A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

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BY

J. W. MELLOR, D.Sc., F.R.S.

VOLUME XIII

WITH 381 DIAGRAMS

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ABBREVIATIONS

aq. = aqueous
atm. = atmospheric or atmosphere(s)
at. vol. = atomic volume(s)
at. wt. = atomic weight(s)
T° or °K = absolute degrees of temperature
b.p. = boiling point(s)
$\theta°$ = centigrade degrees of temperature
coeff. = coefficient
conc. = concentrated or concentration
dil. = dilute
eq. = equivalent(s)
f.p. = freezing point(s)
m.p. = melting point(s)
mol(s) = $\begin{cases}\text{gram-molecule(s)}\\ \text{gram-molecular}\end{cases}$
mol(s). = $\begin{cases}\text{molecule(s)}\\ \text{molecular}\end{cases}$
mol. ht. = molecular heat(s)
mol. vol. = molecular volume(s)
mol. wt. = molecular weight(s)
press. = pressure(s)
sat. = saturated
soln. = solution(s)
sp. gr. = specific gravity (gravities)
sp. ht. = specific heat(s)
sp. vol. = specific volume(s)
temp. = temperature(s)
vap. = vapour

In the **cross references** the first number in clarendon type is the number of the volume; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus **5**. 38, 24 refers to § 24, chapter 38, volume 5.

The oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are considered with the basic elements; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. G. Stokes (*Proc. Roy. Soc.*, **49**. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances *A*, *B*, and *C*, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the triangle represent the single components *A*, *B*, and *C*, the sides of the triangle represent binary mixtures of *A* and *B*, *B* and *C*, or *C* and *A*; and points within the triangle, ternary mixtures. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure *A* will be represented by a point at the apex marked *A*. If 100 be the

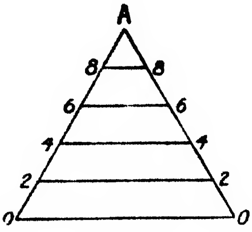


FIG. 1.

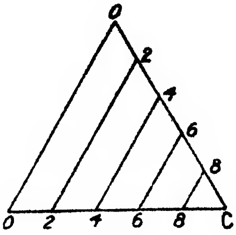


FIG. 2.

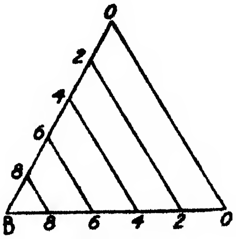


FIG. 3.

standard of reference, the point *A* represents 100 per cent. of *A* and nothing else; mixtures containing 80 per cent. of *A* are represented by a point on the line 88, 60 per cent. of *A* by a point on the line 66, etc. Similarly with *B* and *C*—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig. 4 results. Any point in this

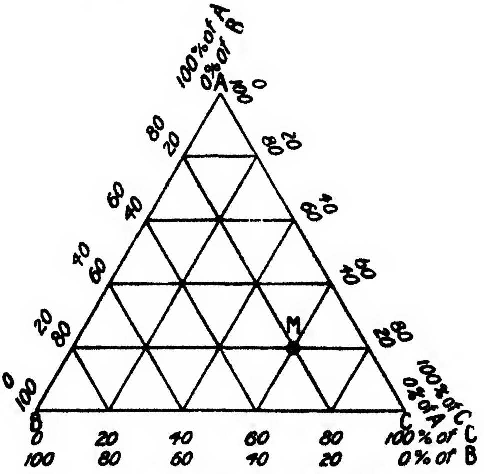


FIG. 4.—Standard Reference. Triangle.

diagram, Fig. 4, thus represents a ternary mixture. For instance, the point *M* represents a mixture containing 20 per cent. of *A*, 20 per cent. of *B*, and 60 per cent. of *C*.

CHAPTER LXVI (*continued*)

IRON (*continued*)

§ 18. The Mechanical Properties of Iron and Iron-Carbon Alloys

The Arabic manuscript of Abu-r-Raihan, *The Book of the Best Things*, written about the tenth century, and described by H. C. Bolton,[1] and J. J. C. Mullet, gave 7·74 for the **specific gravity** of iron, and this value is near the 7·85 accepted to-day. The Arabic manuscript, *Book of the Balance of Wisdom*, by Al-Khazini, written about A.D. 1122, and described by H. C. Bolton, and N. Khanikoff, also gave 7·74 for the sp. gr. of iron. D. G. Fahrenheit gave 7·817; R. Boyle, 7·645—and for soft steel, 7·738, hard steel, 7·704, and spring temper-steel, 7·809; and J. C. . . ., 7·643 for iron, and 7·852 for steel; P. von Muschenbrock, and L. B. G. de Morveau made observations on the sp. gr. of iron. G. Pearson gave values for the sp. gr. of thirty-five different samples of iron and steel, and, for wootz steel, found 7·181 to 7·403; for wootz steel which had been forged, 7·503 to 7·647; for wootz steel which had been melted, 7·200; and for wootz steel which had been quenched from a white-heat, 7·166; Huntsman's hammered steel, 7·826 to 7·916; the same steels quenched from a white-heat, 7·765 to 7·771; soft and tough hammered iron, 7·780 to 7·787; and cast iron, 7·012. T. Bergman gave for steel, 7·643 to 7·784; and for wrought iron, 7·798 to 7·829. Collections of data were published by R. Böttger,[2] E. F. Dürre, and F. W. Clarke.

G. Broling found that the sp. gr. of bar-iron is 7·8439, whereas the same iron in very thin sheet had a sp. gr. 7·6, and that these anomalies may seem to proceed from repulsion between the surface of the iron and the water used in measuring the sp. gr., since the sp. gr. decreased in proportion to the extent of the surface of the metal. The surface, however, had been freed by means of potassium hydroxide from all foreign matters which might prevent adhesion between the metal and water. J. Percy found electrodeposited iron had a sp. gr. of 8·1393 at 15·5°. M. J. Brisson gave 7·788; C. J. B. Karsten, 7·790; A. Baudrimont, 7·6000 to 7·7312, for iron wire in different conditions, and 7·7433 for hammered wire; J. J. Berzelius, 7·8650 to 7·8707; J. A. Poumarède, 7·50 to 7·84 for iron reduced by the vapour of zinc; C. Stahlschmidt, 6·03 for iron obtained by heating the nitride not over 327°; L. Playfair and J. P. Joule, 7·130 for the sp. gr. of iron reduced by carbon; H. Caron, 7·880 at 16° for forged iron fused in hydrogen; 7·847 for wire fused in hydrogen; 7·833 for iron fused in a crucible; and 7·852 for good commercial iron; and H. Schiff gave 7·998 to 8·007 at 10° for iron reduced by hydrogen. K. Ruf gave 7·876 at 20° for the sp. gr. of the metal with less than 0·02 per cent. of carbon; E. Madelung and R. Fuchs gave 7·8544; E. Gumlich gave 7·876; H. Tomlinson, 7·630 for hard drawn, and 7·259 for annealed iron wire; H. Hanemann and E. H. Schulz, 7·899; and R. von Dallwitz-Wegner, 7·86. Amongst

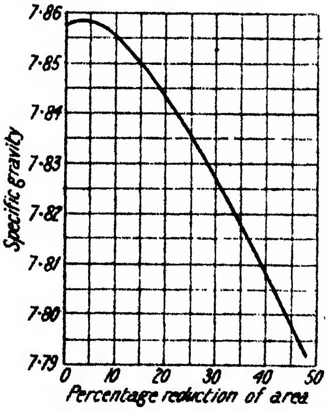


FIG. 179.—The Effect of Cold-work on Armco Iron.

the best results for the sp. gr. of purified iron there are those of J. H. Andrew and A. J. K. Honeyman, who gave 7·864 for the sp. gr. of annealed purified iron, and 0·12716 for the sp. vol.; C. Benedicks, 7·85 for the sp. gr. of purified iron and 0·12739 for the sp. vol.; M. Levin and K. Dornhecker, 7·871 for the sp. gr. of purified and annealed iron, and 0·12705 for the sp. vol.; T. Ishigaki, 7·880; K. Tamaru, 7·882; whilst H. C. Cross and E. E. Hill gave 7·867 for the sp. gr. of electrolytic iron fused in vacuo, and 0·12711 for the sp. vol., the corresponding data for the same iron hot-rolled are 7·8685, and 0·12709; for the same iron annealed at 775°, they are 7·8547 and 0·12731, and when annealed at 900°, 7·865, and 0·12714. R. L. Keynon's results are summarized in Fig. 179.

S. Kaya gave 7·8701 for the sp. gr. and 0·12706 for the sp. vol. of a single crystal where the possibility of intercrystalline pores or spaces is excluded; he said that the sp. gr. of the single crystal of iron may be taken to be about 0·42 per cent. greater than that of polycrystalline iron. W. P. Davey calculated from the X-radiogram data that the sp. gr. of iron is 7·93; L. W. McKeehan, 7·872; and A. Westgren and G. Phragmen, 7·878.

L. Zimmermann and H. Esser measured the sp. vol. of white cast iron at temp. between 0° and 1300°. From the thermal expansion data of K. Honda and H. Endo, and S. Sato, it follows that the sp. gr. of α-iron at 20° is 7·8685—the X-radiogram value is 7·8404; the value for α-iron at 906° is 7·5706—when the X-radiogram value is 7·55. Similarly, the value of γ-iron at 906° is 7·6327, and at 1400°, 7·4077; and the value for δ-iron at 1400° is 7·3900, and at 1535°, the m.p. of iron, 7·3550. The value for molten iron—*vide infra*—at 1535° is 7·0995 when calculated from the expansion data of S. Sato. A. Osawa extrapolated his values for nickel-iron alloys and obtained for γ-iron at 200°, 8·008.

The effect of carbon on the specific gravity of iron.—H. von Jüptner gave for the best representative values for iron alone 7·85 to 7·88; for wrought iron, 7·79 to 7·85; for steel, 7·60 to 7·80; for white cast iron, 7·58 to 7·73; and for grey cast iron, 7·03 to 7·13. S. Rinman, and C. J. B. Karsten gave 7·5 for the sp. gr. of white pig-iron, and 7·1 for that of grey pig-iron. Results were also given by T. Scheerer, B. Kerl, C. Karmarsch, F. Wüst and E. Leuenberger, J. Weisbach, A. Guettier, R. Mallet, E. Maurer, and C. F. Rammelsberg. E. F. Dürre showed the available sp. gr. data to indicate that the sp. gr. of spiegeleisen is diminished if it be melted and slowly cooled; if grey cast iron be melted and rapidly cooled, its sp. gr. is increased; if cast iron be melted under conditions where decarburization can take place, its sp. gr. is increased; and if rods of cast iron be subjected to compression, the sp. gr. is increased. J. E. Hurst gave for the sp. gr. of cast iron, 6·9 to 7·5—mean 7·217; wrought iron, 7·47 to 7·808—mean 7·698; and steel, 7·729 to 7·904—mean 7·852. L. Elsner found the sp. gr. of ordinary steel to be 7·795; hardened cast steel, 7·6578; unhardened cast steel, 7·9288; cast steel, once remelted and hardened, 7·647, and unhardened, 7·647. H. von Jüptner also gave for the sp. gr. of compact iron-carbon alloys:

Carbon . .	0·529	0·649	0·841	0·871	1·0005	1·078 per cent.
Sp. gr. . .	7·841	7·829	7·824	7·818	7·807	7·805

H. C. Cross and E. E. Hill gave for hot-rolled steels:

Carbon .	0·09	0·16	0·25	0·45	0·65	0·87	0·98	1·28 per cent.
Sp. gr. .	7·848	7·857	7·853	7·841	7·831	7·832	7·822	7·812

and for annealed steels:

Carbon .	0·25	0·59	0·73	0·85	0·98	1·15	1·28	1·39 per cent.
Sp. gr. .	7·852	7·836	7·838	7·824	7·823	7·809	7·813	7·816

The smoothed curve for the annealed steel is shown in Fig. 180, and that for the hot-rolled metal almost overlaps. J. H. Andrew and A. J. K. Honeyman's curve likewise is almost overlapping. The curve of M. Levin and K. Dornhecker for hot-rolled steel is shown dotted in Fig. 180, and there is a drop in the curve for the annealed steel which does not appear in the results of H. C. Cross and E. E. Hill, and J. H. Andrew and co-workers. W. Brown gave for the sp. gr. and sp. vol. of steels *A*-series with 0·02 to 0·17 per cent. of silicon, and 0·14 to 0·18 per cent. manganese; and *B*-series with 0·46 to 0·49 per cent. silicon, 0·58 per cent. manganese:

	A-series					*B*-series			
Carbon .	0·028	0·05	0·14	0·89	1·23	0·58	1·00	1·25	per cent.
Sp. gr. .	7·8771	7·8778	7·8638	7·8268	7·7897	7·8132	7·7587	7·7525	
Sp. vol. .	0·12695	0·12694	0·12716	0·12777	0·12827	0·12800	0·12890	·012900	

With up to 0·2 per cent. of carbon, the increase in sp. vol. is 0·0018 c.c. per one per cent. of carbon, and for higher proportions up to 1·25 per cent., 0·0015 c.c. B. Simmersbach made observations on this subject. According to E. Gumlich, if C denotes the percentage amount of carbon, then the sp. gr., D, of alloys with up to $C=1$, is $D=7·876-0·030C$ for slowly cooled alloys; and $D=7·876-0·17C$ for alloys quenched from 850°. H. C. Cross and E. E. Hill gave sp. gr. $=7·855-0·032C$, for the sp. gr. of hot-rolled iron-carbon alloys with up to 1·29 per cent. of carbon, and for the same steels with up to 1·4 per cent. of carbon, when annealed, $D=7·860-0·04C$. J. H. Andrew and A. J. K. Honeyman gave for the sp. vol., $0·12712-0·00052C$. F. Wever represented the at. vol. of austenitic steels by $v=0·1246+0·0004[\mathrm{Mn}]+0·0041[\mathrm{C}]$, where the bracketed symbols represent atomic percentages.

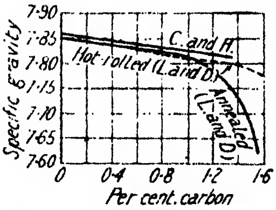


FIG. 180.—The Effect of Carbon on the Specific Gravity of Hot-rolled and Annealed Steels.

G. Hailstone found the effect of the *casting temperatures* on the sp. gr. of cast iron—*vide infra*—with about 1·90 per cent. silicon; 0·10, sulphur; 1·45, phosphorus; 0·27, manganese; and:

Carbon	Total .	3·258	3·246	3·261	3·256	3·281	3·283	3·291	3·295	3·305	3·312 per cent.
	Free .	2·830	2·840	2·862	2·891	2·915	2·926	2·951	2·987	3·012	3·126 ,,
	Comb. .	0·428	0·405	0·399	0·365	0·366	0·357	0·340	0·308	0·293	0·186 ,,
Sp. gr. . . .		7·281	7·262	7·240	7·225	7·201	7·158	7·123	7·085	7·012	7·936
Casting temp. .		1428°	1400°	1390°	1386°	1361°	1348°	1330°	1302°	1272°	1264°

W. H. Hatfield added that the reduction in sp. gr. is partly due to some influence other than the casting temp., and the results agree with H. A. Schwartz that free carbon has a greater influence than combined carbon. One per cent. of free carbon reduces the sp. gr. 0·17; 1 per cent. as free cementite, reduces the sp. gr. 0·025; 1 per cent dissolved in ferrite, 0·115; 1 per cent. of silicon, in soln. in ferrite, 0·060; and 1 per cent. manganese in soln. in ferrite, 0·003. One per cent. of phosphorus in the binary eutectic as Fe_3P reduces the sp. gr. 0·080; and 1 per cent. sulphur present as manganese sulphide reduces the sp. gr. of cast iron 0·2. C. Benedicks said that the addition of one per cent. of manganese increases the sp. vol. 0·00006; with the same proportion of phosphorus, 0·00089; of silicon, 0·00117; and of aluminium, 0·00200. The effects of various elements on the sp. gr. were discussed by H. M. Lane, etc.—*vide infra*, the corresponding alloys of iron.

The effect of mechanical treatment on the specific gravity of iron and of its alloys with carbon.—The early observations of G. Broling are in general agreement with those of later workers. The sp. gr. of the metal usually decreases with *cold-working*; a sample before rolling had a sp. gr. 7·8707, and after rolling 7·8650—the iron was impure since it gave off fœtid hydrogen when dissolved in acids. H. Hädicke found that the hammered metal had a sp. gr. of 7·843, and unhammered 7·838. The effect of cold-work on the densities of metals generally was studied by G. W. A. Kahlbaum and E. Sturm, T. Uêda, W. Spring, J. Johnston and L. H. Adams, and Z. Jeffries and R. S. Archer—*vide* **1**. 13, 18; and the effect of drawing, stretching, or twisting on the density of iron and steel was studied by

E. Heyn and O. Bauer, P. Goerens, H. O'Neil, etc. T. M. Lowry and R. G. Parker found that the sp. gr. of iron filings is less than that of the compact metal from which they were formed—compact iron, 7·8558, filings (cold-worked), 7·8172, decrease 0·0386. J. O. Arnold gave for forged steel, with 99·82 to 99·87 per cent. of iron, 7·8477, and for cast steel, 7·8478. F. Osmond observed that in drawing a wire with a diameter 5·4 mm. and sp. gr. 7·839, the sp. gr. was 7·791 when the diameter was reduced to 3·45 mm., and 7·796 to 7·781 when the diameter was reduced to 0·4 mm. H. M. Howe, W. H. Deering, H. Scott and H. G. Movius, H. E. Doerr, K. Heindlhofer and F. L. Wright, P. Goerens, etc., concluded that the sp. gr. of iron is reduced by cold-working. J. W. Landon found that a piece of wire whose sp. gr. was 7·7097 had a sp. gr. of 7·6160 after being twisted through an angle of 157°, and a sp. gr. of 7·5890 after being twisted through an angle of 228°. The subject was also investigated by E. Houdremont and E. Bürklin, M. Oknoff, K. Tamaru, and T. Uêda. F. C. Thompson and W. E. Millington studied the relations between the sp. gr. and deformation by cold-work with respect to the packing of the atoms of the crystals. They found that very little variation, 7·869 to 7·868, in the sp. gr. of mild steel, of sp. gr. 7·869, pulled in tension with a stress of 14·87 to 21·30 tons per sq. in., occurs until the last section commenced to yield; and with a piece of armco iron, of sp. gr. 7·8580, with the reduction in area in tension of 2·4, 17·8, and 47·5, the sp. gr. were respectively 7·8586, 7·8464, and 7·7927. No change in the sp. gr. occurred until about 5 per cent. reduction of area had occurred, and the decrease in sp. gr. continued until the reduction in area had fallen to 16 per cent. K. Honda, and K. Tamaru discussed the factors involved in the change of sp. gr. by cold-work—*vide supra*, tempering—and the effect is attributed to the closing of blow-holes, and to the weakening of the interatomic forces. H. Hanemann and R. Yamada studied the vol. changes of steel during elastic deformation, and observed that the vol. of mild steel with increasing stress, increases linearly until plastic flow begins; the vol. then increases more rapidly by regular increments, and the curve no longer follows a straight line. The vol. increase $(v-v_0)/v_0\times10^4$ gives a value which rises from zero under a stress of 3·18 kgrms. per sq. mm. to 7·85 under a stress of 41·38 kgrms. per sq. mm.

H. C. Cross and E. E. Hill observed that the effect of hot-rolling is also to decrease the sp. gr. The older observations, which indicate an increase in sp. gr. by cold-working, refer to cast metals in which small cavities are closed up under the hammer, etc. E. Piwowarsky and H. Esser found that the **gas permeability** of cast iron for hydrogen is largely due to microscopic flaws. The porosity of iron is discussed in connection with the corrosion of the metal—*vide infra.* H. O'Neil, B. Beer, J. E. Fletcher, G. Tammann and H. Bredemeier, and A. Marks discussed the **porosity** of cast iron. W. Thörner emphasized the fact that iron always contains pores, and that, where possible, the determinations should be made with the powdered metal. Thus, he obtained for the porosity of iron, in c.c. per kgrm.:

	Specific gravity		Porosity	
	Powder	Compact	Pores	Solid
Ordinary cast iron	7·142	7·042	2·00	140·00
Bessemer steels	7·921	7·826	1·530	126·24
	7·755	7·729	0·530	128·95
Thomas steels	7·968	7·813	2·500	125·50
	7·752	7·700	1·580	128·42

H. O'Neil found that by increasing cold-work in *tension* of armco iron very little alteration in the sp. gr. occurs at first, but the sp. gr. soon decreases about 0·17 per cent., a critical deformation is then reached, for afterwards the sp. gr. ceases to fall and may rise slightly. With further increments of cold-work, the sp. gr. decreases. The overall fall in sp. gr. is about 0·83 per cent. In marked contrast with metallic aggregates, the sp. gr. of single crystals of iron 7·747 was not altered after being subjected to a tensile stress producing a 65-per-cent. reduction of area. T. Ishigaki used a test-piece of armco iron which had been fractured by tensile stresses, and measured the sp. gr. at distances of one centimetre taken successively from the fracture to the lug. The results show that the sp. gr. was least at the point of fracture and increased at increasing distances away. T. Uêda found that the sp. gr. of iron and carbon steel, when stretched, decreases as the tensile stress increases, Fig. 181. If an elongation e be produced by an external force T, $T=eE$, where E is the elastic constant; and if v be the sp. vol., s, the density, and σ, Poisson's ratio, then $dv/v=-ds/s=e(1-2\sigma)$, and by substitution, $ds/s=-E/(1-2\sigma).ds/s$. For a metal with $\sigma=0{\cdot}29$, and $E=2{\cdot}2\times10^4$ kgrms. per sq. mm., $ds/s=-1{\cdot}909\times10^{-5}\ T$. Below the yield-point the sp. gr. decreases slightly and almost proportionally with the stress, but above this point the decrease is more rapid. With carbon steel, the decrease in the sp. gr. is discontinuous at the yield-point, and the magnitude of the decrease decreases with increasing proportions of carbon until, with 0·9 per cent. of carbon, the phenomenon does not occur.

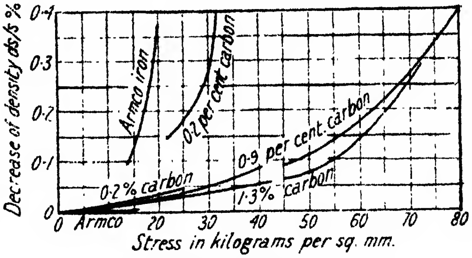


Fig. 181.—The Effect of Tensile Stresses on the Specific Gravity.

H. O'Neil found the sp. gr. of armco iron, between 14° and 16·5°, varied between 7·8393 and 7·8586; and that of single crystals of iron, between 13·3° and 17·5°, varied between 7·747 and 7·754 with *compression* loads up to 45·83 tons per sq. in. After 26 per cent. reduction by compression, the sp. gr. had fallen only 0·07 per cent., and with further work it actually rose above its original value. This is in marked contrast with the behaviour of aggregates of crystals. T. Ishigaki observed the effect of compressing iron and steel at different press., p kgrms. per sq. cm. The results were:

Armco iron		p	0	4,930	7,040	11,970	16,200
		Sp. gr.	7·868	7·866	7·866	7·867	7·867
Carbon	0·3 per cent.	p	0	4,500	7,890	11,830	16,900
		Sp. gr.	7·846	7·844	7·845	7·845	7·844
	0·6 per cent.	p	0	7·040	10,560	12,680	16,900
		Sp. gr.	7·837	7·833	7·835	7·835	7·834
	0·9 per cent.	p	0	5,630	10,700	14,370	16,900
		Sp. gr.	7·828	7·824	7·825	7·826	7·826

The results show that with increasing press. up to about 7000 kgrms. per sq. mm., there is a steady fall in the sp. gr.; an increase then occurs which soon attains a maximum, when it again begins to decrease. The maximum sp. gr. is always less than its initial value. The effect of annealing is gradually to lower the sp. gr. until a tempering temp. of 550° has been obtained when the sp. gr. begins to increase.

J. W. Landon observed a maximum decrease in the sp. gr. of iron, with 0·68 per cent. of carbon, when the iron is subjected to overstrain by *torsion* through various angles:

Angle of twist	0°	70·5°	150°	225°	262°
Sp. gr.	7·7149	7·6678	7·6136	7·5802	7·5757

The results show that the sp. gr. decreases generally as the result of cold-working by twisting. F. C. Lea and W. N. Thomas measured the changes in the sp. gr., D, of steel produced by compressive stresses, S, beyond the yield-point expressed in tons per sq. in. calculated on the original area, and summarized the results by $d=D=0{\cdot}9984+0{\cdot}0_929(250-S)S$. The sp. gr. tends to recover with the lapse of time.

G. Tammann assumed that the decrease in sp. gr. produced by cold-work is due to the production of minute gaps in the slip-planes of the crystal grains; and K. Honda, to the deformation of the space-lattice by internal strain. T. Ishigaki said that the first decrease may be due to these two effects, but the subsequent increase is produced by the closing up of the minute gaps by the higher press. The value of the maximum sp. gr. being smaller than the initial sp. gr. is an effect of the distorted lattice; and the decrease of sp. gr. with higher strains is due to the formation of new intercrystalline gaps. S. Sekito found that the decrease in sp. gr. produced by quenching is due to an expansion of the space-lattice.

The effect of hardening by quenching on the specific gravity of iron and of its alloys with carbon.—Hardening by quenching also lowers the sp. gr., as in the case of cold-working; thus, H. Caron gave the following measurements of a steel rod:

	Before Hardening	Hardened		
		10 times	20 times	30 times
Length . . .	20·00	19·50	18·64	17·97 cm.
Breadth. . . .	0·94	0·96	0·96	1·00 ,,
Thickness . . .	0·93	0·96	0·97	1·00 ,,

and the sp. gr. before hardening was 7·817, and after hardening thirty times, 7·793. H. C. Cross and E. E. Hill's results are summarized in Table XIV. Observations were also made by H. J. French and O. Z. Klopsch. C. Fromme gave for the vol. changes of iron subjected to different heat treatments, original vol., 1·00000; glass-hard, 1·01000; tempered yellow, 1·00495; tempered blue, 1·00060; tempered grey, 1·00425; and annealed at a red-heat, 1·00175. C. Fromme's results show a maximum, or an expansion in volume on passing from the grey annealed to the soft state. C. Barus was unable to verify this, but added that with a more prolonged heating and cooling, it might be possible to obtain the maximum. In one series of observations he found for steel annealed at different temp.:

Annealing temp.	100°	190°	330°	460°	720°	900°	1100°	1300°
Sp. gr. . .	7·7102	7·7251	7·7441	7·7641	7·7793	7·7840	7·7865	7·7856
Sp. vol. . .	0·12970	0·12945	0·12913	0·12880	0·12854	0·12846	0·12843	0·12801

when the values for glass-hard steel are respectively 7·6817 and 0·13018; and for commercial soft steel, 7·81 and 0·1280.

W. Metcalf and J. W. Langley found that steel increases in vol., or decreases in sp. gr. during hardening. The sp. gr. were:

Carbon		0·529	0·649	0·841	0·871	1·005	1·079 per cent.
Ingot		7·841	7·829	7·824	7·818	7·807	7·805
Unhardened rolled steel .		7·844	7·824	7·829	7·825	7·826	7·825
Hardened at	dark redness	7·813	7·806	7·812	7·790	7·812	7·811
	red-heat .	7·826	7·849	7·808	7·773	7·789	7·798
	pale red-heat	7·823	7·830	7·780	7·758	7·755	7·769
	yellow-heat .	7·814	7·811	7·784	7·755	7·749	7·744
	white-heat .	7·818	7·791	7·789	7·752	7·744	7·690

J. H. Andrew and co-workers found that the effect of varying the temp. of quenching on the sp. vol. of steels with carbon up to about 75 per cent. is such that at 800°, the increase in sp. vol. is almost linear, as far as 0·75 per cent. carbon, and the increase is then slower. For a quenching temp. of 1100°, the curve shows a drop in the sp. vol. in the range 0·90 to 1·2 per cent. of carbon, and there appear to be analogous drops in quenching from 900° to 1000° steels with 1·20 to 1·60 per cent. carbon.

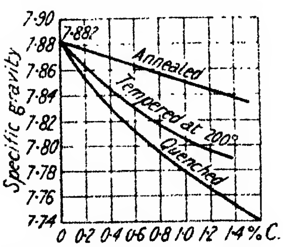


FIG. 182.—The Effect of Annealing, Tempering, and Quenching on the Specific Gravity of Carbon Steels.

K. Tamaru's results for the sp. gr. of quenched, annealed, and tempered steels are summarized in Fig. 182. S. Sekito found that the X-radiograms of quenched steels with different proportions of carbon show that the distances, 2*b*, of the lines (110) with different proportions of carbon, are:

Carbon .	0·12	0·32	0·40	0·51	0·73	0·80	0·90	1·08 per cent.
2*b* . .	56·34	56·33	56·22	56·24	56·14	56·16	56·01	56·17 mm.

so that the lattice expands 0·45 per cent. for 1 per cent. of carbon; the value calculated from K. Tamaru's values for the sp. gr. is 0·44 per cent. This shows that the expansion is mainly due to the expansion of the crystal lattice. The internal stress corresponding with the broadening of the lines is 192 kgrms. per sq. mm., which is of the same order of magnitude as the tensile strength—C. Grad gave 200 kgrms. per sq. mm. The plane at right angles to the plane of maximum at. density—*i.e.* the plane of easiest slip—has the greatest internal stress.

H. Hanemann and E. H. Schulz obtained for steels with 0·16 per cent. C, 0·33 Si, 0·38 Mn, 0·015 S, 0·017 P, and 0·07 Cu:

	Annealed	Quenched at					
		1200°	1105°	1005°	930°	820°	765°
Sp. gr. .	7·863	7·854	7·855	7·861	7·853	7·851	7·855

for steel with 0·51 C, 0·33 Si, 0·62 Mn, 0·023 S, 0·045 P, and 0·07 Cu:

Sp. gr. .	7·854	7·804	7·798	7·801	7·795	7·804	7·844

for steel with 0·86 C, 0·23 Si, 0·25 Mn, 0·033 S, 0·010 P, and 0·020 Cu:

Sp. gr. .	7·857	7·774	7·769	7·772	7·762	7·779	7·839

and for steel with 1·17 C, 0·21 Si, 0·31 Mn, 0·020 S, 0·010 P, and traces of copper:

Sp. gr. .	7·847	7·752	7·759	7·771	7·761	7·810	7·834

The effect of annealing on the specific gravity of steel hardened by mechanical work or quenching.—The effect of annealing is to restore the original sp. gr. diminished by the cold-work. Thus, P. Goerens found a steel wire in which the sp. gr. 7·806, rose to 7·822 on annealing. G. W. A. Kahlbaum and E. Sturm gave 7·7970 for the sp. gr. of annealed piano-wire, and 7·7772 for the same wire cold-drawn—decrease 0·0198. The original sp. gr. was restored on annealing. E. Maurer, E. H. Schulz, B. D. Enlund, and K. Tamaru discussed the subject in connection with the tempering of steels (*q.v.*). C. Chappell and M. Levin found the sp. gr. of cold-worked specimens of steel is about 0·3 per cent. less than that of the annealed metals. Observations were also made by M. Levin and K. Dornhecker, who found that for the sp. gr. of annealed and unannealed iron-carbon alloys:

Carbon .		0	0·11	0·35	0·63	1·00	1·54	2·69	3·05	3·75 per cent.
Sp. gr.	unann.	7·8718	7·8523	7·8422	7·8297	7·8159	7·7957	7·7591	7·7522	7·7343
	ann. .	7·8748	7·8519	7·8425	7·8277	7·8166	7·6422	—	—	—

W. Fraenkel and E. Heymann followed the course of the annealing of quenched steels by the change in the sp. gr. They also observed that with an austenitic steel, having 2·65 per cent. of manganese, and 0·82 per cent. of carbon, at 200°, the sp. gr. rises during the first hour from 7·7801 to 7·8080, and falls to 7·7926 in the first 50 hrs., and rises to 7·7940 in the next 150 hrs. With annealing at a red-heat, the sp. gr. rose to 7·8197. With a steel having 0·50 per cent. of manganese and 0·80 per cent. of carbon, there was only a difference of 0·004 between the maximum and minimum, whilst with the other steel there was a difference of 0·015.

A. Osawa observed that a sample of armco iron, annealed at 1150°, had a sp. gr. of 7·8787 at 20°, and a sp. gr. of 7·8795 after being dipped in liquid air at about −185°, and brought back to 20°. Iron can thus become more compact by cooling to a low temp., possibly owing to the elimination of some pores by the contraction of the metal. H. Hanemann observed the sp. gr. of an unannealed 1·79 per cent. carbon alloy quenched from 1120°, 1130°, and 1140°, before cooling in liquid air, to be respectively 7·7842, 7·6923, and 7·8214, and after cooling in liquid air, respectively 7·6866, 7·8117, and 7·6828; and for alloys quenched from 1100° to 1130°, aged or annealed at 100° to 395°, before and after cooling in liquid air:

Tempered at .		100°	150°	210°	260°	287°	306°	435°	375°	395°
Sp. gr.	Before .	7·8758	7·8979	7·8314	7·7331	7·7084	7·7714	7·7728	7·7794	7·7536
	After .	7·6942	7·7146	7·6993	7·7186	7·7032	7·7560	7·7686	7·7810	7·7485

The observations of H. C. Cross and E. E. Hill, H. A. Dickie, P. Goerens, R. Hay and R. Higgins, E. Heyn and O. Bauer, and F. C. Lea and co-workers show that the effect of annealing on the sp. gr. of cold-worked steel is appreciable in some cases at temp. so low that recrystallization has not commenced. K. Tamaru's results are summarized in Fig. 182—*vide supra*, the tempering of steel. T. Ishigaki observed that with armco iron the sp. gr. 7·862 was reduced by hammering to 7·855. The recovery of the sp. gr. by annealing did not here commence until nearly 700°; in fact, a decrease in the sp. gr. occurred at 500°. This has not been explained. The decrease was also observed in the annealing of specimens which had been subjected to tensile and compression stresses. B. D. Enlund observed a contraction in the sp. vol. during the annealing of quenched steel beginning near 100° and ending about 210°. Thereafter, a pronounced expansion occurs between 250° and 300°. The expansion was also observed by G. E. Svedelius, G. Charpy and L. Grenet, and P. Chévenard. The contraction is attributed by B. D. Enlund to the formation of troostite and the coagulation of cementite, while the expansion corresponds with the decomposition of retained austenite. The subject was discussed by K. Tamaru—*vide supra*, tempering.

E. Heyn and O. Bauer measured the influence of annealing mild steel wire at different temp. on the sp. gr., and found for wires of diameter *d* mm., and the ratios *n* of the elongations due to cold stretching, the sp. gr. before and after annealing:

d	5·22	3·65	3·10	2·65	2·25	1·90	1·60	1·40	1·25
n	—	2·045	2·835	3·88	5·38	7·55	10·65	13·91	17·43
Sp. gr. Before .	7·861	7·840	7·832	7·835	7·828	7·838	7·836	7·841	7·825
Sp. gr. After .	7·862	7·845	7·8405	7·849	7·843	7·8415	7·843	7·847	7·8575

They also found for the cold-drawn wire, 1·25 mm. diameter, annealed at various temp.:

	0°	100°	200°	300°	400°	500°	600°	700°	800°	900°
Sp. gr. .	7·825	7·8275	7·829	7·834	7·836	7·836	7·834	7·8385	7·850	7·8575

The sp. gr. increases with rising temp. E. Maurer observed that cold-worked steels with 0·14 and 0·40 per cent. of carbon attained their maximum sp. gr. when annealed respectively at 150° and 250°. H. C. Cross and E. E. Hill's observations are summarized in Table XIV.

TABLE XIV.—THE SPECIFIC GRAVITY OF QUENCHED AND TEMPERED CARBON STEELS.

Carbon per cent.	Temp. Quenching	Specific Gravity								
				Tempering Temperature						
		Hot-rolled	Water-quenched	150°	225°	300°	375°	460°	525°	600°
0·09	910°	7·848	7·823	7·829	7·809	7·830	7·838	7·845	7·839	7·841
0·28	865°	7·850	7·829	7·837	7·833	7·839	7·842	7·846	7·846	7·844
0·35	865°	7·839	7·802	7·811	7·816	7·829	7·830	7·828	7·829	7·829
0·44	820°	7·839	7·802	7·805	7·809	7·824	7·833	7·834	7·834	7·831
0·47	820°	7·833	7·795	7·796	7·801	7·818	7·825	7·828	7·828	7·831
0·60	810°	7·838	7·785	7·794	7·797	7·818	7·827	7·829	7·828	7·832
0·68	810°	7·832	7·776	7·788	7·789	7·809	7·821	7·824	7·826	7·827
0·87	795°	7·832	7·769	7·784	7·784	7·810	7·824	7·826	7·826	7·830
0·98	795°	7·828	7·762	7·780	7·776	7·804	7·818	7·821	7·823	7·823
1·05	795°	7·825	7·770	7·795	7·792	7·814	7·818	7·821	7·821	7·822
1·12	795°	7·819	7·757	7·781	7·770	7·785	7·805	7·809	7·807	7·813
1·29	795°	7·812	7·758	7·780	7·767	7·787	7·802	7·805	7·807	7·808

H. A. Schwartz measured the sp. gr. of annealed and unannealed white cast iron with different percentages of carbon. E. Maurer determined the sp. gr. of a 0·83 per cent. carbon steel, hardened by quenching from 800°, and annealed at different temp. J. H. Andrew and A. J. K. Honeyman found for carbon steels with 0·08 to 0·25 per cent. of manganese, and 0·08 to 0·175 per cent. of silicon the values shown in Fig. 183 for the sp. vol. (corrected for silicon) for steel quenched from 900° and tempered for an hour at different temp. Tempering at 160° affects only the martensite. At 250°, both austenite and martensite are tempered, but in the higher-carbon steels the tempering of austenite predominates although it is not completed. The tempering at 350° completes the austenite transformation, but some martensite still remains. Tempering is complete at 620°, but this would probably be obtained at a lower temp. For furnace-cooled nickel-chromium steel, with 3·46 per cent. of nickel, 1·80 per cent. of chromium, 0·13 to 0·19 per cent. of silicon, the critical temp., sp. vol. corrected for silicon, and the scleroscopic hardness were :

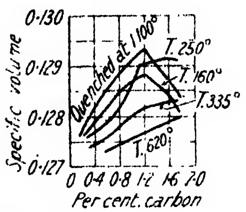


Fig. 183.—The Effect of Annealing and Tempering on the Specific Volume of Carbon Steels.

Carbon .	0·51	0·51	1·28	1·28	1·28	1·50	1·50	1·50 per cent.
Critical temp.	600°	400°	600°	400°	150°	600°	400°	150°
Sp. vol. . .	0·12757	0·12774	0·12781	0·12768	0·12788	0·12790	0·12778	0·12794
Hardness .	30	57	38	48	67	36	47	70

For the same steel, quenched from 1200° and tempered for an hour at the temp. named :

Per cent. C.	Quenched	Tempered				Annealed
	1100°	190°	260°	365°	600°	780°
Sp. vol. . .	0·12843	0·12814	0·12814	0·12790	0·12763	0·12763
Hardness . .	65	65	65	60	52	34
Sp. vol. . .	0·12626	0·12626	0.12626	0.12716	0·12798	0·12788
Hardness . .	29	34	34	49	56	36
Sp. vol. . .	0·12650	0·12647	0·12647	0·12763	0·12803	0·12791
Hardness . .	31	34	34	57	63	40

No change in the sp. vol. occurs until 365° is reached ; the slight increase in hardness is a surface effect. Tempering at 365° results in an incomplete transformation of austenite, but most of the transformation is completed between 350° and 600°. The tempering at 600° is not complete. Heating to 780°, followed by slow cooling, brings the steels back to the fully annealed state.

The energy equivalent of the changes in volume.—As indicated below, E. Heyn and O. Bauer found the sp. gr. of cold drawn mild steel wire to be 7·825, and when annealed at 700°, the sp. gr. becomes 7·838 ; and this corresponds with a decrease of 1·66 mm. per 1000 in a wire 1·25 mm. diam. E. Heyn and O. Bauer explain the reduction in sp. gr. by cold-work, and the increase in sp. gr. by subsequent annealing as follows : E. Rasch has shown that in stretching a metal bar, heat is absorbed so long as the stress is elastic in character ; but on passing the yield-point the heat of the action changes sign, and heat is evolved. In compressive tests, however, E. Rasch found that the heat of the action is positive from the beginning, and on exceeding the yield-point a sudden increase in the heat of the action occurs, but the sign is not changed. From this it might be inferred that the elastic change of form of metals follows a law similar to that which governs the elastic change of form of gases. That is to say, expansion is accompanied by the absorption of heat and a reduction in density ; and compression, by the liberation of heat and increase in density. In contradistinction to this purely elastic change of form stands the purely plastic change of form, which occurs when the internal friction of the metal particles is overcome ; it is accompanied by the conversion of work into heat. This process, as in all cases where work is converted into heat by friction, is not reversible. No change in the sp. gr. would be expected to take place, so long as there were no hollow spaces in the body before undergoing deformation. That is, as long as the change of sp. gr. can be taken as zero and the movement of the particles of the body is not prevented by very high press. Such a deformation of a purely plastic nature cannot be produced in practice, because it is always accompanied by an elastic change of form, even though this, so far as can be judged from the extent of deformation, is very minute in comparison with the former. Since an elastic change of form, as in the case of gases, is accompanied by a storing up of potential energy, a certain amount of potential energy remains stored in metals when deformed in the cold state. Thus, in the cold-drawing of wire, the individual particles become plastically, but also partly elastically, stretched. When the stress is no longer applied, the material partially recovers from the elastic change of form; but this change of form may be partially retained in the material in consequence of the resistance due to friction, which opposes the return to a state of equilibrium; and this remanent elastic tension reveals itself in the reduction of the sp. gr. of the metal. By heating the cold-drawn material the internal friction is moderated, and the elastic tension of the particles is thereby released so that a new state of equilibrium corresponding to the temp. is attained. The sp. gr. must therefore correspondingly increase, as has been already proved by G. W. A. Kahlbaum and E. Sturm for a great number of metals. E. Heyn and O. Bauer obtained an approximate estimate of the remanent elastic stress—namely 33 kgrms. per sq. mm.—from the differences in the sp. gr. before and after annealing.

Let d, l, and s respectively denote the thickness (1·25 mm.), length, and sp. gr. of the annealed wire, and D, L, and S the corresponding values for the cold-drawn wire. Then $dls = DLS$, but the difference in the thickness of the two wires is small enough to be neglected, and then $L = ls/S$; and the elongation $L - l$ becomes $l\{(s/S) - 1\} = 0{\cdot}00166l$, since the sp. gr., s, of the cold-drawn wire is 7·825, and the sp. gr., S, of the wire annealed at 700° is 7·838. This means that the wire, 1·25 mm. diameter, has been shortened $0{\cdot}00166l$—*i.e.* 1·66 mm. per 1000—during annealing. Let E denote the modulus of elasticity, nearly 20,000 kgrms. per sq. mm., and δ the elastic stress in kgrms. per sq. mm. Then, $0{\cdot}001661 = l\delta/E$; or δ, the remanent elastic stress, is nearly 33 kgrms. per sq. mm.—*vide supra*, annealing.

The specific gravity and specific volume of the constituents of the carbon-iron alloys.—O. C. Ralston found that the mean values for the sp. gr. and sp. vol. of the constituents of steel are respectively as follow: Ferrite, 7·864 and 0·1271; cementite, 7·670 and 0·13038; pearlite, 7·778 and 0·12856; austenite, 7·843 and 0·1275; martensite, 7·633 and 0·1310; α-martensite, 7·581 and 0·1319; and β-martensite, 7·800 and 0·1282. This shows that when an austenitic steel is converted into martensite, there is an expansion in vol. The transition from martensite to pearlite involves a decrease in volume although pearlite has a smaller sp. gr. than austenite. G. Tammann and K. Ewig found that at the A_0-arrest, about 210°, the dilation of cast iron corresponds with an expansion of 0·0795 c.mm. per gram of Fe_3C. A. Westgren found the sp. gr. of austenite with 12·1 per cent. of manganese and 1·34 per cent. of carbon to be 7·82; and G. Tammann and E. Scheil gave 7·83 for the sp. gr. of a steel with 1·72 per cent. of carbon. These austenites are impure. A. Osawa obtained 8·008 for the sp. gr. of austenite calculated by extrapolation from the X-radiogram data for nickel steel. S. Sato's value for the thermal expansion gave 8·12 for the sp. gr. of austenite at room temp.; F. Wever's value is 8·04; and K. Tamaru's value 8·097.

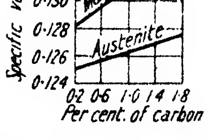


FIG. 184.—The Effect of Carbon on the Specific Volume of Martensite and Austenite.

C. Benedicks said that troostite, sorbite, and pearlite all have the same sp. vol., and that the sp. vol. of austenite is less, and that of martensite greater than that of pearlite. H. von Jüptner gave 7·82 for the sp. gr. of pearlite, and 0·1279 for the sp. vol. J. H. Andrew and A. J. K. Honeyman observed that, as indicated by the sp. vol., the tempering of martensite begins at or below 150°, but it is not complete at 360° in an hour. The sp. vol of fully tempered martensite is the same as that of the corresponding pearlite, indicating that in both conditions of steel, the cementite possesses the same crystalline form. E. Maurer represented the effect of carbon on the sp. vol. of martensite and austenite by the curves Fig. 184. The changes in sp. gr. or sp. vol. during the transformation of austenite to martensite were studied by W. Fraenkel and E. Heymann, H. Hanemann and L. Träger, E. Scheil, M. Levin and K. Dornhecker, K. Honda, F. Wever and P. Rütten, A. Westgren and G. Phragmen, K. Heindlhofer and F. L. Wright, and W. L. Fink and E. D. Campbell. L. Zimmermann and H. Esser studied the sp. vol. of cast iron. K. Honda found that the sp. vol. of austenite, and of the α- and β-martensites, depend on the carbon contents, thus:

	Carbon	0·4	0·7	1·0	1·2 per cent.
Sp. vol.	Austenite .	1·1252	0·1256	0·1260	0·1263
	α-martensite .	0·1276	0·1283	0·1294	0·1300
	β-martensite .	0·1265	0·1268	0·1270	0·1272

and for the sp. vol. of cementite at room temp. and at 1130°, K. Honda and co-workers gave respectively 0·1304 and 0·1350; and for iron, respectively 0·1271 and 0·1331.

The changes in volume during tempering.—The observations of K. Tamaru, and others have been discussed in connection with tempering. According to H. C. Cross and E. E. Hill, carbon steels, with up to 1·30 per cent. of carbon, decrease in density when quenched due to the formation of martensite. The magnitude of this decrease rises with increasing carbon content, reaching a maximum at about 1 per cent. carbon, and then falls off slightly. Upon tempering, the quenched steels gradually increase in density. A decrease in density is noted in the hyper-eutectoid steels when tempered at 225° and this may be ascribed to the tempering of retained austenite. Upon further tempering above 225°, the density of all samples increased, ultimately approaching the density of the annealed steel upon tempering at 600°. The greatest increase in density occurs upon tempering at 300°, the rate of increase then gradually falls off as the tempering temp. is raised to 600°.

Quenched austenite is more stable than martensite at room temp. and up to 200°, so that on tempering up to 200°, martensite needles may be converted into troostite; and if a sample be then cooled in liquid air, needles of martensite appear in a ground mass of unaltered or super-cooled austenite. Water-quenched steel contains martensite mixed with some austenite. On tempering, martensite alters to troostitic and sorbitic pearlite with an increase in vol. The change is at about 100°, and is nearly complete at 200°; and austenite begins to pass into sorbite at about 250°, so that as the temp. rises to 300° to 500°, the sp. vol. decreases by the passage of what G. Tammann and E. Scheil call *distended pearlite*, or troostitic pearlite, into normal pearlite. Any austenite converted at or below 250° furnishes this distended or troostitic pearlite, and any converted above 250° furnishes normal sorbitic pearlite. The pearlite is distended at 100° to 300° because it has a smaller sp. vol. than the martensite from which it was derived. The solid is not sufficiently mobile at these temp. to allow it to contract and fill the spaces that tend to form. Hence, tempered steels have usually a high sp. vol. Ordinary pearlite formed by the slow cooling of austenite has a sp. vol. of 0·12856, whereas the distended pearlite has a sp. vol. 0·1303. O. C. Ralston suggested that if the distended pearlite is sorbite or troostite, the sp. vol. 0·1303 corresponds to a real vol. and is not due to a distortion of the pearlite lattice as a result of its rigidity at the low temp. of the tempering.

According to G. Tammann and E. Scheil, water-quenched steel has about 50 per cent. martensite embedded in a matrix of super-cooled austenite; and steel quenched in liquid air has a sp. vol. of 0·12965 corresponding with about 80 per cent. martensite. K. Honda and H. Endo found that by repeated cooling in liquid air, and warming back to ordinary temp., the sp. vol. could be brought to 0·1303, very nearly the value 0·1310 for martensite. Hence, quenching in liquid air did not completely eliminate the austenite.

The changes in volume on solidification or melting.—H. Moissan found that iron with but little carbon contracts on solidification, but when saturated with carbon, the metal expands on solidification. O. C. Ralston gave $dv/v=0·036$ for the best representative value of the expansion per unit volume for purified iron on melting at 1535°. According to W. C. Roberts-Austen and T. Wrightson, the sp. gr. of solid iron, near its m.p., is 6·95, whilst that of the liquid metal, a little higher in temp., is 6·88. R. Mallet made observations on this subject. T. Wrightson gave for the sp. gr. of cold, solid grey Cleveland iron, 6·95; molten iron, 6·88; and iron in the plastic state, 6·50. C. Benedicks and co-workers found the sp. gr. of liquid iron holding 0·10 per cent. of carbon, which was estimated to increase to 0·2 or 0·3 per cent. of carbon during the experiment, to be 6·92±0·07 at 1550°. This corresponds roughly with a linear shrinkage of $\frac{1}{35}$th in passing from the m.p. to ordinary temp. K. Honda and co-workers obtained the results summarized in Fig. 185. The sp. gr. curve of liquid iron containing different proportions of carbon, and, for comparison, the liquidus curve, are given in Fig. 185. Both curves are of the same general type. At 1600°, the sp. vol., v, and the increase in the sp. vol., δv per 100°, are:

Carbon	0	0·5	1·0	1·5	2·0	3·0	4·0 per cent.
Sp. vol.	0·1397	0·1445	0·1461	0·1471	0·1487	0·1518	0·1566
δv	0·0020	0·0023	0·0025	0·0028	0·0030	0·0035	0·0038

The effect of additions of various elements on the sp. vol. is indicated in Fig. 186.

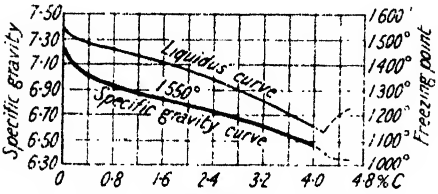


FIG. 185.—Specific Gravity Curve of the Liquid Alloys of Carbon and Iron.

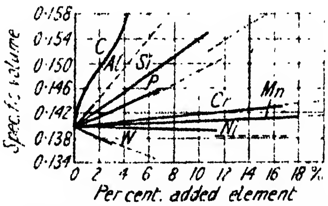


FIG. 186.—The Effect of Various Elements on the Specific Volume of Iron.

According to F. Wüst, the contraction of purified iron from the solidifying temp. is 2·39 per cent. It is diminished by carbon, the addition of 1·7 to 2 per cent. giving a minimum of 1·9 per cent., but then slowly increases as the carbon is further increased. Phosphorus diminishes the contraction to 1·3 per cent. at 1·7 per cent. phosphorus, but further addition increases the contraction. In both series of alloys the formation of mixed crystals diminishes the contraction, but when the limit of solubility is exceeded and iron carbide or iron phosphide is formed, the contraction increases. Silicon diminishes the contraction of iron from 2·37 per cent. to 1·7 per cent. at a content of 18·24 per cent. silicon. Manganese was the only element investigated which increased the contraction, which rose to 2·89 per cent. at 15·5 per cent. manganese. Sulphur diminishes the contraction rapidly up to a content of 1 per cent., afterwards more slowly, but with no minimum value as in the case of phosphorus. Nickel diminishes the contraction of iron very little, with a minimum at about 25 per cent. nickel. Chromium diminishes the contraction uniformly to 1·80 per cent. at a content of 21·4 per cent. chromium. Iron alloys free from graphite show an elongation at the beginning of solidification, the magnitude of which corresponds roughly to that of the solidification period of the alloy. C. Benedicks and N. and G. Ericsson, and C. H. Desch and B. S. Smith gave for iron with 0·03 to 0·04 per cent. of carbon, and for alloys with 3·12 to 3·65 per cent. of carbon:

	0·03 to 0·04 per cent. C				3·12 to 3·65 per cent. C			
	1530°	1545°	1550°	1560°	1300°	1355°	1405°	1465°
Ericsson.	7·18	7·17	7·16	7·17	7·26	7·23	7·23	7·17
D. and S.	6·79	6·05	6·97	6·95	6·93	6·90	6·82	6·77

The mean values for 0·04 per cent. carbon are respectively 7·00 and 7·17 at 1545°, and for 3·40 per cent. carbon respectively 7·25 and 6·86 at 1355°. H. A. Schwartz found the sp. gr. of liquid iron between 1375° and 1500° varies 0·02 grm. per c.c. per degree; and that at 1450°, sp. gr.$=7·16-0·1[Si]-0·7[C]$, where the symbols represent parts per 100. D. W. Berlin gave for carbon-free iron, and iron with 1·2 per cent. of carbon:

	m.p.	1550°	1600°	1650°	1700°
Carbon-free . .	7·4	7·3	7·2	7·0	6·9
1·2 per cent. C.. .	—	7·0	6·9	6·8	6·7

F. Sauerwald and co-workers found the sp. vol. and sp. gr. of grey cast iron—with 3·32 per cent. total carbon; 2·72 per cent. graphite; 2·76, Si; 0·56, Mn; 0·126, S; and 0·492, P:

	700°	800°	840°	900°	1000°	1100°	m.p.		1200°	1300°
Sp. vol. . . .	0·1460	0·1478	0·1484	0·1476	0·1457	0·1444	0·1444	0·1435	0·1445	0·1477
Sp. gr. . . .	6·85	6·77	6·73	6·78	6·86	6·92	6·92	6·97	6·92	6·77
	Solid						Liquid			

The results are plotted for the sp. vol. in Figs. 187 and 188; there is a maximum on the curve at 840°. H. A. Schwartz represented the sp. gr., *D*, of liquid iron, at 1450°, by $D=7·16-(0·1\ Si+0·07\ C)$. Observations were made by G. Dearth and F. Sauerwald, W. Krause and F. Sauerwald, W. Biltz and K. Meisel, and J. J. Saslawsky. According to F. Sauerwald and E. Widawsky, the sp. vol. of molten iron-carbon alloys does not follow the mixture rule, and hence they infer that the liquid metal contains the tritacarbide, Fe_3C. Their results are summarized in Table XV. W. Biltz and K. Meisel calculated 1·05 for the at. vol. of α-iron at absolute zero.

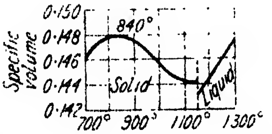


Fig. 187.—The Effect of Temperature on the Specific Volume of Iron.

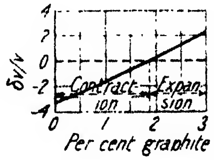


Fig. 188.—The Effect of Carbon on the Specific Volume of Iron.

TABLE XV.—THE SPECIFIC VOLUME OF THE IRON-CARBON ALLOYS.

Carbon per cent.	Liquidus	Specific Volume		Temp. Coeff. $\frac{dv}{dT}\times 10^4$	Specific Gravity	
		at Liquidus	at 1600°		at m.p.	at 1600°
0·0	1533°	0·1402	0·1405	0·05	7·13	7·12
0·5	1480°	0·1408	0·1411	0·06	7·10	7·08
1·0	1458°	0·1412	0·1417	0·06	7·08	7·05
1·5	1422°	0·1416	0·1425	0·07	7·065	7·02
2·0	1382°	0·1418	0·1432	0·07	7·05	6·98
2·5	1341°	0·1419	0·1438	0·08	7·05	6·95
3·0	1290°	0·1419	0·1445	0·08	7·05	6·92
3·5	1232°	0·1418	0·1452	0·09	7·05	6·88
4·0	1170°	0·1415	0·1459	0·10	7·06	6·86
4·2	1150°	0·1414	0·1462	0·10	7·07	6·84

K. Honda and co-workers found for the increase in volume, $\delta v/v$, which occurs during the solidification of cast iron with *Gr* per cent. of graphite, and *C* per cent. of decomposed cementite:

Gr . . .	3·10	2·86	2·38	1·90	1·00	0·22	0·12	0·00
C . . .	46·40	42·80	35·60	28·40	14·95	3·02	1·79	0·00
$\delta v/v$ . . .	2·74	2·22	1·98	0·82	−1·60	−3·07	−3·54	−4·00

The volume changes at the eutectic temperature.—K. Honda and H. Endo estimated that pure iron on freezing at 1530° contracts 4·4 per cent. in volume. The sp. vol. of α-iron at 1450° is 0·1366; and of δ-iron at 1530°, 0·371, and the sp. gr., 7·29. They gave for the sp. vol. of white cast iron with 4·1 to 4·3 per cent. total carbon, and 2·8 to 3·0 per cent. graphite:

	1130° (m.p.)	1150°	1200°	1250°	1300°
Sp. vol.	0·1433	0·1435	0·1445	0·1460	0·1480
Sp. gr.	6·97	6·96	6·91	6·85	6·75

The increase in vol., $\delta v/v$, decreases as well, becoming zero with 2·06 per cent. of graphite (4·1 per cent. of total carbon and 0·38 per cent. of silicon). When no graphite is precipitated, and the metal is 100 per cent. white cast iron, extrapolation shows that the contraction during solidification is 3·6 per cent. The results show the relation between the change of vol. and the liberation of graphite during freezing; and they agree with the assumption that the graphite present in cast iron is a decomposition product of the cementite which is precipitated from the molten alloy during solidification—*vide supra*. F. Sauerwald and co-workers gave for pig-iron of a eutectic composition, 6·85 for the sp. gr. and 0·1460 for the sp. vol. at 700°, the sp. vol. rose to a maximum of 0·1484 (or sp. gr. 6·73) at 840°, and then decreased steadily to the m.p. where a sharp decrease occurred followed immediately by a rapid increase on liquefaction. The abnormal contraction at the m.p. is attributed to the formation of large quantities of cementite in the melt, and the maximum in the sp. vol. curve to the formation of cementite and γ-iron. F. Sauerwald and J. Wecker found the sp. vol., v, and sp. gr., D, of white cast iron before and after melting, to be $v=0·1398$ and $D=7·15$ for the solid, and $v=0·1418$ and $D=7·05$ for the liquid; and for grey cast iron, $v=0·1449$ and $D=6·90$ for the solid, and $v=0·1435$ and $D=6·97$ for the liquid. Consequently, while grey cast iron contracts on melting, white cast iron expands. F. Sauerwald and E. Widawsky found that the contraction of solid grey iron is due to the dissolution of graphite, and that cementite is formed when the grey iron is melted. The data for grey cast iron, and white cast iron are:

		700°	900°	1000°	1150°	1155°	1155°	1160°	1250°	1300°
Grey	Sp. vol. .	0·1456	0·1480	0·1455	0·1450	—	—	0·1455	—	0·1478
	Sp. gr. .	6·87	6·75	6·87	6·90	—	—	6·97	—	6·77
White	Sp. vol. .	0·1340	0·1352	0·1360	—	0·1391	0·1415	—	0·1440	—
	Sp. gr. .	7·46	7·39	7·35	—	7·18	7·07	—	6·92	—
		Solid					Liquid			

L. Zimmermann noted a break in the sp. vol. curve at about 700° with white cast iron, and found that the expansion which occurs on melting is between 1·33 and 1·41 per cent. J. J. Saslawsky studied the atomic volume. W. L. Bragg[3] calculated for the **atomic radius,** 1·40 A.; W. P. Davey, $1·236\times10^{-8}$ cm.; C. Benedicks, $1·26\times10^{-8}$ cm.; M. L. Huggins, 1·23 A. for bivalent iron; and G. Natta, 0·83 A. G. Natta and L. Passerini found that if the radius of oxygen is 1·32 A., that of iron is 0·82 A. Observations were also made by A. M. Berkenheim, E. J. Cuy, V. M. Goldschmidt, H. G. Grimm, E. Herlinger, M. L. Huggins, L. Pauling, J. C. Slater, and E. T. Wherry from which it follows that for tervalent iron atoms, the effective radius is 0·49 to 1·45 A. A. Kapustinsky investigated the effect of solvation on the ionic radius; and F. Wever, the effect of polymorphic transformations. C. Benedicks discussed the sphere of activity of the atoms; P. Vinassa, the mol. number; and J. A. M. van Liempt, the atomic constants.

J. B. A. Dumas[4] observed that iron is scratched by glass of **hardness** 5·6 on Mohs' scale. F. C. Calvert and R. Johnson said that iron is the hardest of all the ductile metals—the hardness of Staffordshire iron being 6 to 7 on Mohs' scale, and that of steel 6. J. R. Rydberg gave 4·5 for the hardness of iron on the same scale. H. F. E. Lenz also reported the results of some tests on the hardness of metals. Actually, P. P. Cioffi found the hardness of iron of a high degree of purity to be about the same as that of annealed copper, that the hardness of iron on Mohs' scale is 5·5, and after heating in vacuo, 4·5. T. Turner observed that the hardness of iron is 1375 when that of copper is 1360, and that of the diamond 3010. These statements serve to illustrate how simple a property hardness was considered to our predecessors; a marked contrast to what the term means to-day. There is also little to indicate the marked change in the hardness which occurs with modifications in the thermal treatment. Hardness may be defined as the resistance of a body against permanent change of shape; or, less rigorously, as T. Turner expressed it, hardness is the property of resisting penetration, so that a hard body is one which under suitable conditions readily penetrates a softer material. The phenomenon is really a complex one, so that hardness varies in kind. The manifestations of hardness vary with the form of stress to which a metal may be subjected, so that phrases like tensile hardness, cutting hardness, abrasive hardness, and elastic hardness have been employed. The usual tests for hardness are *static* in character, but, as T. Turner pointed out, the conditions are different when the penetrating (or other) body is moving with a greater or less velocity. *Dynamic* hardness is exemplified by resistance to the action of a sand-blast, to the pounding of a heavy locomotive on a steel rail, to a projectile, or to a cutting tool in a lathe. The subject has previously been discussed from one point of view—**2**. 20, 7.

S. Bottone assumed that, in general, the closer the atoms are packed, the greater the hardness; hardness varies inversely as the at. vol. Hard metals have a low at. vol., and soft metals a high at. vol. G. Wertheim made a similar observation with respect to tenacity about 1844; and W. C. Roberts-Austen, with respect to the influence of foreign elements on the tensile strength of gold; and F. Osmond, with respect to the influence of various elements on the critical temp. of iron. C. Benedicks pointed out a certain analogy between the atomic volume rule and the gas law that the press. of a gas at a given temp. is proportional to the number of molecules in unit space, for the hardness or the resistance offered by a solid to the entry of another body will increase as the number of atoms in unit vol. is increased. The subject was discussed by L. Gruardet, and C. H. Desch. M. Hanriot observed that iron with a hardness of 57·7 units acquired a hardness of 62·3 after being compressed by a press. equivalent to 10,000 kgrms. per sq. cm.—*vide infra*, the influence of cold-work.

The parallelism between hardness and at. vol. is not rigid, and might be better if the metals were tested under like conditions. P. Ludwik said that the comparison should be made at temp. bearing some relation with the m.p. G. Mars illustrated the idea by calculating the atomic concentrations of a number of steels of known composition and hardness. According to K. Honda, for a given substance having a definite molecular force, its hardness increases with the fineness and strained state of the structure, and for the same structure, and the same degree of strain, the hardness of a substance increases with the strength of its molecular force. C. A. Edwards found that there is an even closer parallelism between the hardness and the m.p. of the metals than with the at. vol. P. Lasareff said that the proportionality between hardness and at. concentration—the reciprocal of the at. vol.—follows from the assumption that the mutual attractive forces of the atoms of different elements is the same function of the distance between them. I. Traube observed a close parallelism between the hardness and internal press.; and C. Benedicks, between hardness and osmotic press.

The various methods for measuring hardness have been summarized by the nomenclature committee of the Iron and Steel Institute in 1902; and reports were issued by the Institution of Mechanical Engineers in 1916, and 1929. The study of the so-called absolute hardness by H. Hertz, F. T. Trouton, etc., was discussed **2**. 20, 7. The summary with some modifications is as follows:

I.—The hardness of a body is determined by the penetration into it of another body.

A.—When the respective positions of both bodies remain unchanged during the operation of testing.

(*a*) The penetration of the foreign body is effected by means of a steady press.
- (1) The depth of penetration, press., constant—*e.g.* J. A. Brinell's indentation test.
- (2) Press. required to produce a fixed depth of penetration.

(*b*) The foreign body is driven in by means of a falling weight.
- (1) The depth of penetration produced by a constant blow—*e.g.* the diamond indentation test, and S. P. Rockwell's test.
- (2) The force of blow is required to produce a fixed depth of penetration—*e.g.* E. G. Herbert's pendulum.

B.—The respective positions of both bodies vary during the operation of testing.

(*a*) By scratching the surface with normal substances of various hardness—*e.g.* T. Seebeck's proposal, and F. Mohs' mineralogical test.

(*b*) By pressing the harder substance against the body to be tested.
- (1) The press. required to plough a way through a certain distance, or in a certain time, a definite portion of the test body—*e.g.* W. J. Keep's drill test.
- (2) The weight of material removed from the test body by a definite press. in a definite time.
- (3) The press. necessary to produce on the test body a furrow of definite width —*e.g.* T. Turner's sclerometer.
- (4) The width of furrow cut in the test body by a definite loading of the cutting agent—*e.g.* A. Martens' sclerometer.
- (5) The number of rotations required to cut a definite depth into a substance by a diamond-tipped borer under a definite load—*e.g.* T. A. Jaggar's and W. J. Keep's processes. The dynamic tests, however, introduce complications which obscure the development of the difficult concept of hardness. H. P. Hollnagel found that soft wrought iron may appear hard when rotated fast enough. Thus, at a speed of 30 ft. per sec., a soft wrought iron disc was cut by a steel tool; at 100 ft. per sec., it cuts the steel tool; and at 300 ft. per sec., it cuts quartz.
- (6) The abrasive hardness discussed by F. Robin, etc.

(*c*) By measuring the height of rebound of a hard body dropped from a given height on to the surface to be tested—*e.g.* A. F. Shore's scleroscope.

II.—The hardness of a body is deduced from the properties of tenacity of the material—*vide infra.*

G. D. Bengough pointed out that the hardness measured by these tests involves two or more variables; and that hardness alone cannot be measured directly. This was also the opinion of W. C. Unwin. The different kinds of hardness are the resultants of different groups of component forces. Thus, according to G. D. Bengough, T. Turner's sclerometer gives readings probably proportional to tenacity and density; A. F. Shore's scleroscope gives readings proportional to the elastic limit, and the elastic hardness so measured would be more accurately called *resilience*; J. A. Brinell's test measures resistance to compression which is nearly proportional to tenacity, the reciprocal of compression; and T. A. Jaggar's test depends on tenacity, density, and elongation. The term *hard* is also applied to metals with a high tensile strength and a low elongation, but the term *coherent* would be more appropriate; metals with a low tensile strength and high elongation could then be called *viscid* instead of soft; metals with a high tensile strength and high elongations could then be called *ductile*; and metals with a low tensile strength and low elongation could be called *weak*.

Observations on the testing of the hardness of iron and its alloys were made by A. H. d'Arcambal, G. Auchy, E. S. Ault, J. C. Ayers, G. W. Barr and co-workers, R. G. C. Batson, C. A. Bauer, C. Benedicks and V. Christiansen, V. Bernard, F. Bollenrath, C. A. Briggs, J. A. Brinell, R. C. Brumfield, D. K. Bullens, G. Charpy, H. le Chatelier and co-workers, J. Class, C. J. B. Cooke, R. H. Coolidge, I. H. Cowdrey, J. W. Craggs, A. E. Crisp, W. J. Crook and H. S. Taylor, N. N. Davidenkoff and G. N. Titoff, C. H. Davis, H. E. Degler, G. H. Denison, H. C. Dews, C. Dillner, P. W. Döhmer, J. W. Donaldson, F. W. Duesing, P. Dufour, J. Durand, H. K. Dutcher. C. A. Edwards and co-workers, J. V. Emmons, R. Esnault-Pelterie, G. S. Evans, A. B. Field, F. Figari, J. E. Fletcher, A. Föppl, M. F. Fogler and E. J. Quinn, A. V. de Forest, F. E. Foss and R. C. Bramfield, H. Fowler, E. Franke, C. de Fréminville, H. J. French and co-workers, T. Friesendorff, J. D. Gat, R. Genders, H. M. German, S. L. Goodale and R. M. Banks, S. H. Graf, C. Grard, R. H. Greaves, L. Grenet, R. Guillery, L. Guillet and co-workers, A. Haar and

T. von Karman, R. A. Hadfield and S. A. Main, B. P. Haigh, P. J. Haler and A. H. Stuart, G. A. Hankins, F. Hargreaves, C. W. Ham and J. W. Huckert, K. Heindlhofer, H. Hencky, E. G. Herbert, W. Herold, F. P. Hitchcock, H. P. Hollnagel, C. W. Holmes, H. A. Holz, K. Honda and co-workers, S. L. Hoyt, H. Hubert, A. Hultgren, F. H. Hurren, J. E. Hurst, M. Ichihara, J. Innes, E. Irion, K. Ito, P. Jannettaz, L. Jannin, J. L. Jones and C. H. Marshall, R. L. Jones, L. Jordan, W. J. Keep, J. O. Keller, E. J. Kelley, F. C. Kelley, O. Keune, R. L. Keynon, H. Z. Kip, H. B. Knowlton, F. Koerber and I. B. Simonsen, S. Kokado, F. Krau, R. Kühnel and co-workers, C. Kugler, W. Kuntze, E. F. Lake, O. H. Lehmann, R. M. Leslie, P. Lieber, P. Ludwik, V. E. Lysaght, D. J. MacAdam, A. McCance, R. Mailänder, A. Mallock, R. Malmström, F. S. Mapes, R. Mather, E. Maurer, E. Menzel, W. J. Merten, A. Mesnager, E. Meyer, H. Meyer and F. Nehl, G. A. A. Middelberg, H. Moore, R. R. Moore, G. Moreau, H. H. Morgan and J. R. Mooney, M. Moser, R. Mouillac, K. H. Müller and E. Piwowarsky, P. Nicolau, P. Nicollet, G. Nidecker, A. L. Norbury, A. L. Norbury and T. Samuel, A. Ohnstein, J. Okubo and M. Hara, T. Y. Olsen, H. O'Neil, A. R. Page, A. L. Parsons, J. G. Pearce, S. N. Petrenko, A. Picarelli, H. R. Pitt, M. Plant, A. Pomp, A. Pomp and H. Schweinitz, A. Portevin, A. Portevin and H. Berjot, L. Prandtl, H. S. and J. S. G. Primrose, G. W. Quick and L. Jordan, E. Rasch, H. S. Rawdon and co-workers, H. Redenz, P. Rehbinder, A. Reichelt, C. O. Reid, M. Retzow, L. Revillon, F. Ricolfi, F. Riedel, A. Ries and L. Zimmermann, F. Robin, S. P. Rockwell, P. le Rolland, A. Rosiwal, P. Rossi, P. Roudie, G. A. Rousch, O. C. Rudolph, G. Sachs, R. Sancery, D. A. N. Sandifer, F. Sauerwald and co-workers, A. Sauveur, N. N. Sawin and E. Stachrowsky, M. Schandt, J. J. Schneider, E. Schüz, M. von Schwarz, F. Schwerdt, G. Sellergren, J. Shaw, G. A. Shires, A. F. Shore, I. G. Slater and T. H. Turner, R. L. Smith and G. Sandland, S. C. Spalding, M. Spindel, A. Stadeler, B. Stoughton and J. S. McGregor, R. Stribeck, M. Suzuki, K. Takahasi, K. Taniguchi, F. C. Thompson, F. S. Tritton, L. B. Tuckerman, T. Turner, F. T. Turpin, W. C. Unwin, F. Waizenegger, L. Waldo, F. Walker, A. Wallichs and H. Schallbroch, A. Wallichs and co-workers, H. L. Whittemore, L. W. Wild, A. Wildometz, S. R. Williams, and F. Wüst and P. Bardenheuer.

E. Meyer showed that in Brinell's test, if P denotes the load in kgrms., and d the diameter of the indentation in mm., $P=ad^n$, where a and n are constants for a given material; or a may be regarded as the load required to give an indentation of unit diameter, and n, the hardenability or capacity of the metal for becoming strain-hardened, either by increased indentation, or by other cold-working operations. n is very nearly 2, and the results are often represented $a=P/d^2$. The subject was discussed by H. Moore, H. O'Neil, T. Baker and T. F. Russell, C. A. Edwards and F. W. Willis, J. J. Schneider, A. Kürth, R. G. C. Batson, B. P. Haigh, etc. According to O. Keune, if B denotes Brinell's hardness of iron; B_1, Brinell's hardness of the standard; S_1, the scleroscopic hardness of the standard; and S_2, the scleroscopic hardness of the specimen, then $B=B_1+(S_2-S_1)B_1/S_1$. Since the different tests for hardness measure different groups of properties, they might be correlated through their components—density, tenacity, etc. As it is, a close agreement is not to be expected, although T. Turner found that the results with his sclerometer, A. F. Shore's scleroscope, and J. A. Brinell's penetration test, are either in agreement with, or proportional to one another. Thus, taking one-sixth of the value of J. A. Brinell's numbers:

	T. Turner's	A. F. Shore's	J. A. Brinell's
Lead	1·0	1·0	1·0
Softest iron	15·0	—	14·5
Mild steel	21·0	22·0	16 to 24
Soft cast iron	21·4	24·0	24·0
Rail steel	24·0	27·0	26 to 35
Hard cast iron	30·0	40·0	35·0
Hard white iron	72·0	70·0	75·0
Hardened steel	—	95·0	93·0

R. A. Hadfield gave the comparison, shown in Table XVI, of J. A. Brinell's ball test, and A. F. Shore's scleroscopic hardness. The subject was discussed by T. N. Holden, and S. N. Petrenko. There is some relation between hardness and tensile strength, as shown by R. A. Hadfield's comparison, Table XVI, of the hardness and the compressive strength, tensile strength, and elastic limit of a great variety of steels. R. H. Greaves and J. A. Jones measured the ratio: Tensile strength (tons per sq. in)/Brinell's number for over a thousand steels, and they observed:

	Ratio
Heat-treated steels with Brinell's number 250 to 400	0·21
Heat-treated steels with Brinell's number $<$ 250	0·215
Medium carbon steels—rolled, normalized, or annealed	0·22
Mild steels—rolled normalized, or annealed	0·23

but no satisfactory explanation of the constancy of the ratio has been given. W. H. Hatfield found that the relation between Shore's hardness and the elastic limit was not always proportional, since the curves sometimes crossed. R. R. Abbott gave a number of empirical factors for converting Shore's hardness, S, into Brinell's hardness, B, for carbon steels: $B=5\cdot6S+14$; for converting Brinell's number, B, into tensile strength in lbs. per sq. in., T, for carbon steels, $T=0\cdot75B-28$; and for converting Shore's number, S, into tensile strength in lbs. per sq. in., $T=4\cdot4S-28$. E. Schüz represented the relation between Brinell's hardness, H, and the tensile strength, T kgrms. per sq. mm., of cast iron by $E=k(H-40)$, where k is a constant. The deviations from the rule were due to the proportion of ferrite and pearlite, and to the size of the graphite flakes.

TABLE XVI.—COMPARISON OF HARDNESS WITH THE TENSILE STRENGTH AND ELASTIC LIMIT OF STEELS.

Hardness		Tensile strength (tons per sq. in.)		Compression (tons per sq. in.)	
Shore's	Brinell's	Yield-point	Maximum stress	Elastic limit and 0·25 per cent. compression	Compression per 100 tons per sq. in.
—	150	20	36	17	49·0
—	175	26	41	19	40·0
34	200	32	46	21	35·0
38	225	38	51	23	31·0
42	250	44	56	26	27·0
46	275	50	61	30	23·0
50	300	56	66	34	19·0
54	325	61	71	38	15·2
57	350	67	76	43	11·3
61	375	73	81	49	8·0
64	400	79	86	55	5·6
68	425	84	91	61	3·8
71	450	90	96	67	2·4
75	475	96	101	74	1·3
78	500	102	106	81	0·6
80	525	107	111	87	0·23
84	550	113	116	94	0·21
86	575	—	121	101	0·20
89	600	—	126	108	0·18
92	625	—	131	115	0·16
95	650	—	136	122	0·14
99	675	—	141	129	0·13
101	700	—	—	136	0·12
—	725	—	—	144	0·11
—	750	—	—	151	0·09
—	785	—	—	159	0·08
—	800	—	—	166	0·07

R. R. Abbott also gave for nickel steels, $T=0\cdot71B-32$; $T=3\cdot5S-6$; and $B=5\cdot0S+48$; for chromium-vanadium steels, $T=0\cdot71B-29$; $T=4\cdot2S-21$; and $B=5\cdot5S+27$; for low chromium-nickel steels, $T=0\cdot68B-22$; $T=3\cdot7S-1$; and $B=5\cdot4S+33$; for high chromium-nickel steels, $T=0\cdot71B-33$; $T=3\cdot7S-3$; and $B=4\cdot8S+58$; and for all steels grouped together, $T=0\cdot70B-26$; $T=4\cdot0S-15$; and $B=5\cdot5S+28$.

J. S. G. Primrose recalculated these results; and J. E. Stead represented the relation between Brinell's number, B, and tenacity by: Tenacity (tons per sq. in.) $=\frac{1}{5}B+6$, or tenacity (kgrms. per sq. mm.) $=\frac{1}{3\cdot2}B+10$. J. Navarro represented the relation between the hardness, B, and the coeff. of the resistance to bending, or the transverse breaking stress, S kgrms. per sq. mm., of cast iron, by $B=3{\cdot}23S+42$. T. Friesendorff studied the mathematical theory of Brinell's test. The relations between the hardness and the other mechanical properties of iron and steel were discussed by T. Baker and T. F. Russell, R. Baumann, G. S. Bell and C. H. Adamson, G. Berndt, H. Bohner, H. M. Brayton, I. H. Cowdrey, H. A. Dickie, P. W. Döhmer, P. Goerens, R. H. Greaves, R. H. Greaves and J. A. Jones, H. Hencky, K. Honda and K. Takahasi, F. Hugueny, E. J. Janitzky, H. von Jüptner, F. Kick, B. Kirsch, A. Kürth, A. Leon, E. Meyer, W. Müller, A. L. Norbury and T. Samuel, J. Okubo, H. O'Neil, V. Pöschl, A. Portevin, F. Reiser, T. F. Russell, F. Sauerwald and K. Knehans, F. Sauerwald and H. Viessen, E. Schüz, O. Schwarz, W. K. Shepard and C. T. Porter, A. F. Shore, T. Swinden and G. R. Bolsover, J. J. Thomas, A. Vierendeel, F. Wüst and P. Bardenheuer. B. D. Saklatwalla and H. T. Chandler applied the probability law of the frequency of errors to the choice of the results of Brinell's test.

F. Auerbach, in applying H. Hertz's method of measuring absolute hardness —**2**. 20, 7—showed that hardness and elasticity are associated quantities in that variations of the one are attended by corresponding variations of the other independent of the body operated upon. His method of calculation is based on the assumption that when the total pressure between a sphere and a plane of a given body is increased up to the elastic limit, the time of yielding is sharply marked either by a permanent set, or by rupture at the area of contact, and the hardness is then determined by the total pressure and the diameter of the impressed area for the time in question. The electrical resistance and hardness also appear to be related in some way, because when one increases, the other also increases. As the temp. falls, the electrical resistance also falls, but usually the hardness is considered to increase as the temp. falls. C. Barus and V. Strouhal, and C. A. Casperson, indeed, estimated the hardness from the electrical resistance of steels (*q.v.*), and K. Heindlhofer, from the magnetic hardness (*q.v.*).

H. O'Neil found that the scratching hardness of single crystals of iron is greatest in a direction parallel to the lobes of the pressure figures; and the hardness is greatest in a direction at right angles to that of the elongation due to cold-work. In aggregates of crystals, the hardness becomes greater in the region of the boundaries of the crystal grains; and in cold-worked metals, etch bands are also super-hardened. H. Gries and H. Esser also measured the hardness of single crystals of iron. W. R. D. Jones and K. G. Lewis, W. Schwinning and E. Strobel, E. Greulich, and F. Sauerwald and co-workers discussed the hardness induced by the cold-work, or cold-deformation—*i.e.* **work-hardening.** Hot-deformation does not have a hardening effect in the same sense, but it causes the metal to recrystallize. M. Mikhailoff and I. Churbanoff studied the hardness of iron broken by tension. B. Stoughton's results for the scleroscopic hardness of cold-rolled, electrolytic iron are shown in Fig. 189; the hardness increases up to a constant value with an increase in the work performed on the iron. The subject was discussed by R. Jonson, M. Guichard and co-workers, and B. Garre.

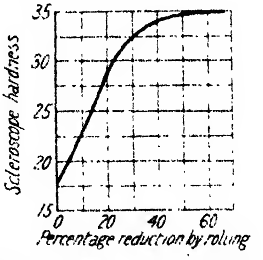


FIG. 189. — The Scleroscopic Hardness of Cold-Rolled Iron.

G. P. Fuller gave 14 to 16 for the scleroscopic hardness of 99·965 per cent. electrolytic iron annealed to remove hydrogen. T. D. Yensen found Brinell's hardness of electrolytic iron, melted in vacuo, to be 60 to 70. D. J. MacNaughtan showed that the hardness of electro-deposited iron is dependent to some extent on the conditions of deposition. Thus, with the pH-value for the H'-ion concentration 4·5 to 4·2, the Brinell's hardness varied from 167 to 195; with pH=3·6 to 3·8, 225 to 244; and for pH=3·3 to 3·5, 256 to 281. Again, with current densities of 5, 10, 15, and 20 amps. per sq. ft., the Brinell's hardnesses of the deposits were respectively 182, 229, 283, and 354. A rise in temp. tends to soften the deposits.

The hardness of electro-deposited iron was attributed to the dissolved hydrogen as such, or as hydride, by L. Cailletet, H. Lee, J. Cournot, A. J. Allmand, H. O'Neil, and N. B. Pilling. D. J. MacNaughtan suggested the proportion of hydrogen in solid soln. is insufficient to explain the high hardness attained ; he also thought that the assumption that the deposit is largely amorphous iron is not a likely explanation ; nor does he favour the assumption that the crystal lattice is distorted by the electrical forces acting during the deposition producing a hardening effect analogous to that of cold-work. The fine-grained character of the crystalline structure, due in part to the action of hydrogen in interfering with crystalline growth, may be a partial explanation of the phenomenon. E. J. Mills found that the electro-deposited iron, cobalt, and nickel are in a condition of tensile stress, whilst with cadmium and zinc, the stress is compressive. G. G. Stoney, W. Kohlschütter and E. Vuillemnier, and R. H. D. Barklie and H. J. Davis made observations on the subject—*vide supra*, theories of hardness, and *vide infra*, electrostriction. The hardness produced by cold-work, etc., was discussed by D. J. MacNaughtan and A. W. Hothersall, C. A. Edwards and K. Kuwada, F. Sauerwald and F. Rakosky, M. Guichard and co-workers, R. H. Greaves, R. Hay and R. Higgins, E. G. Herbert, P. Nicolau, E. A. Ollard, W. P. Sykes and A. C. Ellsworth, and G. Tammann. A. Sauveur and D. C. Lee gave the results summarized in Fig. 190. For J. H. Andrew and A. J. K. Honeyman's observations, *vide supra*, sp. gr. ; and for those of C. Nusbaum and W. L. Cheney on the effect of different rates of cooling eutectoid-carbon steels, *vide* Table XVI, magnetism.

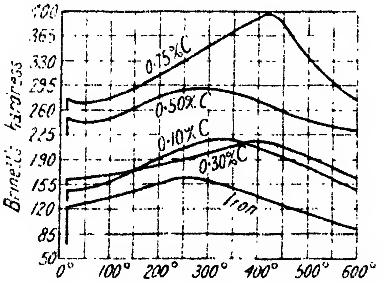


FIG. 190.—Brinell's Hardness of Steel after being Strained at Different Temperatures.

The hardness of steel and cast iron is largely determined by the condition of the carbon. As shown by G. Neumann, the hardness of grey cast iron is more sensitive to the ground mass than to the form of the graphite than is the case with the tensile and bending tests. The subject was studied by T. Klingenstein. The maximum hardness of cast iron occurs when all the carbon is in the combined state ; and also by the particular constituent which predominates in the metal. This is largely determined by the heat treatment to which the metal has been subjected. The exterior of a casting, for instance, is usually harder than the interior. This is due to the chilling of the metal which comes in contact with the mould. For the increase in hardness accompanying the change of austenite into martensite, and the decrease in hardness as the martensite passes into troostite or pearlite, *vide supra*, martensite ; and the hardening and tempering of steel.

The different constituents of steel have their own specific hardness, and H. C. Boynton gave the following relative numbers for Brinell's hardness :

Ferrite	Electrolytic iron	1
	Electrolytic iron quenched	2·15
	Wrought iron	1·5 to 3·6
Pearlite	Steel with 0·13 to 1·52 per cent. C.	1·8 to 10·3
	Steel with 0·35 to 0·86 per cent. C.	3·8 to 4·2
Sorbite	Steel with 0·48 to 0·58 per cent. C.	5·2 to 53·6
Troostite	Steel with 0·58 per cent. C.	88·2
Martensite	Steel with 0·20 to 1·52 per cent. C.	38·9 to 261·6
Austenite	White cast iron with 3·24 per cent. C.	103·4
Cementite	Grey cast iron with 3·24 per cent. C.	272·8

The average values for the sclerometer hardness (calcite, 158 ; quartz, 46,103 ; corundum, 84,809) were :

Ferrite	Pearlite	Sorbite	Troostite	Austenite	Martensite	Cementite
460	2000	2400 to 24,000	40,500	48,000	110,000	125,000

J. A. Brinell found the hardness of Swedish pale grey cast iron to be 179; white cast iron, 460; and mottled cast iron in the grey part, 202, and in the white part, 375. He also found the hardness of Swedish steel with:

Carbon .	0·1	0·2	0·3	0·4	0·5	0·6	0·7 per cent.
Hardness .	97	107	145	156	185	215	232

P. Oberhoffer's results for the influence of carbon on the hardness of steel are summarized in Fig. 191. A. Wahlberg's results are similar, and include those represented by the dotted line. E. Schüz found that the relation between Brinell's hardness and the percentage of combined carbon follows almost a linear law. The results were very little affected by the size of the graphite plates. M. Levin and K. Dornhecker, P. Saldau, and I. G. Slater and T. H. Turner also obtained analogous results. F. Fettweis observed singular points in the hardness of iron at about 600°.

K. Tamaru gave 40 for Brinell's hardness of normalized armco iron; 155 for austenite; 225 for normalized 0·9 per cent. carbon steel; 270 for strained sorbite in 0·9 per cent. carbon steel; 400 for strained troostite in 0·9 per cent. carbon steel; 720 for martensite; 820 for strained cementite, and 640 for natural cementite. According to C. Grard, the hardness of troostite is about 400, and that of sorbite, 270—both are subjected to an internal strain. A. Portevin estimated the Brinell's hardness of cementite to be 400; and K. Tamaru gave the results indicated in Fig. 192, where the unannealed sample is under strain, and amounts to 820 on Brinell's scale; while annealed, or the so-called natural hardness, amounts to 64 on Rockwell's scale, or 640 on Brinell's scale. N. T. Belaiew found that if Δ_0 denotes the distance in microns; μ, pearlite lamellæ—**12**. 66, 15—the Brinell's hardness, H, can be represented by $\Delta_0 H=80$. Hence, for lamellæ with $\Delta_0=0{\cdot}28\mu$, $H=280$ approximately.

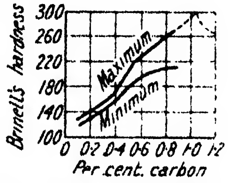


FIG. 191.—The Effect of Carbon on the Hardness of Steel.

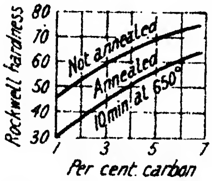


FIG. 192.—The Hardness of Cementite.

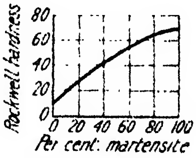


FIG. 193.—The Effect of Martensite on the Hardness of Austenite.

K. Tamaru found that the hardness of austenite in quenched carbon steels depends on the proportion of contained martensite, as indicated in Fig. 193. A similar maximum at about 600° to 630° was observed in the austenite of manganese and nickel steels. The change in hardness which attends the transformation of austenite to martensite was discussed by L. Demozay, W. P. Sykes and Z. Jeffries, etc.—*vide supra.* F. Koerber observed a maximum at 600° in the impact hardness. The observations of R. A. Hadfield and J. Hopkinson, J. O. Arnold and A. A. Read, and E. E. McKee show that there is a separation of carbides in annealing these steels, but K. Tamaru attributed the maximum to the blue shortness of steel—*vide infra,* tensile strength—which, according to K. Honda, is due to the cold-work undergone by the steel during the application of the load. The plastic deformation due to cold-work always lags behind the applied load, and this lag diminishes with rise of temp. Consequently, as the velocity of loading increases, the maximum hardening is displaced towards a higher temp. F. Wüst and E. Leuenberger, W. Köster, O. Reinhold, E. L. Dupuy, H. J. French, Z. Jeffries, T. Matsushita and K. Nagasawa, K. Honda, and T. Inokuty observed a maximum at 200° to 300° in the statical test, and F. Fettweis found that the maximum is displaced to a higher temp. as the velocity of loading is increased. The decreasing hardness with increasing carbon of austenitic manganese steel is attributed to the presence of martensite which increases with decreasing proportions of carbon and manganese. The general results show that Brinell's hardness of austenite is 155 in carbon steels at room temp. A. Sauveur gave 175 to 180; and R. A. Hadfield and J. Hopkinson, 200. K. Tamaru found that Brinell's hardness of martensite in a 1·69 per cent. carbon steel, quenched from 1120°–1130°, is 720. The hardness of the inner portion of a piece of steel quenched in water, and also after immersion in liquid air. The hardness increases with carbon-content up to 0·8 per cent., and then gradually decreases; below 0·7 per cent. of carbon, the outer portion is harder since, owing to the low proportion of carbon, the martensite is well developed; and above 0·8 per cent. of carbon, the outer portion is softer because, in virtue of the high carbon content, more austenite is formed than in the centre. The decrease in hardness with steel with over 0·8 per cent. of carbon is due to the increasing proportion of retained austenite. A. Wahlberg observed that the hardness gave 652 for the maximum hardness of a quenched 0·65 per cent. carbon steel. Observations were made by E. Maurer. A. Katto measured the effect of repeated quenching on the hardness of steel. W. R. Chapin, C. R. Hayward, T. Kase, S. Idei, and K. Honda and S. Idei studied the distribution of the hardness in quenched carbon steel, and M. A. Ammon, and G. Charpy and L. Grenet, the relation of hardness to the depth of carburization of case and hardened steels. C. Y. Clayton, F. J. Walls and A. Hartwell, C. A. Edwards and K. Kuwada, and O. Bauer and W. Schneider found that Brinell's hardness of electrolytic iron is not affected by quenching from 650° to 1258° in iced water, although H. C. Boynton said that there is a 100 per cent. increase in the scratching hardness.

The effect of heat treatment determines to some extent the nature of the dominant constituents of the metal, and these, as just shown, are in a large measure responsible for variations in the hardness of the carbon-iron alloys. J. A. Brinell employed a steel with about 0·01 per cent. of sulphur and 0·026 per cent. of phosphorus, as well as the proportions of carbon, silicon, and manganese shown in Table XVII, and obtained the values for Brinell's hardness shown in the same Table XVII, for steel when subjected to different heat treatments. The effect of the hardening temp. on some steels is indicated in Table XVII.

TABLE XVII.—THE EFFECT OF HEAT TREATMENT ON THE HARDNESS OF STEEL.

Percentage composition			Brinell's hardness			
Carbon	Silicon	Manganese	Direct from rolling-mill	Cooled in charcoal from dull redness	Cooled in charcoal from a white-heat	Quenched from red-heat in water at 20°
0·10	0·007	0·10	109	97	94	149
0·20	0·018	0·40	126	115	109	196
0·25	0·30	0·41	161	143	132	311
0·35	0·26	0·49	172	156	138	402
0·45	0·27	0·45	204	194	151	555
0·65	0·27	0·49	228	202	159	652
0·66	0·33	0·18	255	235	170	578
0·78	0·37	0·20	273	231	176	652
0·92	0·28	0·25	289	258	189	627
1·25	0·60	0·20	302	262	212	627

Hardening temp.	690°	750°	1000°
Carbon 0·10 per cent.	134	163	137
Carbon 0·65 „	235	460	430
Carbon 0·66 „	223	387	387
Carbon 0·70 „	241	744	744

J. A. Jones found that when an annealed bar of armco iron containing 0·05 per cent. of carbon, is reheated to 600° for an hour, the Brinell's hardness with a 10 mm. ball of 1000 kgrms., after various rates of cooling, 8 : slow cooling, 75 ; air-cooled, 87 ; quenched in water and tested after 10 min., 96 ; 1½ hrs., 100 ; 7 days, 107 ; 28 days, 120 ; and 63 days, 136 ; quenched in water and aged for 50 days, 130 ; and then reheated to 100° for an hour, 116 ; or to 200° for one hour, 100. M. Sauvageot and H. Delmas studied the hardness of steels quenched from a high temp. ; and L. Grenet, the hardness of tempered steels. T. Turner gave for the percentage loss of quenching hardness for steel with nearly 0·9 per cent. of carbon when the steel was quenched at different temp., and the hardness measured in different ways :

Percentage loss	100°	200°	300°	400°	500°	600°
Brinell's hardness .	—	13	38	68	94	100
Martens' ,, .	2·5	14·0	41·0	70·6	87·5	95·7
Jaggar's ,, .	1·8	5·4	9·1	23·6	64·0	94·5
Shore's ,, .	3·7	2·7	11·1	33·0	92·5	100

E. Heyn and O. Bauer measured the effect of tempering on the scratching hardness of a 0·95 per cent. carbon steel, quenched from 900°. R. Hay and R. Higgins found that if H_0 denotes the hardness of martensitic steel, and H the hardness on tempering at $\theta°$, then $H=H_0e^{-a\theta}$, where a is a constant. A. Martens obtained a hardness of 277 on a special scale for forged steel with 0·95 per cent. of carbon, this rose to 2775 when the steel was heated to 900° and quenched in water, and on tempering the hardness fell in the following way :

	100°	200°	275°	400°	500°	700°
Hardness . .	2775	2285	1060	595	446	277

The hardness of 0·89 per cent. carbon steel quenched from 850° in water, and then tempered for an hour at various temp. is indicated in Fig. 194—*vide supra*, tempering. The hardness of a sample tempered at 112° is greater than that of the quenched steels, but as the tempering temp. rises still farther, the hardness decreases. The abnormal change at 150° to 200° corresponds with α-martensite, that at 350° to 400°, with β-martensite ; and that at 430° to 450°, with the re-crystallization of the steel. C. Grard found an increase at 100°. Above 450°, the internal stress is removed, and the grain-size increases, and the hardness decreases by tempering—*vide supra*, tempering.

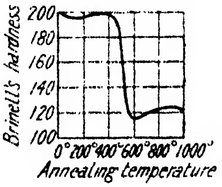


FIG. 194.—The Effect of Tempering on the Brinell's Hardness of Iron.

C. Barus, and L. C. Brant found that hard steel became appreciably softer when kept under ordinary conditions for thirty years ; and C. Barus added that if glass-hard steel tools had been preserved from the beginning of the Christian era they would now be soft as to need re-tempering to be efficient. This statement has probably given rise to the impression that hard and tempered steel will not retain its qualities, and that hard steel is in a metastable state which is afterwards more or less alleviated by tempering. The observations of H. C. H. Carpenter and J. M. Robertson on the hardened and tempered steels of ancient Egypt show that both hardened and tempered steels can retain their mechanical properties and hardness for many thousands of years.

L. Guillet and J. Cournot showed that there is an increase in hardness as the temp. falls, and that there is a fairly large increase in passing from −80° to −190°. The fall in the resilience as the temp. drops is greater the higher the proportion of contained ferrite. Austenite, containing enough nickel, does not show fragility at low temp. ; but pearlitic steels, containing nickel, are fragile in liquid air, but the nickel retards the lowering of the fragility with a decrease in temp. P. Dejean discussed the effect of compression on the resilience or elastic properties of steel. The effect of ageing on the tensile properties of mild steel was discussed by G. Masing and L. Koch, G. Tammann and V. Caglioti, G. Masing, R. S. Dean and co-workers, E. Heyn, and W. Köster—*vide infra*, the tensile strength of iron. L. B. Pfeil found that work-hardened metals are liable to increase in hardness as a result of ageing.

F. C. Thompson examined the effect of grain-size on the hardness of Swedish iron and found that the Brinell's hardness could be increased about 50 per cent. by grain refinement. H. Hanemann and R. Hinzmann found only slight differences in the hardness of steel with grain-sizes ranging from 90 to 20,000μ^2. A. Pomp's data for soft iron with 0·08 per cent. of carbon gave an increase of 15 per cent. with grain refinement. He observed that

Grains per sq. mm. .	68	827	1350	2310	3970
Brinell's hardness .	83	87	89	96	95

W. A. Wood also found that Brinell's hardness, H, increases as the grain-size, $G \times 10^{-6}$ cm. diameter decreases:

$G \times 10^6$.	28·9	8·3	3·9	3·0	2·6	1·9	1·5	1·1
H . .	290	300	313	326	333	361	404	495

A linear curve is obtained from the relation $H = kG^{-2}$, where k is constant; since G^2 is proportional to the surface area of the grain, S, then $H = k'A^{-1}$, where k' is constant. H. S. Rawdon and E. Jimeno-Gil decided that with iron containing 0·07 per cent. of carbon the grain-size has little influence on the hardness; but in general, fine-grained samples had the greater Brinell's hardness; whilst T. Ishigaki observed that with armco iron, the Brinell's hardness decreased as the size of grain increased. S. Shimura and H. Esser showed that with 0·6 to 1·75 per cent. carbon steels, the hardness decreased almost linearly with an increase in the time of annealing, or with an increase in the grain-size of the carbide. The final hardness of all the steels after a prolonged annealing was approximately the same, viz. 121 to 142 on Brinell's scale. The results with a 0·97 carbon steel are summarized in Fig. 195. L. B. Pfeil concluded that neither the grain-size nor, in the case of single crystals, the crystallographic face of the indented plane had any perceptible influence on its Brinell's hardness; although F. Osmond and G. Cartaud had previously reported that the octahedral face has a Brinell's hardness greater than is the case with the cubic-face, and the hardness of the (011)-face is intermediate between the two. H. O'Neil found that the Brinell's hardness of normalized armco iron is lowered considerably by annealing in vacuo; Brinell's hardness is also independent of the grain-size, and different faces of single crystals have the same hardness as aggregates, but the scratch-hardness in different directions on the crystal faces is different. The strain hardening of vacuum-hardened, decarburized iron, shown by the scratch-tests, indicated that the strain-hardening increased somewhat as the temp. is raised from $-185°$ to $+100°$; and similarly also for cold-rolled iron. The results from 100° to 130° are variable. There is a small increase in the scratch-hardness of ferrite at 120°; but the effect with single crystals is small although there are indications of an inflection between 110° and 125°. The subject was discussed by S. V. Belynsky.

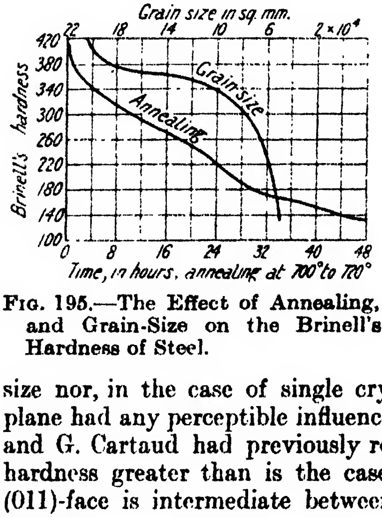


Fig. 195.—The Effect of Annealing, and Grain-Size on the Brinell's Hardness of Steel.

The hardness of cold-drawn steel and iron is greater than that of the annealed material, and the term "hard drawn" has long been applied to unannealed wire. P. Goerens found the Brinell's and the Shore's hardness of wrought iron with 0·11 per cent. of carbon to be:

Reduction area .	0	10·8	25·4	39·8	43·6	48·3 per cent.
Brinell's . .	118	157	176	181	189	201
Shore's . .	24	33	31	39	45	46

and of steel with 0·98 per cent. of carbon to be :

Reduction area .	0	9·1	14·2	22·6	28·3	32·8 per cent.
Brinell's . .	285	325	349	352	350	361
Shore's . .	59	60	56	62	53	52

T. Ishigaki measured the Rockwell hardness of steel before and after it had been subjected to cold-work by tensile straining, and found :

Carbon . .	0·1	0·3	0·3	0·7	0·9	1·1 per cent.
Before cold-work .	65·0	78·0	90·0	95·0	96·0	97·0
After cold-work .	73·2	93·1	95·6	101·5	109·2	106·7

Hence, the hardening effect increases as the proportion of carbon increases, and it attains a maximum with eutectoidal steel. The subject was discussed by W. P. Sykes and A. C. Ellsworth, and W. Broniewsky and J. Krol. M. Hanriot observed that metals are hardened by hydrostatic press., and T. Ishigaki obtained for armco iron, subjected to a compression of p kgrms. per sq. cm., the Rockwell hardness :

p . . .	0	2800	5200	7320	12,400	16,500
Hardness .	40·0	48·0	53·2	56·6	59·0	59·4

The change in the hardness produced by tempering is illustrated by Fig. 196. Assuming that the hardness produced by cold-working depends on internal stress, the latter cannot be increased beyond the yield-point, and consequently the hardness will attain asymptotically a certain maximum value. Thus, the hardness of iron increases rapidly at first, but then gradually tends towards an asymptotic value. The effect of tempering work-hardened armco iron, between 250° and 350°, is to increase slightly the hardness as shown in Fig. 196, and then to decrease somewhat rapidly towards about 470°. A slight hardening occurs in the range 470° to 570°, and the hardness then falls suddenly near 600°. The second hardness is attributed to the development of crystal nuclei occurring immediately before the re-crystallization of cold-worked metals sets in. The sudden softening about 600° is supposed to be due to the release of internal strains attending re-crystallization. The slight hardening of iron and steel between 250° and 350° is explained thus :

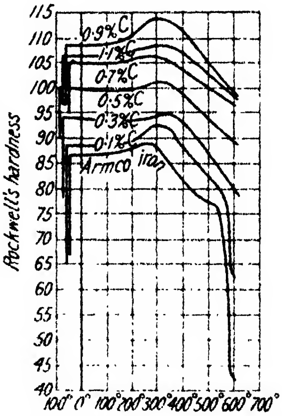


FIG. 196. — Hardness of Tempered Iron and Steel.

> In a severely cold-worked metal some internal strain remains after an applied stress has been released, and thus the metal is considerably hardened, that is, its resistance to slip is greatly increased by the cold-working; but at the same time, it is in a somewhat unstable condition. Consequently, by tempering between 250° and 350°, which results in a violent thermal motion of the atoms, some portions of the internal strain are released at the point of its greatest instability, most of the strain remaining unaffected. Thus the metal becomes a little stable, or becomes more resistant to slip ; that is, the hardness is increased by tempering. The slight hardening in a range between 250° and 350° is probably explained in the same way as above, the only difference being that in the present case, the release of the greatest instability takes place during the stretching at these high temp.

According to R. A. Hadfield, a specimen of steel with 0·045 per cent. carbon had a Brinell's hardness of 90 when tested at ordinary temp., but when tested at −182°, its hardness was 266, that is, about equal to that of a 0·8 carbon steel at normal temp. F. Robin found that the hardness curves of carbon steels show a minimum at about 100°, and a maximum at about 250° ; and that these points coincide with the minimum and maximum resistance to tensile stress. The maximum hardness is followed by a marked and regular fall only in the case of hard steels; with soft steels, there is a downward peak, and the hardness falls rapidly only at about 400° to 450°. Similar effects are encountered in connection with the tensile strength. The presence of phosphorus lowers the variations in the curve, for with 1 per cent. of that element, the curve is almost constant at 215° up to 400°, after which it falls to about 130° at 600°. Abrupt variations in hardness, resistance to tensile stress and crushing, occur only in the case of α-iron. Austenitic steels, with α-iron, give regular and continuous curves like copper and nickel. Observations were made by J. Vietorisz, G. Delbart, F. C. Lea, O. W. McMullen, A. R. Page, H. E. Publow, and H. J. Tapsell and W. J. Clenshaw. The *red hardness* or *hot hardness* of alloy steels was studied by E. G. Herbert, and F. Sauerwald and co-workers.

According to H. M. Howe, M. Rudeloff, and C. Bach, the resistance of cast iron to tensile stresses does not alter up to 300°, but from 300° to 400°, the resistance decreases; and A. Kürth showed that the hardness diminishes slowly with a rise of temp., then rises a little between 200° and 300°, and ultimately falls rapidly above 300°. The tenacity of hard cast iron falls suddenly above 400°, while that of annealed castings falls slowly. F. Robin made observations on cast irons. W. Melle, J. B. Kommers, R. Hugues, P. Goerens and H. Jungbluth, etc., discussed the hardness of cast iron; and H. A. Schwartz, that of malleable iron.

K. Ito found Brinell's hardness, H, of cast iron at different temp. to be:

	−40°	−24°	0°	16°	35°	56°	75°	115°	130°	150°
H . .	159·5	158·0	154·6	150·6	148·2	146·1	146·1	142·2	142·2	139·2

and he represented the relation between hardness and temp., θ, by $\log H_2 - \log H = \alpha(\theta_2 - \theta_1)$, where $\alpha = 0{\cdot}00030$ is the inclination of the straight line, the temp. coeff. of Brinell's hardness. For rolled steel with 0·1 per cent. of carbon:

	−43°	−21°	0°	20°	40°	55°	75°	115°	130°	148°
H . .	114·5	113·2	113·2	111·8	109·2	109·2	108·4	107·2	104·6	104·6

where $\log H_2 - \log H_1 = 0{\cdot}00020(\theta_2 - \theta_1)$. For rolled steel with 0·7 per cent. of carbon:

	−40°	−21°	0°	10°	40°	55°	75°	115°	129°	145°
H . .	239·0	237·2	229·9	225·8	223·7	223·7	221·8	217·8	216·2	212·6

where $\log H_2 - \log H_1 = 0{\cdot}00025(\theta_2 - \theta_1)$. For rolled steel with 1·5 per cent. of carbon:

	−42°	−26°	1°	16°	35°	55°	75°	95°	115°	147°
H . .	302·0	293·5	285·8	283·0	274·4	274·4	267·4	261·8	259·8	255·5

where $\log H_2 - \log H_1 = 0{\cdot}00040(\theta_2 - \theta_1)$. The hardness thus increases considerably with a fall of temp. The hardness and temp. coeff. of rolled steel are greater than with cast specimens. The relation between the coeff. of hardness, α, and the m.p. T_m, on the absolute scale, of a number of metals can be represented by $T(\alpha + 0{\cdot}000145) = 2{\cdot}5$. This is similar to A. Mallock's relation between the temp. coeff. of Young's modulus, and C. Schaefer's relation for the temp. coeff. of the torsion modulus. G. Mahoux studied the effect of electromagnetic waves on the hardness of steel.

F. Robin compared the **abrasive hardness**, or abrasive wear of steels by rubbing the metal against abrasive paper, at a given speed, under a definite pressure, for a given time, and finding the loss in weight. He observed that carbon steels do not wear inversely proportionally to their percentage of carbon. They show a minimum of resistance to wear on emery-paper at about 0·4 per cent. of carbon. Purified and fine-grained metals offer most resistance. Phosphorus greatly increases the resistance to wear. Small quantities of manganese and silicon diminish the resistance to wear in the case of carbon steels, which is the opposite to what is found in regard to lubricated wear on a polished surface. Cast iron is more resistant to wear if it contains phosphorus or is composed largely of cementite. Its wear on abrasive paper reveals the peculiarity of being very high to commence with and subsequently falling to a very low value. Basic pig-iron and chilled castings offer the highest amount of resistance, although this does not apply to their penetrative hardness. Quenched and annealed steels (martensite, osmondite, and sorbite) possess a very high degree of resistance to wear in the vicinity of the eutectoid. This resistance does not increase with higher percentages of carbon. Austentite is specially resistant to wear. With a relatively low penetration hardness, the wear is comparatively inconsiderable. The austenitic alloy steels especially reveal this property. Steels containing nickel and manganese in high percentages are exceedingly resistant. Manganese steel offers a high degree of resistance which varies with the speed and with the pressure of the test. Pearlitic chromium steels similarly wear but little, particularly in the case of annealed steels. Annealed steels containing a double carbide wear with the greatest ease, and pearlitic steels containing tungsten and molybdenum show the same property. Vanadium considerably improves the resistance of steels to wear with emery-paper.

The subject was discussed by C. B. Dudley, J. E. Howard, S. J. Rosenberg, and A. Stadeler. The abrasive hardness was discussed by A. L. Boegehold, A. M. Cox, L. Guillet, G. A. Hankins, K. Honda and R. Yamada, L. Jannin, H. M. Kerscht, T. Klingenstein, G. L. Norris, W. H. Phillips, F. Robin, S. J. Rosenberg, S. Saito, E. H. Saniter, and M. Suzuki; and the endurance of rail steels, etc., in service, and the wearing qualities of iron and steel, by J. M. Blake, J. A. Brinell, A. Capron, N. N. Davidenkoff, T. G. Digges, A. Dormus, J. R. Freeman and co-workers, C. Frémont, H. J. French, H. J. French and H. K. Herschman, H. Friedrich, M. Füchsel, A. Hasch, F. Heimes and E. Piwowarsky, F. P. Hitchcock, L. Jannin, L. Jordan, J. F. Kayser, R. Kühnel, O. H. Lehmann, L. Lubimoff, P. Lucchini and M. Ros, M. Marqueyrol and M. Merklen, P. Mast, H. Meyer and F. Nehl, F. K. Neath, W. H. Parker, E. Piwowarsky, G. Ranque, C. O. Reid, S. J. Rosenberg and co-workers, J. Seigle, R. Spazier, M. Spindel, A. Stadeler, H. W. Swift, L. Thibaudier and H. Viteaux, A. A. Timmins, and A. K. Zaitzeff. M. Fink discussed the wear of steel rails as a result of oxidation associated with sliding friction. J. O. Arnold, E. G. Coker and K. C. Chakko, R. E. Crompton, C. Frémont, H. J. French and T. G. Digges, H. Friedrich, E. G. Herbert, K. Honda and K. Takahasi, J. E. Hurst, A. J. Langhammer, W. J. Merten, M. Okochi and M. Okoshi, W. H. Phillips, R. Poliakoff, H. Pommerenke and R. Dewert, W. Ripper and G. W. Bailey, W. Rosenhain and A. C. Sturney, H. D. Smith and I. Hey, T. E. Stanton, T. E. Stanton and R. G. C. Batson, T. G. Digges, and P. V. Vernon discussed the cutting properties of tool steels, and the cube law of cutting speed as used to develop the heat theory of durability; and A. Kessner, the drilling test.

I. Traube [5] represented the **internal pressure** of solid iron by 239,000 megabars. F. C. Thompson gave 323,900 for annealed, normalized, and quenched and tempered iron. R. von Dallwitz-Wegner calculated 336,837 atm. for the internal press. of wrought iron. S. Sekito calculated 192 kgrms. per sq. mm. for the value of the internal stress, and this is the same order of magnitude as the tensile strength. T. W. Richards gave 587 kilomegabars. Observations on the subject were made by J. H. Hildebrand and co-workers—*vide supra*, for internal strains and stresses. R. F. Mehl gave 587 kilomegabars for the internal press. and for the maximum disruptive internal press. 1884 kgrms. per sq. mm. R. von Dallwitz-Wegner gave 336,837 atm. for the internal cohesion at 0°, and 309,881 atm. at 100°.

G. Quincke gave 949·7 to 997 dynes per cm. for the **surface tension** of molten iron, and 25·8 to 27·1 sq. mm. for a^2, the **specific cohesion.** F. C. Thompson gave 1350 dynes per cm. for the surface tension between tempered iron and cementite. W. Krause and F. Sauerwald measured the surface tension and sp. cohesion of grey cast iron :

C : Mn : Si : P	.	1225°	1250°	1300°	1350°	
3·32 : 0·56 : 2·76 : 0·49	a .	826	846	880	926	$da/d\theta=0{\cdot}80$
	a^2.	12·01	12·37	13·09	13·84	
		1150°	1200°	1250°	1310°	
3·52 : 2·1 : 0·36 : 1·6	a .	1054	1071	1088	1108	$da/d\theta=0{\cdot}34$
	a^2.	14·6	15·17	15·68	16·39	
		1245°	1300°	1350°	—	
1·4 : 0·29 : 1·27 : 7·44	a .	957	1013	1065	—	$da/d\theta=1{\cdot}04$
	a^2.	13·79	14·92	16·02	—	

G. Drath and F. Sauerwald obtained for cast iron at 1267°, 1277°, 1310°, and 1318°, respectively, the surface tensions $\sigma=936$, 938, 917, and 914 dynes per cm., and the sp. gr. 6·81, 6·80, 6·75, and 6·74. The surface-tension forces between the crystal grains of a metal were discussed by G. T. Beilby, F. L. Brady, M. Brillouin, P. Curie, C. H. Desch, G. Quincke, G. Tammann, and F. C. Thompson; and F. C. Thompson attempted to correlate these forces with other properties of the metals, particularly the elastic limit. M. Born and O. F. Bollnow estimated the cohesive force of the atoms on the lattice to be $6{\cdot}25\times10^{11}$ dynes per sq. cm. W. B. Hardy discussed the range of cohesion at the surface of iron and steel. F. Sauerwald and E. Jänichen found that the force of adhesion of compressed iron powder increased with temp., but at high temp. a decrease occurs owing to crystallization. The tensile strength depends on the degree of compression and the grain-size of the powder. The **diffusion** of the different elements in iron is discussed in connection with alloys of the respective elements and iron, and in connection with cementation; M. Ballay studied the Ludwig-Soret phenomenon in liquid and solid alloys.

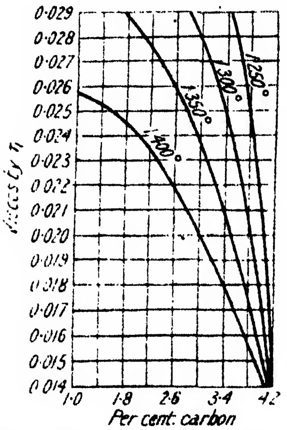


Fig. 197.—The Viscosity of Cast Irons with Different Proportions of Carbon.

K. Honda and S. Konno found the coeff. of normal **viscosity**, at 20°, of steel with

Carbon		0·18	0·38	0·67	1·17	1·75 per cent.
$\eta\times10^{-8}$	Not annealed	4·94	5·12	5·93	5·06	7·20
	Annealed at 850°	2·68	3·51	4·30	4·27	—

and K. Iokibe and S. Sakai gave for iron, and iron-carbon alloys:

Carbon	—	0·55	0·90	1·30 per cent.
$\eta\times10^{-8}$	12·89	12·90	7·70	9·82

Observations were also made by O. Boudouard, P. Chevenard, N. N. Feigin, O. Holz, J. E. Hurst, C. Johns, J. J. Porter, M. Riddell, D. Saito and K. Hayashi, and A. Wimmer; while H. Thielmann and A. Wimmer measured the influence of temp. on the viscosity of cast iron, Fig. 197. B. Gutenberg and H. Schlechtweg gave $1{\cdot}4\times10^{8}$ c.g.s. units for the inner friction of iron. Taking the fluidity of aluminium at about 800° as unity, D. Saito and K. Hayashi said that the fluidity of crucible steel at about 1600° is 46. G. Subrahmaniam gave 14×10^{8} for iron, and K. Iokibe and S. Sakai, 13×10^{8}—*vide infra*, plastic flow. A. L. Kimball and D. E. Lovell gave $4{\cdot}16\times10^{15}$ c.g.s. units for the internal friction of annealed Swedish iron, and $2{\cdot}33\times10^{15}$ c.g.s. units for cold-rolled mild steel.

The **internal or molecular friction** of a solid is measured in terms of the diminution in amplitude, or rather the logarithmic decrement of the amplitude, calculated for conditions where the friction of air is eliminated, when a metal wire, suitably loaded and supported is set in torsional oscillation, when the amplitudes of the vibration decrease more or less gradually until finally rest ensues. With small deformations, H. Tomlinson observed that the logarithmic decrement is independent of the amplitude, and independent of the vibration of the period when the wire has been allowed to rest for a considerable time after any change has been made in the arrangements, and when a large number of oscillations have been executed previous to the testing. H. Tomlinson said that the internal friction cannot resemble fluid friction because, for such velocities as are here employed, the internal friction of fluids is proportional to the velocity, nor can it resemble the extent friction of solids because the latter is not nearly so independent of the velocity as is the internal friction, nor would the logarithmic decrement be independent of the amplitude. The term viscosity applied by W. Thomson (Lord Kelvin) to what is here called internal friction is rather metaphorical. It is true that a substance which is infinitely viscous is a solid, for the component parts are held so tenaciously as to prevent permanent deformation; but, as emphasized by C. Barus, the impression conveyed in speaking of a very "viscous body" and of a "solid body" are very different. The conception of the viscosity of liquids, as well as the hypothetical proportionality between frictional resistance and velocity, was introduced by Isaac Newton in his *Philosophiæ naturalus principia mathematica* (London, 2. 9, 1687). He said: *resistentia quæ oritur ex defectu lubricitatis.* The theory of the "viscosity" of solids was discussed by F. Auerbach, W. Hallock, A. L. Kimball and D. E. Lovell, E. M. Horsburgh, R. H. Canfield, F. Braun, E. Cohn, J. A. Ewing, J. Hopkinson, F. Kohlrausch, F. Neesen, M. Brillouin, W. Thomson (Lord Kelvin), E. Warburg, W. Weber, R. Clausius, O. E. Meyer, J. C. Maxwell, L. Boltzmann, T. Nissen, E. Butcher, and J. Pernet.

C. Barus found that the viscosity of solid steel decreases as the hardness of the metal increases; or the internal or molecular friction of steel is greater in proportion as the metal is softer, and he said, in illustration, that as regards hardness and viscosity, hard steel may be compared with sealing-wax, and soft steel with tallow. C. Barus said that the relationship between viscosity and hardness is as follows:

> Suppose a stress to be so distributed in a solid that its application at any interface is nowhere sufficient to produce rupture. Then that property of a solid in virtue of which it resists very small forces (zero-forces) acting through very great intervals of time (∞-times) may be termed the viscosity of the solid. That property in virtue of which it resists the action of very large forces (∞-forces relatively) acting through zero-time may be termed the hardness of the solid. Since the application of forces in such a way as accurately to meet either of these cases is rare, we have in most practical instances mixtures of viscous resistance and hardness to encounter. We may reasonably conceive that in the case of viscous motion the molecules slide into each other or even partially through each other by interchange of atoms, so that the molecular configuration is being continually reconstructed; that in the other case (hardness) the molecules are urged over and across each other and that therefore the intensity of cohesion is in this case more or less thoroughly impaired. In most cases of scratching, the action is indeed accompanied by physical discontinuity of the parts tangentially strained. The interpenetration of the molecules of a viscous substance is necessarily favoured by temperature.

C. E. Guye and E. Mintz found that the internal friction of steel increases up to about 100°, then falls, and passes through a minimum value at about 200°, it then increases very rapidly. The changes are reversible because they can be observed on a rising or on a falling temp. The influence of temp. on the viscosity is diminished by previous annealing, and it increases when the load on the vibrating wires is increased. H. Tomlinson observed two critical points in the internal friction one about 550°, and one about 100°. M. Ishimoto found in the internal friction curves a minimum near 65° on both the heating and cooling curves; there was a maximum at 183° on the heating curve, and one at 173° on the cooling curve. There is a bend in the curve at 260°, and anomalous changes cease up to 500°. H. Tomlinson found the logarithmic (base 10) decrement of a torsionally oscillating hard-drawn wire to be 0·001214, and of an annealed wire, 0·000914. Observations were made by G. Subrahmaniam, A. G. Hill, P. Oberhoffer and A. Wimmer; and K. Iokibe and S. Sakai—*vide infra*—noted the change in the logarithmic decrement produced by heat-treatment.

The viscosity of steel varies with the character and amount of twist it has received. Fig. 198, by C. Barus, represents the angular distortion in radius as a function of the time in hours when wires of all degrees of hardness are exposed to temp., θ, of 100°, 190°, and 300°, respectively. The annealing temp. is indicated in brackets. Curves are included for the angular distortion for 100° when the rate of twist, $\tau=3°$; and likewise for a rate of twist $\tau=6°$ when the values for the angular distortion have been divided by 2. For $\theta=190°$, values are given for both $\tau=3°$ and $\tau=6°$. Each curve consists of two parts, an anterior ascending branch showing the motion at the high temp. θ, and a descending branch showing the elastic effect of cooling from θ to the temp. of the room. The results show that the viscous deformation is much more influenced by temp. when the steel is hard than when it is soft; that is, the viscosity decreases with temp.—*cæteris paribus*—at greater rates in hard steel than with soft steel. At the same temp. θ, the differences in viscosity are very large when the temper lies between glass-hard and annealed at 350°; intermediate differences within this interval are larger in proportion as the hardness is greater. When the temper lies between annealed at 350° and soft, differences of viscosity at the same temp. are relatively small. Consequently, the variations in viscosity due to temper are very pronounced during the first stage of annealing, and nearly vanish during the second stage. The effect of tempering on the viscosity is thus analogous to its effect on the electrical resistance, and the thermoelectric force.

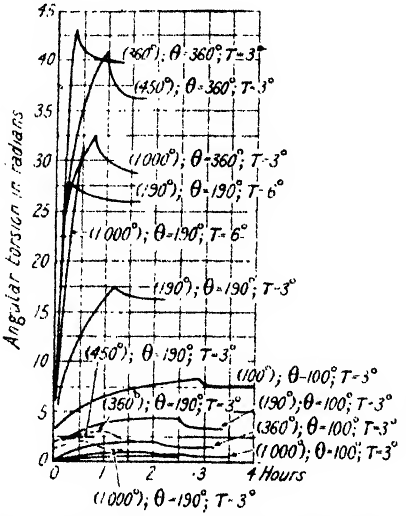


FIG. 198.—Viscous Deformation Increasing with Time for Different States of Temper and Temperature.

For the same degree of hardness, the viscosity increases at an accelerated rate with temp. In Fig. 198, for $\theta=100°$, the large viscous interval between the results of the metal annealed at 100° and at 360° is in striking contrast with the smaller viscous interval for metal annealed at 360° and at 1000°; for $\theta=190°$, the interval between the results with metal annealed at 190° and at 360° is greatly increased, but the increase is not so great for the interval between the metal annealed at 360° and at 1000°; and for $\theta=360°$, the interval in the second phase of annealing—360° to 1000°—is largely increased. Hence, steel wire annealed from hardness at $\theta°$ has a marked tendency to suffer viscous deformation at $\theta°$; and this tendency decreases with great rapidity in proportion as the temp. of exposure falls below $\theta°$.

C. Barus added that since at a depth of 10 miles below the surface of the earth the temp. is at least as high as 450°, it follows that if the earth were made of steel, in the state of maximum viscosity, the rigidity 10 miles below the surface would be *nil*, so far at least as the action of a continuous shearing press. is concerned.

The viscous deformation of steel increases much more rapidly than the rate of twist, and it is as much as 3 in the case of steel annealed at 190°, and more than 10 in the case of steel annealed at 1000°. It is therefore probable that the viscous relations of soft steel to hard steel vary enormously, and even change sign as the stress producing viscous motion passes from high to low values. For rates of twist less than 3°, steel is less viscous, and the viscosity is more susceptible to the influence of temp. in proportion as it is harder; and for rates of twist exceeding 6°, steel is less viscous and more susceptible to the influence of temp. in proportion as it is softer.

The effect of strains of whatever kind applied in sufficient intensity to homogeneous soft steel results in a marked decrease in the viscosity of the originally soft metal. The diminution increases with the intensity of the strain. The viscous effect of a tensile strain applied in any degree to the same originally soft metal is, after straining, almost *nil* in comparison. F. Kohlrausch, F. Streintz, and H. Tomlinson have studied these phenomena. C. Barus measured the time-variation of viscous deformation in the case of soft steel transformed by temper, drawing strain, traction, and torsion, with intense and moderate values of stress. In all cases, a given loss of viscosity is attended by a simultaneous increase in hardness.

Repeated torsional oscillation was shown by G. Wiedemann, and Lord Kelvin to reduce the internal friction, and they found that a large influence is exerted by a long rest, either with or without oscillation, and that a considerable diminution, both temporary and permanent, can be produced by raising the temp. of the wire to 100°. Thus, according to H. Tomlinson, a well-annealed iron wire, when tested 10 min. after suspension, had a logarithmic decrement, due to internal friction, of 0·003011, after an hour, 0·001195, and after a day, 0·001078. After the last period, the friction became sensibly constant, and remained the same after 4 days, so that the wire had accommodated itself to the conditions. F. Streintz, G. Wiedemann, and F. Kohlrausch called the period during which the diminution occurs, *the period of accommodation.* H. Tomlinson added that the reduction of the internal friction by oscillation and rest had not reached a minimum, because, on repeatedly heating the wire to 100°, and allowing it to cool, the logarithmic decrement rapidly diminished, until, after 6 days, on each of which the wire was heated to 100° and allowed to cool slowly, it became 0·000412 when further repetition of the process no longer affected the friction sensibly. The greater part of the diminution occurred after the first heating and cooling, but several repetitions were needed to produce the minimum. A temporary rise of temp. not exceeding 100° had a marked effect on the internal friction: for instance, the logarithmic decrement at 0° was 0·000412 and about one-fourth this value or 0·000112 at 98°. At this temp., the internal friction was a minimum, because with a further rise of temp., the logarithmic decrement increased. The internal friction in iron at 98° is thus very small, and this is shown by the fact that only about 3000 vibrations are required before the amplitude is reduced to one-half of its initial value by internal friction. Consequently, if a wire and its appendages be made to vibrate in vacuo, and the temp. be kept constantly at 98°, with a vibration period of 10 secs., more than 8 hrs. would elapse before an initial amplitude of 100 would be reduced to 50. The internal friction under these conditions is only one-thirtieth of its original amount. When the wire is fully accommodated, a small change in the conditions will produce a disturbance; thus, a mechanical shock, a change of load, a slight rise of temp., or a rotation of the molecules by magnetic stress, will require fresh oscillations to be made before the friction reaches its minimum. The time taken by a wire to re-accommodate itself when the accommodation has been disturbed by a change of temp. depends considerably on the direction of the change. Thus, if a wire be re-heated from room temp. to 100°, re-accommodation is effected in a much shorter time than when the accommodation has been disturbed by lowering the temp. from 100° to room temp.

O. E. Meyer referred viscosity to partial molecular rotation, and this view was adopted by F. Kohlrausch. These rotations are similar to those postulated by R. Clausius in developing a theory of shear. L. Boltzmann assumed that the elastic forces are dependent on the present and preceding deformations of the body. The effect of the earlier states of stress on the existing stress diminishes with intervening time, but is independent of intervening states of stress. Different viscous deformations are superposable. T. Nissen modified L. Boltzmann's theory to suit the atomic theory, and he distinguished forces producing and retarding motion, and the purely elastic forces which obtain when viscous motion has subsided. F. Braun concluded that elastic and viscous deformations are the result of the action of forces of different origin, and he refers viscous motion to the partial rotations postulated by W. Weber, and F. Kohlrausch. E. Warburg referred viscosity to the partial rotations of molecules of a form other than spherical. T. Nissen based a theory on the conditions under which æther enters the intermolecular spaces when a body is deformed by stress.

C. Barus employed J. C. Maxwell's theory in which the effect of twisting is to be referred to the motion of molecules which accompanies it. The molecules, together with their component atoms, are thus placed in new relative positions; therefore unstable configurations during the course of such motion are continually broken up into configurations of smaller potential energy and greater stability. Hence, finally, the observed decrease of viscosity. By reversing the sign of the twist the original configurations can be only partially restored, even for small permanent set, such as is here in question; and the effect of prolonged and repeated twisting is stiffness and constant viscosity, because all the molecules have collapsed into configurations of minimum stability, and the intrinsic molecular energy is the potential minimum compatible with the given conditions. Again, the molecular condition of iron at its recalescence temp. may be regarded as almost chaotic; the number of configurations made unstable because they are built up of disintegrating molecules is therefore a maximum, so that the viscosity will here be a maximum. C. Barus regarded glass-hard steel as a stage of temper which is undergoing incipient annealing at ordinary temp. Annealing is attended by chemical decomposition of the carbides, so that the molecular configuration of glass-hard steel is in a state of incipient change, and it contains more unstable configurations than steel in other states of temper. Hence, on J. C. Maxwell's theory, glass-hard steel, despite its extreme hardness, is the least viscous of the whole group of tempered and soft steels. According to C. Barus, viscosity and hardness can be clearly distinguished as follows:

> Imagine a round harder body sliding tangentially along the plane of a softer body without rotation. Let there be sufficient pressure on the round body normal to the plane of the softer body to insure cohesion at the point of contact. Then the softer body is subjected to a *simple shear* along the line of scratching. If the motion is sufficiently slow, the soft body may yield viscously and there will be no scratching. If the motion is sufficiently fast, the soft body will generally be scratched. Hence hardness and viscosity are each resistances against simple shearing, according as the tangential motion of the hard body is sufficiently rapid or sufficiently slow, respectively. The conditions for the occurrence of quiescent friction may therefore be stated thus: if there is sufficient time given for the molecules of two bodies to react on each other at the point of contact, the friction is quiescent. If the time be insufficient, friction is kinetic.

H. Tomlinson considers that both the temporary and permanent alterations of the internal friction of iron produced by raising the temp. not above 100°, are partly due to mere agitation of the molecules, but the permanent effects are probably not wholly an effect of molecular agitation because maintaining the temp. at 100° for some time does not bring down the friction anything like so much as repeated heating and cooling. The slow shifting backwards and forwards of the molecules induced by repeated heating and cooling, is, in a great measure, responsible for the permanent decrease of the internal friction. Similarly, the shifting backwards and forwards of the molecules caused by torsional oscillation produces a permanent diminution—*vide infra* for the effect of magnetization on viscosity. A. Guillet, and H. le Chatelier discussed the effect of the physical properties of iron on the damping down of the oscillations of a bar.

The **plastic flow** or **plasticity** of metals was discussed by E. N. da C. Andrade,[6] R. Becker, R. H. Canfield, H. and F. le Chatelier, J. Dejmek, J. H. S. Dickenson, R. Eisenschitz and co-workers, W. Fahrenhorst and E. Schmid, J. E. Fletcher, H. J. French, H. J. French and W. A. Tucker, N. P. Goss, J. N. Greenwood, B. P. Haigh, H. Hencky, E. Heyn, H. Hoff and G. Sobbe, E. M. Horsburgh, H. M. Howe and A. G. Levy, Z. Jeffries, Z. Jeffries and R. S. Archer, E. Kieft, F. Körber and co-workers, W. Kuntze, C. E. Larard, W. Lode, P. Longmuir, H. V. Loss, P. Ludwik, O. Manfred, H. Meyer and F. Nehl, H. F. Moore, A. Nadai, A. Nadai and co-workers, E. B. Norris, J. T. Norton and B. E. Warren, J. Orland, J. Puppe, R. L. Peek and D. A. McLean, L. B. Pfeil, W. Prager, H. Preussler, C. Ranque and P. Henry, M. Ros and A. Eichinger, W. Rosenhain and J. McMinn, G. Sachs, F. Sauerwald, F. Sauerwald and co-workers, F. Schleicher, E. Schmid and co-workers, A. Schob, J. Seigle, H. Shoji, E. Siebel and co-workers, F. T. Sisco, W. Tafel, G. I. Taylor and H. Quinney, F. C. Thompson and W. E. W. Millington, P. A. Welikhoff and N. P. Stchapoff, W. M. Wilson, and J. K. Wood. According to H. Shoji, if P denotes the plasticity of a metal, and dv/dw the final velocity per unit length caused by a load w_0 exceeding the elastic limit, then $P=(1/w_0)(dv/dw)$. The laws of flow were discussed by H. Meyer and F. Nehl, and E. N. da C. Andrade; and by W. Rosenhain, the behaviour of crystals under plastic deformation—*vide supra*, slip-bands. The effect of plastic deformation on the crystal structure was discussed in connection with the X-radiograms, and with slip-bands. A. Robertson and G. Cook studied the transition from the elastic to the plastic state. If the applied stress exceeds the elastic limit, the metal begins to flow perceptibly; and the rate of this flow expressed as a percentage elongation represents the ductility of the metal. The definitions were discussed by A. E. H. Love, and W. C. Unwin; H. Shoji said: "Suppose a metal be loaded by a constant weight so slightly beyond its elastic limit that the cross-section of the metal is not altered by the tension. Let V be the velocity of the elongation per unit length, w_0 the intensity of the stress corresponding to the elastic limit, when $V=0$, and w the intensity of the applied stress diminished by w_0; then the plasticity P can be defined by the equation $P=(1/w_0)(dV/dw)$." The theory of the subject was discussed by K. Bennewitz, A. E. H. Love, L. Boltzmann, A. A. Michelson, H. V. Wartenberg, G. Masing, H. Lorentz, R. Becker, V. Volterra, and H. Shoji. P. Kreuzpointer found that steel with granular structure flows less readily than steel with a "mushy" structure although both may have the same tensile strength and percentage elongation. He devised an arrangement which rang a bell when a test-piece was pulled by the hands showing that a force so slight suffices to cause an elongation of the test-piece. A. le Chatelier found that a metal may be broken by a tensile stress above a certain temp., with loads that produce permanent elongation. With a constant temp., the deformation under a given load has a decreasing value tending towards equilibrium; the deformation increases more rapidly than the loads, whilst the stress increases and the strain decreases with the speed of loading; deformation under shock is inversely proportional to the shock; under an increase in temp., the deformation increases, and the resistance decreases. Cast iron at 15° can support the following loads in tons per sq. in. for the time stated in the number of minutes without breaking:

Time .	0·5	1·0	5·0	15	60 mins.
Load .	25·21	24·63	23·87	23·49	22·86 tons per sq. in.

According to J. Cournot and K. Sasagawa, the time-elongation curves of metals at 600° show that the following increases in load were needed to pass from the viscosity limit to a rate of flow eq. to 16×10^{-4} mm. per hour with wires 100 mm. long: mild steel, 4·2 to 5·2 kgrms. per sq. mm.; semi-mild steel, 4·3 to 5·6 kgrms. per sq. mm.; high-speed steel, 14·0 to 19·0 kgrms. per sq. cm.; nickel-chromium alloy, 32·0 to 36·0 kgrms. per sq. mm.; and silicon-chromium steel, 30·0 to 35·5 kgrms. per sq. mm. J. J. Kanter and L. W. Spring found that steels which have undergone small amounts of flow do not seem to have deteriorated, the tensile properties, including elongation and reduction of area, remaining approximately what they were before the flow tests. Since little or no deterioration occurs or should be expected (unless through oxidation), and since with ductile metals at temp. above 315°, 10 per cent. or more of flow or elongation are necessary before the material starts out on its final stretching preceding rupture. Any slight flow or deformation brought about by stresses below the proportional limit are not seriously objectionable unless the distortion interferes with service. Carbon increases the resistance to flow. At low temp. where grain-size is a prime factor governing the strength, carbon increases the strength by refining the grain; at low temp., deformation is accompanied by great strain hardening, and continuous flow sufficient to rupture is observed only at loads approaching the tensile strength. At temp. above 425°, the grain-size is still small, but the grains themselves are not so brittle as at strain-hardening temp.; they are plastic enough to change their form under stress without splitting, and without forming slip-bands. In this plastic state, strength by mere virtue of number or multiplicity of grain does not obtain. The subject was studied by C. L. Clark and A. E. White, and J. L. Cox.

L. Klein discussed the **friction** between wood and iron; P. E. Shaw and

E. W. L. Leavey, and B. S. Hedrick, the friction of iron in vacuo against iron, nickel, aluminium, silver, and copper; J. S. Rankin, the friction of iron against glass, and brass; G. A. Tomlinson, the friction of copper, aluminium, iron, nickel, and glass; and O. H. Lehmann, the friction of ordinary cast iron against steel and against hard and soft cast iron. J. S. Stevens discussed the molecular contact during friction of one surface on another. F. Sauerwald and E. Jänichen studied the cohesion of the compressed powder.

A. Masson [7] observed the **velocity of sound** in iron to be 5015·9 to 4940·2 metres per sec.; A. Kundt, 5092·9 metres per sec.; and G. Wertheim gave 5123·8 metres per sec. between 15° and 20°, for iron wire, 4912·9 metres per sec. between 10° and 20°; for soft steel, 4982·0 metres per sec. between 15° and 20°; and for the same steel tempered blue, 4880·4 metres per sec. at 10°. G. Chrystal, and F. Robin noticed discontinuities at 120° and 250°; and G. Wertheim at 100°. G. Wertheim inferred that the velocity of sound in iron and steel is increased by a rise of temp. not exceeding 100° because of the increase in the longitudindal elasticity. He found that the percentage *increase* in longitudinal elasticity between 15° and 100° is 4·90 for annealed iron, 6·91 for annealed iron wire, 2·79 for annealed cast steel, 23·20 for annealed steel wire, and 5·18 for steel tempered blue. H. Tomlinson, however, found that both the torsional and longitudinal elasticities of iron and steel are *decreased* by about 2·5 per cent. when the temp. is raised from 0° to 100°. True, the longitudinal elasticity may be greater at 100° than it is at 0° provided a start be made from 0° and the wire has not been previously heated to 100°, but the apparent temporary increase is really a permanent one, and if the wire be repeatedly heated to 100° and then cooled, the elasticity is less at the higher temp. if sufficient rest after cooling has been allowed. The pitch of the musical note produced by a steel wire or steel tuning-fork is lower as the temp. is raised, and this more than corresponds with the mere change in dimensions. G. Tammann and co-workers studied the formation of Chladni's figures.

F. Robin examined the **acoustic properties** of iron. When the dry metal is heated, the duration of the sound diminishes slowly from, generally speaking, 10° to 20°, then more rapidly, and finally very rapidly, between 50° and 100°. At 90° the curve falls rapidly, and attains a minimum at about 120° to 130°, when the sound is hardly more than a confused murmur. On continuing the heating, the curve is seen to rise again, and the duration of the sound increases rapidly from 150° onwards to about 220° or 250°, where it reaches a maximum. From this point the duration increases very slowly until 325° to 350° is reached, when the fall becomes more rapid and the sound dies away finally at about 540°. It should be noted that on reaching red-heat, at about 500°, the bar still gives out a sound at least four times greater, generally speaking, than the sound given at 120°. The duration of the sound decreases very rapidly in steels, starting from normal temp., and attains a minimum at about 120°, which may be measured in the case of hypereutectoid steels. The peaking of the curve of resonance decreases, and the minimum rises with the percentage of carbon. It is less accentuated in proportion as white iron is approached. As may be seen on inspecting the curves of the duration of the sound, complete extinction of sound only occurs in the case of the annealed hypo-eutectoid between 100° and 140°. Grey irons no longer display sonorousness, and the phenomenon is no longer distinctly observable. The maximum resonance on heating is in the vicinity of 250°; it approaches 200° when the proportion of carbon increases; its distinctiveness and its absolute value increase with the amount of combined carbon contained in the metal. The resonance gradually diminishes and finally becomes extinguished at a little below nascent red-heat. Slag reduces and a little carbon favours resonance; sulphur diminishes the sonorous properties, but at ordinary temp. phosphorus has very little influence. For alloy steels, *q.v.*, J. A. Anderson found the velocity of sound in iron vapour to be between 990 and 1650 metres per second.

Innumerable tests have been made on the **mechanical properties** of iron and steels. A selection for some of the alloy steels is made in connection with the different alloys. For industrial purposes, in different parts of the world, probably thousands of samples are tested every day; and metals are manufactured to satisfy certain specified mechanical tests.

The *elastic limit* is the greatest load per unit of original cross-section which does not produce a permanent set; the *proportional limit* is the load per unit of original cross-section at which the deformations cease to be directly proportional to the loads; and the *yield-point* is the load per unit of original sectional area at which a marked increase in the deformation of the specimen occurs without increase of load—*cf.* **1.** 13, 17. The definitions were discussed by J. E. Howard,[8] and T. D. Lynch.

In 1809, L. B. G. de Morveau made some observations on the **tensile strength** of the metals, and found that the weight in kilograms which could be supported by an iron wire 2 mm. in diameter was 250; a copper wire, 137; a silver wire, 85; etc. G. Wertheim measured the tenacity of some metals, in kilograms per sq. mm., and found for iron, 50·3; copper, 31·6; silver, 16·4; etc. G. Wertheim said that the tensile strengths of the metals vary as their at. wts.—*vide supra*, hardness. There are many collections of data. The following is based on that of F. Auerbach. In illustration of the values given for the **elastic modulus** of iron, E, in kgrms. per sq. mm., N. Katzenelsohn gave for forged iron, 19,024; G. Wertheim, 20,869; G. Pisati and G. Saporito-Ricca, 21,450; M. Baumeister, 20,500; H. Tomlinson, 19,810; K. F. Slotte, 19,385; for annealed iron, G. Wertheim gave 20,794; for cast iron, P. A. Thomas gave 21,740; O. Wagner, 21,300; W. Pscheidl, 11,713; W. Voigt, 12,800; and A. Gray and co-workers, 15,750. Similarly, for forged steel, G. Wertheim gave 18,810; for annealed steel, 17,280; and for cast steel, 19,555. For cast steel, G. Pisati gave 18,490; W. Voigt, 20,400; E. H. Amagat, 20,395; O. Wagner, 20,560; and for mild steel, A. Gray and co-workers gave 21,700; and C. P. Weston, 19,380; for soft steel, 20,705; for medium steel, 20,910; and for hard steel, 20,600. A. L. Kimball and D. E. Lovell gave for the elastic modulus of annealed Swedish iron $18{\cdot}9\times10^{11}$ dynes per sq. cm., and for cold-rolled mild steel, 21×10^{11} dynes per sq. cm. H. Tomlinson gave for hard steel, $21{\cdot}360\times10^{6}$ and 1862×10^{6} grms. per sq. cm. for hard drawn, and 198×10^{6} grms. for annealed iron wire; and G. Angenheister, for hardened steel, 18,206; and for soft steel, 18,875; and G. F. C. Searle, 19,810—*vide supra*, Table XVI. As indicated below, the actual values for any particular samples must obviously depend on the composition of the metal, and on its previous history. W. Sutherland gave for the best representative values for iron, in kgrms. per sq. mm., 20,000, with the extremes 18,610 and 21,440. Observations on the elastic limit were made by C. H. Desch, J. Galibourg, E. Goens and E. Schmid, J. E. Howard, A. Jaquerod and H. Mägeli, P. Kreuzpointer, H. K. Landis, G. Lanza, P. F. Lee and H. A. Schade, P. le Rolland and P. Sorin, K. Prosad, C. A. P. Turner, and L. B. Turner. The results of D. K. Froman, for Young's modulus with small stresses, are summarized in Fig. 199. A. Mallock observed that there is a similar relation between the temp. coeff. of the modulus of elasticity and the m.p. as that which obtains between the temp. coeff. of the hardness and the m.p. L. C. Tyte discussed the deviations from Hooke's law.

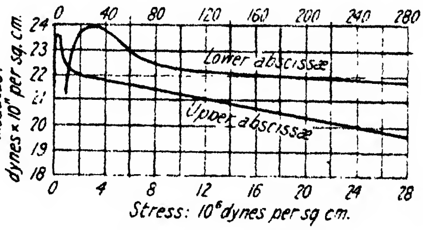


FIG. 199.—Young's Modulus with Small Stresses for Steel.

G. Wertheim gave for the elastic modulus of iron at 15°, 100°, and 200°, respectively 20,794, 21,877, and 17,700; and for that of cast steel, respectively 19,561, 19,014, and 17,926. N. Katzenelsohn found that with iron of elastic limit 19,024, the percentage decrease between 0° and 100° is 2·33. A. Wassmuth obtained a similar result. K. F. Slotte gave for the elastic limit of iron :

	8·4°	20·4°	30°	40°	50°	60°
E . .	19,687	19,385	19,226	19,137	19,037	19,004

A. Gray and co-workers gave $a = -0{\cdot}0_3136$ for the temp. coeff. of the elastic limit of iron. G. A. Shakespear obtained similar results, while M. C. Noyes obtained $0{\cdot}0_3460$ for steel; and G. Pisati obtained for iron, the following results for the elastic limit, E, and the temp. coeff., $a \times 10^5$:

	0°	20°	60°	100°	140°	180°	220°	260°	300°
E .	21,483	21,441	21,336	21,212	20,981	20,625	20,267	19,723	19,175
$a \times 10^5$.		10	12	27	34	41	47	60	69

and for steel :

	0°	20°	60°	100°	140°	180°	220°	260°	300°
E .	18,518	18,481	18,391	18,232	18,085	17,925	17,720	17,550	17,372
$a \times 10^5$.		10	13	26	18	24	28	25	26

K. Wimmer gave 7427 at 0°, 6298 at 100°, and computed 10,508 at −273°; and K. R. Koch and R. Dieterle, for steel with 0·0085 per cent. of carbon annealed at 620°, $1{\cdot}455 \times 10^{-6}$ kgrm. per sq. cm. at 12°; $1{\cdot}360 \times 10^{-6}$ at 200°; $1{\cdot}250 \times 10^{-6}$ at 400°; and $1{\cdot}0455 \times 10^{-6}$ at 600°; C. Schäfer gave $1{\cdot}835 \times 10^{-6}$ at 20°; and E. Grüneisen $2{\cdot}168 \times 10^{-6}$ at 18° for 0·1 per cent. carbon steel, and $2{\cdot}132 \times 10^{-6}$ at 18° for 1·0 per cent. carbon steel. J. R. Benton found the ratio of the elastic limit at −186° and at ordinary temp. to be 1·180; and C. Schäfer found a 0·02250 increase in the elastic limit per degree between 20° and −186°. K. Honda and T. Terada found that the coeff. of elasticity, E, of Swedish iron rose from $1{\cdot}802 \times 10^{12}$ with a load of 1689 grms. per sq. mm. to $1{\cdot}968 \times 10^{12}$ with a load of 11,700 grms. per sq. mm. H. Schlechtweg, and G. H. Kuelegan and M. R. Houseman studied the subject. W. Sutherland said that if E denotes Young's modulus at $\theta°$, and E_0 its value at the absolute zero, then, if θ_m denotes the m.p. of the metal, $E/E_0 = 1 - 0{\cdot}823\theta/\theta_m$, for temp. up to about 102°, but it is imperfect at the m.p., since it gives finite values at that temp., whereas the value ought to be zero. A. Gray and co-workers found for Young's modulus of mild steel $2{\cdot}1279 \times 10^{12}$ dynes per sq. cm., at 20·3°, and $2{\cdot}0939 \times 10^{12}$ at 80·3°—a diminution of 0·000247 per degree; for soft iron they gave $1{\cdot}5521 \times 10^{12}$ at 16° to 22°, and $1{\cdot}5321 \times 10^{12}$ at 94° to 96°—a diminution of about 0·000156 per degree. E. P. Harrison and S. K. Chakravarti observed that the elastic modulus does not reach a maximum as the temp. rises, but decreases continuously so that between 27° and 140° for annealed wires, $E = E_0\{1 - 0{\cdot}000934(\theta - 30) - 0{\cdot}0_6733(\theta - 30)^2\}$, when E_{30} is $18{\cdot}95 \times 10^{11}$ dynes per sq. cm. H. L. Dodge found the modulus of elasticity, E, of mild steel (0·162 per cent. carbon) in 10^{-11} dyne per sq. cm. :

	22°	142°	263°	398°	466°
$E \times 10^{-11}$ . .	19·3	18·9	18·2	16·9	14·6

A. Mallock gave 1·27 for the ratio of Young's modulus at −273° and at 0°. F. Sauerwald and co-workers attributed the brittleness of a-iron at the temp. of liquid air to the ready cleavage of the crystals at that temp.

K. Honda and T. Tanaka found that the effects of carbon on the modulus of elasticity, E, and modulus of rigidity, K, for iron alone are respectively $2{\cdot}087 \times 10^{12}$ and $8{\cdot}34 \times 10^{11}$; and for alloys with carbon :

Carbon . . .		0·10	0·20	0·40	0·59	0·81	1.02	1·19	1·48 per cent.
$E \times 10^{-12}$	Annealed .	2·045	2·025	2·070	2·040	2·030	1·906	1·981	1·930
	Quenched .	1·942	1·931	2·000	—	1·928	1·911	1·880	1·820
$K \times 10^{-11}$	Annealed .	8·13	8·11	8·21	8·19	8·15	8·17	8·06	7·97
	Quenched .	7·92	7·88	7·92	—	7·78	7·78	7·74	7·65

The presence of carbon in general decreases both moduli. The zig-zag character of the curves is attributed to impurities. Whilst the tensile strength of carbon steels is increased by quenching, the moduli of elasticity and rigidity are decreased in all cases. This fact was noted by K. Honda and H. Hasimoto.

H. Tomlinson observed that after a wire has suffered permanent extension, the temporary elongation which can be produced by any load becomes less as the interval between the period of permanent extension and that of applying the load becomes greater. This increase of elasticity is greater in proportion for large loads than for small ones. The increase of elasticity takes place whether the wire be allowed to remain loaded or unloaded between the period of permanent extension and that of testing for the elasticity. The rate of increase of elasticity varies considerably with different metals; with some, the maximum elasticity is attained in a few minutes, with others, as with iron and steel, not till some days have elapsed. The elasticity can be increased by heavily loading and unloading several times, the rate of increase diminishing with each loading and unloading. A more or less decided departure from Hooke's law—**1.** 13, 17—always attends recent permanent extension, even when the weights employed to test the elasticity do not exceed one-tenth of the breaking weight. L. C. Tyte found that all the metals he investigated deviated from Hooke's law over the whole range. The amount of deviation differed for the same material subject to different heat-treatments, and cold-working. For annealed metals, the deviations increased with an increase in the size of crystals. H. Tomlinson observed that the departure is diminished very noticeably in the case of iron and much less so in the case of other metals, by allowing the wire to rest for some time, either loaded or unloaded, it is also diminished by repeated loading and unloading. Permanent extension with all metals, provided the wire has not been kept heavily loaded for some time, produces a decrease of elasticity if the strain be not carried beyond a certain limit. If the extension be carried beyond this limit, a further permanent increase of length causes an increase of elasticity. In the case of iron, heavy loading for some time so increases the elasticity that even when the extension would have caused diminution of elasticity without such continued loading, the latter will, if sufficient time be allowed, change this diminution into an increase—but not so with copper. With iron which had been heavily loaded for some time, the ratio of the temporary elongation to the load producing it becomes less as the load employed becomes greater, until a certain limit is attained dependent on the extent of the previous heavy loading. With other metals, and with iron which has suffered permanent extension without allowing the load producing the extension to remain for any appreciable time on the wire, the elongation increases in a greater proportion than the load. This behaviour of iron, as well as the fact that this metal does not, until many hours have elapsed, attain its maximum elasticity, after having undergone permanent elongation, is attributed to the great cohesive force of the metal. When a fixed load is applied to steel at a constant temp., there is an initial flow which results in an elongation of the steel. This elongation ceases after a time, if the load is not too great. This indicates a strain hardening of the material. If the load be constant, there is a slower elongation, or *secondary flow*, which continues under a constant load of sufficient magnitude until it is followed by a *final rapid flow* which immediately precedes the fracture of the metal. H. F. Moore represents the phenomena as elastic deformation, slip, and fracture. The elastic deformation is represented by a slight stretching, or compression, or a lateral displacement (shear). This deformation disappears when the stress is released. As the stress is increased, some of the atomic bonds in the crystal-grains are broken along certain planes, the divorced atoms slide over other atoms, find new partners,

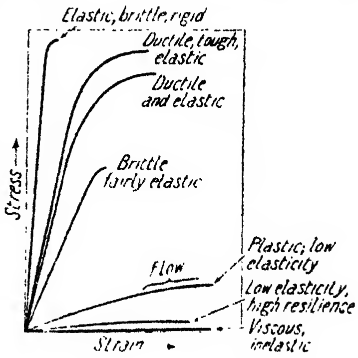
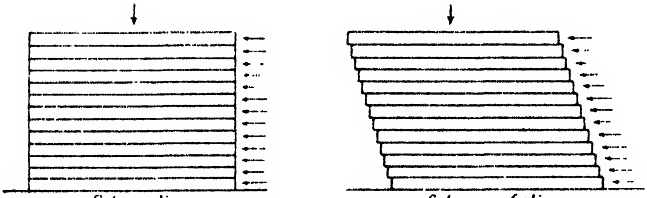


Fig. 200.—Some Types of Stress-Strain Curves.

and form new bonds. It is remarkable that after a brief period of rest for readjustment, the new bonds seem to be stronger than the old—*e.g.* in cold-drawn steel the slip is attended by an increase in strength. The action at this stage is the phenomenon of slip discussed above. The planes of slip across the crystal grains appear microscopically as lines, or *slip-bands*. H. P. Hollnagel represented the different types of stress-strain curves by Fig. 200. H. F. Moore likens the slip to the action of an oblique pressure on a pack of cards—Fig. 201—and added : The slipping continues, some of the broken atomic bonds do not form new bonds, and minute cracks appear, until finally the cracks spread and a fracture occurs. The relations of stress to strain are illustrated by Fig. 202. *OE* represents the first stage of elastic deformation ; slip-bands begin to appear at *E* when the stress is *AE*, after that, the curve deviates from a straight line, and when the load is released, the material has acquired a small permanent set. *E* represents the proportional limit or elastic limit ; the yield-point is represented by *Y*, so that when the stress attains the value *BY*, a general slip occurs, and after that fracture. With very brittle materials, fracture may occur before the stress becomes large enough to show a well-marked yield-point. Under repeated loading a stress well below the ultimate tensile strength will start a fracture in metal which finally spreads to failure of the entire cross-section of a piece. This spread under repeated loading is very much slower that the spread under a single increasing load. Thousands or even millions of cycles of stress may be required to develop the final failure. This repeated stress fracture spreads slowly, like a minute hack-saw cut, but its rate of progress is accelerated, and just before fracture it is almost as rapid as is the spread of fracture under a single increasing load. In fact, a typical fatigue failure usually shows two distinct zones : (i) A smooth surface where the crack has spread slowly and the walls of the crack are battered smooth by repeated opening and closing, (ii) a rough " crystalline " surface indicating the very much more sudden fracture of the core of the piece. The subject was discussed by K. Yuasa.


Before slip

Side view of slip

FIG. 201.—Formation of Slip-bands (Diagrammatic).

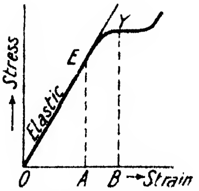


FIG. 202.—Relation of Stress and Strain.

According to Hooke's law, if S denotes the extension, and P the stress, $S=kP$, where k is a constant ; but, as just indicated, the results of accurate observations deviate a little from the rule. C. Bach said that F. A. Schulze's formula $S=kP^m$ gives better results when m is a constant greater than unity. For example, T. E. Stanton observed that in his tests, the relation between permanent strain, S, and stress, P, can be represented by $P=39{\cdot}37S^k$, where k is nearly 0·25 for some specimens of mild steel. R. Mehmke has made a collection of the formulæ which have been suggested in place of Hooke's law, in order to represent the observed results empirically. E. Hartig, and E. Grüneisen and F. A. Schulze assumed that the elastic modulus increases linearly with increasing stress, so that $dP/dS=E-cP$, where c is a constant ; and this can be written $S=E^{-1}(P+b_2P^2+b_3P^3+\ldots)$, where b_2, b_3, . . . are constants. This resembles I. O. Thompson's formula, $S=aP+bP^2+cP^3$. W. Voigt also supposed that the increase in the elastic modulus with increasing stresses is in accord with a power series. P. Debye assumed that the modulus of elasticity is a function of the interatomic distance. G. Wertheim made an assumption of this kind in 1848, for he gave the formula Ed^7=a constant when d denotes the mean distance apart of the atoms. P. Debye's hypothesis is not in accord with the behaviour of solid soln. where the change in the modulus is greater than can be explained by a small change in interatomic distances. According to H. von Wartenberg, every elastic deformation of a metal composed of grains is really made up of pure elastic deformation and of an elastic after-working, having a time factor. Single crystals do not exhibit elastic after-effect. The pure elastic deformation of a metal is independent of the previous treatment. The limit of proportionality of a metallic conglomerate is the stress at which the most unfavourably situated crystal slips, and it follows that there is no such limit for single crystals. The elastic limit is the stress at which the elastically deformed crystals fail to bring back the displaced crystals to their original position. The subject was discussed by A. Berliner, W. Geiss, G. A. Tomlinson, G. S. Meyer, M. Polanyi, G. Tammann, E. Goens and E. Schmid, P. Bechterew, G. Cook, G. Masing, H. Mark, L. Boltzmann, J. E. Wiechert, A. A. Michelson, J. Okubo, J. C. McConnel and D. A. Kidd, E. Heyn, M. Mesnager, F. Sauerwald and H. G. Sossinka, A. V. Stepanoff, and E. Houdremont and H. Kallen.

J. E. Stead worked out a theory for the relation between the cold-working of steel and the tensile strength. He stated that there are at least three stresses to consider: (i) the stress, S_1, required to destroy the cohesion between the atoms in the space-lattice of the crystal, and this is assumed to be constant: (ii) the stress, S_2, required to produce internal slip; it is a characteristic of each steel; it increases exponentially with the amount of slip, and depends on the amount of slip which has already taken place; and (iii) the stress, S_3, required to produce external slip; it is characteristic of each steel; and it increases linearly with the amount of slip that has taken place. He said:

> When a test-piece is stressed, the stress rises elastically until the initial value of S_2 is reached, and then internal slip takes place. The crystallites being in a state of unstable equilibrium owing to internal stresses, when slip takes place this equilibrium is upset and a position of stable equilibrium is attained, in which the internal stresses have disappeared. This necessitates considerable slip taking place, such slip constituting the yield-point slip. This is nearly all internal, but is accompanied by some slight external slip to conform with the movement that has taken place in the crystallites. While the crystallites are settling down into a position of equilibrium, the stress remains the same and the slip produces no hardening effect. That is to say, the piece cannot withstand any higher stress than S_2 without further slip. As soon as the equilibrium position is reached, any further slip produces an increase in S_2. That is to say, to produce further slip the stress must be increased, and with each increasing slip there is an increase in the value of S_2. However, the slip that takes place is partly internal and partly external, the proportion of external to internal increasing as the slip increases. Thus, hardening is due partly to the increase of S_2 and partly to that of S_3. Though the initial value of S_2 is less than that of S_3, the former increases with slip more rapidly than S_3, so that a point is reached when the value of S_2 is equal to the value of S_3. As the values of S_2 and S_3 approach each other, the ratio of external slip to internal increases until, when S_2 and S_3 are equal, the slip becomes wholly external. This continues until the breaking point is reached. The breaking stress may be equal to S_1, but of that there is no evidence one way or the other.

J. T. Bottomley noted the great difference between the tenacity of iron when loaded by slow degrees, and when loaded quickly; and this recalled the increase in the portative power of a magnet with gradual loading—*vide infra*. H. J. French and W. A. Tucker, and A. Michel and M. Matte showed that when a specimen of steel is subjected to a constant load, it passes through four phases: (i) an instantaneous extension; (ii) a slow extension; (iii) a constant increase; and (iv) a rapid increase accompanied by fracture. The permanent deformation and fracture was discussed by M. Malaval, and A. H. Leblond; and the expansion of cast iron under tension, by E. Piwowarsky and O. Bornhofen; and the change of dimensions under torsional stresses, by T. Uêda.

C. A. Edwards and L. B. Pfeil, working with single crystals of iron, containing 0·13 per cent. carbon, 0·023 Si, 0·44 Mn, 0·028 S, and 0·020 P, found that the limits of proportionality ranged from 1·725 to 2·69 tons per sq. in.; the tensile strength, from 9·38 to 15·38 tons per sq. in.; the modulus of elasticity, from 11,200 to 13,320 tons per sq. in.; and the elongation, from 30·5 to 53·65 per cent. With two exceptions, the tensile strengths fall within a range of 1·27 tons per sq. in., the average of 8 tests is 9·98 tons per sq. in. with maximum and minimum values, respectively, 10·65 and 9·38 tons per sq. in. H. C. H. Carpenter's values for the tensile strength ranged from 9·61 to 9·94 per sq. in. Observations were made by G. I. Taylor and C. F. Elam, F. Sauerwald and G. Elsner, P. Ludwik, A. B. Kinzel, J. Königsberger, A. Kroitzsch, W. H. Hatfield, R. L. Templin, O. Schwarz, J. Galibourg, J. Seigle, A. R. Page, F. G. Martin, J. A. Jones, F. W. Duesing, H. Poellein, P. Régnauld, R. Rimbach, C. H. Carus-Wilson, R. H. Graham, J. E. Howard, E. Bernardon, C. Cornut, J. H. Wicksteed, E. Marke, L. Tetmajer, W. P. Davey, A. Pomp, A. Vosmaer, J. W. Langley, K. Daeves, C. C. Schrott and G. M. Case, J. E. Howard, and T. B. Focke. The tensile strengths of small crystals were more variable than large ones. C. A. Edwards and L. B. Pfeil consider that the lowest value for the tensile strength in a single crystal will be obtained when two slip-planes make angles of 45° to the axis of stress, that is, when two planes coincide with a plane of maximum shear, and that higher values for tensile strength will be obtained when no planes make this angle. The important factor is the angle between the planes and the axis of stress, and not the relative position of the planes and the surface of the specimen. It is not clear whether an iron crystal during a tensile pull gives way upon the dodecahedral-planes or on the cube-planes. Slip in a crystal usually occurs most easily on the planes containing the greatest number of atoms per unit area, and in the case of α-iron, these are the rhomb-dodecahedral or (110)-planes. Observations, however, favour the assumption that slip in α-iron takes place on the cubic or (100)-planes. The limits of proportionality have an average of 2·19 tons per sq. in.; the results are all low when compared with that for crystalline iron where the value attains 8 tons per sq. in. No relation between the tensile strength and the limit of proportionality was observed. The elongation shows a tendency to vary in accord with the tensile strength; the data were very variable when compared with the tensile strength. The modulus of elasticity averages 12,016 tons per sq. in. There are no wide variations in accord with general observations that the condition of a metal—cold-worked, annealed, etc.—has but a small effect on the elastic modulus. F. Sauerwald and co-workers observed that single crystals of α-iron at the temp. of liquid air readily rupture along the face of the cube. According to F. Osmond and C. Frémont, the mechanical properties of single crystals are a function of the crystallographic planes in relation to the direction of stress. The extreme brittleness displayed along the planes of cleavage is associated with high plasticity in other directions. G. P. Fuller found that the yield-point of 99·965 per cent. electrolytic iron, annealed to remove hydrogen, is 23,000 lbs. per sq. in., and the tensile strength is 40,000 lbs. per sq. in. The metal can be annealed at a high temp. and quenched without affecting its properties.

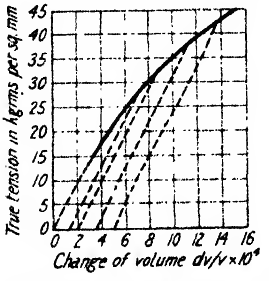


FIG. 203.—The Effect of Tensile Stresses on the Volume of Steel.

H. Quinney observed that the Ac_3-arrest with single crystals was not influenced perceptibly by strains; and the subject was studied by J. Seigle, and H. Griess and H. Esser. F. Sauerwald and T. Sperling observed that the Ac_1-arrest of iron is lowered by deformation; the Ar_1-arrest is raised about 1°; the Ac_3-arrest is lowered about 4°; and the Ar_3-arrest is raised about 4°. H. Hanemann and R. Yamada observed that the sp. vol. of steel is increased temporarily by elastic stress, and permanently if it be deformed when in a state of plastic flow. The dotted lines, Fig. 203, show that the vol. of a number of steels increases with increasing tension; and the continuous curve represents the increase in vol. which occurs when plastic flow begins. B. MacNutt and A. Concilio observed that when stressed in a testing machine, steel makes noises. The load at which the first noise is heard is constant for a given material, and it occurs in the neighbourhood of the yield-point.

The physical properties of steel are mainly dependent on (i) the previous history of the metal; (ii) the chemical composition, *i.e.* the relative proportions of the other elements present; (iii) the distribution of the different structural constituents, *i.e.* the relative proportions of ferrite, cementite, etc., present; and (iv) the size of the grains. F. Sauerwald and K. A. Pohle found that the brittleness of iron below 0° is not appreciably affected by the grain-size. L. Ljamin found that the tenacity of different steels varied as the size of the pearlite grains at the same finishing temp.; and A. Sauveur obtained the results indicated in Table XVIII,

TABLE XVIII.—THE RELATION BETWEEN THE GRAIN-SIZE AND TENSILE STRENGTH.

Size of grain in 0·0001 sq. mm.	Tensile strength (kgrms. per sq. mm.)	Elongation (per cent.)	Reduction of area (per cent.)
148	69·2	15·0	20
118	70·3	19·0	22
62	77·7	22·5	35

and found that if A denotes the average area of the grains in sq. mm., the tenacity, T, in kgrms. per sq. mm., is $T=75{\cdot}5-0{\cdot}004A$. Observations on the effect of the grain-size on the mechanical properties have been made by J. O. Arnold, F. C. Thompson, W. E. Dalby, W. H. Bassett and C. H. Davis, R. Arrowsmith, W. Rosenhain and J. C. W. Humfrey, R. E. Paine, E. Houdremont and co-workers, E. Schüz, H. von Jüptner, F. Osmond, O. von Keil and O. Jungwirth, and H. T. Angus and P. F. Summers. C. A. Edwards and L. B. Pfeil found that a test-piece with 28 crystal grains per sq. mm. had a tensile strength of 17·2 tons, and with decreasing grain-size the tensile strength remained steady until about 84 crystals per sq. mm. were present, after which, the strength increased rather rapidly to about 20 tons per sq. inch at a crystal-size of 145; with a crystal-size of 166, the tensile strength fell to 17 tons per sq. in.; and any further decrease in crystal-size had little effect since the tensile strength remained about 17 tons per sq. in. for all samples with a finer grain than 166. The curve thus shows a definite maximum which also corresponds with the maximum for the limits of proportion. The cause of the discontinuities has not been explained. It was not due to the contact of the metal with hydrogen or nitrogen.

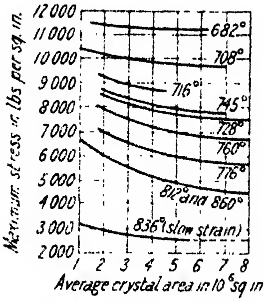


FIG. 204.—The Effect of the Grain-size of Crystals on the Tensile Strength at Different Temperatures.

C. A. Edwards and L. B. Pfeil observed that decarburized ferrite aggregates gave practically constant maximum stress and elongation values as the grain-size decreased from 27 to 307 grains per sq. mm. W. Rosenhain and J. C. W. Humfrey summarize their results, Fig. 204, as follows:

> Commencing with the material at the higher temp., that is, well above Ar_3, it possesses the mechanical properties and the microscopic behaviour of an aggregate of crystals, themselves relatively strong, embedded in a viscous fluid. Throughout the γ-range these characteristics are maintained although the actual fluidity of the intercrystalline cement no doubt diminishes steadily with decreasing temp. The allotropic modification which occurs at Ar_3 affects the crystals alone without altering the character and properties of the cement; as a consequence of the allotropic change, the crystals become very considerably weaker, so that the relative importance of crystals and cement from the point of view of strength is reversed after passing Ar_3; the crystals now being relatively weak, yield first, while the cement is relatively hard and stiff. This change makes itself felt in two ways: in the first place, the tenacity-temp. curve drops suddenly and follows a totally different course from that which governed its path in the γ-region, and in the second place, the strength of the material is now very largely dependent upon the crystal-size,

since the proportion of the harder and stronger cementing material is much higher in a fine-grained structure than in a coarse-grained one, and the presence of this harder material makes itself felt more directly, and also indirectly by acting as a stiffening which resists the tendency of the crystals to undergo plastic deformation. The fact that this influence of crystal-size is really due to the presence of an amorphous cement is further confirmed by the observations which show that if the rate of straining is extremely slow the influence of crystal-size practically disappears, this being in accordance with the view that at these slow rates of straining the cement even at this lower temp. will undergo viscous flow. The allotropic change at Ar$_2$, although clearly indicated by discontinuities in all tenacity-temp. curves, does not make itself felt very strongly in any of the observations, and beyond the fact of establishing the existence of a mechanical discontinuity the observations throw little light on the nature of the change from β- to α-iron. The bearing of the results of these observations on the allotropic theory of the hardening of steel is of some interest. An inspection of the temp.-tenacity curves clearly shows that the allotropic change at Ac$_3$, or Ar$_3$, brings with it the greatest change in mechanical properties. The question whether the β-modification of iron plays the principal part in the hardening of steel is still an open one. The shape of the curve does not justify any very definite extrapolation towards the ordinary temp., although it seems tolerably certain that if the γ- or β-curve could be produced down to the ordinary temp. it would correspond to material very much harder than α-iron. Whether, however, these two curves would retain their relative positions, thus making the γ-iron the harder at the ordinary temp., or whether the two curves may cross, cannot be concluded from these observations. All that can be definitely said is that at least one important transformation takes place in iron at a temp. near 900°, and that this transformation results in the formation of a considerably harder and stronger body, usually called γ-iron. A similar but much smaller change is indicated definitely at the temp. of Ar$_2$, and it is difficult to reconcile the occurrence of such a discontinuity with C. Benedicks' theory which regards β-iron as a soln. of γ-iron and α-iron. On the other hand, the observations, apart from the mechanical discontinuity, do not indicate any very striking difference between β- and α-iron.

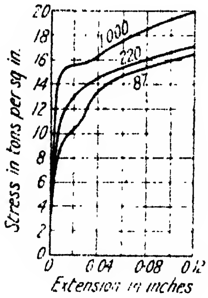


FIG. 205.—The Effect of Grain-size on the Stress - Elongation Curves.

R. Arrowsmith's observations on the effect of grain-size on the extension of armco iron at the yield-point are summarized in Fig. 205, for a sample annealed at 1050° for 7 hrs. when the number of grains was 87 per sq. mm., annealed at 920° for 90 min. when 220 grains per sq. mm. were present, and annealed at 770° for 19 hrs. when 1000 grains per sq. mm. were present. F. C. Thompson found that for a number of metals the elastic limit, E, is very nearly $E=1{\cdot}5n\sigma/d$, where n denotes the number of crystals per sq. cm., σ denotes the surface tension, and d denotes the thickness of the intercrystalline film. This expression assumes that the elastic limit is a measure of the strength of the intercrystalline junctions. Sufficient data are not available for satisfactory tests. The subject was discussed by W. von Moellendorff and J. Czochralsky, and T. W. Hardy. H. Hanemann and R. Hinzmann found only a slight variation in the tensile strength of steels with a grain-size ranging from 90 to 25,000μ^2.

W. S. Farren and G. I. Taylor found an increase in the internal energy of the metal in an overstrained state, and with mild steel they estimated an increase of 14 per cent. of the work done. Confirmatory results were obtained by H. Quinney. P. Lasareff said that the elastic limit of iron is proportional to $N^{5/8}$, where N is the number of atoms per c.c. The theoretical basis of the formula means that the intercrystalline forces can be neglected, the intermolecular force is proportional to the atomic concentration and a certain power, the same for all metals, of intermolecular distance—*vide supra*, hardness. E. Marke, T. Morris, W. E. Koch, T. H. Beare, W. M. Wilson and W. A. Oliver, and R. R. Kennedy and G. J. Oswald found that titanium, even in small proportions, considerably lessened the grain-growth, and H. Hanemann observed that with graphite present as coarse grains, the tensile strength of iron was 10 to 14 kgrms. per sq. mm., whilst it was 20 to 24 kgrms. per sq. mm. when present as fine grains. See hydrogen, for the effect of that element.

E. H. W. Tafel and H. Scholz discussed the distribution of the stresses in test-bars of different shapes. L. H. Appleby, W. Ast, C. Bach, C. Bach and R. Baumann, W. Bagshaw, J. Barba, T. H. Beare and W. Gordon, A. L. Boegehold, H. Bornstein, H. Brearley, P. Breuil, R. Buchanan, R. H. Cabena, R. C. Carpenter, F. J. Cook, A. H. Dierker, J. W. Donaldson, J. Durand, H. J. French, W. Gordon and G. H. Gulliver, W. Hackney, P. A. Heller, H. A. Holz, H. M. Howe and co-workers, H. Hubert, T. H. Johnson, B. Kirsch, P. Kreuzpointer, R. Kühnel, O. Leyde, J. T. Mackenzie, J. D. Mackinson, R. S. MacPherran, A. Martens, A. Mesnager, R. Moldenke, J. Muir, A. L. Norbury, P. Oberhoffer and W. Poensgen, D. A. Oliver, J. G. Pearce, A. Portevin and co-workers, A. Pouilloux, J. S. G. Primrose, P. Reusch, G. H. Roberts, E. V. Ronceray, W. H. Rother and V. M. Mazurie, M. Rudeloff, F. Sauerwald, H. B. Seaman, J. Seigle, J. Shaw, H. H. Shepherd, T. G. Staub, A. le Thomas and R. Bois, W. C. Unwin, E. R. Verity and A. Binns, G. B. Waterhouse, G. Welter, T. D. West, M. O. Withey, and W. Wood examined the influence of the form of the test-pieces on the results; E. P. Withrow and L. C. Niedner, and J. G. Pearce, the effect of machining and removal of skin; R. H. D. Barklie and H. J. Davies, the effect of films of electrodeposited metals; E. G. Coker, the effect of polishing; F. J. Cook, K. L. Zeyen, J. and L. Treuheit, and J. E. Stead, the mode of casting; J. E. Hurst, the effect of temp. of casting—*vide infra*; J. Bauschinger, B. Blount and co-workers, H. Stradtmann, J. T. Bottomley, H. Lebasteur, E. Maitland, the effect of the time of loading on the results; and O. Bauer, K. Hopfer, O. Knaudt, A. Pomp and S. Weichert, R. L. Templin, L. C. Tyte, H. Wald, and F. Wüst and W. C. Huntington, the degree of accuracy attainable in the tests.

A. Pomp measured the effect of cold-work on the tensile strength, in kgrms. per sq. mm., and Brinell's hardness of electrolytic iron, and of iron with 0·03 per cent. carbon; 0·01, silicon; 0·29, manganese; 0·028, sulphur; and 0·019, phosphorus. The results are indicated in Table XIX. F. C. Thompson and

TABLE XIX.—EFFECT OF COLD-WORK ON THE MECHANICAL PROPERTIES OF IRON.

	Thickness		Tensile strength		Hardness		Elongation per cent.
	mm.	Decrease per cent.	per cent.	increased		Increase—per cent.	
Electrolytic Iron	4·0	0·0	24·7	0·0	52	0·0	41·5
	3·5	12·5	28·8	16·6	78	50·0	34·2
	3·0	25·0	32·9	33·2	95	82·7	11·4
	2·5	37·5	37·1	50·3	109	109·7	8·6
	2·0	50·0	41·7	68·8	112	115·4	4·3
Iron	4·0	0·0	32·6	0·0	62	0·0	40·0
	3·5	12·5	41·4	27·0	91	46·0	14·3
	3·0	25·0	47·8	46·7	121	95·1	13·3
	2·5	37·5	55·6	70·6	135	117·7	6·0
	2·0	50·0	61·3	88·1	159	165·5	6·0

W. E. W. Millington studied the effect of varying diameters on the elastic constants of wires, and found the results indicated in Table XX. R. L. Sanford and co-workers also found that the effect of wear on steel wires is to increase the tensile strength per unit area.

TABLE XX.—THE EFFECT OF VARYING DIAMETERS ON THE ELASTIC CONSTANTS OF WIRES.

Diameter (inch)	Tons per sq. inch			Percentage elongation in $4\sqrt{\text{area}}$	Reduction of area (per cent.)
	Elastic limit	Yield-point	Maximum stress		
0·300	18·0	24·0	34·5	35·0	62·0
0·232	18·0	23·9	35·1	35·1	63·2
0·176	18·6	24·0	34·7	35·3	64·0
0·128	17·0	22·8	35·0	36·0	66·3
0·092	17·0	21·8	34·6	36·8	67·4
0·064	16·3	20·4	34·2	39·2	69·1
0·040	15·6	19·8	34·1	41·4	70·3
0·036	15·2	20·0	34·1	42·5	71·2

P. Goerens represented the effect of cold-work in terms of percentage reduction of area on the tensile properties of a soft basic Bessemer mild steel, on a medium steel, and on a hard steel, by Fig. 206—the dotted curves refer to percentage elongations, the others to tensile strengths. P. Goerens gave for the elastic modulus $E \times 10^6$ kgrms. per sq. cm. for drawn wire, and $E^1 \times 10^6$ for the annealed wire :

Carbon . .	0·07	0·12	0·27	0·55	0·62	0·78	0·98 per cent.
Drawn . .	96·5	70·4	70·4	86·5	44·3	58·5	32·8 ,,
$E \times 10^6$ . .	2·00	1·985	1·99	2·00	2·00	2·00	1·98
$E^1 \times 10^6$ . .	2·00	2·01	2·02	2·05	2·09	2·19	2·01

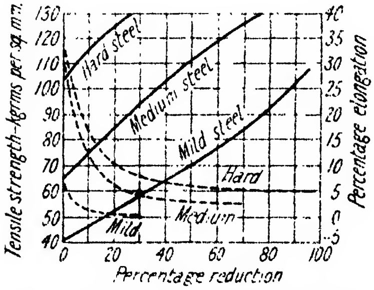


FIG. 206.—The Effect of Cold-work on the Tensile Strength of Steel.

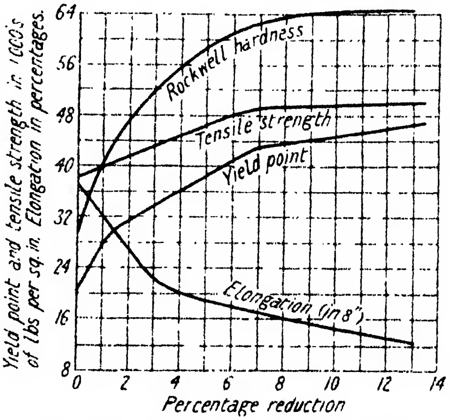


FIG. 207.—The Effect of Cold-work on Armco Iron.

R. M. Brown found that cold-drawing does not much affect the elastic modulus of iron and steel, but it may double the tensile strength. For mild steel, the limit of proportionality is increased by cold-drawing. H. Eicken and W. Heidenhain found that with a 0·26 per cent. carbon steel, with a 15 per cent. reduction in diameter, the tensile strength rose from 85 to 180 kgrms. per sq. mm. R. L. Keynon's results with armco iron are summarized in Fig. 207. Observations were made by I. Adachi, F. J. Cook, W. Broniewsky and J. Krol, C. A. Edwards and J. C. Jones, E. Fangmeier, J. Feilen, J. R. Freeman and A. T. Derry, R. Giraud, K. Honda and R. Yamada, E. J. Janitzky, W. Knackstedt, W. Köster and H. Tiemann, E. Marke, A. de Marneffe, F. S. Merrills, R. W. Miller, F. Pacher and F. Schmitz, L. B. Pfeil, A. Pomp, A. Pomp and W. Albert, W. Püngel, S. H. Rees, E. L. Rhead, W. Rosenhain, F. Sauerwald and co-workers, T. Swinden and G. R. Bolsover, and R. L. Templin. E. Grüneisen gave $E \times 10^6 = 1{\cdot}329$ for cast steel with 2·7 per cent. of graphite and 0·8 per cent. of combined carbon, and $E \times 10^6 = 1{\cdot}050$ for cast iron with 3·0 per cent. of graphite and 0·5 per cent. of combined carbon. For the relation between tensile strength and hardness, *vide supra*, Table XIX. L. Rürup examined the changes in composition of steel during mechanical treatment, and found :

	Total C	Combined C	Mn	P	Si
Crucible steel . . .	0·804	0·80	0·249	0·030	0·201
After rolling . . .	0·800	0·78	0·263	0·0465	0·0238
Annealed wire . . .	0·801	0·775	0·2625	0·0415	0·235

F. Schmitz gave for the averages of 200 basic steel bars, and 200 acidic steel bars, with carbon ranging from 0·45 to 0·54 per cent. :

	Elastic limit (kgrms. per sq. mm.)	Breaking stress (kgrms. per sq. mm.)	Elongation (per cent.)	Reduction area (per cent.)
Basic steel . .	38·46	71·73	16·83	40·58
Acidic steel . .	39·93	72·39	16·49	36·07

A. Sattmann studied the effect of the mechanical treatment of acid and basic steel ingots. The acid steel had 0·19 per cent. of carbon, a tensile strength of 26 tons per sq. in., an elongation of 24·5 per cent., and a reduction area of 59 per cent.; whilst the basic steel had 0·15 per cent. of carbon, a tensile strength of 22·8 tons per sq. in., an elongation of 28·5 per cent., and a reduction of area of 65 per cent. When reduced at different temp., by a rapid-striking hammer, from a thickness of 0·39 in. to one of 0·35 in., the mechanical properties were those indicated in Table XXI. The acid metal hammered at 200° could be bent double when cold, but showed small cracks at the bend; that hammered at 320° (blue-heat) broke when bent at an angle of 20°. The basic metal with a similar treatment could be bent double but showed slight cracks. The bars subjected to a temp. of —19°, had a lower tensile strength but a much greater elongation and reduction of area than the bars treated at slightly higher temperatures. The best temp. for the mechanical treatment of ingot metal would appear to be that of a bright red-heat. The effect of annealing the hammered bars is shown in Table XXII. The bars, which had been treated at a bright white-heat, became much softer and more ductile by this treatment; but those treated at somewhat lower temp. were not softened to so considerable an extent. The results show that heating the material to a yellow- or a blue-heat has no influence on the properties of the cooled-down bar. Heating

TABLE XXI.—MECHANICAL PROPERTIES AFTER HAMMERING AT DIFFERENT TEMPERATURES.

Temperature (degrees C.)	Acid metal			Basic metal		
	Tensile strength (tons per sq. inch.)	Elongation (per cent.)	Reduction of area (per cent.)	Tensile strength (tons per sq. inch)	Elongation (per cent.)	Reduction of area (per cent.)
− 19	26·3	15	59·8	25·2	19·5	64·0
+ 10	31·3	7	55·7	28·3	7·5	64·6
40	31·5	7	50·6	30·4	7	55·5
200	37·0	4	37·8	30·7	7	57·2
320	37·5	4	47·2	30·7	7	56·7
600	27·6	12	56·0	27·2	10	56·0
800	27·0	16	56·2	25·6	21·5	64·7
1000	26·9	22·5	64·5	24·1	22	67·6
1100	26·2	22·5	62·5	23·3	21	67·3
1300	26·3	18·5	61·0	22·9	19·5	68·9

TABLE XXII.—THE EFFECT OF ANNEALING HAMMERED BARS AT DIFFERENT TEMPERATURES.

Temperature (degrees C.)	Acid metal			Basic metal		
	Tenacity (tons per sq. inch)	Elongation (per cent.)	Reduction of area (per cent.)	Tenacity (tons per sq. inch)	Elongation (per cent.)	Reduction of area (per cent.)
200	25·4	27	64·7	22·7	30·0	69·3
320	26·2	24	62·4	22·9	28·5	68·5
600	26·0	26	61·1	23·3	29·0	69·4
800	26·0	24	64·1	22·8	31·0	69·2
1000	26·4	24	65·1	23·1	29·0	71·6
1100	27·2	24	64·9	22·7	33·0	71·8
1300	25·7	22	63·9	22·4	30·0	73·0
Not heated	26·0	24·5	59·0	22·8	28·5	65·0
Tested at −19°	25·8	19·0	63·9	23·1	26·5	80·8

to a white-heat affects the quality of the acid metal, but does not appear to have much influence on the basic metal. The effect of heating the hammered bars to various temp. and then plunging them into water at 6° is shown in Table XXIII.

TABLE XXIII.—THE EFFECT OF QUENCHING HAMMERED BARS FROM DIFFERENT TEMPERATURES.

Temperature (degrees C.)	Acid material			Basic material		
	Tensile strength (tons per sq. inch)	Elongation (per cent.)	Reduction of area (per cent.)	Tensile strength (tons per sq. inch)	Elongation (per cent.)	Reduction of area (per cent.)
200	24·3	22·5	65·3	23·9	26·0	65·5
320	24·2	24·6	65·6	23·6	28·0	69·4
600	26·5	16·0	62·7	24·9	22·0	67·3
800	36·4	13·0	54·8	38·3	14·5	56·6
1000	31·3	20·0	66·6	29·3	15·0	69·1
1100	32·2	20·0	61·1	29·6	15·0	63·6
1300	39·8	10·0	43·6	30·7	12·0	65·5

In both cases there is a first maximum tensile strength at 800°, followed by a drop and then by a further increase. The basic steel heated to a blue-heat gave much better results on testing than did the acid metal. With the exception of the bars heated to a white-heat, annealing softened the metal completely. Those heated to the temp. of 1300° still remained hard even after this annealing. J. Czochralsky, L. Guillet, Z. Jeffries and R. S. Archer, F. Körber, F. Körber and K. Wallmann, A. Lundgren, W. Püngel, T. F. Russell, F. Sauerwald, and C. W. Yearsley discussed the effect of cold-work on the tensile properties of steel; H. van de Loo, the effect of pickling and galvanizing; and K. Honda, the effect of the forging temp. on the tensile strength.

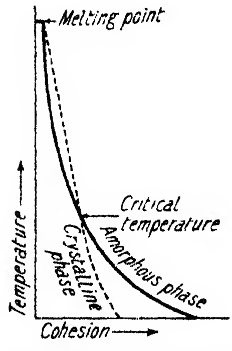


FIG. 208.—Idealized Tensile Strength Curves for Amorphous and Crystalline Materials.

Z. Jeffries and R. S. Archer assume that the effect of temp. on the tensile strength of metals agrees with the assumption that the cohesion depends on the relative magnitudes of (i) the intercrystalline cohesion, *i.e.* the cohesion of the assumed amorphous material between the grains, and (ii) the intercrystalline cohesion, *i.e.* the cohesion within the crystal grains. Analyzing the curves of the relation between the rupture strength and temp. with metals which suffer no allotropic change within the range of temp. considered, Fig. 208,. has shown that (i) at the higher temp., the intercrystalline cohesion is the smaller of the two, so that rupture occurs along the grain boundaries. Plastic deformation or viscous flow is characteristic of amorphous materials, and it resembles the flow characteristic of that of liquids, where the viscosity is very large at low temp. Whilst the rupture strength of a crystal depends on temp. and is independent of the duration of loading, the resistance to the deformation of an amorphous body varies with the rate and duration of loading. A large load exerted for a short time is equivalent to a smaller load applied for a longer time. Here, the tensile strength decreases linearly with temp., and can be represented by the relation: $S=S_0-a\theta$, where S_0 denotes the tensile strength at 0°, S, the tensile strength at θ°, and a is a constant showing the rate of decrease of S with temp. Again, (ii) at the lower temp., the intercrystalline cohesion is the smaller of the two, so that rupture occurs across the grains themselves. Here, the tensile strength increases very rapidly with temp. and the relation between temp. and tensile strength, S, was found by D. H. Ingall to be best represented by an exponential equation. There is a temp. at which the two forms of cohesion are equal—*the critical cohesion temperatures.* In accord with the suggestion that metals behave as if they are composed partly of a crystalline and partly of a viscous solid, and that the viscous flow occurs at the higher temp., and the critical cohesion temp. marks the minimum limiting temp. for viscous flow, D. H. Ingall said :

> For this reason it is suggested that the straight line or lower temperature curve is the all important one to the engineer, for, at a temperature beyond it, that is, beyond the critical inflection temperature which limits it, a metal or alloy will only be of mechanical use when it is subjected to a stress which is insufficient to overcome the resistance to flow due to friction, etc., or a cycle of stresses which do not give time for flow.

S. Dushman represented the relation between the tensile stress, S, and the absolute temp., T, by the exponential equation : $S=S_0e^{A/T}$, where, by analogy with numerous other chemical and physical reactions, the term A can be represented by Q/R, where R is the gas constant 1·986 cals., and Q denotes the heat, or may be energy, of the reaction per gram-atom or gram-molecule at the absolute temp. $T=0°$, or it may be the heat of the evaporation per gram-atom or gram-molecule respectively. S. Dushman and I. Langmuir also represented the relation between the rate of diffusion of metals into one another as a function of temp., so that if D denotes the diffusion constant at $T°$ K., and D_0 a constant, then $D=D_0e^{-Q/RT}$, where Q denotes the heat of diffusion per gram-atom or gram-molecule. When, say, zinc diffuses into iron, the diffusion occurs by an interchange of adjacent atoms, Q may be regarded as the energy required for a gram-atom of zinc to replace an equivalent amount of iron.

If Q denotes the latent heat of evaporation, then, according to L. Boltzmann's hypotheses—**1.** 12, 9—the amplitudes of vibration of the different atoms are not equal, but vary from zero to infinity in accord with a definite distribution law. Consequently, at any given temp., there are some atoms for which the energy of vibration is in excess of that required to separate them completely from the space-lattice, and the probability of the occurrence of atoms of such a high energy content will govern the rate of evaporation, so that if P denotes the probability that an atom will evaporate at the temp. T, then $P=P_0e^{-Q/RT}$, where $P=P_0$ when T attains its maximum value, *i.e.* when the temp. is indefinitely large. Here, P decreases as T decreases. Hence, continued S. Dushman, the probability that an atom in a grain boundary will be able to move past an adjacent atom is proportional to $e^{-Q/RT}$, where Q denotes the energy involved in this motion per gram-atom of the metal. The tensile strength is a measure of this probability, and thus the variation of tensile strength with temp. assumes the form indicated above. R. Becker studied the plastic deformation of crystals from the crystallographic point of view. He said :

> Under the action of shearing stresses there occurs a gliding of the material on definite crystallographic planes, and in some cases also the direction of gliding within the surface is determined crystallographically. The lowest shearing stress required to initiate the gliding is known as the elastic limit. . . . This limit is never measured exactly ; it is possible only to state that load which, with the measuring arrangement used, is just sufficient to produce an observable extension. . . . We assume that on the body to be deformed we apply such a load that on the crystallographic gliding plane a shearing stress, s, is effective which is less than the limiting stress, S, and we consider especially a definite gliding plane. In consequence of the irregular thermal motion, the force acting along the gliding plane will undergo irregular oscillations about the average value, s. If now the limiting value, S, is exceeded for a short time, a gliding action will suddenly be started during such an instant. . . . The plasticity of a crystal is thus affected by thermal oscillation phenomena, which leads to the consequence that at one instant gliding will occur on one plane and at another instant on another plane, the occurrence of gliding on any particular plane being governed by the law of probability.

He then calculated the rate of plastic deformation, U, and found that it can be represented by $U=U_0e^{-a(S-s)^2}/RT$, where a is a constant connected with the elastic modulus, and the quantity $a(S-s)^2$ represents an amount of energy equivalent to Q in the preceding equations. J. Frenkel assumed that gliding is similar to that of two toothed surfaces, but R. Becker objected that if so, a stress, S, would be required to produce a shearing break and not a plastic deformation. It is characteristic of plastic deformation that it must proceed with a definite velocity. W. Rosenhain stated that when mild steel undergoes plastic deformation, 10 per cent. of the work done is converted into heat, and the remainder does internal work of some kind. The subject was investigated by H. Quinney, W. S. Farren and G. I. Taylor, and C. H. M. Jenkins and M. L. V. Gayler. W. Braunbek has tried to describe the phenomena of fusion, and ionic conductivity in accord with L. Boltzmann's probability theorem.

According to P. Ludwik, the physical properties of metals, not alloys, when plotted against equal fractions of their absolute m.p., almost coincide—*e.g.* if the absolute m.p. of a metal be 1255°, the metal at half this temp. has nearly the same tensile strength as another metal at half the absolute temp. of its own m.p. M. Plaut said that the elastic properties of metals indicate that the force required to displace a particle in a solid is small for small displacements, increases linearly up to the limit of proportion, and then increases more slowly up to a maximum, after which, it falls, ultimately becoming zero when the cohesion is overcome. The area beneath the resulting curve gives the work of separation; and the work of separation is given by the heat of sublimation. The tensile strength of solids falls below the values calculated from this assumption, although the Brinell's hardness is approximately proportional to the heat of sublimation except in the case of substances with a marked cleavage—*e.g.* graphite has a large heat of sublimation but is weak in one direction. The increase in the hardness of cold-worked metals is not explained on this hypothesis.

E. Grüneisen-derived an equation of state for solids, and calculated values for the cohesive forces between atoms—$6{\cdot}25\times10^{11}$ dynes per sq. cm. for iron, and $6{\cdot}02\times10^{11}$ dynes per sq. cm. for nickel. G. Tammann found that with iron, slip-bands appeared with a stress of 2370 kgrms. per sq. cm. when the elastic limit was 5840 kgrms. per sq. cm. The corresponding numbers for nickel were 788 and 5570; and for lead, 25 and 102. R. F. Mehl studied the interatomic forces of metals; and G. Moressée, *La resistance des matériaux, résultante des forces atomiques*, and from the dynamics of the rotation of the atoms, and other assumptions, calculated a value for the elastic limit and its variation with temp. He thus calculated the elastic limit of iron, at absolute zero, to be 2300 kgrms. per sq. cm.; at 15°, 1400 kgrms. per sq. cm.; and at 1027°, 368 kgrms. per sq. cm. For steel, he calculated:

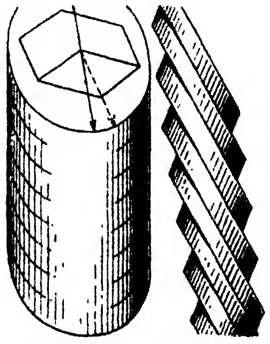
	200°	400°	600°	800°	1000°	1200°	1300°
Elastic limit .	3160	2440	1800	1240	480	200	0

M. Born calculated values for the cohesive strength of ionic lattices, and obtained values for the energy of the lattice, U per gram-molecule, of the alkali halides in agreement with observation. J. E. L. Jones and co-workers were also able to deduce values for the elastic moduli, and the surface energy. This also shows that an approach is being made to obtain a theory of cohesion based on atomic structure. M. Born, indeed, assumed that the mechanical cohesion of the space-lattice, and the chemical attraction of the ions are one and the same. F. Zwicky calculated the theoretical rupture or tensile strength from the lattice energy U. There is a marked discrepancy between the measured tensile strength, and the calculated cohesive force. This was discussed by S. Dushman. The explanations of G. Cook, E. Goens and E. Schmid, A. A. Griffiths, K. Hohenemser and W. Prager, E. Jaenichen and F. Sauerwald, T. M. Jasper, A. Joffe, H. Kotte, P. Nemenyl, M. Polanyi, W. Prager, H. Reissner, W. Schmidt, A. Schob, H. Tertsch, and J. H. C. Thompson, A. V. Stepanoff, H. Mussmann, W. Fahrenhorst and E. Schmidt, O. Manfred, and W. Widder are in agreement with that of A. Smekal, who said:

> The only logical conclusion to account for the difference between technical and theoretical rupture strength of materials is the assumption that ordinary technical materials are far from being homogeneous, as we have always assumed, but that they have many fine, microscopic and submicroscopic holes, cracks and other inhomogeneities, which decrease the technical strengths as compared with the molecular strength. The former is thus determined on the basis of a microscopic stress distribution, behind which there is hidden a quite different sort of microscopic stress distribution which depends on the inhomogeneities present in the material. . . . The old experience that coarsely crystalline material possesses a lower (technical) strength than finely crystalline, thus receives a very obvious explanation. If this view is correct, the strength of any material should be considerably increased if care is taken to reduce to a minimum the occurrence of cracks and other inhomogeneities by choice of correspondingly small dimensions and careful thermal treatment of the body under test. In fact it has been known for a long time, for example, that very thin wires are much stronger than thicker wires ; in the ideal limiting case of a single chain of molecules, the rupture strength would become of the same magnitude as the molecular strength. . . . From the above remarks we must conclude that the technical strength does not represent, in general, a physical constant characteristic of a given material, whereby the practical significance (of such a value) is naturally not taken into consideration. The physicist requires for his purpose a modification of the material which is as free from flaws as possible and reproducible in every respect, and that is the *single crystal*. As a matter of fact, it is found that not only the rupture strength but also, as has been shown by G. von Hevesy, the electrolytic as well as thermal conductivities are quite different in the polycrystalline state from those of single crystals.

and with that of F. Zwicky, who said :

> A. Smekal thinks that actual crystals are never of an ideal geometrical structure, but are made up of a great many microscopic blocks leaving cracks and other imperfections between them. We might call such a structure a mosaic crystal, according to a term used by P. P. Ewald. A. Smekal correlated this conception with a great many facts such as electric conductivity, electric strength, photo-electric absorption, etc. He succeeded in determining the size of the elementary blocks in a half empirical way, and he found that they contain in the case of rock-salt and in many other cases about 10,000 atoms each. As A. Smekal's considerations enable us to understand a great number of facts, it has to be concluded that the formation of cracks and blocks cannot be of a purely accidental nature. Otherwise, the surface cracks should occur in all kinds of different sizes on different samples. But then, it is impossible to understand why the technical breaking strength is a relatively well-defined quantity, as the different samples of a crystal would break on application of widely varied specific stresses.



Basal plane before slip *Lateral view after slip*

Fig. 209.—Mechanism of Slip with Crystals of Zinc.

According to A. Smekal, the rupture strength of a single crystal must increase with a decrease in the dimensions of the crystal until it approaches molecular strength, and that for any given material there is an upper limit for these dimensions. Z. Jeffries found the tensile strength of a tungsten ingot of diameter 200×25 mils. to be 18,000 lbs. per sq. in., of a swaged rod 26 mils. diam., 215,000 lbs. per sq. in., and of a drawn wire 1·14 mils. diam., 590,000 lbs. per sq. in.—by extrapolation, in the limiting case as the diameter approaches atomic dimensions, the tensile strength will approximate 800,000 lbs. per sq. in. A. A. Griffiths, M. Polanyi, and A. Smekal showed that the rupture strength, S, is related with the surface energy, σ, by an expression analogous with $Sl > 2\sigma$, where l denotes the elongation, or grain diameter. The calculated value of l, about 5×10^{-6} cm., is about 500 times greater than the distance at which the attractive forces between the atoms should vanish. To evade the difficulty it was assumed that the rupture strength increases when the elongation required for rupture is less than 5×10^{-6} cm. This means that the rupture of a single crystal is not a definite magnitude corresponding with the cohesive forces. With single crystals of zinc, the round wire during elongation becomes a flat ribbon, the width of the ribbon being slightly greater than that of the original wire. G. Masing and M. Polanyi represented the mechanism of the slip of single crystals of zinc by Fig. 209. The diagram on the left represents the basal plane; the large arrow indicates the direction of maximum shear, and the small arrow lying in a direction parallel to one of the prism sides gives the direction of slip. The elongation is accompanied by a continued strengthening of the crystal, due, according to M. Polanyi, to the bending of the slip planes so that the resistance to slip is increased. M. Polanyi suggested that this result is due to changes in the crystal units themselves; whilst W. Geiss and J. A. M. van Liempt attribute the phenomenon to the deformation of the atoms. The subject was discussed by W. Rosenhain and J. McMinn. D. A. G. Bruggeman discussed the elastic anisotropy of iron.

Observations show that there is an increase in the rupture strength with increasing fineness of grain, and there is a further increase by cold-working. M. Polanyi, and E. Schmid showed that the rolling or drawing of a metal does not destroy the crystal unit, but there is merely a re-orientation of certain planes so that they lie in the direction of the axis of the wire or the plane of rolling--*vide supra*, the crystals of iron. The crevices in the lattice structure of the crystals are independent of temp., and the relation between surface tension and rupture strength, indicated above, means that the effect of a variation of temp. in the one case will be attended by a similar effect in the other case. Surface energy decreases almost linearly with temp., and the tensile strength should therefore follow a similar relation. Surface tension increases with a decrease in grain-size, and this is also the case with the tensile strength. If there be no great variation with temp. in the cohesional forces between atoms, the latent heat of evaporation will be a measure of the lattice energy, but the latent heat of evaporation decreases almost linearly with temp., so that the cohesive strength should similarly decrease with temp.

There is an increase of the free energy of a metal when it is hardened by deformation. Z. Jeffries and R. S. Archer found that cold-work increased the tensile strength, the yield-point and the hardness, while the elongation and reduction of area are decreased by it. The cold-worked metal, however, immediately after working has a lowered elastic limit, but there is a recovery to the original value by ageing or by low temp. annealing. The actual treatment necessary for elastic recovery is dependent on the composition of the metal, and the extent of the deformation during the cold-working. G. von Hevesy, W. Geiss and J. A. M. van Liempt, and S. Dushman showed that the diffusion of one element into another is very much less with single crystals than it is with the rolled metal. Diffusion can occur only through an interchange of places among individual atoms owing to thermal agitation and a consequent disturbance of the lattice. In agreement with the failure of diffusion with single crystals, it is difficult to understand how such phenomena could occur in an undisturbed lattice. Diffusion is more rapid with fine crystalline wire than it is with coarse crystalline wire, indicating that the diffusion occurs along the boundaries of the crystal grains. According to R. Becker, lattice disturbances are the necessary condition for the subsequent interchange of position amongst the atoms. At a given temp., these interchanges occur the more frequently the more the structure is unlike that of a single crystal. In recrystallization, the disturbed lattice is restored to the undisturbed state and the mechanism again involves an interchange of position amongst the atoms. The probability, P, of such an interchange is given by $P=P_0e^{-Q/RT}$, where Q denotes the difference in the potential energy of the atoms in the deformed lattice as compared with that in the undeformed lattice. This is in accord with the fact that the temp. of recrystallization is decreased by cold-working, and R. Becker also showed that grain-growth must similarly increase with temp.

The observations of Z. Jeffries, and W. H. Bassett and C. H. Davis show that the rate of grain-growth varies with temp. as indicated by the equation $G=G_0e^{-Q/RT}$, where G represents the average area of the grain. J. Czochralsky, and G. Masing found that the grain-size increases rapidly with temp. at rates which indicate large values of Q. According to S. Dushman, the cold-working of metals also decreases the rate of grain-growth. This corresponds with an increase of Q with working just as was observed for the case of tensile strength tests. This means that the resistance to the motions of the atoms in forming grains is increased by the mechanical working, or, expressing the same idea in other words, the probability that atoms in adjacent grains will readjust themselves to form a continuous lattice is decreased because these grains have been deformed by working.

According to P. Ludwik, cold-working distorts the space-lattice owing to a movement along the gliding planes; an increase of strength is caused by the breaking action of the gliding planes which increases with the magnitude of the deformation until the crystal ultimately becomes homotropic. The detrimental action of alternating stresses is attributed to a reversal of the movement along the gliding planes—*vide supra*, the crystallization of iron. O. W. Ellis discussed the degree of deformation required to produce a decrease of tensile strength in the cold-working of metals. A. H. Leblond found that when steel bars nicked across opposite surfaces are tested in the tensile machine, the fracture occurs along two planes inclined at angles of 45° with the planes of the nicked surfaces, and meeting at an angle of 90°.

The work performed when a test-piece is broken by the tensile test was discussed by M. Born and O. Stern, P. Ehrenfest, M. Ensslin, W. S. Farren and G. I. Taylor, K. Honda, H. Hort, K. Ljungberg, G. Wulff, and M. Yamada. R. Plank discussed the thermodynamics of the heating of metals which attend elastic and permanent deformation. A. Robertson and G. Cook studied the transition from the elastic to the plastic state. According to O. Faust and G. Tammann, the elasticity of a metal can be increased by alternately slowly increasing the pressure beyond the first limit of elasticity, and then releasing it, until finally an upper limit of elasticity, corresponding with the limiting pressure which produces flow in the metal, is reached. The metal has, therefore, been hardened by slowly increasing the pressure. The hardening of metals is ascribed, not to formation of a harder crystalline form, or to a change to the amorphous condition, but to a diminution in the size of the crystallites of which the metal is composed, owing to the formation of systems of sliding surfaces. The hardening is, therefore, a preparation for flowing, the latter occurring when the systems of sliding surfaces have sufficiently increased. The subject was discussed by H. P. Hollnagel, W. Kuntze and co-workers, A. F. Torres, J. Vietorisz, J. G. Docherty and F. W. Thorne, G. Cook, A. Lundgren, H. O'Neil and H. Greenwood, C. Benedicks—see plastic flow; and R. Plank studied the elongation, and the reduction of area in tensile tests; L. Hartmann, the permanent deformation; and R. H. Greaves, and E. L. Hancock, the overstrain—*vide supra*.

J. Russner discussed the relations between the tensile properties, the sp. ht., and the electrical conductivity; J. Divis, the relation between tensile strength and electrical resistance; O. Leyde, F. Wüst and P. Goerens, A. Campion and H. W. Watts, and W. C. Unwin, the relations between structure and composition, and the mechanical properties; and F. C. A. H. Lantsberry, C. W. Yearsley, and M. Kralupper, the mol. changes in steel under tension. H. Sieglerschmidt found that if E denotes the elastic modulus; D, the density; A, the at. wt.; and a, the coeff. of thermal expansion, $E=CD(Aa)-n$, where C and n denote constants.

S. H. Rees observed that there is a slight increase in the maximum load, yield-point, and elastic limit of a strained, 0·85 per cent. carbon steel as a result of annealing at 200°, and a complete recovery on tempering at about 600°. J. R. Freeman and R. D. France found that cold-rolled electrolytic iron had the greatest tensile stress perpendicular to the direction of rolling, and that ductility was highest in the direction of rolling. J. A. van den Broek summarized his results as follows: (i) When mild steel is cold-worked and properly aged or tempered and subsequently tested in the same direction as that of the cold-working, its elastic limit may be raised more than 100 per cent., and from 10 to 20 per cent. beyond the stress at which cold-working was discontinued. (ii) When mild steel is cold-worked in one direction and properly aged or tempered, but tested in either one of two senses of a different direction, then its elastic limit may be raised some 50 per cent. (iii) When mild steel is cold-worked in one direction and properly aged or tempered but tested in the opposite direction, then the elastic limit remains at the value of the original elastic limit, but the yield-point is raised. (iv) When mild steel is cold-worked in any direction and tested in any direction, without any ageing or tempering, then the elastic limit falls below the value of the original elastic limit, often down to zero. (v) Tempering cold-worked steel at temp. from 100° to 300° C., or ageing cold-worked steel, has a tendency to perfect its elastic properties. Tempering merely accelerates the effects of time. The subject was investigated by A. Pomp and co-workers, A. Portevin and E. Pretet, H. Poellein, and E. Mayer.

The orientation of the crystals by cold-work has been discussed in connection with the structure of the crystal lattice of iron. From the observations of M. Masima and G. Sachs, R. G. Karnop and G. Sachs, P. W. Bridgman, and E. Grüneisen and E. Goen, T. Kawai said that in a metal with crystals belonging to the cubic system, it may be assumed that Young's modulus is smallest in the (100)-direction, largest in the (111)-direction, and greater than the mean of these two in the (110)-direction. A polycrystalline metal in which the microcrystals are oriented at random, is isotropic with respect to Young's modulus; but if the metal be stretched or drawn, it becomes aelotropic, for a definite axis of the microscopic crystals takes the axial direction of the bar by rotation due to cold-working. In the case of iron and steel, the (110)-axis of the crystals gradually takes the direction of the axis of the bar by increasing cold-work, and consequently the modulus is slowly increased. With copper, aluminium, and nickel, the (111)-axis of the microcrystals takes the axial direction of the bar by cold-working, and consequently the modulus is rapidly increased by cold-working.

L. Aitchison and L. W. Johnson examined the effect of testing materials in the direction of rolling or forging, and in other directions. The fibrous structure, frequently obvious in rolled steel, can be compared with the grain of wood, so that directions which are taken longitudinally and transversely to the directions of rolling can be said to be taken *along the grain* and *across the grain* respectively. A selection from the results is given in Table XXIV. All the samples except that indicated were normalized, and the tensile results are expressed in tons per sq. in. The results show that the values for the elastic limit, yield-point, and maximum stress are almost uniform, the values for the Izod or notched-bar test are different when taken longitudinally and transversely, and the value for the notched-bar test taken longitudinally increases as forging progresses. The fatigue strengths of specimens taken parallel and at right angles to the grains do not show large differences, but the difference is in favour of the longitudinal material; thus:

TABLE XXIV.—MECHANICAL PROPERTIES OF STEEL TAKEN LONGITUDINALLY AND TRANSVERSELY.

	Casting		First forging		Second forging		Third forging		Second forging (hardened and tempered)	
	Long.	Trans.	Long.	Trans.	Long.	Trans.	Long.	Trans.	Long.	Trans.
Elastic limit .	16·4	16·3	20·2	19·6	20·8	20·8	20·1	18·9	25·5	25·3
Yield-point .	20·3	20·4	21·2	21·5	21·2	21·2	20·6	19·3	25·7	25·7
Max. stress .	38·3	38·9	36·4	36·5	35·5	35·6	36·0	36·0	40·5	40·2
Elongation (per cent.) . .	19·7	18·2	30·8	29·0	33·4	22·2	33·1	28·5	29·8	21·2
Reduction of area (per cent.)	25·8	23·6	57·4	48·4	58·3	23·8	58·7	43·5	66·9	38·2
Izod value (ft.-lbs.) . .	16·7	17·0	34·0	27·3	61·7	30·0	74·0	29·0	59·0	16·3

	Longitudinal	Transverse
Cast (normalized)	±13·0	±12·6
First forging (normalized)	±16·2	±15·0
Second forging (normalized)	±16·2	±13·5
Third forging (normalized)	±16·0	±15·5
Second forging (hardened and tempered)	±19·5	±17·0

T. D. Yensen found that for electrolytic iron, melted in vacuo, the limits of proportion were 11 kgrms. per sq. mm.; the tensile strength, 25 kgrms. per sq. cm.; the elongation, 60 per cent. on a 50·8 mm. test-piece; and the reduction of area, 85 per cent. The effect of carbon has been the subject of numerous investigations. J. O. Arnold, working with steels containing 0·03 to 0·08 per cent. of silicon; 0·01 to 0·10, manganese; 0·02, phosphorus; 0·01 to 0·03, sulphur; and 0·02 to 0·04, aluminium, obtained for the tensile properties, in tons per sq. in., of rolled bars, *R*, normalized by heating to 1000° and cooling in air; and of bars annealed for 72 hrs. at 1000°, *A*, and cooled in the luted muffle for 100 hrs. with

Carbon		0·08	0·21	0·38	0·59	0·89	1·20	1·47	per cent.
Elastic limit	*R*	12·19	17·08	17·95	19·82	24·80	35·72	32·27	
	A	8·82	9·02	9·55	11·36	16·81	16·19	10·08	
Max. strength	*R*	21·39	25·39	29·94	42·82	52·40	61·65	55·71	
	A	18·34	21·25	25·02	31·87	36·69	32·87	22·33	
Elongation	*R*	46·6	42·1	34·5	19·9	13·0	8·0	2·8	per cent.
	A	52·7	42·3	35·0	22·0	4·5	6·0	19·0	,,
Reduction area	*R*	74·8	67·8	56·3	22·7	15·4	7·8	3·3	,,
	A	76·7	65·7	50·6	23·3	4·2	4·9	17·7	,,

The annealed steels with 1·20 and 1·47 per cent. of carbon included respectively 0·28 and 1·14 per cent. of graphitic carbon. C. R. Jones and C. W. Waggoner found the stress deformation shown in Fig. 210; and the mechanical tests, expressed in lbs. per sq. in., for steels with 0·14 to 0·17 per cent. of manganese; 0·15 to 0·19. silicon; 0·010 to 0·013, phosphorus; and 0·012 to 0·014, sulphur, as well as for iron with 0·058, carbon; 0·071, manganese; 0·008, silicon; and a trace of phosphorus, when they were annealed for 2 hrs. at 1000°, and cooled in the furnace, are:

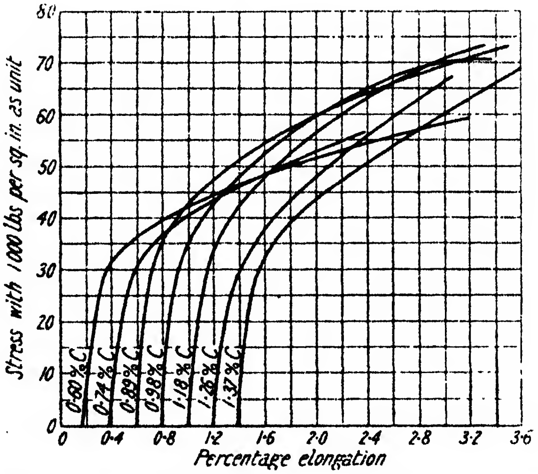


FIG. 210.—Stress-Elongation Diagram for Steels with Different Proportions of Carbon.

Carbon	0·058	0·6	0·74	0·89	0·98	1·18	1·26	1·37	per cent.
Max. strength	45,800	76,500	81,250	95,250	94,600	90,400	84,100	89,000	
Breaking load	22,800	72,750	79,600	93,100	94,600	90,400	84,100	89,000	
Elastic limit	26,000	28,500	28,500	32,000	27,500	25,500	23,500	23.500	
Elongation	28·0	20·0	14·0	13·5	8·0	3·0	2·5	broke	per cent.
Reduction area	75·7	29·5	18·2	12·6	11·3	5·96	2·38	,,	,,

F. W. Harbord gave for steels, with about 0·02 per cent. of sulphur; 0·02, phosphorus; 0·020 to 0·98, silicon; and 0·160 to 0·217, manganese, annealed for 30 mins. at 900°, in lbs. per sq. in.:

Carbon . .	0·130	0·180	0·254	0·468	0·722	0·871	0·947	1·36 per cent.
Max. strength .	48,100	62,350	66,000	72,700	96,780	112,900	114,700	99,769
Elastic limit .	29,100	35,500	38,300	40,400	—	—	—	—
Elongation .	45·0	33·5	32·5	28·0	16·5	11·2	10·0	5·5 per cent.
Reduction area	71·16	60·24	54·84	46·26	25·86	15·84	15·42	5·58 ,,

H. H. Campbell gave for steels with 0·013 to 0·019 per cent. sulphur; 0·14 to 0·29, phosphorus; 0·012 to 0·013, silicon; 0·068 to 0·20, manganese, heated to 950° except in the last case where the heating was 1050°, and cooled in the furnace, in lbs. per sq. in.:

Carbon	0·42	0·70	1·04	1·61	1·72 per cent.
Max. strength . .	64,420	90,500	111,500	96,350	95,000
Elastic limit . .	41,800	39,700	46,800	48,500	45,200
Elongation . . .	19·4	16·5	10·5	7·5	7·5 per cent.
Reduction area . .	44·5	20·5	10·9	6·8	6·3 ,,

J. Bauschinger's results are indicated in Table XXIV, and Fig. 210. T. Ishigaki also found the maximum stress, in kgrms. per sq. cm., increased with the proportion of carbon up to 0·9 per cent., and thereafter decreased; thus:

Carbon . .	0	0·1	0·3	0·5	0·7	0·9	1·1	1·3 per cent.
Max. stress .	3380	3700	5200	5750	7550	8800	8200	7860

H. Wedding gave, in tons per sq. in.:

Carbon . . .	0·20	0·30	0·40	0·50	0·60	0·70	0·80	0·90	1·0 per cent.
Tensile strength .	26·2	30·0	35·0	37·1	39·6	50·8	58·0	61·2	65·4
Elongation . .	26·2	19·4	19·0	18·1	16·3	8·3	5·7	7·5	6·0 per cent.
Reduction of area	62·0	52·2	55·0	34·7	34·2	9·9	3·8	12·3	12·2 ,,

K. Johansson gave for the percentage elongation, *E*, and the tensile strength, *T*:

Carbon . .	0·06 to 0·10	0·10 to 0·15	0·15 to 0·22	0·22 to 0·28 per cent.
E . . .	21·6 to 24·1	24·1 to 26·7	26·7 to 29·8	29·8 to 32·4
T . . .	25 to 30	22 to 25	20 to 24	20 to 22
Carbon . .	0·28 to 0·22	0·33 to 0·38	0·38 to 0·45	0·45 to 0·50 per cent.
E . . .	32·4 to 35	35·5 to 38·7	38·7 to 43·2	43·2 to 47·0
T . . .	18 to 20	16 to 20	15 to 18	14 to 16
Carbon . .	0·50 to 0·55	0·55 to 0·60	0·60 to 0·68	0·68 to 0·75 per cent.
E . . .	47·0 to 50·8	50·8 to 54·6	54·6 to 57·1	57·1 to 63·5
T . . .	12 to 15	10 to 12	8 to 10	5 to 10

According to E. J. Rang, the effect of increasing the proportion of carbon is to increase the elastic limit and ultimate tensile strength of steels; with very high carbon steels, the elastic limit is indefinite because, under load, the elastic limit is continuously being reached, and the small amount of cold-work thus done on the bar forms a new elastic limit. As a result, the stress-strain curve, though continuous, is not a straight line. The subject was discussed by E. H. W. Tafel, J. Dessent, J. O. Arnold, C. R. Jones and C. W. Waggoner, and W. A. Scoble. M. Moser said that during elongation in the tensile test, steel does not flow uniformly, but in zones. Each zone stretches at first until a certain degree of hardness is attained and then remains nearly stationary with the hardness unaltered until another zone elongates. Only when all the zones in the test-piece have been elongated does a further uniform increase in hardness set in over the whole elongated part. E. Schüz, etc., studied the relation between the tensile strength and hardness (*q.v.*), and they found that the tensile strength in general increased with the proportion of combined carbon; and M. Hamasumi, that the tensile strength increased with the rate of cooling. A. Pomp and A. Lindenberg studied the effect of nitrogenization. For the embrittling effects of occluded hydrogen, *vide infra*, corrosion. J. V. MacCrae and R. L. Dowdell studied the effect of deoxidation on the tensile strength of cast steel.

C. R. Jones and C. W. Waggoner added that all the curves for maximum strength or tenacity have the general form predicted by H. M. Howe from a consideration of the microscopic constituents. His curves show a maximum at or near the eutectoid ratio for the iron-carbon diagram. B. Stoughton has suggested that the intimate mixture of the crystalline constituents when the steel is near the eutectoid ratio has the effect of increasing the molecular attraction between the crystals, thus raising the maximum strength of the material; for below the eutectoid the pearlite is surrounded by a network of soft ferrite, while above it is surrounded by a network of cementite, both of these networks having a weakening effect upon the attraction between the molecules of the crystals. Although the experimental maximum seems to occur at a lower percentage of carbon than predicted by H. M. Howe, the curves show a strong confirmation of the theories of H. M. Howe, and B. Stoughton. The results indicate that pure iron should have a tensile strength of about 40,000 lbs. per sq. in., and that the tensile strength of the series of annealed crucible steels tested increased about 630 lbs. for each 0·01 per cent. of carbon up to 0·89 per cent., after which the strength gradually decreased. The elastic-limit-carbon curves seem to follow the same general law as the maximum strength-carbon curve, the maxima for the curves plotted occurring at the same percentages of carbon. The variation of the stresses at the elastic limit, however, is much less marked than the variation of the maximum strengths, and in other tests that the writers investigated the results were either irregular or showed more than one critical point. The curves for total elongation or ductility, and reduction of area are similar; and indicate that there is a critical point in each corresponding to the percentage of carbon which gives maximum strength. This critical point may represent a minimum value or a marked change in the direction of the curve. E. L. Dupuy's results for the percentage reduction of area with the temp. and percentage of carbon as variables, are summarized in Fig. 211. E. Greulich represented the relation between the reduction of area, ϕ, Brinell's hardness, elongation, or tensile strength, y, by $y=a+b \log \phi$, where a and b are constants.

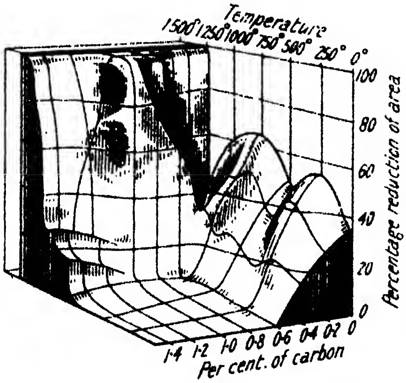


FIG. 211.—The Percentage of Area at Different Temperatures and with Different Proportions of Carbon.

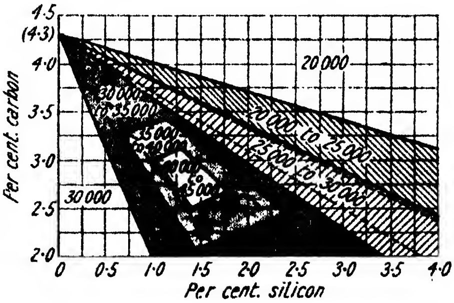


FIG. 212.—Constitution and Tensile Strength of Cast Iron.

According to P. Bardenheuer, and G. Neumann, the form and degree of fineness of the separated graphite are the dominant factors in determining the tensile strength, bending strength, and resistance to shock of grey cast iron as cast, as annealed at 850°, as quenched in oil, and as quenched and then annealed at 600° to 650°. The nature of the ground mass influences the hardness, but the highest tensile strength is obtained with the minimum amount of graphite provided it is evenly distributed throughout the metal in fine flakes. F. B. Coyle studied the tensile strength of cast iron, and found that the results can be represented by diagram, Fig. 212, where the dotted lines refer to E. Maurer's diagram of the constitution of cast iron—*vide supra*, Fig. 58. The numbers in the diagram are intended to represent the tensile strengths of cast irons, expressed in lbs. per sq. in., and whose compositions fall in the regions concerned. Analogous diagrams were prepared for cast irons with 2 per cent. of nickel, and with 0·50 to 0·75 per cent. of chromium, and with combinations up to 0·25 to 1·25 per cent. of nickel and 0·25 to 0·75 per cent. of chromium.

W. R. Webster examined a great number of steels in the attempt to find a relation between the strength of steel and its chemical composition; and the subject was also taken up by H. H. Campbell, who gave the following formulæ: Let C denote 0·01 per cent. of carbon; P, 0·01 per cent. of phosphorus; Mn, 0·01 per cent. of manganese; and *R*, a variable to denote the heat-treatment, then, the ultimate stress in lbs. per sq. in., for acid steel where the carbon is determined by combustion, is $40,000+1000C+1000P+x\text{Mn}+R$; and when the carbon is determined by colour, $39,800+1140C+1000P+x\text{Mn}+R$. While for basic steel, where the carbon is determined by combustion, the ultimate stress is $41,500+770C+1000P+y\text{Mn}+R$, and where the carbon is determined by colour, $42,000+820C+1000P+y\text{Mn}+R$. Table XXV gives the coeff. x for acid steels with over 0·4 per cent. Mn, and Table XXVI, the coeff. y for basic steels with over 0·3 per cent. Mn. Any formula expressing the relation between the strength of steel and its chemical composition can have only a limited application because of the influence of other variable conditioning factors; it is therefore assumed that the conditions of manufacture are similar to those which were employed for the standards from which the formulæ were deduced. Observations on the subject were made by J. Bauschinger, A. C. Cunningham, E. Demange, V. Deshayes, H. M. Howe, J. E. Hurst, J. B. John-

TABLE XXV.—MANGANESE.

C per cent.	0·42 per cent.	0·44 per cent.	0·46 per cent.	0·48 per cent.	0·50 per cent.	0·52 per cent.	0·54 per cent.	0·56 per cent.	0·58 per cent.	0·60 per cent.
0·10	160	320	480	640	800	960	1120	1280	1440	1600
0·15	240	480	720	960	1200	1440	1680	1920	2160	2400
0·20	320	640	960	1280	1600	1920	2240	2560	2880	3200
0·25	400	800	1200	1600	2000	2400	2800	3200	3600	4000
0·30	480	960	1440	1920	2400	2880	3360	3840	4320	4800
0·35	560	1120	1680	2240	2800	3360	3920	4480	5040	5600
0·40	640	1280	1920	2560	3200	3840	4480	5120	5760	6400
0·45	720	1440	2160	2880	3600	4320	5040	5760	6480	7200
0·50	800	1600	2400	3200	4000	4800	5600	6400	7200	8000
0·55	880	1760	2640	3520	4400	5280	6160	7040	7920	8800
0·60	960	1920	2880	3840	4800	5760	6760	7680	8640	9600

TABLE XXVI.—MANGANESE.

C per cent.	0·35 per cent.	0·40 per cent.	0·45 per cent.	0·50 per cent.	0·55 per cent.	0·60 per cent.
0·05	550	1100	1650	2200	2750	3300
0·10	650	1300	1950	2600	3250	3900
0·15	750	1500	2250	3000	3750	4500
0·20	850	1700	2550	3400	4250	5100
0·25	950	1900	2850	3800	4750	5700
0·30	1050	2100	3150	4200	5250	6300
0·35	1150	2300	3450	4600	5750	6900
0·40	1250	2500	3750	5000	6250	7500

son, H. von Jüptner, A. Kroitzch, H. K. Landis, F. C. Lea, A. Ledebur, W. N. Lipin, M. Merriman, W. Minty, H. O'Neil, B. Osann, F. Osmond, E. Rasch, P. G. Salom, J. K. Smith, R. H. Thurston, H. Wedding, and J. Weyrauch. C. D. Mathews found the tensile strength of grey cast iron with 1·5, 2·0, and 2·5 per cent. of silicon to be respectively 25,600, 24,370, and 24,660 lbs. per sq. in. J. E. Hurst discussed the attempts made to show the relation between the composition and properties of cast iron by formulæ and diagrams.

R. A. Fessenden, G. Wertheim, W. Sutherland, and H. Tomlinson observed a relation between the tensile properties of the metals and their at. vol., and W. C. Roberts-Austen showed that except in cases where chemical combination occurs, the introduction of atoms of elements with a small at. vol. raises the tensile strength of a metal. R. A. Fessenden's relation is Tensile strength$=0{\cdot}5280T_mv^{-4/3}$, where T_m denotes the m.p. of the metal on the absolute scale, and v the at. vol.—*vide* **1.** 13, 17.

J. O. Arnold and A. McWilliam represented the effect of the constitution of steel, on the tensile properties, by diagrams analogous to those of Fig. 213. The *first stage*, I, Fig. 213, contains sorbitic pearlite associated with emulsified cementite, and it is very dark on etching; the maximum tensile strength is about 70 tons per sq. in., and the elongation on 2 ins. is about 10 per cent. The *second stage*, II, Fig. 213, contains pearlite with semi-segregated cementite, and it is dark on etching; the maximum tensile strength is about 55 tons per sq. in., and the elongation on 2 ins. is about 15 per cent. The *third stage* contains laminated pearlite with completely segregated cementite, and it exhibits a gorgeous play of colours when lightly etched; the maximum tensile strength is about 35 tons per sq. in., and the elongation on 2 ins. is about 5 per cent. The *fourth stage* has laminated pearlite passing into massive cementite and ferrite; the maximum tensile strength is about 30 tons per sq. in. The different stages may sometimes be observed in juxtaposition on one piece. R. Hugues, H. Meyer and W. Wesseling, and S. S. Steinberg discussed the effect of heat-treatment on the mechanical properties.

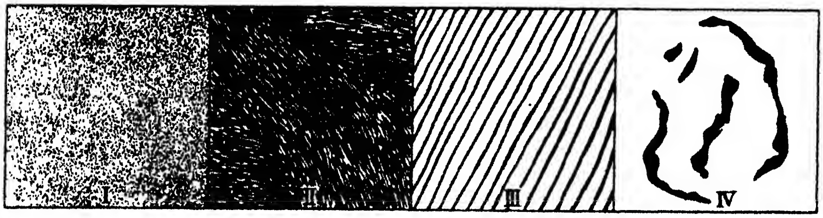


FIG. 213.—Stages in the Formation and Disruption of Pearlite.

O. Bauer and W. Schneider said that the breaking stress of electrolytic iron is not affected by quenching from 650° to 1258° in iced water. H. Hanemann measured the tensile strength, in kgrms. per sq. mm., of some hypereutectoidal steels quenched from different temp., and obtained the results indicated in Table XXVII. The

TABLE XXVII.—THE EFFECT OF QUENCHING TEMPERATURE ON THE TENSILE STRENGTH OF HYPEREUTECTOIDAL STEELS.

Carbon (per cent.)	750°	800°	850°	900°	950°	1000°	1050°	1075°
0·99	44·95	29·61	17·07	14·42	10·07	6·37	—	—
1·15	53·61	52·75	43·73	35·78	21·51	16·82	—	—
1·22	—	48·62	47·88	50·71	37·77	24·92	17·17	—
1·33	—	51·43	54·38	54·63	41·23	30·22	20·03	—
1·45	—	61·42	61·72	60·91	42·66	38·88	29·41	—
1·56	—	51·28	48·87	51·18	55·40	52·19	49·28	42·45

results show that for each steel there is a quenching temp. which gives the strongest metal; this temperature rises with the carbon-content, but when it is exceeded, the strength of the metal is impaired. The greatest strength was obtained by quenching in a lead-zinc bath at 300°. Tempering at 350° yielded a steel with a maximum tensile strength, and this agrees with E. Heyn and O. Bauer's observation that a steel heated to 900° and quenched at 14° to 18°, gives a maximum solubility when tempered at 900°. It is therefore suggested that the osmondite structure gives the maximum tensile strength. A. Jung concluded from his observations on the influence of heat-treatment on the tenacity and microstructure of hypereutectoidal steels : (i) The temp. to be employed in hardening hypereutectoid steels are restricted to a definite range, which is lower and narrower the smaller the carbon content. (ii) The ultimate strength increases to a maximum for a given carbon content as the temp. of quenching falls. (iii) For equal quenching temp., the ultimate strength increases with the carbon content. (iv) The same quenching temp. should be used for different media. (v) The greatest strength is attained by quenching in water and then tempering at 350°. (vi) By quenching in water and tempering, a comparatively brittle material, with high tenacity, is obtained; while by quenching in a medium at the same temp. as that employed for tempering, a lower tenacity and greater toughness is obtained. (vii) Different forms of heat-treatment cannot be made to produce identical results ; identity of results can be obtained only for any one property of steel. (viii) The mechanical properties depend on the state of the carbon and also on the structure of the metal. (ix) A martensitic structure gives the greatest hardness, a troosto-sorbitic structure gives the greatest tenacity, while a pearlitic structure gives the great elongation. (x) It was not possible to detect any consistent influence of the carbon content on the mechanical properties of the specimens under the conditions employed. The subject was discussed by L. Faure, M. Kuroda, and A. Pomp and A. Lindenberg.

H. Hanemann and R. Kühnel studied the hypoeutectoidal steels, hardened by quenching at 950°, and then tempered 2 hrs. in water at 100°; 1 hr. in rape oil at 200° ; 40 mins. in a bath of sodium and potassium nitrates at 300°, 400°, and 500°. The results are summarized in Table XXVIII. The tensile strength is expressed in kgrms. per sq. mm. For the 0·34 per cent. carbon steel annealed at 500° after quenching in water, the numbers were respectively 79·9, 15·0, and 51·0, and after quenching in water, 80·1, 15·0, and 51·0; for the 0·65 per cent. carbon steel quenched in oil, 84·7, 10·0, and 51·0; and quenched in oil, 84·7, 9·5, and 51·0. G. Welter found that the mechanical properties vary 10 per cent. by cooling under different conditions.

TABLE XXVIII.—THE EFFECT OF QUENCHING AND SUBSEQUENT TEMPERING ON HYPOEUTECTOIDAL STEELS.

Carbon per cent.	Quenched in	100°			200°			300°			400°		
		Tensile	Elong. per cent.	Red. per cent.	Tensile	Elong. per cent.	Red. per cent.	Tensile	Elong. per cent.	Red. per cent.	Tensile	Elong. per cent.	Red. per cent.
0·05	Oil	57·9	11·0	63·2	44·8	11·7	75·0	48·8	11·5	75·0	47·8	12·0	75·0
	Water	56·6	11·5	63·2	43·0	11·85	75·0	43·7	12·2	75·0	45·8	12·4	75·0
0·20	Oil	146·7	2·5	9·8	143·3	5·0	36·0	122·4	8·0	47·5	102·9	11·0	51·0
	Water	103·5	9·0	51·0	90·0	10·5	55·0	82·9	10·7	58·1	73·5	11·2	63·2
0·34	Oil	168·6	3·0	11·6	155·6	6·0	27·5	134·4	8·5	36·4	111·2	10·0	48·2
	Water	148·2	5·6	15·4	143·6	7·1	21·7	134·2	9·8	24·3	111·6	10·0	36·0
0·50	Water	174·3	0·0	0·0	188·8	1·5	0·0	176·6	4·5	17·2	153·6	7·0	36·0
0·65	Oil	170·0	0·0	0·0	174·2	0·0	0·0	189·2	2·3	5·9	149·0	5·8	36·0
	Water	136·7	0·0	0·0	185·8	1·0	4·0	164·5	4·0	15·4	147·2	6·3	36·0

The highest, lowest, and average tensile strength of cast iron given were respectively 9·08, 5·09, 7·19 tons per sq. in.; by E. Hodgkinson and W. Fairbairn, 10·5, 4·9, and 6·83 tons per sq. in.; by W. Wade, 20·5, 4·2, and 9·1 tons per sq. in.; by T. Turner, 15·7, 4·75, and 10·22 tons per sq. in.; by W. C. Unwin, 17·3, 14·9, and 15·7 tons per sq. in.; and by E. Adamson, 13·74, 15·62, and 14·8 tons per sq. in. E. Adamson's results show that with total carbon 3·56 to 3·57; graphitic carbon, 2·98 to 3·04; combined carbon, 0·54 to 0·59; silicon, 1·46 to 2·00; sulphur, 0·072 to 0·11; phosphorus 0·59 to 1·20; and manganese 0·65 to 0·90, considerable variations in the phosphorus, silicon, and manganese makes very little difference to the results. The elastic limit varies with the proportion of combined carbon; if all the carbon is in the combined state, the range of proportionality extends up to the point of fracture even when a pearlitic matrix is present. If the iron contains a small matrix of ferrite when the carbon is wholly graphitic, there is so low an elastic limit that some—*e.g.* I. N. Hollis—say that the material has no well-defined modulus of elasticity, or elastic limit. The yield-point of commercial cast iron also coincides with rupture, so that the elongation and reduction of area are negligibly small. G. A. Akerlind gave 40,000 to 50,000 lbs. per sq. in. for the tensile strength of malleable cast iron and 1 to 6 per cent. for the elongation, and 0·75 to 3·0 per cent. for the reduction of area. Hence, cast iron is about half as strong as the malleable. Observations on the elastic properties of cast iron were made by F. B. Coyle, J. T. Mackenzie, A. Thum and H. Ude, W. R. Needham, J. B. Kommers, E. J. Lowry, J. E. Hurst, K. Emmel, B. Osann, and O. Smalley. C. Frémont said that the elastic limit of cast irons is from one-fifth to three-fifths of that of steel; and the elastic limit occurred with 0·45 to 0·80 per cent. of the ultimate load. According to A. Thum and H. Ude some of the modern cast irons have a tensile strength of 30 kgrms. per sq. mm. where 18 to 20 kgrms. per sq. mm. was formerly thought to be very good. H. A. Schwartz discussed the tensile strength of malleable cast iron. W. C. Unwin gave 19·8 tons per sq. in. for the highest and 12·8 tons per sq. in. for the lowest tensile strength of malleable cast iron. W. H. Hatfield gave for the maximum stress of European or Réaumur's malleable cast iron 19·78 to 27·07 tons per sq. in., 3·5 to 6·0 per cent. elongation in 2 ins.; and 3·5 to 6·0 per cent. reduction in area; and for the American, or blackheart, malleable cast iron, 19·41 to 22·85 tons per sq. in. for the maximum stress, 10·0 to 14·0 per cent. elongation in 3 ins., and 7·7 to 17·5 per cent. reduction in area. H. Hanemann found that with graphite present as coarse grains, the tensile strength of cast iron was 10 to 14 kgrms. per sq. mm., and with the graphite in fine grains, 20 to 24 kgrms. per sq. mm. Many observations have been made on the influence of the separation of graphite on the mechanical properties of cast iron—*e.g.* by A. G. Ashcroft, P. Bardenheuer and K. L. Zeyen, O. Bauer, J. W. Bolton, K. Emmel, C. Gilles, C. Henning, E. Jüngst, P. Kleiber, T. Klingenstein, A. E. Macrae, E. Maurer, A. E. Outerbridge, E. Piwowarsky, H. Rolle, P. A. Russell, J. Seigle, K. Sipp, A. E. M. Smith, R. Stotz, A. Thum and H. Ude, O. Wedemeyer, T. D. West, F. Wüst and co-workers, and A. Zenges—*vide supra*, graphitization. A. Thum and H. Ude suggested that structurally cast iron can be regarded as a "notched steel" because the carbon flakes produce minute notches and so lower the mechanical properties of the metal.

P. Goerens observed the effect of tempering and annealing on cold-worked iron with 0·080 per cent. of carbon; 0·39, Mn; 0·008, Si; 0·056, S; and 0·059, P. The results are summarized in Fig. 214. Tempering at 100° gives a perceptible result, and near 520° there is an abrupt change from about 45 kgrms. per sq. mm. to 40 kgrms. per sq. mm. at 600°, which is about the normal value. The elongation and reduction of area behave in a corresponding way. Observations were made by P. F. Lee and co-workers, H. E. Publow and co-workers, and F. G. Sefing and M. Surls. The effect of the duration of the annealing is summarized in Fig. 215. J. Orland studied the influence of pearlization below the Ar_1-arrest on the mechanical properties. P. Ludwik found for cast iron annealed at 900°, and cast steel annealed at 700°, and tested at the following temp.—the ultimate strength is expressed in kgrms. per sq. mm.:

		20°	225°	335°	407°	617°	807°	835°
Iron	Strength	42·5	45·0	45·0	34·0	13·8	3·8	3·6
	Elongation	21	4	18	21	45	39	—
	Reduction	68	57	61	68	95	89	88 per cent.

		20°	250°	330°	412°	485°	617°	722°
Steel	Strength	53·5	60·2	57·6	55·0	34·7	22·0	10·7
	Elongation	16	5	9	19	20	32	35
	Reduction	63	43	54	55	62	80	63 per cent.

F. C. Lea and O. H. Crowther observed a maximum in the tensile strength, and yield-point of iron at 300°; and F. C. Lea observed a maximum in the tensile strength of armco iron at about 230°, a minimum in the elongation at about 100°, and a maximum at 350°. The elastic limit in tension had a minimum at 230°. H. J. Tapsell and W. J. Clenshaw obtained similar results. E. L. Dupuy found a maximum in the tensile strength and a minimum in the reduction of area at 250° in a 0·15 per cent. carbon steel rising to 330° in a 0·91 and 12·5 per cent. carbon steel, in which two the minimum in the reduction area was not perceptible. F. A. Epps and E. O. Jones observed a minimum in the elongation of wrought iron between 100° and 150°; and A. Sauveur and D. C. Lee, a minimum in the strength of steel. A. Goffey and F. C. Thompson observed changes at 70°, 120°, 170°, 230°, 290°, 310°, and 350°, and with steels, in addition, and at 90°, 190°. The meaning of the singularities is unknown—*vide supra*.

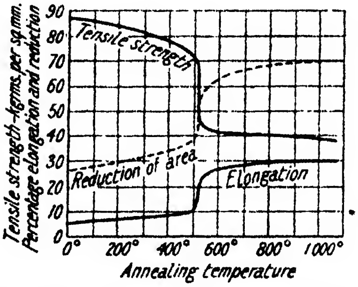


FIG. 214.—Effect of Temperature of Annealing on the Tensile Properties of Cold-drawn Wire.

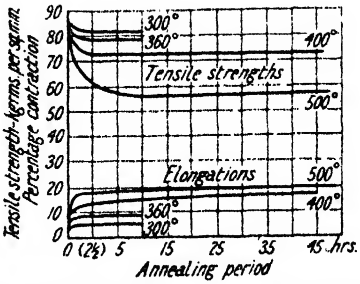


FIG. 215.—Effect of Temperature and Time of Annealing on the Tensile Properties of Cold-drawn Wire.

W. Eilender found that the changes produced by the ageing of quenched steel, containing 0·032 per cent. of nitrogen, are very remarkable. Thus, the tensile strengths after quenching from 680°, and after ageing for 14 days at 20°, were, respectively, 39·1 and 44·8 kgrms. per sq. mm., whilst the corresponding elongations were 33·0 and 2·7 per cent., and the reductions of area 61·0 and 2·5 per cent.

In 1863, K. Styffe found that the strength of iron and steel is not diminished by cooling to −40°; and C. Pardun and E. Vierhaus observed no loss in the mechanical properties of cast iron occurred by cooling it to low temp., but a change occurred when the temp. dropped to −80°. The cause of the alleged brittleness of cast iron in winter is due to shrinkage stresses, or, in the case of pipe systems, to the action of the frozen earth in which they are embedded. In 1886, T. Andrews investigated the effect of cooling down to −45°, on the strength of railway axles, and found the metal was more brittle at these low temp. F. Steiner also observed what he called "crystalline brittleness" at −50°. M. Rudeloff found that the cooling of weld iron to −20° did not markedly affect its toughness, but ingot metal became brittle; cooling to −80° caused both these metals to become brittle. Crucible steel became very brittle at −80°, but at −20° was not much affected. Basic bessemer steel was more affected by cooling than open-hearth steel. The bending capacity was reduced from 100 to 85 in the latter case, and from 100 to 81 in the former case. J. Dewar showed that at −280°, iron has double the tensile strength it possessed at 15°. A soft steel wire of 0·098 in. diameter at 15° broke with a stress of 420 lbs., and at −182°, with 700 lbs.; while an iron wire broke at 15° with 320 lbs., and at −182°, with 670 lbs. Observations were also made by C. Schäfer, F. Sauerwald and K. A. Pohle, W. H. Johnson, T. Matsuda, and J. R. Benton. R. A. Hadfield found that low temp. in the vicinity of −182° increased the tenacity or breaking load of iron and iron alloys; the ductility as measured by the elongation is reduced from 30 to 40 per cent. with mild steel, to practically *nil*. The same changes occur with the softest wrought iron, as with steels with 0·10 to 1·50 per cent. of carbon, so that the presence or absence of carbon has very little influence. Pieces of mild steel immediately after immersion, break instantly when struck with a hammer, and there is an entire absence of ductility. Thus, a sample of steel with 0·045 per cent. carbon; 0·07, silicon; 0·005, sulphur: 0·004, phosphorus; a trace of manganese; and 99·82, iron, gave:

	18°	−80°	−100°	−193°	−273°
Tenacity . .	20	27	30	44	(70) tons per sq. in.

A similar sample with 21 tons per sq. in. tenacity and 25 per cent. elongation gave at −182° a tenacity of 54 tons per sq. in., and elongation *nil*. The presence of nickel was found to counteract the tendency of iron to become brittle at these low temp. R. A. Hadfield also observed that with Swedish iron having 0·045 per cent. of carbon, the tensile strength in tons per sq. in. and the percentage reduction of area were for the annealed metal respectively 44·0 and 0·0 at −185°, and 18·5 and 75·0 at 18°; whilst for the quenched metal, these values were respectively 54·0 and 0·0 at −185°, and 20·5 and 72·0 at 18°. O. Reinhold gave for the tensile strength in kgrms. per sq. mm., and for the percentage reduction of area, of soft iron with 0·04 per cent. of carbon:

	−70°	20°	320°	400°	460°	520°	590°	620°
Tensile strength .	48·0	42·6	58·7	42·6	33·2	26·3	16·2	13·7
Reduction area .	70·0	73·0	65·0	74·6	80·3	86·5	93·0	95·8 per cent.

The question has been raised whether iron which has been exposed to a low temp. is afterwards more brittle than before the exposure. A. von Frank said that there is no evidence of any change in metal which has been exposed to the temp. of a European winter in mountainous districts, −22° to −25°; or to an Arctic winter. E. Bernardon found that the test-pieces exposed to great cold showed no marked difference when tested at ordinary temp. F. Steiner, and H. Gollner observed no apparent alteration in the bending tests of wrought iron, annealed cast iron and steel which had been cooled to −50°, and then returned to the original temp. of the room; and G. Mehrtens, no permanent deterioration in the metal of a prolonged exposure at about −88°.

The term **shortness** is often used synonymously with **brittleness**—*e.g.* in the ceramic industries a short clay is one with a low plasticity and in consequence with a tendency to rupture; and in the metallurgical industries the term is applied to a metal with a tendency to rupture under shock or stress, particularly when the stress is suddenly applied, and when the metal breaks without much elongation or reduction of area. Shortness is the opposite to toughness (not hardness). If the metal is brittle when hot, it is said to exhibit **red-shortness or hot-shortness**; when cold, **cold-shortness**; and when at a blue temper heat, about 300°, **blue-shortness.** The evolution of these apparently simple terms is curious. In an early translation of Pliny's *Historia naturalis*, by P. Holland, in 1610, the term *colsar* is used for cold-shortness; in 1637, P. Vernatt and T. Whitmore spoke of *colshire* or *coleshire* iron; in 1665, D. Dudley called it *coldshare* iron; in 1677, A. Yarranton used the term *coldshore;* and "red-short" and "cold-short" occur in a tract, *Beware of Bubbles*, by J. Moxon, dealing with W. Wood's patent for the manufacture of iron, and published about 1828. For red-hardness, *vide infra*, tungsten-steels. L. Aitchison discussed the difficulties which attend the formulation of a definition of brittleness.

F. Sauerwald and co-workers said that the brittleness of α-iron at the temp. of liquid air, −155°, is a consequence of the tendency of the crystal to split along the crystal planes. With a system of two crystalline phases, the limit for brittleness can be raised from −155° to −98° to −90°. The brittleness—cold-shortness—which develops in some alloy steels was attributed by H. Hüttenhain to the separation of graphite consequent on the metastable iron: iron carbide system being resolved into the stable iron : carbon system—*vide* the action of sulphur on iron. H. H. Lester investigated the brittle range of some chromium-nickel steels.

A peculiar brittleness is exhibited by iron between 200° and 400°, so that deformation, such as bending, within this range of temp. causes the metal to become more brittle after cooling to room temp. than would occur with a similar amount of deformation at room temp. The temper colour of iron in this range of temp. is bluish, so that the range of temp. is called *blue-heat*, and the brittleness, *blue-brittleness* or *blue-shortness*. Early reports on the ultimate strength of iron when heated showed that a maximum strength was obtained at about 260°, and from there up to over 500° the strength gradually decreased. In 1828, J. L. Fremery and P. St. Brice observed that a specimen of wrought iron, with a tensile strength of 43·4 kgrms. per sq. mm., at ordinary temp. had a strength of only 7·8 kgrms. per sq. mm. at a red-heat. K. Styffe found no change occurs in the tenacity of steel when heated up to 200°, but with soft iron there is an increase in strength between 100° and 205°. J. Kollmann observed that wrought iron maintains its strength up to 93° and then gradually weakens, the weakening goes on rapidly after 400° ; while Bessemer steel behaves in the same way except that the temp. at which the changes occur are higher—there is a constant strength up to 205° and a gradual decrease then begins, and it becomes greater above 500°. J. E. Howard found that the strength of steel decreases to a point between 93° and 150° when it increases until 260° ; after that the metal gradually weakens. The maximum strength with a harder steel occurs at a lower temp. The results with cast iron were almost constant up to about 480° when, at about 820°, the value is about half that of steels. The reduction of area decreased with temp. up to the point of maximum strength after which it increased ; the elongation was greatest at ordinary temp. M. Rudeloff observed that heating the metal to 250° has the same deleterious effect on the subsequent mechanical treatment of weld iron as it has on ingot iron ; as the temp. exceeds 300°, both weld iron and ingot iron steadily decrease in strength ; with weld iron, the elongation on fracture increased proportionally, but with open-hearth steel it reached a maximum at 350°. Hence, 300° is the limit below which the temp. must not fall when weld iron is subject to mechanical treatment, and for open-hearth steel, the temp. differs from this only slightly. Up to 250°, both open-hearth steel and weld iron steadily increased in strength, while the elongation diminished rapidly. The safety of the metal in use is not endangered up to 250°. The modulus of elasticity of open-hearth steel increased as the temp. was raised up to 250°. W. Fairbairn, G. Pisati and G. Saporito-Ricca, H. C. H. Carpenter, M. Leblant, M. Rudeloff, C. Bach, and G. Charpy all place the maximum resistance to tensile fracture at about 250° ; and R. H. Thurston, W. Fairbairn, W. G. Kirkaldy, and E. Adamson, between 250° and 300°. J. H. Andrew and H. A. Dickie, and K. Honda and R. Yamada attributed temper-brittleness to the separation of carbides along the grain boundaries during slow cooling. According to M. A. Grossman, the brittle range in steels with a low percentage of alloying element is due to a small proportion of retained austenite when the steel is quenched. The retained austenite is broken up more or less completely at a certain temp. and the resulting brittle, submicroscopic particles of α-iron, interspersed throughout the mass, make the specimen brittle.

The effect of temp. on the mechanical properties was also measured by R. G. Batson, G. R. Bolsover, G. R. Brophy, G. Charpy, H. le Chatelier, C. L. Clark and A. E. White, E. W. Fell, I. Fetchenko-Tchopivsky, F. Fettweis, J. R. Freeman and G. W. Quick, C. de Fréminville, H. J. French, R. H. Greaves and J. A. Jones, L. Grenet, L. Guillet and M. Balley, T. Inokuty, P. L. Irwin, Z. Jeffries, Z. Jeffries and R. S. Archer, J. J. Kanter and L. W. Spring, F. Körber and co-workers, F. Körber and A. Dreyer, F. Körber and A. Pomp, A. Kühle, A. Kurzwernhart, P. Ludwik, H. Lüpfert, L. H. Marshall, E. Maurer and R. Mailänder, F. Pester, A. Portevin, E. Preuss, G. C. Priester and O. E. Harder, F. Sauerwald and co-workers, P. Schönmaker, H. Schottky, K. Schichtel and R. Stolle, H. Scott and H. G. Movius, L. W. Spring, G. Wazau, and L. R. van Wert, R. Willows and F. C. Thompson, etc.

R. H. Thurston, W. Fairbairn, W. G. Kirkaldy, and E. Adamson observed a decrease in the elongation and an increase in brittleness between 250° and 300°; H. C. H. Carpenter, a minimum elongation at about 130°; and A. Martens, and M. Rudeloff a minimum resistance to tensile stress at 50°. The elongation and reduction of area rise from 300° or 400° upwards; and the minimum elongation occurs at about 150°, a temp. rather lower than the resistance to stress. The decreased elongation and the increased resistance to fracture as the temp. rises, explains the brittleness at a blue-heat, studied in 1877 by F. Valton. C. Bach, and M. Rudeloff found that with 0·16 to 0·20 per cent. carbon steels, the elongation previous to fracture reaches a minimum at 200°, but no definite relation was observed between composition and the variation in the resistance to fracture at different temp. The metals which behaved best when heated had the greatest tenacity and elongation before fracture. M. Leblant found that the maximum at 250°, and the minimum between 80° and 150° appear to occur at higher temp. as the proportion of carbon increases. According to P. Ludwik, the changes in the elastic limit during ageing, and at a blue-heat as well as blue brittleness, are due to changes in the solubilities of the minor constituents in the steel. A similar hypothesis was employed by W. J. Brooke and F. F. Hunting to explain the brittle zone with armco iron between approximately 900° and 800°.

L. Aitchison, L. H. Appleby, A. H. d'Arcambal, C. Bach and R. Baumann, H. W. Baker and A. H. Gibson, J. H. Baker, T. Baker, E. Bernardon, G. W. Barr and co-workers, J. Bartel, R. G. Batson and J. H. Hyde, A. Baykoff, N. I. Belaiew and N. T. Goudtsow, H. Bonte, H. Bouasse, J. M. Bregowsky and L. W. Spring, W. Brockbank, A. Brovot, J. D. Brunton, H. Buchholtz and E. H. Schulz, A. Campion, R. C. Carpenter, H. Carrington, W. Cassie, G. Charpy and A. Cornu-Thénard, P. Chevenard, P. Chevenard and A. M. Portevin, J. Christie, A. S. Clark, E. F. Cone, G. Cook, J. L. Cox, H. C. Cross, N. Czako, K. Daeves, W. E. Dalby, N. Davidenkoff and G. Sajzeff, V. A. Davidenkoff, W. B. Dawson, R. R. Devries, J. H. S. Dickenson, H. A. Dickie, T. G. Digges, J. W. Donaldson, P. Drosne, H. K. Dyson, H. Edert, J. V. Emmons, F. A. Epps and E. O. Jones, P. Eyermann, F. A. Fahrenwald, P. Fischer, R. do Fleury, F. B. Foley, L. Fraichet, C. Frémont, H. J. French, H. J. French and W. A. Tucker, Y. Fukuie, G. Gabriel, J. Galibourg, A. W. Germer and R. N. Wood, F. Goerens and F. P. Fischer, P. Goerens, P. Goerens and G. Hartel, C. Grard, F. Graziani, R. H. Greaves, J. N. Greenwood, E. Greulich, J. J. Guest, R. Guillery, L. Guillet, L. Guillet and co-workers, G. H. Gulliver, H. I. Hannover, M. Hanszel, J. F. Harper and R. S. MacPherran, A. B. Harrison, P. Henry, H. D. Hibbard, A. H. Hiorns, H. A. Holz, J. E. Howard, H. M. Howe, A. K. Huntington, C. Huston, D. H. Ingall, L. Jannin, Z. Jeffries, Z. Jeffries and R. S. Archer, G. R. Johnson, J. B. Johnson, J. B. Johnson and S. A. Christiansen, W. R. Johnson, D. Jouraffsky, W. Kahlbaum and co-workers, H. Kamura, J. Kanter and L. W. Spring, J. F. Kayser, W. J. Keep, F. Kintzle, B. A. Kjerrman, O. A. Knight, H. B. Knowlton, F. Körber and co-workers, W. Köster, P. Kreuzpointer, R. Kühnel, W. Kuntze, W. Kuntze and G. Sachs, H. K. Landis, O. Lasche, A. Lautz, J. H. Lawrence, F. C. Lea, F. C. Lea and O. H. Crowther, A. Ledebur, W. E. Lilly, A. Lindenberg, P. Ludwik and co-workers, A. Lundgren, T. D. Lynch and co-workers, D. J. MacAdam, G. P. McNiff, R. S. MacPherran, C. E. MacQuigg, A. McWilliam and E. J. Barnes, M. Mahoux, R. Mailänder, M. Malaval, V. T. Malcolm, A. Martens, W. Mason, T. Matsumura and G. Hamabe, M. Matweieff, K. Memmler and A. Schob, A. N. Mitinsky, R. G. Morse, K. H. Müller and E. Piwowarsky, J. Muir, F. Nakanishi, W. R. Needham, J. T. Nichols and co-workers, J. Nodder, P. Oberhoffer, W. Oertel, G. A. Orrok and W. S. Morrison, M. Orthey, N. S. Otey, J. G. Pearce, E. N. Percy, H. Perrine and C. B. Spencer, L. Persoz, W. Pinegin, A. J. S. Pippard, E. Pohl, A. Pomp, A. Pomp and A. Dahmen, G. W. Quick, E. J. Rang, W. del Regno, O. Reinhold, F. Rittershausen, F. Robin, M. Ros and A. Eichinger, W. Rosenhain and D. Hanson, O. Ruff, G. Sachs, F. Sauerwald and co-workers, A. Sauveur, E. Scharffenberg, E. Schiebold and G. Richter, C. C. Schneider, W. Schneider and E. Houdremont, A. Schob, H. Schottky and co-workers, E. Schüz, W. A. Scoble, J. Seigle, J. Seigle and F. Cretin, P. Siebe, E. Siebel, E. Siebel and A. Pomp, C. A. Smith, J. H. Smith, M. B. Smith, R. H. Smith, B. F. Spalding, A. P. Spooner, L. W. Spring, L. W. Spring and H. J. French, L. W. Spring and J. Kanter, H. Stäger, P. Stephan, R. Stribeck, H. W. Swift, W. P. Sykes, R. L. Templin, J. L. Terneden and M. von Rath,

A. F. Torres, E. Touceda, L. B. Turner, H. Ude, C. Upthegrove and A. P. White, G. Urbanczyk, M. Vitmos, E. C. Wadlow, O. Wawrziniok, F. W. Webb, W. R. Webster, P. A. Welikoff and co-workers, G. Welter, T. D. West, A. E. White, A. E. White and C. L. Clark, H. E. Wimperis, H. Wright, and H. J. Young, made observations on the tensile and elastic properties of iron and steel.

H. Perrine and C. B. Spencer gave the results indicated in Table XXIX for the ultimate strength in lbs. per sq. in., and the percentage elongation and reduction of area of Bessemer steel with 0·196 per cent. of carbon; and cast iron with 2·69 per cent. According to P. Ludwik, iron annealed at 900°, gave for the tensile strength in kgrms. per sq. mm., and the percentage expansions and reduction of area:

TABLE XXIX.—THE EFFECT OF TEMPERATURE ON THE TENSILE PROPERTIES OF IRON AND STEEL.

		25°	93·5°	204·5	260°	315·5	426·5°	537·5°
0·39 per cent. C	Elongation . . .	34·33	31·30	25·33	26·00	31·55	47·77	52·66
	Reduction area .	56·63	54·84	49·90	48·78	50·16	78·54	89·57
	Strength . . .	72,530	66,940	73,550	75,380	74,780	54,015	32,580
0·23 per cent. C	Elongation . . .	43·33	31·00	27·11	29·11	32·89	54·72	61·18
	Reduction area .	67·28	61·03	56·78	57·60	61·69	82·03	91·63
	Strength . . .	59,955	59,255	69,060	69,400	65,908	44,953	26,315
0·196 per cent. C	Elongation . . .	27·33	—	25·78	21·67	26·45	31·11	49·00
	Reduction area .	36·99	—	41·64	37·51	38·36	51·85	80·17
	Strength . . .	81,310	—	73,180	74,580	79,930	63,520	36,450
2·69 per cent. C	Strength . . .	21,140	—	20,400	—	19,500	17,750	12,810

	20°	275°	335°	407°	617°	835°	1200°
Tensile strength .	33·4	44·5	37·1	27·0	7·6	2·2	1·3
Elongation . .	21	7	18	21	45	—	—
Reduction . .	68	51	61	68	95	88	—

and for steel annealed at 700°:

	20°	250°	330°	412°	485°	617°	722°
Tensile strength .	45·0	57·2	52·6	44·5	27·8	15·0	7·0
Elongation . .	16	5	9	19	20	32	35
Reduction . .	63	43	54	55	62	80	63

H. J. French's tensile tests of iron at elevated temp., show that in the blue-heat range the tensile strength is higher than at room temp. although the reduction of area and elongation are lower. Z. Jeffries obtained similar results; and F. Robin observed that Brinell's hardness is greater at a blue-heat than at room temp. Z. Jeffries and R. S. Archer's experiments illustrate the greater hardening of iron for a given deformation-drawing from 0·042 to 0·025 in. at a blue-heat, 275°, than at room temp., for the tensile strengths lbs. per sq. in., and the percentage elongations, and reductions of area were:

	Tensile strength	Elongation	Reduction of area
Room temp.	85,720	2·60	70·0
275°	111,000	1·58	67·0

Hence the wire drawn at a blue-heat is stronger, but less plastic, than that drawn at room temp. Observations on the effect of temp. on the elastic limit are not concordant. J. E. Howard found that the elastic limit decreases with rise of temp.; W. Mauksch, that the stress with wrought iron at 200° is about half its value at ordinary temp., but rises to its original value at 300°; A. K. Huntington's curve shows no maximum in the blue-heat; C. Bach, and A. Martens observed a maximum at about 200°; and H. J. French found a maximum at 200° where the value is about 14 per cent. greater at 200° than it is at room temp. Observations were made by R. Hay and R. Higgins, R. L. Keynon, F. A. Epps and E. O. Jones, A. Kühle, H. Hubert, A. Pomp, R. C. Carpenter, K. Honda, and G. Delbart. According to E. Houdremont and co-workers, if T_0 denotes the tensile strength of unworked steel, and T is the tensile strength after being drawn from a cross-sectional area F_0 to one of F, then $T=T_0+a \log (F_0/F)$, where a denotes a constant.

A. le Chatelier found that all metals may be broken by a constant tensile stress applied above a certain temp., and that the elongation depends on the load. With a constant temp., the deformation under a given load has a decreasing value tending towards equilibrium; the deformation increases more rapidly than the loads, while the stress increases and the strains diminish with the speed of loading. Deformation under shock is inversely proportional to the shock; and with an increase in temp., the deformation increases and the resistance decreases. Cast iron at 15° can support the following loads without breaking in the periods of time stated:

Time . . .	0·5	1·0	5	15	60 mins.
Load . . .	25·21	24·63	23·87	23·49	22·86 tons per sq. in.

A. le Chatelier postulated that at temp. in the vicinity of 90°, any permanent deformation of iron gives rise to an irreversible transformation which tends to raise the tensile strength and decrease the ductility. The transformation requires a certain amount of time for its completion, but takes place more rapidly the higher the temp. Above 300°, however, the transformation is less effective in producing strength and hardness because of incipient annealing. F. Fettweis identified A. le Chatelier's transformation with the elastic recovery after overstrain. G. C. Priester and O. E. Harder observed a minimum in the tensile strength of 0·29 per cent. carbon steel between 100° and 200°, and a maximum at 300°. K. Yuasa observed that in tension, torsion, and crazing tests between ordinary temp. and 349°, armco iron in tension at 250° showed 320 breaks or sudden yieldings as it began to fail, but no breaks at 20° and 295°. Steels with 0·19, 0·5, 0·68, and 0·80 per cent. of carbon gave a diminishing number of breaks as the proportion of carbon increased until, with eutectoidal steel having 0·85 per cent. of carbon, no breaks were observed. Steels with 0·9, and 1·1 per cent. of carbon showed an increasing number of breaks as the proportion of carbon increased. Distinct sounds were heard as the breaks appeared in the stress-strain diagrams. According to A. Michel and M. Matte, several kinds of elongations are produced when a wire is maintained for a long time under a constant load, and at a raised temp. (i) an instantaneous elastic elongation, (ii) a slow elongation which proceeds with decreasing rapidity, and can be resolved into an elastic elongation with retarded elasticity or reactivity, and a permanent elongation, (iii) if the load is sufficient, the foregoing elongation is followed by another which proceeds with constant rapidity and corresponds to a so-called "viscous" deformation, (iv) after a certain time the rapidity of elongation increases very rapidly up to the breaking-point of the test-piece; this period corresponds to the striction.

A. Sauveur and D. C. Lee observed that in the case of electrolytic iron a maximum tensile strength is obtained at 250°, whilst steels containing respectively 0·10, 0·30, and 0·50 per cent. of carbon reach their maximum strength at a temp. slightly in excess of 300°. With 0·75 per cent. carbon, the maximum strength occurs at 400°. Consequently, the blue-heat phenomenon does not occur at the same temp. with all grades of iron and steel, and it is probable that, as the carbon increases, the temp. imparting maximum strength likewise increases. Electrolytic iron at room temp. has a tensile strength of 40,000 lbs. per sq. in., while at 250° its strength is 56,000 lbs. per sq. in., an increase of 40 per cent. Steel containing 0·10 per cent. carbon increases in strength from 68,000 lbs. to 86,000 lbs., or 26 per cent.; steel with 0·30 per cent. carbon, from 80,000 to 88,000, or 10 per cent.; steel with 0·50 per cent. carbon, from 110,000 to 126,000, or 15 per cent.; and steel with 0·75 per cent. carbon, from 140,000 to 145,000, or 4·3 per cent. Iron and very soft steel increase in strength by tempering at a blue-heat very much more than higher-carbon steel. It should also be noted that the increase of strength is preceded by a decrease of that property.

W. Rosenhain and J. C. W. Humfrey studied the tenacity deformation, and fracture of soft steel—0·106 per cent. C; 0·075, S; 0·050, P; 0·395, Mn; and a trace of silicon—at high temp. Some results with annealed wire are summarized in Fig. 216. The results show that with a fast rate of straining, a maximum stress of 42,400 lbs. per sq. in. was attained, while with a slower rate of straining the maximum stress was 40,250 lbs. per sq. in. The curves are fractionally identical in shape, but the curves with the slower tests lie below those with the faster rates of applying the stress, and the curves are practically parallel to one another. The two upper curves also indicate the influence of the mean size of the crystal grains. Near the Ar_1-arrest the two curves coincide. The effect of the average grain-size of the crystals is indicated in Fig. 204. The effect of temperature on the tensile properties of iron was investigated by R. G. Batson and H. J. Tapsell, C. E. Corson, H. L. Dodge, P. Fischer and V. Ehmcke, J. R. Freeman and G. W. Quick, L. Guillet and co-workers, W. H. Hatfield, H. M. Howe, L. M. Jordan, F. Körber and co-workers, J. H. G. Monypenny, E. Popl and co-workers, O. Reinhold, A. Sauveur, R. Waddell and L. Johnson, and A. E. White and C. L. Clarke. R. S. MacPherran observed that the maximum tenacity at elevated temp. is lowered by nickel, but is not much affected by chromium. R. B. Wilhelm's results for a medium carbon steel—with 0·37 to 0·40 per cent. C; 0·63 to 0·69, Mn; 0·11 to 0·14, Si; and approximately 0·012, P; and 0·037, S—are shown in Fig. 217. F. Körber and H. Hoff, and A. Pomp and co-workers, and P. Bardenheuer and K. L. Zeyen, examined the effect on the mechanical strength of over-heating cast iron.

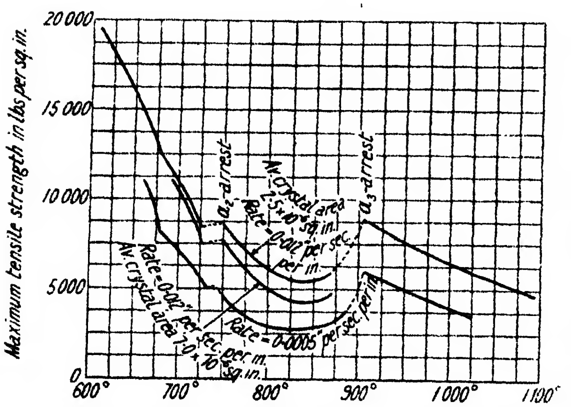


Fig. 216.—The Effect of Temperature on the Tensile Strength of Soft Steel.

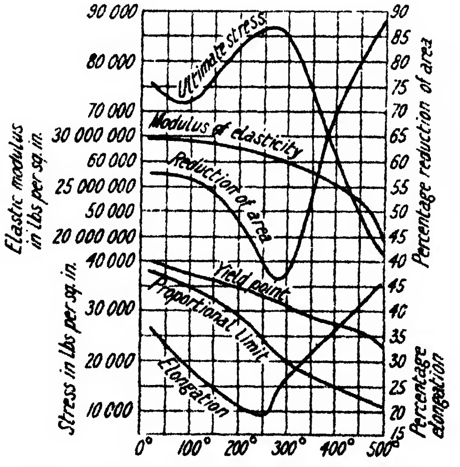


Fig. 217.—The Effect of Temperature on the Tensile Properties of Steels.

The decrease in Young's modulus due to stretching in the cold state and its subsequent recovery by ageing at room temp., or in boiling water, was studied by J. Bauschinger, J. Muir, L. B. Pfeil, C. W. Yearsley, and M. Rudeloff; C. A. Seyrich observed that with a cold-drawn, steel wire, the modulus had not recovered six months after drawing; and in another sample, P. Goerens observed no appreciable effect had occurred in three months. K. Honda and R. Yamada found that a decrease in the modulus produced by stretching had not occurred after being heated for 30 mins. at 100° to 200°, and with a sample of mild steel, severely cold-worked, no recovery of the modulus had occurred in six months, an annealing at above 600°

was required for the recovery. Measurements of the tensile strength of armco iron, mild steel, and nickel steel by T. Kawai are summarized in Figs. 218 and 219 - the hardness of these metals is indicated in Fig. 196. The recovery of Young's modulus by annealing mild steel is shown by the dotted line whose ordinates and abscissæ are on top and on the right of the diagram. E. Heyn, and G. Sachs attributed the decrease of the modulus by cold-working to the internal stresses set up by cold-working; and K. Honda and R. Yamada interpreted this explanation in terms of the atomic force. E. Murata, and T. Kawai showed that there is a release of an internal stress during annealing. T. Kawai observed that the increase in the internal stress during cold-working makes Young's modulus decrease; but the phenomenon may be more or less obscured by an increase in Young's modulus which is due to a change in the orientation of the crystals during cold-working whereby the orientation of the crystals is made to coincide with the direction of the axis of the bar or wire. O. A. Knight found that heating a wire while subjected to a load increased its resistance to deformation.

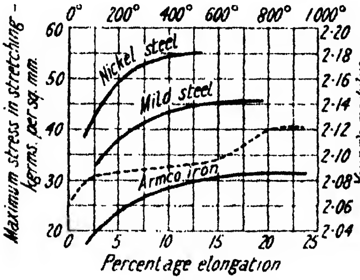


FIG. 218.—Maximum Stress in Stretching.

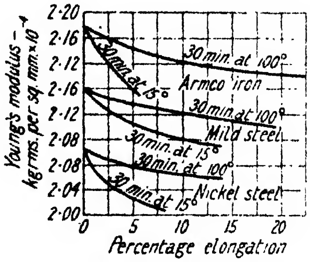


FIG. 219.—Young's Modulus of Stretched Iron.

According to C. Codron, if S denotes the sectional area of the tensile test-piece, and S', the sectional area on breaking, the coeff. of **ductility** or of malleability can be defined as $1-S'/S$, and it is a function of the reduction of area. The results by C. Codron are summarized in Fig. 219. The critical periods of ductility in steels containing different elements were found to be very variable. M. Leblant found a minimum reduction in area near 200° with extra hard steel, and at 300°, with hard steel; the corresponding elongation is a minimum between 200° and 300°. E. Preuss observed that with a pearlitic nickel steel with 0·15 per cent. of carbon, and 3 per cent. of nickel, a minimum elongation occurred at 300°, and a slight decrease in the reduction of area at the same temp. The brittleness, therefore, appears to be a minimum at these temp. F. Robin discussed the application of these results to the forging of metals; P. Junkers, the decrease in the resistance to deformation with increase of forging temp.; O. W. Ellis, the effect of temp. on the malleability of iron and steel; A. F. Shore, the measurement of toughness; and R. Stumper, the effect of the final rolling temp. on the mechanical properties. The ductility was discussed by P. Ludwik, and J. Vietorisz.

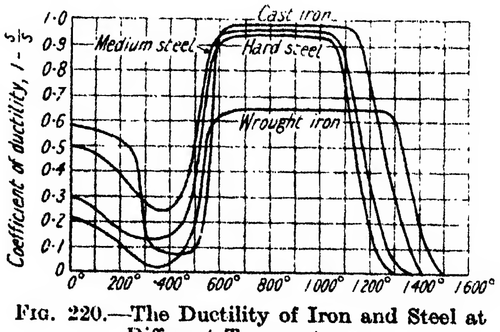


FIG. 220.—The Ductility of Iron and Steel at Different Temperatures.

Following H. J. Gough's study[0] on the **fatigue** of metals—*vide infra*—if a specimen be loaded up to a point B, Fig. 221, and the load removed, then, if no permanent elongation occurs, the materials are said to be perfectly elastic; the loading and unloading curves, *AB*, and *BA*, are the same, and the phenomena are reversible. Actually, however, when the load is *p*, while the sample is being loaded, the elongation is *OC*, and with the same load *p*, while the sample is being unloaded, the elongation is *OD*. The difference, *CD*, thus represents a lag or hysteresis in the strain when the stress is *p*. *Elastic hysteresis* is applied to the case where no permanent sets occur on removing the load, but a strain exists in other parts of the cycle. Again, if no strain disappears when the stress on a solid is removed, the material is perfectly plastic, but with all metals some strain is recovered when the stress is removed. If *AB*, Fig. 221, represents the stress-strain curve, and *b* the total strain, then when the stress is removed, a permanent elongation, *AC*, may be recorded, and this is called the *permanent set* or *plastic strain*; and *Cb* represents the *elastic strain* released by unloading. In a third case, Fig. 221, when the load is maintained at *B*, plastic strain sets in, producing the plastic strain *BF*. This strain increases at a decreasing rate, being very rapid at first, and thereafter slower and slower so that the whole process occupies days or weeks. When the stress is relieved by unloading, some elastic strain is recovered, but there remains a permanent set *AG*. In some cases the permanent set diminishes until some lower value, *AH*, is attained. The subject was discussed by J. V. Howard and S. L. Smith, W. E. Dalby, W. Kerr, M. F. Sayre, and A. Pomp and A. Dahmen. The plastic strain, *BF*, under load is often called the **creep**; and the decrease in the permanent set, *GH*, with no load can be called **elastic after-effect**—that is, *die elastische Nachwirkung*—elastic afterworking—or **elastic hysteresis or lag.** Both phenomena are cases of creep, and, according to H. J. Gough, are the same phenomenon due to the same cause. The permanence of the dimensions of steel under stress at an elevated temp. was discussed by W. H. Hatfield, and L. Jannin.

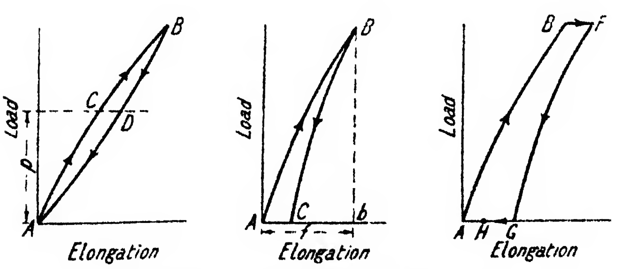


FIG. 221.—Elastic Hysteresis Loop.

In the stress-strain or load-elongation diagram, the elastic limit is taken as the load at which a deviation from Hooke's linear relation—**1.** 13, 17—is first apparent, this point is also called the *limit of proportion, P*; from a second point of view, the elastic limit may be the first permanent set which is observed on removing the load; this point is the so-called *limit of restitution, R*; and from yet a third way of considering the problem the elastic limit corresponds with a point of inflection on the stress-temperature curve; this point is called the *thermal limit* of proportionality.

As a result of the observations of J. P. Joule, and Lord Kelvin (W. Thompson), it was found that if thermal losses due to radiation, conduction, etc., are allowed for, cold is produced when a metal is strained by opposing an elastic force, and heat is developed when a metal is yielding to an elastic force; and with cyclic stresses, there is an average temp. of the metal which does not vary since heat is neither absorbed nor evolved. If a stress, p, is applied at the absolute temp., T; and ϵ denotes geometrical deformation produced by a temp. of 1° when the body is kept under a constant stress; c, the sp. ht.; D, the density; and $J+$, the mechanical equivalent of heat, then, assuming perfect elasticity, Lord Kelvin showed that the elevation of temp. produced by the sudden application of stress is $T\epsilon p/JcD$.

According to H. J. Gough, it has been observed that metals like copper, cast iron, and untempered steel undergo plastic strain when small stresses are applied, and they show no definite *P*, *R*, or *T* limits; while iron, mild steels, and many other metals show definite *P* and *R* limits which are generally in good agreement. J. A. Ewing observed that definite hysteresis loops were always obtained by direct tension with wires of iron, steel, brass, and copper; J. J. Guest and F. C. Lea, that definite hysteresis loops occurred with mild steel under all ranges of torsional stresses, though with up to a certain stress no creeping under load was observed. B. Hopkinson and G. T. Williams, with direct stresses, and F. E. Rowett, with torsional stresses, also found elastic hysteresis with low stresses. C. A. P. Turner found that the thermal limit of proportionality is generally lower than the *P*-limit; E. G. Coker observed that the fall of temp. was linear up to a stress corresponding with *P*, after which, proportionality ceased, and a sharp reversal occurred when the yield stress was reached; E. Rasch, and J. R. Lawson and J. A. Capp observed a general agreement between the *P*- and *T*-points, but elasticity was imperfect. Fatigue and **overstrain** were studied by R. Cazaud, H. F. Moore, R. H. Greaves, Z. Jeffries and R. S. Archer, J. W. Landon, J. K. Wood, H. P. Troendly and G. V. Pickwell, R. W. Bailey, H. J. French and co-workers, J. S. Brown, F. C. Lea and co-workers, D. Hanson, P. Henry, E. Honegger, and R. Liljeblad.

The elastic limit or yield-point represents the maximum distortion which a body can suffer and yet return to its original form. If the strain is not much greater than the elastic limit, the restoration of the original form will take place very slowly. The metal exhibits **elastic recovery.** Thus, we are told that some steel bridges may sag during a heavy week's traffic, but recover during a week-end's rest. It is possible to apply a much greater stress than the elastic limit provided the stress be very quickly applied. Thus, B. Hopkinson has shown that a wire with an elastic limit of 17·8 tons per sq. in. withstood a stress of 35·5 tons per sq. in. applied for less than the thousandth part of a second. Z. Jeffries and R. S. Archer thus describe the phenomenon of fatigue: When hot-rolled or mild steel is tested in tension, the first part of the stress-strain diagram is a straight line representing the elastic deformation up to about half the tensile strength. When a bar of this material is loaded to a stress well beyond the yield-point, on removing the load, it will have lost its elasticity; and the second application of the load furnishes a new stress-strain diagram which curves away from the straight line representing the proportional deformation, and the proportional or elastic limit is reduced almost to zero. If, however, the bar is allowed to rest for a few weeks after the first loading beyond the yield-point (over-straining), before the second tensile stress is applied, it will have recovered its elasticity, and may have a new proportional limit higher than the original limit. This **recovery** of elasticity takes place slowly at ordinary temp., and more rapidly as the temp. is raised; thus, J. Muir found that the recovery of elasticity is as complete after a few minutes at 100°, as it is in 2 weeks at room temp.; and at 250°, the time required for the recovery is measured in seconds or fractions of a second.

R. H. Greaves concluded from his observations on the recovery of elastic properties after simple overstrain in tension: The rate of recovery of elasticity varies greatly with different steels, the harder steels in general recovering more slowly. The greater the degree of overstrain, the longer the time required to bring about recovery at a given temp., or the higher the temp. required to bring about recovery in a given time. All steels show some progress towards recovery at atm. temp., but in the case of the harder steels, it is very slow. The effect of 30 years' rest at atm. temp on an overstrained crucible steel having 1·22 per cent. carbon, was about the same as the effect of holding the metal for 1 hr. at 100°, and considerably less than the effect of holding it for an hour at 125°. E. G. Coker, and E. J. McCaustland also found that there is a certain amount of recovery with overstrained mild steel and wrought iron at 0°, after which the recovery proceeds no further. According to Z. Jeffries and R. S. Archer, the recovery of elasticity on ageing at ordinary temp., or on heating at temp. up to about 300°, is attended by an increase in hardness, and tensile strength, and by a loss of plasticity. Elongation is usually reduced to a marked degree although the reduction of area is less affected. Hence, the change that occurs is, in general, a hardening and stiffening.

Z. Jeffries and R. S. Archer added that while the proportional limit in tension can be greatly increased—nearly doubled—by overstrain in tension followed by ageing, or heating at low temp., the limit in compression is not similarly increased. In fact, it has been reported that the gain in the tensile proportional limit is almost exactly compensated by the loss in the compressive proportional limit, so that the total elastic range is not greatly changed. J. A. van den Broek, however, found that by stretching and reheating, the tensile proportional limit of mild steel can be almost doubled while still retaining the original compressive proportional limit. H. M. Howe discussed cases where (i) the overstrain strengthens the metal against a later stress in the same direction, but weakens it against a stress in the opposite direction; and (ii) one in which it strengthens the metal in all directions though to a degree which varies with the direction of the later stress, being greater for stresses which are in the same direction as the overstrain itself.

Z. Jeffries and R. S. Archer hold that the blue-heat phenomenon and that of elastic recovery are both due to a spontaneous increase in resistance to motion of the slip-planes formed during deformation.

It is supposed that immediately after motion begins on a slip-plane the resistance is less than the shearing strength of the unbroken crystals. Deformation tends to progress by continued motion on this plane, until brought to a halt by end-resistance—that is, by the interference of adjacent grains. If the deforming load is removed immediately after slip has started and time is allowed for elastic recovery, then the resistance to motion on the plane of slip spontaneously increases to a value equal to or greater than the resistance to the formation of a new slip-plane. Further deformation must then take place on new planes. The time required for this increase in resistance is less as the temp. rises, so that at about 250° to 300° the change is practically instantaneous and occurs during the progress of any ordinary deformation, such as a tensile test. The result is that at a blue-heat a given *external* deformation produces more internal deformation, or cold-working, and hence more *hardening*, than the same amount of external deformation effected at room temp. This statement applies to deformations effected within a short period of time, such as during an ordinary tensile test. If the deformation which takes place during the tensile test at room temp. could be effected very slowly so that there was time for elastic recovery during the test, we should expect the tensile strength to be increased to an extent comparable with the increase obtained at a blue-heat. According to the theory here described, the blue-heat properties of iron are due to certain peculiarities of the process of deformation, and are not specific properties of crystalline iron. The yield-point, tensile strength, Brinell hardness, elongation and reduction of area are all properties whose measurement necessarily involves plastic deformation. The true elastic limit, on the other hand, being the stress at which plastic deformation begins, cannot be affected by the mechanism described, nor can the modulus of elasticity. Unless there is an allotropic change (change in atomic arrangement), it is to be expected that both elastic limit and elastic modulus will decrease continuously as the temp. rises. There is a lack of sustaining evidence of any allotropic change in these temp. regions, and recently E. C. Bain has found by X-ray analysis that iron at 300° has the same body-centred cubic lattice as at room temp.

In the so-called **bending test** for ductility, a bar of iron is bent by steady pressure or by hammering, until an angle of 180° is attained, or until the iron ruptures. In the latter case, the angle at which the fracture occurs on the outside of the bend is noted. The test is usually carried out at ordinary temp., but in order to detect red-shortness, or a high sulphur-content, the test may be carried out at about 900° or 1000°. In the nicked bending test the test-piece is nicked all round, before bending, so that the fracture shows the texture—fibrous or crystalline. These tests are generally used as guides in the workshop.

The subject was discussed by L. Aitchison and L. W. Johnson,[10] L. H. Appleby, C. Bach, P. Bardenheuer, J. Bartel, G. S. Bell and C. H. Adamson, B. Blount and co-workers, E. Brinckmann, G. Charpy, G. Cook, J. G. Docherty, B. A. Firth, J. E. Fletcher, H. Herbst, E. Houdremont and H. Kallen, E. Houdremont and R. Mailänder, S. Ikeda, L. Jannin, W. E. Johnston, T. von Kármán, W. J. Keep, G. H. Keulegan, R. L. Keynon, A. B. Kinzel, G. Klein and W. Aichholzer, R. Kühnel, W. Kuntez, M. Lautz, P. Ludwik, H. Lüpfert, A. Lundgren, A. Martens, G. Mehrtens, E. Meyer, H. Meyer, R. Mitsche, R. Moldenke, J. Muir and D. Binnie, E. Nusbaumer, J. G. Pearce, S. N. Petrenko, L. Piedbœuf and M. Remy, A. Pinegin, H. Pommerenke, F. Roll, W. Rosenhain and A. J. Murphy, M. Rudeloff, H. R. Sankey, H. Schottky, A. Schuchart, E. Schüz, W. A. Scoble, H. Scott, J. Seigle, E. Siebel, C. A. M. Smith, E. K. Smith and L. Lichtenfeld, R. Stribeck, O. Thallner, A. Thum and H. Ude, and H. E. Wimperis. The effect of nitrogenization was studied by A. Pomp and A. Lindenberg.

R. Schöttler, and C. Bach discussed the fact that the tensile strength of cast iron calculated from the bending tests is greater than the value obtained by applying a direct tensile stress. P. Goerens and G. Hartel measured the angle through which bars of 0·085 per cent. carbon steel could be bent at different temp. The curve for the **bending angles** required for fracture shows a sharp minimum between 400° and 500°; and the bending angle becomes rapidly less as the temp. falls from, say, 0° to —75°. O. Reinhold measured the bending angles of steels at different temp., and obtained similar results. M. Koepke and E. Hartig, and G. Mehrtens showed that wrought iron, whether cooled down to —100° or not, is somewhat more rigid than steel when tested by shock or bending. The bending number becomes less, but whereas steel behaves well, wrought iron cracks on its convex surface after a few blows. F. Steiner, and H. Gollner found that a wrought iron test-piece could be bent 180° at —50° without fracture, but a nicked test-piece could not be bent to so great an angle at this temp. as was possible at the normal temp. The fracture at the reduced temp. was of a crystalline nature, and that at ordinary temp. was of a fibrous nature. Annealed cast iron and steel which in their normal condition could be bent double without difficulty, withstood a slight bending at —50°, and, on the third light blow, it snapped like glass; E. Kuczera and E. Reinisch, and M. Koepke and E. Hartig also made observations on this subject. Steel bars which had been cooled showed a greater resistance to impact than uncooled bars—for the effect of cooling steel on the structure, etc., *vide supra*, austenite and martensite. G. Meyersberg studied the effect of work, and of the dimensions of the test-piece on the bending test.

P. Goerens measured the **flexibility** of iron in terms of the number of times it can be bent backwards and forwards to certain angles before it breaks off. The course of the flexibility curve corresponds with the tensile strength curve; up to 520°, the flexibility is influenced to a slight degree rising from 11 to 16; there is an abrupt jump to 27 at this temp.; and a subsequent rise in the annealing temp. is accompanied by a small rise of the bending number to 32. If the annealing coarsens the grain, there is a fall in the bending number. According to W. Herold, by slowly raising the load on the bending-test machine, the strength can be augmented in some cases 30 per cent. above the result of the short-time test. A change of structure is produced in the long-time test. In the case of annealed and quenched pearlitic and martensitic steels, there is a separation of the two solid phases so that the harder phase is driven to the grain boundaries which slow up more clearly giving the impression that the structure has been coarsened. In the case of pearlitic steels, the cementite migrates to the grain boundaries, and, in the neighbourhood of the fracture, it consists of ferrite with granular pearlite at the grain boundaries. J. W. Cuthbertson studied the subject. J. Muir and D. Binnie discussed the overstraining of iron by bending.

The **transverse strength** of iron is measured by the so-called transverse or cross-breaking test in which a bar of iron of standard size is supported as a beam and loaded centrally under standard conditions. The strength is measured by the central load the beam will carry without rupture; the deflection of the beam before rupture gives a rough measure of the toughness. The test is favoured for cast iron. Observations were made by E. Hodgkinson[11] in 1824. The standardization of the test has been discussed by a committee of the American Society of Mechanical Engineers, by W. J. Keep, J. E. Stead, J. A. Mathews, R. R. Devries, G. W. Dress, H. C. Dews, G. R. Johnson, C. Jovignot, R. Kröhn and F. Kintzle, E. C. de Segundo and L. S. Robinson, G. S. Bell and C. H. Adamson, J. B. Kommers, J. G. Pearce, W. R. Needham, J. Navarro, W. C. Unwin, G. Hailstone, and W. J. Millar. Working with samples of cast iron having a span of 36 ins., breadth 1 in., and depth 2 ins., averages of 1344 tests gave: ultimate strength, 3740 lbs., ultimate deflection, 0·400 in., and modulus of rupture, 50,490 lbs. per sq. in. J. A. Mathews obtained the results indicated in Table XXX, with cast iron having 3·56 to 3·78 per cent. of total carbon; 2·68 to 3·08, graphitic carbon; 0·70 to 1·04, combined carbon; about

0·45, manganese; 0·8, phosphorus; 0·1, sulphur; and silicon. E. Adamson found for cast iron with 3·56 to 3·58 total carbon; 2·98 to 3·05, graphitic carbon; 0·54 to 0·59, combined carbon; 1·30 to 2·00, silicon; 0·072 to 0·11 sulphur; 0·59 to 1·20, phosphorus; and 0·65 to 0·90, manganese, the transverse strength in 3 ft. was 27·5 to 38·5 cwts.; the deflection, 0·314 to 0·386 in.; and the moment of resistance, 16·588 to 20·796. J. Bauschinger's results are indicated in Table XXX.

TABLE XXX.—TRANSVERSE STRENGTH OF CAST IRON.

Silicon (per cent.)	Span (inches)	Mean centre load (lbs.)	Modulus of rupture (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)
1·50	12	3000	47,100	25,600
	18	1935	45,600	
	24	1425	44,700	
2·00	12	2900	45,500	24,370
	18	1835	43,200	
	24	1265	39,700	
2·50	12	2880	45,200	24,660
	18	1905	44,900	
	24	1400	44,000	

H. Meyer gave for the effect of temp. on the modulus of rupture (tons per sq. in.), and the maximum deflection in inches:

	18°	85°	155°	370°	580°	810°
Modulus of rupture .	23·6	21·9	21·3	21·0	16·0	6·2
Max. deflection .	0·30	0·28	0·28	0·30	0·57	0·79

L. H. Appleby[12] measured the resistance of iron to **shearing and torsional stresses,** and found that open-hearth steel had a torsional limit of 20·09 tons and a breaking stress of 39·29 tons per sq. in., while the shearing resistance was 29·7 tons per sq. in. Some results of the breaking stress, in tons per sq. in., are indicated in Table XXXI. The numbers in brackets refer to the number of twists on a length of 30 diameters which were found after fracture. J. Bauschinger's results for the tensile and compressive strengths, the transverse strength, the shearing strength, and the torsional strength are indicated in Table XXXI; and those of L. H. Appleby, in Table XXXII. J. Platt and R. F. Hayward found that the shearing strength is always less than the tensile strength; and that the ratio shearing strength : tensile strength increases as the tenacity increases and is 85 per cent. for wrought iron, 81 per cent. for mild steel, 64 to 70 per cent. for steels with a high proportion of carbon, and for cast iron, 40 per cent.; the torsional strength is greater than that of the direct shear, and the ratio varies with the tenacity and nature of the materials. The modulus of elasticity in torsion is about 40 per cent. of the modulus in tension. E. G. Izod, and J. Goodman obtained higher results than J. Platt and R. F. Hayward for the shearing strength of cast iron. E. G. Izod

TABLE XXXI.—MECHANICAL PROPERTIES OF IRON AND STEEL.

	Tensile strength	Compressive strength	Bending test	Torsional strength		Shearing strength
				Limit	Rupture	
Cast iron . . .	12·517	—	—	—	14·417 (0·04)	12·338
Wrought iron . .	25·410	—	—	8·928	26·042 (10·56)	22·436
Cast steel . . .	29·060	23·131	39·495	20·094	39·286 (0·90)	29·700
Forged steel . .	28·415	—	51·351	11·163	30·878 (7·64)	24·436
Bessemer steel . .	34·465	-	66·267	17·857	38·231 (16·03)	18·933

gave for the ultimate tensile stress of cast iron, 9·7 to 13·7 tons per sq. in., and for the ultimate shearing stress, 13·9 to 17·4 tons per sq. in. J. Goodman gave for cast iron, 10·9 to 11·5 tons per sq. in. for the ultimate tensile strength, and 12·9 to 13·0 tons per sq. in. for the ultimate shearing stress. W. Püngel discussed the effect of cold-work on the torsion strength of steel.

Observations with iron, etc., were made by G. C. Anthony, W. Bader and A. Nadai, A. J. Becker, G. S. Bell and C. H. Adamson, B. Blount and co-workers, T. H. Burnham, E. G. Coker, G. Cook, G. K. Elliott, J. V. Emmons, O. Föppl, C. Frémont, A. Glazunoff, J. J. Guest and F. C. Lea, E. L. Hancock, P. Henry, W. Herold, A. G. Hill, L. J. Johnson and J. R. Nichols, W. Jolley, J. B. Kommers, W. Kuntze, C. E. Larard, F. C. Lea and F. Heywood, E. Lehr, W. Lode, P. Ludwik, P. Ludwik and co-workers, D. J. MacAdams, L. Perard, P. Régnauld, M. Rudeloff, A. Sauveur, H. A. Schwartz, W. A. Scoble, F. B. Seely and W. J. Putnam, J. Seigle, J. Seigle and co-workers, Y. Sekiguchi, K. Sipp, C. A. M. Smith, J. H. Smith and F. V. Warnock, R. L. Templin and R. L. Moore, V. Vieweg and A. Wetthauer, P. B. Whitney and G. K. Dohner, and F. P. Zimmerli and co-workers.

TABLE XXXII. MECHANICAL TESTS OF CARBON STEELS (kgrms. per sq. mm.).

Carbon (per cent.)	Tensile strength limits	Tensile strength	Compressive strength limits	Compressive strength	Transverse strength limits	Transverse strength	Shearing stress	Torsional strength limit
0·14	30	44	28	48	38	--	34	—
0·19	33	48	30	54	42	—	37	15
0·46	35	53	34	63	40	83	36	15
0·51	34	56	33	70	42	93	40	--
0·54	35	56	34	61	40	86	39	15
0·55	33	56	35	62	42	88	40	--
0·57	33	56	34	66	45	96	36	16
0·66	37	63	38	66	44	86	43	17
0·78	37	65	38	73	47	88	41	18
0·80	40	72	44	97	47	76	48	20
0·87	43	74	39	89	47	77	50	20
0·96	49	83	50	99	69	85	58	27

In the fracture of iron by alternating torsional stresses, fracture may occur when the total distortion is small or inappreciable. H. Gough found that with single crystals of α-iron, the direction of slip is the octahedral direction. At any point on the surface of the specimen there will exist a plane on which the value of the shear stress resolved in the contained octahedral directions is a maximum for all similar resolved shear stresses. Slip will not, in general, occur on this plane, unless the plane coincides exactly with a dodecahedral (110), icositetrahedral (112), or hexakis-octahedral (123) plane of the crystalline structure (and then only when conditions of perfect symmetry obtain). In other cases, the distortion is produced by slipping on two planes, each of which corresponds to one of the above crystal planes. These slip-planes are situated on opposite sides of the plane of maximum resolved shear stress, although not, in general, equidistant from that plane. Each slip-plane is determined by the consideration that it is subjected to a greater value of resolved shear stress than any other possible slip-plane on the same side of the plane of maximum resolved shear stress. The slip-bands will, in general, be of a duplex type, the *average* slope being that of the trace of the plane of maximum shear stress on the surface of the specimen. The limits of slope of the slip-bands will agree with the traces of the planes of slip. Under very small deformations, the slip-bands appear either as short separate traces of the slip-planes, or of a combination of these traces, and can be identified as such. Under great deformations, however, the component slopes of the slip-bands are difficult to resolve, and sometimes they cannot be resolved at all. In the latter case they present a very wavy, branched appearance bearing no appreciable relation to the crystalline structure. Observations on single crystals were made by J. Königsberger. For mild steel,

E. G. Izod, and J. Goodman respectively gave 26·9 and 23·6 tons per sq. in. for the ultimate tensile strength, and 21·0 and 18·9 tons per sq. in. for the ultimate shearing stress. The ultimate shearing stress of cast iron—free from blow-holes and springiness—is greater than the ultimate tensile strength. J. Frenkel discussed the theory of the shearing strength of crystals; D. Binnie, the overstraining of steel by torsion; G. H. Gulliver, and C. Frémont, the shearing strength of iron and steel. W. Jolley found the measurements with cast iron to be unsatisfactory. M. Majima found that when the elastic limit of mild steel is exceeded in torsion, the deformation becomes plastic, and with a constant twisting couple the angle of twist ultimately reaches an upper limit. After several hours the material recovers its elasticity, the recovery being nearly proportional to the time of rest. If, then, the twisting couple is increased, elastic deformation is produced, and up to the new elastic limit the stress-strain relationships are approximately equal to those observed within the original elastic limit. The results are satisfactorily explained by the slip-band theory. P. Chevenard measured the variation with temp. of the torsional rigidity of some carbon steels, and found that the variation with temp. of the inverse squares of the times of oscillation only represents the apparent variation of the torsion modulus up to 300°. Above 300°, the decrements showed a rapid increase. The anomaly in the elasticity of carbon steels is directly proportional to the carbon content. L. di Lazzaro found that when torsional and tensile stresses are applied simultaneously, the torsion modulus diminishes, and rises again after the tension has been released.

According to H. Tomlinson, the longitudinal and torsional elasticity of iron are not so much affected by raising the temp. as is the case with internal friction. The torsional elasticity of annealed iron is temporarily decreased 2·693 per cent. when the temp. is raised from 0° to 100°; an annealed wire tested with a certain load at 12° was temporarily elongated 0·751 mm.; when heated to 100°, 0·793 mm.; and when cooled again and tested 24 hrs. afterwards, 0·725 mm. Thus, as with torsional elasticity, there is a permanent increase of elasticity, and a temporary decrease of 2·58 per cent. Time is here an important factor, for the elasticity immediately after cooling is appreciably less than it is after a long rest. With both torsional and longitudinal elasticity, after an iron wire has been permanently extended by traction, the elasticity is permanently increased by long rest. The carrying power of a magnet, also, can be considerably increased by putting on the load in small quantities at a time, with long intervals of rest between. All this is taken to mean that if the molecular arrangement of iron be disturbed by any stress whatever, exceeding a certain small limit, the molecules will not assume at ordinary temp. those positions which will secure a maximum of elasticity, until after a rest of many hours. K. Yuasi's observations were indicated in connection with the tensile tests. H. J. Tapsell and W. J. Clenshaw studied the subject.

For the **torsion modulus,** in kgrms. per sq. mm., C. A. Coulomb gave for iron, 7,651; G. Pisati, 8,082; N. Katzenelsohn, 7,505; M. Baumeister, 7,975; A. Gray and co-workers, 8,230; C. Schäfer, 7,337; H. Tomlinson, 7,590; and F. Horton, 8,280. For the torsion modulus of steel, W. Voigt gave 8,070; H. Tomlinson, 7,731; G. Pisati, 8,262; A. Gray and co-workers, 7,965; G. F. C. Searle, 7,872; F. Horton, 8,470; and F. A. Schulze, 8,022. For **Poisson's ratio,** P. Cardani gave 0·321; J. D. Everett, 0·310; M. Baumeister, 0·304; J. R. Benton, 0·288; N. Katzenelsohn, 0·272; H. Tomlinson, 0·281; J. Morrow, 0·263; A. Mallock, 0·253; O. Littmann, 0·243; C. Schäfer, 0·247; and E. Grüneisen, 0·280 for steel with 0·1 per cent. of carbon to 0·287 for steel with 1·0 per cent. of carbon. H. Polnick calculated Poisson's ratio, w, from $w=0·5\text{-}tEk$, where E denotes Young's modulus, $21·3\times10^{-11}$ c.g.s. units, and k the coeff. of compressibility, $0·606\times10^{11}$, so that $w=0·285$, when E. Grüneisen observed 0·28. Observations were also made by W. P. Wood, C. Frémont, E. G. Izod, W. E. Lilly, W. C. Popplewell, E. L. Hancock, C. A. M. Smith, E. Siebel and A. Pomp, C. Bach, O. Bretschneider, T. Reimers, J. J. Guest, G. Moreau, E. Goens, F. W. Alexander, and J. Seigle and F. Cretin.

A. E. H. Love and others have studied the mathematical theory of elasticity and shown that for simple torsion, in static testing, and in the range where stress is proportional to strain W, the energy absorbed per unit vol. is $W=C_1S_a^2/2F$, where C_1 is a constant; S_a, the maximum stress in torsion; and F, the modulus of torsional elasticity. Likewise also for tension or compression, $W=C_2S_b^2/2E$, where C_2 is a constant; S_b, the maximum stress in tension or compression; and E, the modulus of elasticity in tension. In the case of reversed stresses, W, the amount of energy involved per unit vol. per cycle of stress at the endurance limit, is $W=(S_1^2+S_2^2)/2E$, where E is the modulus of elasticity; S_1, the maximum stress per unit area; and S_2, the minimum stress per unit area. If the cycle does not involve a reversal of stress, $W=(S_1^2-S_2^2)/2E$, when S_1 and S_2 are both values in tension or both in compression.

J. Goodman showed that as the range of repeated stress on a steel is decreased, the maximum stress that can be carried successfully an indefinitely large number of times is increased; and H. F. Moore and T. M. Jasper showed that whilst this relation holds for normalized steels over a considerable range, with heat-treated steels, when the elastic limit and yield-point approach proportionately nearer the ultimate strength, the limits of endurance do not follow J. Goodman's relation; and the upper limit of the range then rarely goes beyond the yield-point of the material. The endurance limit represents the maximum stress a metal can withstand in repeated stress for an indefinitely large number of cycles. If the repeated stress of a ferrous metal is run at a stress very little above the endurance limit, it will usually fail before it has reached 2,000,000 cycles, whereas if the metal is repeatedly stressed at or near the endurance limit, it will withstand at least 100,000,000 cycles without failure, and in some cases as much as 900,000,000 cycles.

In his study of the kinetic theory of solids, W. Sutherland showed that if F denotes the modulus of shear at any temp. T° K.; F_0, the modulus of shear at 0° K.; and T_m, the absolute temp. of the m.p., then $F/F_0=1-(T/T_m)^2$. A. E. H. Love, and A. Morley have shown that for an isotropic elastic solid, if B represents the bulk modulus, $E=9BF/(F+3B)$, and $B=FE/(9F-3E)$; and W. Sutherland deduced for the bulk modulus, $B=2hJc\delta/9a\{1/(aT)-4\}$, where J denotes the mechanical equivalent of heat; h, the sp. ht.; δ, the density; a, the coeff. of linear expansion; c, a constant which is nearly unity; and T, the absolute temp. at which the test is made. Since J and c are constant, and δ may be taken to be constant over the range 0° to 1400° F., the equation assumes the form $B=kh/a\{(1/aT)-4\}$, where k is a constant. H. Brearley investigated the energy involved in bringing a steel to the yield-point. T. M. Jasper examined these relations for steel. The results in Table XXXIII for $W=(S_1^2+S_2^2)/2E$ were calculated by T. M. Jasper—for static tests where S_2 is zero, and $W=S_1^2/2E$. The results show that the value of the energy involved per complete cycle of stress for a specific wrought ferrous metal at the endurance limit, is nearly constant; and the energy involved in bringing the stress to the static yield-point under different temp. below 510°, is a constant; above 510°, the value of the modulus changes abruptly

TABLE XXXIII.—THE ENERGY ABSORBED IN BRINGING STEEL TO THE YIELD-POINT.

Temp. (°F.)	Yield-point (tons per sq. in.)	S_1 (lbs. per sq. in.)	E (lbs. per sq. in.)	$S_1^2/2E$	Per cent. deviation from mean
65	38·8	87,000	30,000,000	126	− 3·4
212	37·0	82,800	28,000,000	123	− 5·7
392	37·0	82,800	25,300,000	135	+ 3·6
572	33·44	75,000	22,400,000	126	− 3·4
752	33·6	75,300	19,500,000	145	+11·1
842	31·32	70,300	18,200,000	135	+ 3·6
932	28·68	64,200	16,700,000	123	+ 5·7

indicating a possible critical point. G. D. Newton, and F. Schleicher discussed the energy necessary to shear steel at a high temp. H. H. Lester, and H. H. Lester and R. H. Aborn discussed the behaviour of the atoms within a crystal of iron when stressed up to and beyond the elastic limit. C. Schäfer observed a relation between the temp. coeff. of the torsion modulus, λ, and the m.p. of metals corresponding with that observed in the case of the temp. coeff. of the hardness. J. H. Poynting observed that when a loaded wire is twisted, it lengthens by an amount proportional to the square of the angle of twist; and that with a wire previously straightened by heating under tension, the lengthening is the same for all the loads which were tried. Hence, the only function of the load is to straighten the wire. He also discussed the theory of the phenomenon.

The modulus of elasticity in shear, the modulus of transverse elasticity, or the modulus of **rigidity,** of iron at 15° is, according to W. Sutherland, 750×10^{-6} gram per sq. cm. For the ratio at 100° with that at 0°, A. W. Napiersky gave 0·979; F. Kohlrausch and F. E. Loomis, 0·960; and H. Tomlinson, 0·950. Lord Kelvin (W. Thomson) gave for the absolute value between 0° and 20°, per gram per cm., 790×10^{-6}; H. Tomlinson, 751×10^{-6} to 773×10^{-6}; G. Pisati, 811×10^{-6}; F. Kohlrausch and F. E. Loomis, 694×10^{-6}; A. T. Kupffer, 713×10^{-6} to 742×10^{-6}; C. Schäfer gave $0·734\times10^{-6}$ kgrm. per sq. mm. at 20°; E. Grüneisen, $0·828\times10^{-6}$ at 18°; and B. Gutenberg and H. Schlechtweg gave for the average rigidity of iron, $7·8\times10^{11}$ dynes per sq. cm. For drawn steel having 1·0 per cent. of carbon, E. Guye and V. Freedericksz gave $0·857\times10^{-6}$ kgrm. per sq. mm. at $-196°$; $0·829\times10^{-6}$ at 0°; and $0·811\times10^{-6}$ at 100°; K. Iokibe and S. Sakai, $0·7985\times10^{-6}$ at 24°; $0·750\times10^{-6}$ at 216°; $0·706\times10^{-6}$ at 418°; $0·649\times10^{-6}$ at 595°; and $0·518\times10^{-6}$ at 650° with wire having 0·0085 per cent. of carbon, annealed at 800°; and K. R. Koch and E. Dannecker gave for annealed wire with 1·0 per cent. of carbon, in kgrms. per sq. cm.:

	20°	200°	400°	600°	800°	1000°	1200°
Torsion modulus $\times10^6$.	0·805	0·764	0·712	0·461	0·277	0·270	0·181

H. Tomlinson gave 704×10^{-6} grm. per sq. cm. for hard-drawn and also annealed iron wire, and W. P. Wood gave for the torsion modulus, in lbs. per sq. in.:

Hard-drawn	Tempered			
0·56 to 0·58 % C	0·76 to 0·83 % C	0·44 % C	0·67 % C	0·78 C
11,299,000	11,427,000	11,299,000	11,437,000	10,607,000

For steel with 0·35 and 0·90 per cent. carbon annealed at 900°, T. Kikuta gave for the coeff. of rigidity, $E\times10^6$ kgrms. per sq. cm.:

	20°	199°	443°	631°	795°	924°
0·35 per cent. C $E\times10^6$ . .	0·823	0·784	0·713	0·533	0·324	0·211
	20°	221°	446°	619°	780°	937°
0·90 per cent. C $E\times10^6$ . .	0·805	0·764	0·695	0·5295	0·321	0·262

and for steel wire with 0·55, 0·90, and 1·30 per cent. carbon, K. Iokibe and S. Sakai gave for coeff. of rigidity $E\times10^6$ kgrms. per sq. cm.:

	43°	207°	399°	600°	
0·55 per cent. C $E\times10^6$ . .	0·783	0·765	0·737	0·562	—
	56°	187°	419°	616°	
0·90 per cent. C $E\times10^6$ . .	0·782	0·762	0·683	0·600	—
	29°	221°	412°	599°	700°
1·30 per cent. C $E\times10^6$ . .	0·773	0·758	0·739	0·640	0·447

K. Honda and T. Terada gave $0·75\times10^{12}$ at 14° for the coeff. of rigidity with a load of 3113 grms. per sq. mm. G. H. Keulegan and M. R. Houseman studied the subject. A. Gray and co-workers found for the modulus of rigidity of mild steel: $7\cdot9648\times10^{11}$ dynes per sq. cm. at 17·0°, and $7\cdot7704\times10^{11}$ at 89·2°—a diminution of 0·000338 per degree; and for soft iron, $8\cdot2855\times10^{11}$ at 13·6°, and $8\cdot0125\times10^{11}$ at 93·8°—a diminution of 0·00041 per degree. T. Kawai observed that there is a decrease in the modulus of rigidity of iron and mild steel due to cold-working until a minimum is attained, after which, the amount of decrease diminishes with an increase in the degree of cold-working. K. Iokibe and S. Sakai studied the effect of temp. on the rigidity. P. W. Bridgman found that under a press. of 10,000 kgrms. per sq. cm., the rigidity of steel is increased 2·2 per cent. *Vide infra* for the effect of rigidity on magnetization. K. Honda and H. Hasimoto found that the rigidity is slightly decreased by an increase of carbon; it is decreased by quenching, and increased by annealing. The effect of annealing was studied by F. P. Zimmerli and co-workers, and T. Kawai.

A. Mallock observed that the elastic rigidities of iron and steel are identical at the same temp., and this value diminishes slowly from ordinary temp. to a red-heat. The limits of the elasticity of the two are widely different: very small for iron, and increasing with the carbon-content of the steel. Just below 800°, the rigidity and elastic limits begin to diminish rapidly. The changes in viscosity and rigidity are not coincident with the change of state, and this is particularly noticeable in steels with a high proportion of carbon. The diminution in the rate of subsidence of torsional oscillations in wires was studied by H. Streintz, O. Feussner and E. Ramb, G. S. von Heydekampf, O. Föppl, S. Higuchi, and G. Pisati. A. Gray and co-workers observed that the rate of subsidence of the amplitude is slower at the lower temp. Analogous results were obtained for soft iron. F. C. Lea observed two discontinuities in the torsional rigidity modulus of mild steel at 120° and 230°; and discontinuities were also observed in a 0·57 per cent. carbon steel. *Vide supra*, the viscosity of iron.

According to H. Tomlinson, the loss of torsional rigidity produced by twisting or stretching a wire beyond the limits of elasticity is partly diminished by rest. The loss is more sensible with large arcs of vibration than with small ones. The influence of rest is more apparent with large vibrations than with small ones. Continued vibration through large arcs has a similar effect on the rigidity to that produced on the longitudinal elasticity by heavily loading and unloading. The effect of vibrating hard steel through a large arc for several minutes makes temporarily the rigidity determined for large vibrations greater than that determined from smaller vibrations. The torsional rigidity is temporarily depressed by the passage of a powerful electric current, but is very little, if at all, altered by currents of moderate intensity. The torsional rigidity of iron is temporarily diminished to a small extent by a high magnetizing force. Both these effects are independent of changes produced by the current in the temp. of the wire.

E. L. Hancock showed that (*a*) an overstrain in either tension or torsion destroys the elasticity of the material, but that this elasticity gradually returns when the piece is allowed to rest, the elastic limit becoming, in some cases, greater than its original value, and the modulus of elasticity the same as its original value. (*b*) That the elastic properties of the overstrained material are restored by immersion for a short time in boiling-water. (*c*) That recovery is not aided by repeated impact from a light hammer. (*d*) Materials overstrained in either tension or compression lose their elasticity for stress of the opposite kind, but the elasticity is restored by rest. (*e*) The carbon-steels seem to recover more quickly than the nickel steels. This, however, has not been shown conclusively by these tests, but all evidence goes to show that it is true.

Observations on the resistance of metals to impact were made by Leonardo da Vinci,[13] E. Mariotte, P. de la Hire, M. de Cessart, W. J. Gravesande, F. J. de Camus, J. V. Poncelet, G. Juan, M. Rambourg, J. R. Perronnet, L. de Maupéon, etc. E. Hodgkinson [14] applied the impact or shock test to iron in 1833. E. D. Estrada examined the effect of a sudden application of the load on the tensile properties of wrought iron and steel. He found that some fractures were finely granular or silky; in some cases a small load suddenly applied will produce a permanent set, and, in general, the elongation increases and the elastic limit diminishes with loads suddenly applied. Elongation is a function of the time, since it increases as the time diminishes though the ultimate resistance remains the same. The tests applied to iron and steel with the object of finding their mechanical properties can be grouped as static and dynamic; and it has been found that the dynamic tests—illustrated by the so-called impact test—show characteristics of the metal which are not revealed by the static tests. The **impact or shock test** may be applied to notched or un-notched bars. It gives an idea of the toughness or brittleness or resilience of the metal. T. E. Stanton and L. Bairstow, and P. Welikhoff observed that with un-notched bars, the results of the tensile impact tests are virtually the same as those obtained with static tensile tests.

Observations were also made by T. Asano, L. Aitchison, N. Akimoff, J. H. Andrew and R. Hay, T. Andrews, J. O. Arnold, L. Auspach, H. Bancke, P. Bardenheuer, R. Baumann, M. Belanger, G. Berndt, B. Blount and co-workers, H. T. Bovey, E. Brechbühl, P. Breuil, R. C. Carpenter and H. Diederichs, G. Charpy, G. Charpy and A. Cornu-Thénard, H. le Chatelier, E. G. Coker, A. L. Colby, A. Cornu-Thénard, N. Davidenkoff, N. Davidenkoff and K. Yureff, P. Dejean, M. Delbruck, M. Denis, M. Derihon, G. Dilber and H. T. Hannover, E. H. Dix, W. A. Doble, J. G. Docherty, P. H. Dudley, F. W. Duesing, B. W. Dunn, J. Durand, C. A. Edwards and F. W. Willis, H. C. Ehrensberger, H. A. Elliott, A. Elmendorf, F. Eloy, L. E. Endsley, H. Enshaw, P. Fain, H. J. Fereday, F. Fettweis, P. Fillunger, P. Fischer, F. B. Foley and co-workers, C. de Fréminville, C. Frémont, S. R. Fuller and W. A. Johnston, A. Gagarine, A. Gossner, W. A. Gibson, W. Giesen, P. Goerens, E. P. Gooch, W. F. M. Goss, H. J. Gough and A. J. Murphy, R. H. Greaves, R. H. Greaves and H. Moore, L. Grenet, M. Guillery, L. Guillet, L. Guillet and co-workers, L. Guillet and L. Révillon, R. A. Hadfield, R. A. Hadfield and S. A. Main, J. H. Hall, H. I. Hannover, F. Harboard, W. H. Hatfield, W. K. Hatt, W. K. Hatt and E. Marburg, W. K. Hatt and W. P. Turner, P. Heymans, E. Heyn, E. Höeg, W. Honiger, A. Horzenberger, H. M. Howe, S. L. Hoyt, H. Hubert, J. C. W. Humfrey, D. H. Ingall, E. G. Izod, F. H. Jackson, L. Jannin, J. B. Johnson, R. M. Jones and R. Greaves, W. R. D. Jones, H. Jungbluth, C. Jungst, H. Kamura, T. Kawai, W. J. Keep, A. B. Kinzel and W. Crafts, H. B. Knowlton, F. Körber and co-workers, F. Körber and J. B. Simonsen, H. Kreuger, E. Kuhlmann, E. F. Lake, F. C. Langenberg, G. Lanza, F. Laszlo, E. Leber, A. Ledebur, M. Legrand, F. Leitzmann, A. Leon and P. Ludwik, J. M. Lessells, P. Longmuir, P. Ludwik, P. Ludwik and R. Scheu, A. Lundgren, T. D. Lynch, D. J. McAdam, C. McGarvey, J. S. Macgregor and B. Stoughton, D. R. MacLachlan, A. McWilliam and E. J. Barnes, W. T. Magruder, R. Mailänder, C. E. Margerum, A. Martens, A. Martens and E. Heyn, A. Martens and F. W. Hinrichsen, S. S. Martin, T. Matsushita and K. Nagasawa, H. S. Mattimore, K. Memmler, M. Merriman, J. T. Milton, M. A. Mimey, O. Miyagi, R. W. Moffatt, H. F. Moore, H. F. Moore and co-workers, R. R. Moore, G. Moreau, J. F. Morrison and A. E. Cameron, M. Moser, J. H. Nead, F. Nehl, J. A. Newlin and T. R. C. Wilson, E. Nusbaumer, W. Oertel and L. A. Richter, J. Okubo, J. Okubo and M. Hara, A. Olry and P. Bonet, T. Y. Olsen, A. Ono, A. E. Outerbridge, R. Pawliska and M. Schmidt, J. G. Pearce, A. Pérot, A. Pérot and H. M. Lévy, F. Pester, S. N. Petrenko, H. P. Philpot, J. A. Pilcher, R. Plank, H. Pommerenke, A. Pomp, E. Preuss, M. Prevez, H. S. Primrose and J. S. Glen, G. W. Quick, H. S. Rawdon and S. Epstein, P. Régnauld, C. Richardson and C. N. Forrest, N. Richardson and E. K. MacNutt, C. H. Ridsdale, F. Robin, R. Rötscher and M. Fink, F. Rogers, C. V. Roman, W. Rosenhain, M. Rudeloff, S. B. Russell, G. Sachs, H. R. Sankey, H. R. Sankey and J. K. Smith, F. Sauerwald and H. Wieland, M. Schaper, A. Schmid, M. Schmidt, E. Schneider, W. Schneider, P. Schönmaker, F. Schule and E. Brummer, E. Schulz and R. Fiedler, R. Sergeson, W. Schwinning, A. E. Seaton and A. Jude, H. Seehase, E. Seidl, E. Simonet, W. A. Slater and G. A. Smith, C. A. M. Smith, E. B. Smith, J. P. Snow, J. Snyders and P. A. M. Hackstroh, R. V. Southwell, H. J. Stagg, T. E. Stanton, T. E. Stanton and L. Bairstow, T. E. Stanton and R. G. Batson, R. Stribeck, Z. Takao, O. Thallner, J. J. Thomas, W. N. Thomas, F. C. Thompson, R. H. Thurston, H. D. Tiemann, T. Tredgold, E. U. Tschudi, W. C. Unwin, J. E. P. Wagstaff, R. G. Waltenberg, C. L. Warwick, O. Wawrziniok, W. R. Webster and L. Baclé, P. Welikhoff, G. Welter, T. D. West, H. L. Whittemore, and A. B. Wilson.

T. Kawai worked out the impact energy diagram of armco iron, mild steel, nickel steel, and nickel-chromium steel. The results are summarized in Figs. 222 and 223. In the usual form of the test, the impact energy required just to break the test-piece is determined. The impact energy is expended partly on heating the specimen, and is not stored up as potential energy, so that when the stress is reversed, the test-piece does not return to its previous length, and the elastic limit is reduced—*vide supra* for the effect of slow and rapid loading in the tensile strength test. T. Kawai found that the stress-strain relation with the impact test is not affected by the mode of applying the stress, that is, whether the stress is steadily increased, or whether it is applied and released several times in the stage of loading. The greater part of the impact energy is expended in producing an elastic and plastic strain in the test-piece. The former is at once returned to the pendulum hammer as rebound energy, and the latter is absorbed by the test-piece. T. Kawai found that the apparent absorbed energy varies linearly with the number of impacts, and a similar relation obtains between the apparent absorbed energy and the elastic strain energy of the test-piece. The relation between the bending and the net absorbed energy in the impact test is illustrated by Fig. 223 for notched bars 10×10×54 cu. mm. The results for the stress-strain energy of impact are summarized in Fig. 224. The energy absorbed in the impact test was discussed by G. Charpy and A. Cornu-Thénard, A. Cornu-Thénard, K. Honda, F. Körber and R. Sachs, M. Moser, and R. Yamada. R. W. Boyle discussed the compression waves produced in the metal by impact.

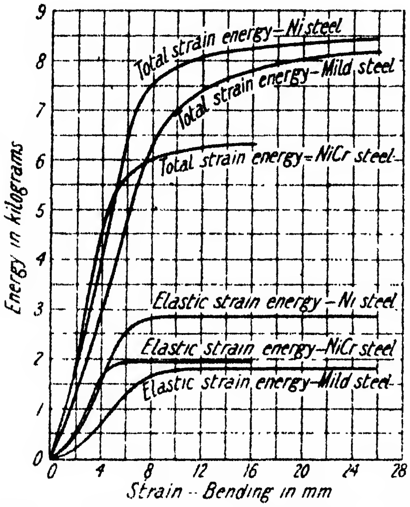


FIG. 222.—The Total Strain of Impact.

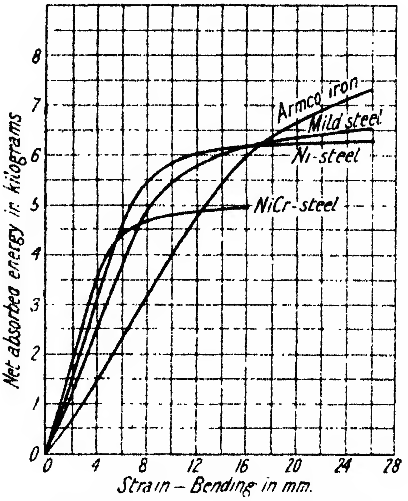


FIG. 223.—The Net Absorbed Energy of Impact.

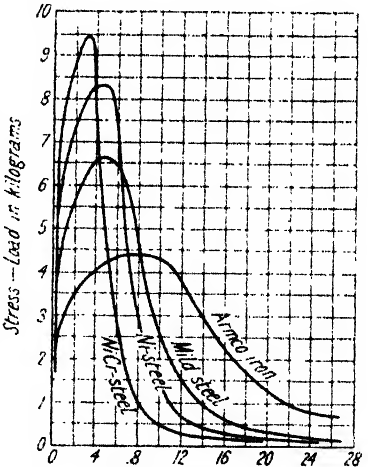


FIG. 224.—The Stress-Strain Energy of Impact.

The fundamental principles underlying the test were discussed by R. Plank, and he showed that rupture in the tensile test is totally different from rupture by the impact tensile test; in the static test there is a gradual increase in the applied stress, whereas with the dynamic test the stress suddenly increases to a maximum and then decreases. The stress-strain impact test was also examined by M. Moser, T. Inokuty, S. B. Russell, H. A. Dickie, T. Ishigaki, R. Mailänder and F. P. Fischer, W. Kuntze, F. Fettweis, K. Honda, R. H. Greaves, R. H. Greaves and J. A. Jones, A. McCance, J. Cournot, H. Sawagawa and R. de Oleveira, R. W. Moffatt, A. Gessner,

L. Jannin, E. Brechbühl, J. H. Hall, E. Preuss, O. Bauer, E. Heyn and O. Bauer, H. M. Howe, L. Klein, A. Mimey, H. Bornstein, F. N. Menefée and A. E. White, W. J. Keep, A. E. Outerbridge, A. M. Portevin, F. J. Cook, J. B. Kommers, J. G. Pearce, H. A. Schwartz, H. J. Tapsell and W. J. Clenshaw, A. N. Talbot and F. E. Richart, F. Körber and H. A. von Storp, W. Schwinning and K. Mathaes, S. Watanabe, Y. N. Morozoff, and R. Yamada. G. Delbart studied the impact toughness of cold-worked steel.

T. Sutoki observed that with 0·3 and 0·5 per cent. carbon steels, the highest temp. at which the test-pieces were abruptly broken by the impact test were 600° and 650°, respectively. A test-piece of a brittle material breaks abruptly at a maximum stress, but in the case of a tough material, the breaking occurs in several steps. The bending of the test-piece increases almost linearly with a rise of temp., but from 200° to 300° it begins to decrease, falling, at about 550°, almost to the value at ordinary temp. Above 550° it rapidly increases. K. Honda, T. Inokuty, and T. Sutoki discussed the theory that the thermal brittleness is the combined effect of work hardening and of the softening due to temp. R. W. Moffatt found that grey iron castings have a low impact resistance at room temp.; and this becomes less and less as the temp. is reduced below the f.p. The impact resistance of straight carbon steel castings decreases as the temp. falls below f.p., so that at −35° the resistance is only one-fourth of its value at room temp. The heat-treatment of these castings increases the resistance so that the value at −40° compares favourably with that at room temp. Low-carbon castings have a higher impact resistance than high-carbon castings. For the effect of hydrogen, see that element.

G. Charpy examined the impact toughness of iron by the notched-bar impact or shock test, between 80° and 600°. The work, in kilogrammetres per sq. cm., done by a hammer of weight W, falling a height H with a rebound h, when a denotes the effective sectional area of the fracture, is $W/(H-h)/a$. G. Charpy found a maximum in the vicinity of 200° and a minimum in the neighbourhood of 500°, and at higher temp. the toughness rapidly increased. A. le Chatelier, and E. Ehrensberger also measured the toughness of iron in terms of the notched-bar impact test at ordinary temp. L. Guillet and L. Révillon's observations agree with those of G. Charpy. The subject was also investigated by P. Breuil, W. H. Hatfield, R. A. Hadfield, P. Fillunger, R. Stribeck, T. Sutoki, F. Robin, and G. Goldberg,

E. W. Kaiser observed that the effect of cooling is very marked with the notched-bar impact test of wrought iron, and much more so in the case of steel. Mild steel lost 85·5 per cent. of its notched toughness when cooled from 15° to −20°; whilst under the same conditions wrought iron lost only 42·3 per cent. L. Aitchison found that most plain carbon steels give a marked drop in the notched-bar test at a low temp.—and generally between normal air temp. and −40°; between −40° and −80° the drop is small, and in some cases there is a small rise in value.

P. Goerens and G. Hartel found that, with a steel containing about 0·85 per cent. of carbon, between −75° and 1000°, the curves for the work on impact, or the resilience, in kilogrammetres per sq. cm. of effective section, are regular and show maxima at about 35° and 600°, with a minimum at 400°. Above 600° the work required for fracture falls off very rapidly, likewise also below 35°, so that at −75° the steel is very brittle. No discontinuities have been observed at the critical temp. R. H. Greaves and J. A. Jones found a maximum at 100° to 150° in the notched-bar tests; the exact position depends on the form of the test-pieces and the striking velocity. O. Reinhold's results with steels containing 0·08 C, 0·24 Si, 0·36 Mn, 0·050 P, and 0·04 Si; 0·15 C, 0·28 Si, 0·49 Mn, 0·034 P, and 0·03 S; 0·25 C, 0·12 Si, 0·39 Mn, 0·048 P, and 0·038 S; and 0·04 C, 0·23 Si, 0·51 Mn, 0·036 P,

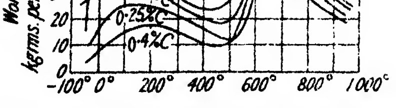


FIG. 225.—The Effect of Temperature on the Impact Work Required for Fracture.

and 0·015 S, are summarized in Fig. 225, and they illustrate the effect of carbon as well. A. Pomp used a soft iron with 0·07 per cent. carbon; he found that when heated to various temp. above 1000°, and slowly cooled, the toughness decreases, and this the more rapidly the higher is the temp., and a minimum brittleness is attained. R. M. Brown observed that cold-drawing greatly reduces the resistance to impact of mild steel, and a minimum is attained with a 30 per cent. reduction of area. A. Ono found that the cold straining of mild steel reduces its resistance to impact, but the resistance is restored on annealing. A steel containing 0·065 per cent. of carbon, after annealing at 920°, withstood 1010 blows; after annealing, followed by 8 per cent. straining, it withstood 940 blows; after annealing, straining, and again annealing:

Annealing temperature .	450°	500°	600°	700°	800°	900°	980°
Blows resisted . .	1013	1013	1013	496	553	1104	572

F. Wüst and E. Leuenberger made some observations on this subject. For L. Aitchison and L. W. Johnson's observations on the notched-bar test taken longitudinally and transversely, to the direction of forging, *vide supra*. The impact strength (notched bar) of mild steel castings was found to decrease on ageing at 250° for 1 hr. after forging to a reduction in area of 7 to 10 per cent., but not nearly to the same extent as it does after complete annealing. The values for the annealed metal at 20° to −20° were consistently below 2 mkgrms. per sq. cm., whereas those for the aged metal varied from about 6 mkgrms. per sq. cm. at 20° to about 2 to 3 mkgrms. per sq. cm. at −20°. A. B. Kinzel and W. Crafts studied the effect of inclusions on the impact test.

A. E. Seaton and A. Jude found that some nuts of connecting-rods broke down under conditions which could not be explained by the results of ordinary tensile tests, or of the alternating tensile stress tests. The repeated impact test was therefore investigated by J. O. Arnold, W. K. Hatt and E. Marburg, A. Pérot, M. Denis, T. E. Stanton and L. Bairstow, J. B. Johnson, J. B. Kommers, L. Bairstow, and J. O. Roos. According to T. E. Stanton and L. Bairstow, the angle of the notch in repeated impact tests has no influence on the number of blows which occasion fracture, for this depends solely on the relation between the diameter of the bar at the bottom of the notch, the diameter of the test-piece, and the distance between the supports. E. Nusbaumer compared the results of the simple impact test, and of the repeated impact test with Swedish iron, 0·07 to 0·46 per cent. carbon steels, nickel steels, and nickel-chromium steels subjected to different heat-treatments. It was found that the resistance always varies in the inverse ratio to the fall, and the rate of repetition of the stress—with the one exception of hardened nickel-chromium steel. The influence of the rate of the repetition of the impacts becomes less and less as the depth of fall increases, so that, provided the shock be sufficiently intense, the number of blows required to break the test-piece remains virtually the same, no matter what the rate of repetition of the test may be. H. Hanemann and R. Hinzmann found that the impact values with the notched-bar test are altered considerably by variations in the grain-size of the metal; and A. B. Kinzel and W. Crafts examined the effect of inclusions in the steel on the results.

A. E. Seaton and A. Jude found that the resistance to fracture with repeated impact-tests decreases as the proportion of carbon increases from 0·15 to 0·30 per cent.; and T. E. Stanton and L. Bairstow obtained a similar result provided the impacts are below a certain intensity. A. McWilliam and E. J. Barnes obtained the same results as A. E. Seaton and A. Jude. Steel with 0·75 to 0·80 per cent. of carbon offers a good resistance to repeated shock. According to J. O. Arnold, J. E. Stead and A. W. Richards, C. E. Stromeyer, and J. B. Kommers, phosphorus, and nitrogen in steel have an unfavourable influence on the repeated shock test; according to P. Longmuir, occluded hydrogen is deleterious; and, according to T. E. Stanton, J. H. Smith, and E. F. Lake, nickel, and titanium do not increase the resistance of steel to repeated shocks. E. Nusbaumer found that with carbon steels the resistance varies directly with the percentage of carbon as long as this percentage does not exceed 0·25 to 0·30, but with over this amount the resistance has a tendency to diminish, and this tendency is increased by hardening. In other words, the semi-hard steels always have a greater resistance than the mild steels. Hard steels resist better than mild steels (except in the hardened state), but not so well as the semi-hard steels. Swedish iron does not apparently display any greater resistance than soft steel. Generally speaking, the nickel steels have a greater resistance than soft carbon steels, but they do not appear to be superior in this respect to semi-hard steels. This is true only in cases where the depth of fall is not excessive; when the shock attains a certain intensity, the influence of the nickel disappears and the steel tends to behave like a simple carbon steel, no matter what the percentage of nickel may be. A second exception arises in the case of the steels containing from 0·30 to 2 per cent. of nickel, which in the hardened state display extraordinary resistances, far higher than those of the best carbon steel. The steel with 0·30 per cent. of nickel behaves almost as well or even better than steels containing a higher proportion of nickel (with the exception of the steel with 25 per cent. of nickel, and rolled). Finally, the nickel-chromium steels display much greater resistance than ordinary carbon steels, or even than nickel steels; but, of the nickel chromium steels, the dead-soft steel is the most resistant, and the semi-hard variety is the steel which gives the least satisfactory results. It has been said that, generally speaking, the resistance varies in inverse ratio to the depth of fall. Nickel steels, and in particular those containing both nickel and chromium, are much more sensitive than carbon steels to any variation in the depth of fall. This sensitiveness reveals itself by a considerable increase in the resistance once the depth of fall decreases.

A. E. Seaton and A. Jude found that hardening increases the resistance of steel to repeated shocks; but A. McWilliam and E. J. Barnes obtained a contrary result, and they also found that a sorbitic structure is unfavourable to the resistance of soft steels to repeated shock. According to E. Nusbaumer, hardening followed by annealing slightly increases the resistance of carbon steels. Its influence is, however, more appreciable with steels containing less than 0·30 per cent. of carbon than it is with the "hardening steels." Thus, semi-hard steels, hardened and annealed, are always higher in resistance than hard steels that have undergone similar treatment. Owing to the same phenomenon, hardening followed by annealing markedly raises the resistance of steels containing a low percentage of nickel (0·30 per cent. of nickel), but leaves steels with 2 per cent. of nickel practically unchanged. Lastly, it diminishes the resistance of nickel-chromium steels, but seems to have more influence upon soft nickel-chromium steels than on semi-hard steels. The latter, once hardened and annealed, display rather more resistance than the former when similarly treated. This is the reverse of what is found in the annealed (normalized) state. Hardening (not followed by annealing) considerably raises the resistance of Swedish iron, and, particularly, of mild steel—at least when the depth of fall is not excessive. In the opposite case (and this is a general observation applicable to all steels independently of their composition) the influence of the depth of fall becomes paramount and obliterates every other influence, *e.g.* that of the rate of repetition of the stress, of the chemical composition, and of the thermal treatment. Quenching either fails to affect or tends to diminish the resistance of semi-hard steel; it reduces to zero that of the "hardening" steels. The presence of nickel, either alone or combined with chromium, exaggerates to an extraordinary degree the effect of the quenching. The resistance of steel with 0·30 per cent. of nickel which has been quenched is, as a regular thing, equal to more than twenty-five times that of the same steel annealed, that is, for low depths of fall. That of steel containing 28 per cent. of nickel and quenched is, similarly, equal to nearly ten times that of the same steel after annealing; on the other hand, the steel with 25 per cent. of nickel subjected to the operation of quenching undergoes a sudden diminution in its resistance (nearly one-half). The nickel-chromium steels also have their resistance raised to a notable degree, but it is in the soft steels that the phenomenon is most marked, and in the semi-hard steels in which it is the least so. Lastly, in most cases overheating notably diminishes the resistance of all steels.

According to T. E. Stanton, the resistance of steel to repeated impacts agrees with its resistance to simple impact when the number of impacts determining fracture is small, but not so if the number of shocks is large. J. O. Roos obtained concordant results with endurance, rotary bending, and repeated impacts, but added that, in general, endurance under alternating tests is the reverse of the endurance under simple impact. L. Bairstow, however, believed that there is a complete lack of agreement between the results of the repeated shock test and those of alternating stresses. According to E. Nusbaumer, if the curves of resilience are comparable with those of the resistance to repeated shocks, it will appear at first sight as if there was no relationship between the two types of test. There is, however, a relation between the brittleness test and the repeated shock test. Every time the same steel in the same physical state (possessing the same essential constituents) undergoes—for any reason—a diminution of resilience, its resistance to repeated impact diminishes likewise ; and, on the other hand, whenever (under the same conditions) the resilience remains sensibly constant the resistance to repeated impact does not vary. It should be noted as a corollary to the foregoing proposition that the differences between the resistances of a normalized steel and a more or less overheated steel are greater in proportion as the depth of fall is less. Here is found once again the influence of the depth of fall which, as we know, tends to mask every other factor.

Fracture takes place by progressive fissuration. There exists at each point of fracture a dullness occasioned by the fact that the edges of the crack have become roughened or dulled by rubbing against one another, and the crack has enlarged until the moment when, the section having become too small, the test-piece has broken suddenly, yielding this time a crystalline fracture. This crystalline fracture invariably consists of a central band more or less wide and perpendicular to the line which joins the points of impact. Austenite is the particular constituent which offers the most resistance to repeated shocks, ferrite offers a far lower degree of resistance, and, finally, of all the constituents, martensite is the one whose resistance is lowest and, generally speaking, very closely in the vicinity of zero.

C. Frémont plotted the crushing curves at 15°, 800°, and 1300° for a soft steel with the tensile strength of 35 kgrms. per sq. cm. The curves were similar. F. Robin found that at a red-heat the ratio of the resistances is the same for static and dynamic crushing. The work done during static crushing was found to be less than during dynamic crushing. A. Martens gave for the static and dynamic work, in kilogrammetres per sq. mm., necessary to reduce the depth to a certain percentage of the height at a single blow :

	Soft steel				Soft steel			
Reduction depth .	95	90	80	70	95	90	80	70 per cent.
Compression (static) .	11·2	32·8	100·7	204·5	11·1	39·0	82·0	168·7
Crushing (dynamic) .	66·3	148·7	401·2	802·8	77·3	170·2	409·3	774·2

He showed that the proportion of work necessary to produce a certain reduction in depth increases with the intensity of the crushing, and to more than the anticipated proportionate number. C. Codron measured the resistance, in kilogrammetres per sq. mm., of forged metals to compression at different temp., and found :

	0°	100°	200°	300°	400°	500°	600°	700°	800°	1000°	1200°	1400°
Cast iron . .	50	50	49	48	47	44	40	36	28	18	8	0
Wrought iron . .	40	49	39	38	37	34	30	25	20	12	8	4

The values would be different with other modes of testing. With malleable metals the yield in the press. may be quadruple, triple, or double that of the hammer working at an average speed. With elastic metals, like steels at a red-heat, the coeff. of the relative yield falls, and the compression requires nearly the same amount of mechanical energy as does forging. The coeff. of the yield may here vary from 0·3 to 0·7. The work, in kilogrammetres per sq. mm., found by F. Robin for two steels at different temp., by static and dynamic compression, was as follows :

	0·07 per cent. carbon			0·9 per cent. carbon		
	15°	275°–290°	500°	15°	200°	500°
Elastic limit	35·2	17·5	19·9	108	110·7	60·7
Work Static	11·04	10·2	6·5	16·0	13·3	14·4
Work Dynamic	24·55	24·3	12·74	34·2	25·1	27·5

The curves for the static stresses up to a red-heat diverge completely from the curves of dynamic stresses. Soft metals like lead, tin (cold), and steels at a red-heat give higher values for the dynamic work for equal amounts of deformation ; and as the hardness and elasticity increase, the difference between the static and dynamic work may become less, or even reversed as in the case of the nickel, chromium, and tungsten steels, because of the work lost in the drop weight. The special austenitic steels, and often the martensitic steels, display this property. F. Robin extended this subject to the work of the drop-hammer, and the press. in forging metals. F. Sauerwald found that at moderate temp. the application of press. did not increase the size of grain of powdered iron, not previously worked in the cold, but at a higher temp. an increase in grain-size was observed.

C. de Fréminville[15] investigated **the effect of vibrations** on the tensile properties of steel. He said that in metallic rods and bars, elementary vibrations are propagated with but a very slight loss in work, and are reflected back again from the ends of these conductors. If these vibrations encounter the reflected vibrations, considerable stresses result. Excessive stresses leading to breakages may be set up by waves, or considerable vibrations being arrested in their course, at some point within the mass. C. Frémont, and C. Faroux found that, at this point, these vibrations occasion cracks, for the prevention of which any mode of strengthening the piece is absolutely useless. R. A. Henry studied the propagation of vibrational pressures within elastic bodies, and concluded that if there is complete synchronism between the vibratory movement a solid body may assume the periodic repetition of the stress, the vibratory movement becomes exceedingly exaggerated and develops elastic stresses wholly disproportionate to the intensity of the isolated stresses. He also showed that for any simple cylindrical body subjected in the direction of its axis to a simple sinusoidal pulsation applied to one extremity, the other being fixed, periodicities exist at which the body will undergo fracture, independently of what the amplitude of the pulsation may have been. A. Boudouard, and A. Guillet investigated the influence of various factors on the resistance to vibrations of cylindrical bars vibrating in diapason, and found that fracture occurred with stresses far below the ordinary elastic limit. Puddled iron resisted the vibrations better than did dead soft steel; and the number of vibrations necessary to fracture a bar of steel varies inversely as the percentage of carbon. Hardening diminishes the resistance of hard steels to vibrations. J. Resal made some observations on the subject, and E. Nusbaumer concluded from his observations that : (i) In carbon steels, the resistance, in the annealed state, varies in direct proportion to the percentage of carbon ; the rise in resistance, corresponding with a relatively slight increase of carbon, is considerable. Quenching markedly diminishes the resistance, but affects hard steels to a much greater extent than soft steels. Quenching followed by an annealing is the treatment that ensures the maximum resistance. (ii) In nickel steels, the resistance, in the annealed state, varies in direct proportion to the percentage of nickel. Quenching reduces the resistance. Quenching followed by annealing gives the most marked resistance. The 2 per cent. nickel steel, quenched and annealed, is distinctly superior to the best carbon steel. (iii) In nickel-chromium steels, the resistance varies inversely with the hardness of the steel, except in the quenched state. Hard nickel-chromium steels, quenched and annealed, display less resistance than semi-hard steels, which, in turn, again display less resistance than mild steels. In contradistinction to what occurs with carbon steels or with nickel steels, quenching considerably raises the resistance of nickel-chromium steels. It seems, moreover, to affect hard steel to a greater extent than it does mild steel. Quenching, followed by annealing, gives the minimum resistance. Any treatment that increases the tensile strength of nickel-chromium steel appears likewise to increase its resistance to vibratory stresses. (iv) An important fact is that all the steels, no matter what their nature (carbon, nickel, or nickel-chromium), ended by breaking, notwithstanding that they were being worked at less than their elastic limit. Thus, a steel may break by vibration without its effective deflection having attained that calculated from its elastic limit.

The question : What is the effect of repeated stresses on the tendency of metals to fracture ? was raised by W. A. J. Albert [16] in 1829, and later by H. James and D. Galton. In 1837, E. Hodgkinson stated that the repetition of any stress, however small, would permanently deform a metal exposed to the stress ; and in 1848, J. Thomson, however, added that the limits of proportionality might be initially very low, and in consequence small permanent sets might result from the first application of relatively small stresses, but a secondary result would be that the limits of proportionality would be greatly widened, so that subsequent applications of initial small stresses would produce no further deformation. Mysterious failures in fracture, and in the testing of wrought iron, etc., for railway bridges, appear as if (i) the ultimate strength of the metal deteriorated with time, or else (ii) failure was due to the mere repetition of the applied stresses. In 1849, a Royal Commission was appointed to inquire into this subject; it was found that the first hypothesis did not explain the phenomenon, but it was shown that a metal could fracture by the frequent repetition of a stress less than the statical ultimate stress, and that the failure was not due merely to the presence of a vibration, although vibration acted as an accelerating agent.

Metals will break under the repeated application of a stress very much less than what would be required to produce rupture if the stress were applied gradually and continuously. The strength of a piece of metal when tested in the ordinary way is not a sure guide for material which is to be subjected to a series of vibrating stresses such as might occur in the piston of an engine, in steel springs, in the axles of a railway carriage, in the supports for railway bridges, etc. F. Braithwaite attributed the breakage of some girders to a similar phenomenon. W. Metcalf found that hard steels suffer less from vibrations than do soft steels. W. Fairbairn investigated this subject for the Board of Trade, and he showed that a beam with a statical breaking load of 12 tons might withstand 3×10^6 applications of a load of 3 tons, but with a greater load, fracture occurred with a correspondingly smaller number of reversals. Hence, a safe vibrating load can be applied which can be sustained indefinitely. A. Wöhler concluded :

> Wrought iron and steel will rupture at a unit stress not only less than the ultimate static strength of the material, but even less than the elastic limit, if the stress is repeated a sufficient number of times. Within certain limits, the range of stress rather than the maximum stress determines the number of cycles before rupture. For a given maximum or a minimum unit stress, an increase of range of stress decreases the cycles necessary for rupture. For a given minimum or maximum unit stress, there appears to be limiting range of stress which may be applied indefinitely without producing rupture. As the maximum applied unit stress increases, this limiting range of stress decreases.

A. Wöhler found the safe unit stress for wrought iron under an alternating stress might be 8600 lbs. per sq. in. ; but under tension, it might vary from 3300 to

19,300 lbs. per sq. in.; and that the range of stress was constant if the ultimate stress fell below 3300 lbs. per sq. in. The alternating stress for untempered cast steel might be 12,800 lbs. per sq. in.; and in one direction only, from 11,500 to 35,000 lbs. per sq. in. For cast spring steel, the stress might vary from 96,000 to 128,0000 lbs. per sq. in. A. Wöhler's work was confirmed by L. Spangenberg, and B. Baker. The subject was followed up by J. Bauschinger, and he concluded that:

(i) A tension stress above the yield-point up to the applied stress, even if the bar is immediately re-tested: upon the release of the load and the lapse of time, the yield-point increases even above the previous maximum applied stress. This increase is noticeable even after one day, and may continue for even years. (ii) A tension stress above the yield-point reduces the elastic limit (determined by delicate measurements of deformations) often down to zero. Upon the release of the load and the lapse of time, the elastic limit increases, reaches the applied stress after several days, and may rise above this stress after sufficient lapse of time. (iii) A tension stress which lies above the elastic limit immediately, the more so the higher the initial stress. When the applied stress approaches the yield-point, the elastic limit reaches a maximum, and is lowered when the yield-point is exceeded. (iv) As a rule, a stress above the yield-point lowers the modulus of elasticity. Upon the release of the stress and the lapse of time, the modulus increases, and after several years is found to be considerably above the original value. (v) Severe jars, as by cold-hammering, lower the elastic limit which has previously been raised by over-stress and rest. If the hammering produces tension, the elastic limit decreases down to its original value, but otherwise it remains above it. (vi) Heating followed by subsequent cooling, will again reduce the elastic limit and yield-point which have been increased by overstress and rest. For low-carbon steel the effect becomes noticeable at 350° if the cooling is rapid, and at 450° if the cooling has no effect on the two limits. With wrought iron the effect is produced at about 400° both for rapid and slow cooling. (vii) Rapid cooling lowers the elastic limit and yield-point, especially the former, more effectively than slow cooling. Rapid cooling usually decreases the elastic limit to zero, or nearly zero, after heating up to 500°, and surely by heating up to cherry-red heat. This is true for wrought iron, low-carbon steel, and Bessemer steel. Slow cooling even after heating to a cherry-red heat does not produce such a great decrease. (viii) A stress in tension (or compression) beyond the elastic limit reduces considerably the elastic limit in compression (or tension) the more, the higher the applied stress is above the original elastic limit. Even relatively small transgressions of one elastic limit will produce the opposite elastic limit. A period of rest will not again increase the elastic limit, as is possible by loading in one direction above the yield-point. (ix) Gradually increasing alternating stress in tension and compression will not decrease the opposite elastic limit unless one of the original limits is exceeded. (x) An elastic limit in tension (or compression) which has been lowered by previous stress above the elastic limit in compression (or tension) can again be increased by applying a gradually increasing alternating stress, but it can be increased only up to a value which is considerably below the original elastic limit. (xi) Repeated stresses between zero and an upper limit which coincides with or is close to the elastic limit will not cause rupture. The elastic limit, however, must not previously have been raised artificially by tension or cold-working, nor must there be any flaws in the material. In the latter respect homogeneous material like low-carbon steel is especially sensitive. (xii) Repeated stress between zero and an upper limit in tension which coincides with or lies slightly above the elastic limit will increase the elastic limit, and the more so the greater is the number of repetitions, but not above a certain limiting value. (xiii) If by the previous action (as in xii) the elastic limit is increased above the applied stress, fracture will not take place; but if the applied stress is so high that the elastic limit cannot be augmented to this value, failure must take place after a limited number of repetitions. (xiv) If a material is to withstand an indefinite number of repetitions of alternating stress, then the applied stress must not exceed the natural elastic limit.

J. Bauschinger understood by the *yield-point* the unit stress at which a metal shows an increase of deformation without additional stress; and he explained his use of the term *natural elastic limit* by supposing a material with an artificially raised elastic limit would have its elastic limit reduced to a certain value by applying alternating stresses below this artificial limit, and that this new elastic limit would be the same as that obtained when an elastic limit which has been reduced is gradually increased by applying a slowly increasing alternating stress.

The effect of surface conditions on the resistance of metals to repeated stresses was studied by F. C. Lea and co-workers, D. J. McAdam, and R. H. D. Barklie and H. J. Davies.

The fact that when metals are fractured by repeated stresses, the fracture has a crystalline appearance led to the assumption that the metal gradually develops a crystalline structure under the influence of repeated stresses. There has been some discussion as to whether vibration and shock, under ordinary working conditions, can cause a metal to become crystalline and brittle. P. Argall, for instance, held that this is probably the case; whilst R. W. Raymond supported the opposite view. According to P. Kreuzpointer, the mode of breaking a metal may produce a crystalline fracture even though the metal is uniformly fibrous. Iron and those classes of steel which are supposed to be capable of crystallizing under shock and vibrations will not break until long after the primary or original elastic limit and the yield-point have been passed, and the metal has "flowed" more or less. The natural and inevitable consequence of "flow" in iron and steel is to break up and reduce the size of crystals and fibres; hence, the forces which operate to break and destroy a structural member of whatever kind are directly antagonistic to the formation of crystals out of fibres, these forces being fibre producers, as it were, from the moment they become active until the point of rupture is reached. This tendency is increased as the point of rupture is approached, since flow is most rapid in iron and steel just before the metal breaks, as is proved by the reduction or contraction of area at the point of rupture, and by the amorphous condition of "detail" fractures of iron and steel. Consequently, the theory of the crystallization of iron and steel under stresses and strains is based upon a misconception of the nature and properties of those metals, because the low heat or the heat that can possibly be produced in service, as well as stress and strain, with their effects analogous to mechanical work produced under hammer and roll, all tend to break up crystals in iron and steel, to make them smaller instead of making them larger, or permitting the formation of a new structure. R. A. Hadfield stated that all the fractures he had observed were more likely to have been the result of defective heat-treatment, than to have been produced by changes in the molecular structure of the metal. The subject was discussed by H. M. Howe, F. Rogers, C. H. Risdale, J. E. Stead, and E. B. Grub. R. W. Raymond does not consider that W. Fairbairn believed in crystallization as an explanation of the fracture, and there is no proof that a metal which has undergone much vibration has a more crystalline fracture than it originally possessed. When the bars which ruptured under fatigue showed a coarsely crystalline structure, this was not due to crystallization produced by cyclic stresses but rather to overheating, to defective chemical composition, or to faulty treatment in manufacture. J. Bauschinger proved that millions of repetitions of a stress do not alter the structure of the metal, nor reduce the ultimate static strength. A. E. Outerbridge said that brittle cast iron, after being subjected to repeated shocks, may become less brittle because a molecular annealing may occur at ordinary temp. which releases the strains in castings. The subject was discussed by A. Ledebur, and J. O. Arnold. H. Hädicke found that the repeated hammering—15,000 blows—of a piece of iron an inch square changed the fibrous to a granular structure. The blows went beyond the limit of elasticity, but if not subjected to this excessive treatment the metal does not change in this way.

According to P. Oberhoffer and W. Oertel, commercial iron shows a maximum grain-size after a 10 per cent. deformation between 700° and 800°, but with electrolytic iron this is not the case. The grains of electrolytic iron, however, do continue to grow at this temp. W. Riede showed that many alloy steels—Si-Mn, Cr, and Ni-Cr steels—as well as carbon steels, show a recrystallization of the material when subjected to rapidly alternating stresses.

Just as the *elastic limit*, or, in ductile metals, the *yield-point*, is the important criterion in the resistance of static stresses, so with alternating or repeated stresses the *endurance limit* is the important criterion, and with impact stresses the important criterion is the *modulus of resilience* or the capacity to absorb energy up to the elastic limit. Repeated stresses may vary from zero or from a positive or negative minimum to a positive maximum, so that the range of the stress is the algebraic difference between the maximum and the minimum stress. The **endurance limit** is the stress that may be applied to a given material for an indefinitely large number of cycles without producing rupture; or it may be regarded as the number of repetitions of a given stress required to cause failure. The term **fatigue** refers to the phenomenon of fracture under repeated stresses—*vide supra*. It is assumed that the metal becomes "weakened" by the repeated stresses, and then breaks more readily.

Excepting the eighth conclusion, the general results of J. Bauschinger have not been disproved. H. F. Moore and J. B. Kommers found that hot-rolled, 0·18 per cent. carbon steel wire, reduced by cold-stretching from 0·50 to 0·44 in., had originally an elastic limit of 38,200 lbs. per sq. in. and an ultimate strength of 61,500 lbs. per sq. in., and an endurance limit of ±28,000 lbs. per sq. in., and after the cold-stretching the endurance limit was ±41,000 lbs. per sq. in. after having been heated to 260°. Hence the elastic limit in compression which was reduced to zero by cold-stretching must have been restored to something like 41,000 lbs. per sq. in., and possibly a period of rest would have had a similar effect. G. Sulzer said that the stresses lead to cracking when they exceed the elastic limit, no matter how high the tensile strength of the metal may be; and C. B. Dudley, that breaking occurs when the calculated maximum stress reached half the ordinary elastic limit. T. E. Stanton and L. Bairstow found that the elastic limit after a certain number of alternating tensile and compression tests is lower than the original elastic limit; and L. Bairstow showed that the iron and steel adapt themselves to these variations so as to remain perfectly elastic and to exhibit no trace of fatigue. The variations of the elastic limit of tensile strength are slighter than those of the elastic limit of compressional strength, so that it is the latter which determines the permissible variation of stresses. Similar conclusions were obtained by J. H. Smith with alternating tension and compression; and by J. E. Howard, and L. B. Turner with rotatory bands.

The life or endurance of a metal can be referred to the number of repetitions of a stress of a given range of magnitude. The stress may be direct, bending, or torsional, or a combination of these stresses. The results of T. E. Stanton and J. R. Pannell with a reversed bending test on mild steel are summarized in Fig. 226, and the curve is sometimes called the *S/N*-curve. The endurance limits of stress on a 10 million reversals basis are ±12·75 tons per sq. in.; the limiting range of stress on a 10 million reversals is 25·5 tons per sq. in., using reversed stresses, or the limiting range of stress on a 10 million reversals basis is 12·75 tons per sq. in. The general type of curve is the same for various other modes of applying the test, and with many different materials. The curves become more and more nearly horizontal to the *N*-axis as the endurance increases. The curves have a certain formal resemblance to the so-called human endurance curves, where, owing to muscular fatigue, the speed of, say, a Marathon runner becomes less the greater the distance traversed. The question has arisen whether a material will fail at all stresses if the number of repetitions be sufficiently high, or whether there exists a limiting range of stress which would never produce failure. E. M. Eden and co-workers were unable to find a limit of stress, however slight, for which the necessary number of alternations required to produce fracture becomes infinite. C. E. Stromeyer denied the existence of any relation between resistance to alternating stresses, elastic limit, and breaking strain.

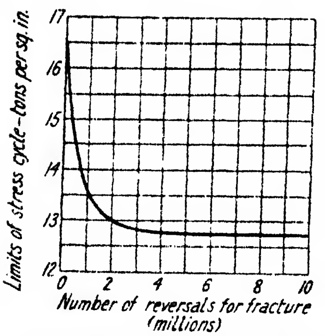


FIG. 226.—Endurance Curve of Mild Steel.

The subject has been discussed by K. Aders, C. R. Austin, F. Bacon, L. Bairstow, W. B. Bartels, O. H. Basquin, R. G. Batson and co-workers, K. Baumann, P. Billet and H. Wantz, R. M. Brown, G. R. Brophy, H. Buchholtz and E. H. Schulz, C. H. Bulleid,

R. Cazaud, C. L. Clark and A. E. White, G. Colonnetti, J. L. Cox, J. F. Cunningham and J. Gilchrist, J. Czochralsky and E. Henkel, C. H. Desch, H. Deslandres, W. Deutsch, H. C. Dews, C. B. Dudley, E. Duryea and J. Mayer, E. M. Eden, E. M. Eden and co-workers, A. Esau, W. H. Finley, O. Föppl, J. R. Freeman and co-workers, H. J. French and co-workers, Y. Fujii, T. S. Fuller, J. C. Gardner, J. Geller, H. W. Gillett, J. C. Godsell, H. J. Gough and co-workers, J. H. Grindley, L. Guillet, G. H. Gulliver, R. G. Guthrie, G. A. Hankins, G. A. Hankins and G. W. Ford, D. Hanson, O. E. Harder, V. B. Harley, K. Heindhofer and H. Sjövall, W. Herold, B. Hopkinson, E. Houdremont and R. Mailänder, S. A. Houghton, J. E. Howard, C. E. Inglis, P. L. Irwin, D. S. Jacobus, L. Jannin, T. M. Jasper, C. F. Jenkin, C. F. Jenkin and G. D. Lehmann, C. H. M. Jenkins, H. Kändler and E. H. Schulz, J. J. Kanter and L. W. Spring, H. W. Keeble, C. H. Keulegen, R. L. Keynon, Y. Kidani, W. Knackstedt, F. Körbor and A. Pomp, J. B. Kommers, W. Kuntze and co-workers, K. Laute, K. Laute and G. Sachs, F. C. Lea and co-workers, E. Lehr, J. M. Lessells, R. E. Lewton, K. Ljungberg, C. C. Longridge, F. F. Lucas, P. Ludwik, P. Ludwik and R. Scheu, A. Lundgren, D. J. McAdam, F. F. McIntosh and co-workers, P. G. McVetty, R. Mailänder, F. S. Merrils, J. Miller, H. F. Moore and co-workers, R. R. Moore, W. Müller and H. Leber, W. R. Needham, F. H. Norton, J. Oehschläger, A. Ono, R. E. Peterson, E. Pohl and co-workers, W. C. Popplewell, E. Preuss, V. Prever and E. Balma, H. S. Prichard, W. Riddlesworth, F. Rittershausen and F. P. Fischer, T. L. Robinson, T. Robson, F. Rogers, W. Rohn, J. O. Roos, W. Rosenhain, F. W. Rowe, N. A. Schaposhnikoff and co-workers, W. Schneider, W. Schwinning and E. Strobel, J. Seigle and F. Cretin, R. Sergeson, C. Shiba and K. Yuasa, W. R. Shiner, A. Shimizu, J. H. Smith and co-workers, T. A. Solberg and H. E. Haven, E. P. and B. H. Stenger, R. Stribeck, C. E. Stromeyer, H. J. Tapsell and W. J. Clenshaw, H. R. Thomas and J. G. Lowther, A. Thum and co-workers, J. R. Townsend and C. H. Greenall, L. B. Tuckerman and C. S. Aitchison, C. A. P. Turner, G. B. Upton and G. W. Lewis, G. Welter, J. K. Wood, and J. G. R. Woodvine, etc.

H. J. Gough concluded that a definite limiting range of stress exists for an indefinitely large number of reversals, and it can be determined, for all practical requirements, by the endurance test on a basis of 10 million reversals. He also studied the effect of alternating torsional stresses on a single crystal of α-iron. A. Thum and W. J. Wiss found that by subjecting steel to 5,000,000 reversals of a load just below the fatigue strength and then repeating the treatment several times after increasing the load by 1 kgrm. per sq. mm. every time, the fatigue limit may be increased by as much as 20 per cent. If the load is increased after fewer reversals the material acquires a greater strength at the cost of a shorter effective life. Previous cold-work increases the fatigue strength and the capacity of the metal to withstand overload in dynamic tests. According to H. J. Gough and D. Hanson, armco iron after being exposed to repeated stresses about 40 millions in number and 0·4 ton less than the limiting fatigue range, shows, microscopically, dark slip-bands consisting of fine lines which appear to be masses of slip-bands rather than one slip-band widened by attrition. It is doubtful if continuous slipping occurs on the planes first formed. A mobile film was postulated to explain the behaviour of overstrained metal, particularly with respect to the gradual recovery of elasticity after overstrain, but it does not readily account for the fact that recovery of elasticity can be attained by subjecting overstrained material to reversals of stress at high speed. Failure under repeated stresses does not appear to differ essentially from failure under static stresses. When a sufficient stress is applied, slip occurs within certain crystals in the material, resulting in local strain-hardening, and when the stress is reversed further slip takes place, but not on the original slip-band, which has been strengthened by the previous slip. This process is repeated, and if the range of stress is not too great the metal may be sufficiently strengthened to withstand an indefinite number of reversals of that range of stress without further slip occurring. In this way the formation of a very large number of slip-bands within the fatigue range may be explained. The subject was studied by H. F. Moore and T. Ver.

According to W. Herold, the structure of pearlitic steel at the point of fracture by fatigue under repeated stress shows that the cementite has been forced towards the grain boundaries, whilst lamellar pearlite has been crushed and converted into granular pearlite, giving the metal a very coarse-grained structure. In martensitic steels the hard η-phase becomes crushed into small particles which are forced through the softer ϵ-phase towards the grain boundaries. In some austenitic steels after fracture by fatigue, cementite may be observed at the grain boundaries, although the presence of this constituent is not visible in the original structure; in other cases, the fatigued metal has a nodular structure which cannot further be resolved. In general, steels which have been hardened and tempered lose their capacity for damping, *i.e.* for converting energy into heat by internal friction after being subjected to repeated stresses sufficient to produce failure by fatigue. G. S. von Heydekampf studied the effect of cold-work on the fatigue or endurance limit of steel and found that the fatigue limit is raised by cold-work, and similarly with the safe working range of repeated reversals of stress.

Attempts have been made to find a relation between the safe range of the stress, and the mean stress of the cycle, by W. Gerber, H. Lippold. W. Launhardt, O. H. Basquin, F. Schäffer, J. Gilchrist, J. Weyrauch, J. Goodman, F. Rogers, B. P. Haigh, A. Wöhler, J. B. Johnson, J. H. Smith, H. J. Gough, H. F. Moore and T. M. Jasper, T. M. Jasper, H. F. Moore and F. B. Seely, C. E. Stromeyer. F. C. Lea, etc. Attempts have also been made to find a relation between the endurance, and other physical properties—*e.g.* hardness, tensile strength, and impact tests—by H. J. Gough, R. R. Moore, P. D. Merica and co-workers, W. M. Corse and G. F. Comstock, R. L. Templin, T. E. Stanton and R. G. Batson, T. E. Stanton and L. Bairstow, H. R. Sankey, etc. C. Mimey, N. Davidenkoff, P. Breuil, A. Portevin, H. Seehase, R. Stribeck, and H. le Chatelier discussed the transformations of impact energy into thermal energy during the impact testing of steel. The effect of the shape of the specimen, and of sudden changes in the section of the specimen tested—by flaws, holes, etc.—has been discussed by A. Wöhler, J. O. Roos, B. P. Haigh, W. N. Thomas, J. S. Wilson and B. P. Haigh, E. M. Eden and co-workers, C. E. Inglis, K. Suyehiro, E. G. Coker, G. I. Taylor and A. A. Griffith, L. Bairstow, H. W. Gillett and E. L. Mach, F. C. Lea, T. E. Stanton, H. F. Moore and co-workers, etc.; the effect of the surface finish, by E. M. Eden, G. A. Hankins and M. L. Becker, H. F. Moore and J. B. Kommers, J. Sondericker, W. N. Thomas, A. A. Griffith, etc.; the effect of internal stresses, by H. F. Moore and co-workers, L. Aitchison, H. W. Gillett and E. L. Mach, S. Whyte, etc.; the effect of surface decarburization, by C. R. Austin; and the effect of corrosion, by D. J. McAdam, B. P. Haigh, and R. R. Moore—*vide infra*.

The possibility of applying the elastic formulæ of W. J. M. Rankine, A. J. C. B. de St. Venant, and C. A. Coulomb, which has been developed on the assumption that the metals are homogeneous and isotropic, turns on the fact that although the metal is really an aggregate or a colony of minute crystalline grains, and that the formulæ are consequently not true for individual grains, or for small groups of grains, yet with large aggregates the formulæ are statistically true in the same sense that mortality statistics enable the death rate of a *community* to be predicted, but are not applicable to *individuals*. The subject has been discussed by J. J. Guest, W. A. Scoble, R. G. Batson, B. P. Haigh, E. L. Hancock, L. B. Turner, C. E. Stromeyer, D. J. McAdam, H. F. Moore and J. B. Kommers, H. F. Moore and T. M. Jasper, and T. E. Stanton and R. G. Batson. The effect of the speed of repetition upon the fatigue range was discussed by O. Reynolds and J. H. Smith, J. B. Kommers, H. J. Gough, H. F. Moore and T. M. Jasper, T. E. Stanton and J. R. Pannell, G. A. Hankins, W. Mason, B. P. Haigh, etc. O. Reynolds and J. H. Smith with alternating bends, L. Bairstow with alternating tension and compression, and J. O. Arnold with repeated impacts observed that the resistance of the metal varies inversely as the rapidity of the reversal of the stresses, but B. Hopkinson with periodic tensile tests, and J. O. Roos with rotary bending tests came to the opposite conclusion; while T. E. Stanton, and E. M. Eden and co-workers concluded from alternating bending tests that there is no relation between the endurance and rates not exceeding 2,000 alternations per minute. T. E. Stanton and L. Bairstow, T. E. Stanton, J. B. Kommers, and E. M. Eden and co-workers, showed that in the alternating bending tests, deep grooves and even tool marks on the test-pieces spoil the results; and C. de Fréminville, and C. Frémont attribute this to the fact that deep grooves and tool-marks stop vibrations—*vide supra*, the action of vibrations. L. Aitchison and L. W. Johnson discussed longitudinal and transverse tests—*vide supra*. The effect of understressing was examined by J. H. Smith, H. F. Moore and T. M. Jasper, E. G. Coker, etc.; and the effect of overstressing, by J. H. Smith, H. F. Moore and co-workers, etc.

Railway engineers have noticed that with axles and rails, hard metals resist alternating bending stresses far better than soft metals, and this is in agreement with the observations of T. E. Stanton and L. Bairstow, and J. E. Howard. The last-named reported that steels with 0·75 to 0·80 per cent. of carbon resist very well rotary bending stresses, while with higher or lower percentages of carbon the resistance is not so good—*vide infra*, repeated impact tests. Impurities like slag, manganese sulphide, etc., were found by M. Longridge, M. Ziegler, and C. B. Dudley to act injuriously on alternating bending or rotary stresses, and repeated impacts. In the solidification of these impurities, owing to their contraction, they leave minute fissures and flaws within the steel, and these enlarge under the influence of repeated stresses. According to C. E. Stromeyer, J. O. Arnold, J. E. Stead, and J. B. Kommers, phosphorus and nitrogen favour resistance to alternating bending stresses, but not to repeated shocks; according to T. E. Stanton, J. H. Smith, and E. F. Lake, nickel and titanium favour resistance to alternating bending stresses, but not to repeated shocks; and, according to P. Longmuir, occluded hydrogen makes the steel more susceptible to fracture by repeated shocks. E. Biard said that the relative breakage of railway axles owing to the development of cracks, is as follows: Open-hearth steel, 1; Bessemer steel, 0·625; crucible steel, 0·333; puddled steel, 0·256; crystalline iron, 0·213; and fibrous iron, 0·092. A. Boudouard also found that puddled iron resists vibrations better than soft steel.

F. Rogers, T. E. Stanton, B. Blount and co-workers, and E. M. Eden and co-workers found that the hardening of steel raises its resistance to alternating bending stresses, and annealing has the converse effect; J. C. Gardner obtained similar results with rotary bending stresses; J. H. Smith, with alternating tensile and compressive stresses; and A. E. Seaton and A. Jude, with repeated shocks. A. McWilliam and E. J. Barnes said that hardening diminishes the resistance of steel to repeated shocks; and A. Boudouard, to vibrations. F. Rogers, and A. W. Richards and J. E. Stead found that overheated steel has a poor resistance to alternating bending stresses, but the metal can be restored by a suitable heat-treatment. A. Boudouard, and A. W. Richards and J. E. Stead found that a sorbitic structure, obtained by hardening and annealing, favours the resistance of steel to vibrations and alternating bending stresses; but, according to A. McWilliam and E. J. Barnes, not so with repeated impact tests on soft steels. E. M. Eden and co-workers found that no heat treatment improves resistance to alternating bending stresses, tension, or compression by raising the permissible load; the sole advantage of heat-treatment is to increase the number of alternations before fracture under a given load. L. Bairstow found that a fatigued steel—*i.e.* a steel whose elastic limit has been displaced by repeated stresses—regains its ordinary limit after testing for several months, or on treatment with boiling water—*vide infra*, recovery. According to E. P. and B. H. Stenger, there is one certain quenching temp. for steel to yield a maximum fatigue strength, and with high-carbon steel this corresponds with the A_{cm}-point.

L. Aitchison and L. W. Johnson found that the fatigue strength is higher with specimens cut parallel to the direction of forging than it is with specimens cut at right angles to that direction. H. F. Moore observed that the failure by fatigue of the metals he examined was due to the growth of minute flaws and cracks; and it is generally agreed that fracture takes place gradually by the development of a flaw, which, to begin with, may be microscopic. For K. Yuasa's observations, *vide supra*, tensile tests. According to J. A. Ewing and J. C. W. Humfrey, A. E. Seaton and A. Jude, W. Schwinning and E. Strobel, and T. E. Stanton and L. Bairstow, the development takes place either by slip-bands or twinnings. A. E. Seaton and A. Jude, F. Rogers, T. E. Stanton and L. Bairstow, and W. Giesen consider that the flaw develops by preference within the ferrite.

The observations of J. A. Ewing and co-workers on the development of slip-bands and cracks when a metal is subjected to alternating stresses, have been previously discussed. T. E. Stanton and L. Bairstow obtained confirmatory results. One of the characteristic features of fractures due to stress reversals is the fact that they occur abruptly without the local drawing out and necking associated with ordinary tensile tests with ductile materials. This phenomenon fits very well into the slip-band hypothesis. In agreement with some observations of H. F. Moore and J. B. Kommers, H. J. Gough and D. Hanson found that with armco iron the endurance limit may be greater than the static yield-point. Analogous cases where the endurance limits are higher than the proportional elastic limits have been reported by H. F. Moore and T. M. Jasper, R. R. Moore, D. J. McAdam, and J. M. Lessells. H. J. Gough and D. Hanson observed that with static stresses, below the limit of proportionality, there is no indication of strain, but for stresses above the proportional limit, definite markings developed like the slip-bands produced by elastic strain; with alternating stresses, just below the limit of proportionality, after 11,750,000 cycles, surface markings developed on only a few crystals, the other crystals showed no evidence of stress, and with stresses a little above the proportional elastic limit, the markings were the same as before, but more crystals were affected. With stresses greater than the static yield-point, but less than the endurance limit, dark areas appeared on some of the crystals. These areas contained numerous slip-bands, proving that the slip-bands develop at stresses below the endurance limit, and that the production of these bands is not a criterion of ultimate failure by fatigue. D. J. McAdam, and A. M. Binnie studied the corrosion fatigue of iron—*vide infra*, corrosion.

L. Bairstow found that a specimen of axle steel with a yield-point of 55,700 lbs. per sq. in. and an ultimate strength of 85,500 lbs. per sq. in., when subjected to

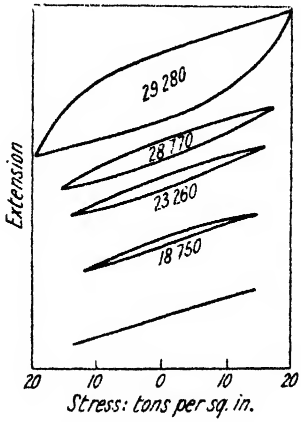


Fig. 227.—Elastic Hysteresis under Repeated Stresses.

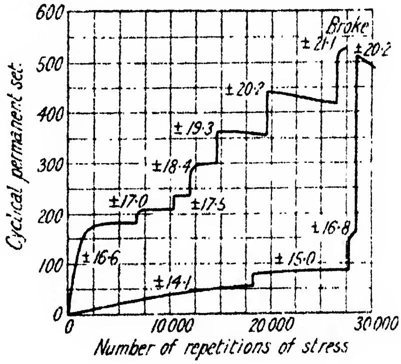


Fig. 228.—Effect of Reversals on the Permanent Set.

equal and opposite stresses of 31,600 lbs. per sq. in., gave a straight line as the cycle of extensions, but as the number of cycles increased to 18,750, the width of the hysteresis loop was about 11 per cent. of the original elastic extension. As the stress on the specimen was increased to 33,600 lbs. per sq. in., the width of the loop increased, so that with a stress of 45,200 lbs. per sq. in., and 29,280 cycles, the loop became very wide. At lower stresses the width of the loop tended to a constant value as the number of cycles increased, and at higher stresses the width of the loop decreased with an increase of cycles. When the stresses were not completely reversed, a "permanent extension" was developed, due to the repeated stresses, and he called it the *cyclical permanent set.* Observations on the hysteresis loops were made by J. A. Ewing, B. Hopkinson and G. T. Williams, F. E. Rowett, J. J. Guest and F. C. Lea, J. Arnott, H. F. Moore and J. B. Kommers, H. J. Gough and D. Hanson, J. H. Smith, J. H. Smith and G. A. Wedgwood, etc.

L. Bairstow studied the development of the cyclical permanent set with reversals (Fig. 228). At each stress range the cyclical permanent set appears to be approaching a constant value, which was in some cases temporarily preceded by a higher value. The constant values attained with the two specimens shown increased with the intensity of the applied range. L. Bairstow plotted these constant values of the cyclical permanent set against the applied stresses, and obtained an approximate straight line intersecting the stress axis at a positive value. He concluded that a range of stress was indicated under which the material would possess or attain a state of perfect elasticity under indefinite repetitions of the stress range. This means that the fatigue range is an elastic range. In the case of reversed stresses no permanent extension occurred during the test.

The phenomenon of **creep** (Fig. 228) was studied by R. W. Bailey, L. Bairstow, R. G. Batson, R. G. Batson and H. J. Tapsell, H. J. Tapsell and co-workers, H. J. Gough and D. Hanson, W. Herold, W. Kerr, F. Körber and A. Pomp, F. C. Lea, W. Mason, K. Memmler and K. Laute, L. S. Moisseiff, E. Pohl and co-workers, A. Pomp and co-workers, A. Pomp and W. Enders, W. Rohn, W. Rosenhain, L. W. Spring, H. Stäger, etc.—*vide supra,* plastic flow. H. F. Moore and J. B. Kommers stated that when a metal is stressed above a certain value, plastic yielding and creep occur with certain unfavourably placed crystals. This, they said, causes a local redistribution of internal stresses, which may cause an increase or decrease of stress in the immediate vicinity. A local increase of stress acting on a suitably placed cleavage plane may cause further slip, which induces a further redistribution of the stresses. With some ductile metals, creep may produce a sudden yielding at a particular load, and in others it may continue until it reaches a maximum. This creep increases as the stress increases, until finally a stress is reached at which the creep continues indefinitely and the metal fails. If the creep under a certain stress has ceased, the portions of the metal which have not suffered plastic deformation will be under a higher stress than those which have slipped. When the stress is reduced, slip may occur in those parts previously free from slip. When the stress reaches zero the redistribution of stress continues in the form of the so-called elastic after-effect. Hence, creep and elastic after-effect are two aspects of the same process, the one positive creep and the other negative. H. F. Moore and J. B. Kommers continued:

> The well-known fact that metal which is stressed below its endurance limit is strengthened is in itself sufficient to show that even at these lower stresses there must be an action in the material which is not elastic. It is difficult to conceive how elastic action could strengthen the material, but it is easily understood how inelastic action could do this. The evidence of slip-bands and hysteresis loops at stresses less than the endurance limit of the material is further evidence that a material has the power of adjusting itself to cycles of stress if these cycles of stress are within certain limits. That a process of strain-hardening is going on under repeated stresses below the endurance limit is evidently quite as possible as it is under the action of static stresses above the yield-point.

The creep at an elevated temp. was studied by F. C. Lea and co-workers, who found that, at a given temperature, there is a limiting creep stress above which the material is viscous; at ordinary temp., and with stress above the static yield-point, specimens may show a fairly steady creep for hours, but the creep eventually ceases if the stress is below the ultimate strength. This shows that at a given temp. there is a stress below which creep ceases, and above which it is continuous. H. F. Moore and J. B. Kommers added that "the limiting range of stress appears to be that range below which molecular slips can take place in the material, but after which new bonds may be established. This new bonding is materially helped by raising the temp., and also by permitting slip to take place in very small increments during the application of cycles of stress. If the applied stress exceeds a certain value the relative movement of the molecules is too great to permit re-bonding, and molecular separation occurs, which results in the formation of a fatigue crack and final failure."

L. Bairstow compared the yield in static and fatigue tests. In Fig. 229 the curve *FABC* represents the ordinary load-elongation static test for axle steel; while the curve *FEJHBC* represents the total elongation produced by repeated stresses, when the upper limit of the safe range coincides with the ordinates of this curve. Thus the repeated application of a safe range of stress with a superior limit, *OG*, produces a total permanent set equal to *GH*; *FE* represents half the safe range of stress and it produces no permanent elongation. Between this stress and the static yield-point, the permanent set is greater with a repeated stress than with a static stress. The two curves are the same at the static yield stress, and remain so for higher stresses, so that the curve *FEJHBC* is continuous. Hence, for stresses below the yield-point, iron and steel can maintain an unstable condition for a considerable time under cyclic stress. The first application may not show a measurable extension, but the extension may be greatly augmented under a constant cycle of repeated stress. The region *EABJE* can be explored by repeated stresses, but not by a single application of stress as in a static test. According to H. F. Moore and J. B. Kommers, this indicates that the elastic limits and yield-points of static tests cannot be correlated with endurance limits. C. L. Clark and A. E. White studied the effect of temp., and found that if y denotes the stress in lbs. per sq. in., and x the duration of the stress in hours, $y = ax^b$, where a and b are constants for a particular metal. They found for steels:

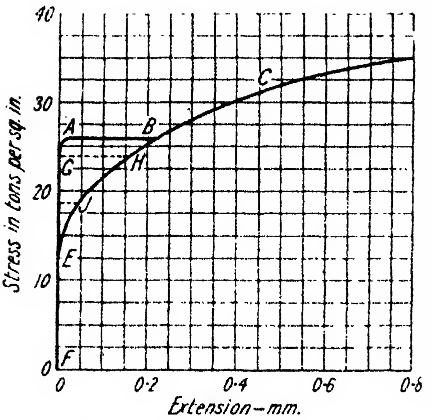


FIG. 229.—Permanent Set of Static and Repeated Loading.

	0·13 per cent. C		0·38 per cent. C		
	593°	538°	677°	593°	538°
a	9566	24,125	7670	16,300	27,275
b	−0·1477	−0·1333	−0·1600	−0·1384	−0·1375

While the term *fatigue* is an effect which will finally lead to fracture, the term **recovery** is applied to the opposite effect. J. A. Ewing found that overstrained iron or steel gradually approaches its original unstrained state with time, and J. Muir added that the recovery may occupy 17 days, but the recovery may be accelerated by raising the temp. to 100°. The observations of J. H. Smith, and of H. F. Moore and T. M. Jasper, show that for any degree of overstressing there is a limiting number of reversals below which the fatigue range is not affected, and that this limiting number decreases as the magnitude of overstraining increases. Overstressing has a greater effect on hard than it has on soft steels. Where the effects of overstressing are negligible, it is assumed that recovery has taken place. H. J. Gough defines recovery as that process by which a metal attains, or tends to attain, a state of elasticity from a non-elastic state. (i) *Recovery by the application of repeated stresses.* Some metals, under safe ranges of stress, have a large primary hysteresis loop; and under the application of repeated stresses the loop diminishes in width so that a state of elasticity is attained and maintained indefinitely. Hence, repetitions of a safe range of stress constitute an effective agent of recovery. In some cases a similar phenomenon occurs with unsafe ranges of alternating stresses. (ii) *Recovery by rest.* There is nothing to show that a state of elastic hysteresis is affected by rest, but with ranges of stress exceeding the limiting range, J. H. Smith and G. A. Wedgwood, W. E. Dalby, and H. J. Gough showed that rest has a marked effect in diminishing the area of the hysteresis loop. Recovery by rest occurs whether the specimen is under stress or free from stress. (iii) *Recovery by mild heat-treatment.* J. Muir, and R. H. Greaves have shown that a mild heat-treatment—*vide supra*—accelerates the recovery produced by resting. (iv) *Recovery by annealing.* If an annealed specimen with a definite primitive limit of proportionality and yield-point be subjected to repetitions of a range of stress, the primitive limits are rapidly readjusted; and if, after a few repetitions, the specimen be annealed, the primitive properties of the material reappear. E. G. Coker, and E. J. McCaustland discussed the effect of low temp. on the recovery of steel from overstrain.

Several hypotheses have been suggested to explain fatigue. The crystallization hypothesis has been discussed. J. Goodman assumed that a range of alternating stress should be regarded as a live load superposed on a statical load, so that the live load has the destructive effect of a suddenly applied load. This does not agree with the general form of the S/N-curve. J. Bauschinger's range of natural elastic limits did not imply any mechanism by which the elasticity was attained. J. A. Ewing and J. C. W. Humfrey applied their theory of deformation by slip, or slip-bands. G. T. Beilby, and W. Rosenhain developed the theory of the production of an amorphous phase by deformation through mechanical strain. B. P. Haigh assumed that the change from the crystalline to the amorphous phase precedes the gliding action, so that the glide is a result of the change of phase and not the cause, as assumed by G. T. Beilby. The actual slip is a protective agency against fatigue, and not a contributory cause. Once a cyclic state has been established, the inelastic work done per cycle is a function of the range of applied stress, whether that range is safe or unsafe. Hypotheses on the subject have been developed by A. A. Griffith, S. L. Smith and J. V. Howard, C. F. Jenkin, and W. E. Millington and F. C. Thompson. H. J. Gough thus summarizes B. P. Haigh's theory of the hysteresis:

> In a metallic test-piece subjected to repeated stresses, certain molecules are in unstable positions, some being ready to be projected from the crystalline lattice into the vitreous state. Under repeated stresses, a dual process of crystallization and decrystallization is in action. This is equally true whether the range is safe or unsafe; also, as the change of state is associated with gliding motion resisted by friction, the process will not be thermo-dynamically reversible, and work will be done on the specimen by the external forces producing a hysteresis loop. B. P. Haigh has likened this dual action, with the ensuing heat loss, as equivalent to the action of a reversed heat engine with a considerable thermal leakage. Under safe ranges of stress, the dual actions of ravage and repair will either balance each other, resulting in a steady rate of evolution of heat, or the repair forces may slightly preponderate and the heat evolution will gradually diminish. When the applied range is increased, the dual action occurs at a greater number of zones, and more actively at each of the original zones. The mechanism is still the same, molecules being cyclically projected from and into the crystalline lattice by an orderly arrangement of replacement. So long as this continues, the limiting range of stress has not been exceeded. At some stage, however, the simultaneous movement of such a large number of neighbouring molecules renders impossible the previous orderly replacement, and cavities form which subsequently develop into cracks. The fatigue range has been exceeded, and the process is now mechanically, as well as thermo-dynamically, irreversible. Thus, the limiting condition is that the dual processes of crystallization and decrystallization shall no longer balance each other, but produce cumulative effects.

H. E. Tresca[17] showed that homogeneous and isotropic solid substances under deformation obey the laws of the flow of liquids, and that, from this point of view, solids can be regarded as liquids possessing a greater or less degree of viscosity; and F. Robin found that the law is applicable to wire-drawing and to the rolling or forging of carbon steels. The crushing of a body depends on its physical condition and geometrical form, and it is usual to keep the shape of the test-piece constant—a straight cylinder with circular bases. The bases undergo friction from the crushing surfaces so that the flow of the metal is different at the extremity bases and at the middle. The cylinder generally bulges out so that the equatorial or medium diameter is greater than the diameters at the ends. H. E. Tresca also observed that under the influence of shock, delivered at the same rate, the resulting deformations are larger, the greater the intensity of the shock; and on similar test-pieces the deformations are similar and proportional to the shock. The specific work performed by shocks of equal intensity, in kilogrammetres per c.c., on similar shaped solids of similar materials, results in equal amounts of crushing deformation. J. V. Poncelet showed that the greater the amount of deformation on the surface receiving the shock, the less the lag on the bases; the difference in the deformation at the two bases increases with the intensity of the shock; and the form of the cylinder under compression is symmetrical only in the case of static compression. The median bulge is greater the more slowly the test is conducted, and the less smooth the bases of support—*vide supra*, plastic flow.

A. Martens, C. Codron, and F. Robin discussed the work done during the deformation, as well as the resistance to crushing as affected by the dimensions of the test cylinders, the number of blows delivered, and the rate of succession of shocks by impact. According to F. Robin, in the neighbourhood of atm. temp., the resistance to crushing (Fig. 230) of pearlitic carbon steels varies but little. If the metal be cooled the resistance increases, and there is a sudden rise at about −80°, and a high value is attained at −185°. The resistance to crushing at −185° is a little more than one and a half times its value at 15°, that of steels containing free cementite is very high at these low temp. A rise in the temp. from 0° to 300° diminishes the resistance of carbon steels to crushing. The curve is not uniform throughout this interval, but assumes a wavy direction, which more often than not is distinguished by a marked fall in the resistance at about 100°. At about 300° all the curves of the carbon steels attain a minimum. The resistance to crushing is at this temp. lower than it is at any other except when a red-heat is reached. Above 300° the curves rise, and the resistance to crushing increases up to about 500°, where it reaches a maximum which occurs probably a little below the exact temp. of 500°. Above 500° the resistance of the metal decreases rapidly up to 1000°, carbon steels being ranged at that temp. in the same order as at the ordinary temp. Above 1000° with highly carburized steels, or above 900° with mild and dead-soft steels, the diminution of the resistance to crushing in terms of the temp. takes place very slowly. Steels containing free cementite are somewhat resistant at about 1300°, and commence to split beneath the shock and to lose their cohesion. Dead-soft steels, on the contrary, are still forgeable at 1480°, where their resistance to crushing reaches about 1·5 kilogrammetres per c.c. At higher temp. the metal burns or fuses, and is no longer forgeable. The curvature appears to be very nearly uniform at a red-heat; at a nascent red-heat, only in the case of steels with a high percentage of carbon; soft steels and dead-soft steels appear to present two successive bends towards 500° and 600°. The difference between the maximum and the minimum resistance to crushing does not vary greatly in its absolute value. This difference does not depend on the percentage of carbon, but seems rather to bear a ratio to the amount of foreign elements present, and, in particular, to elements dissolved in the iron.

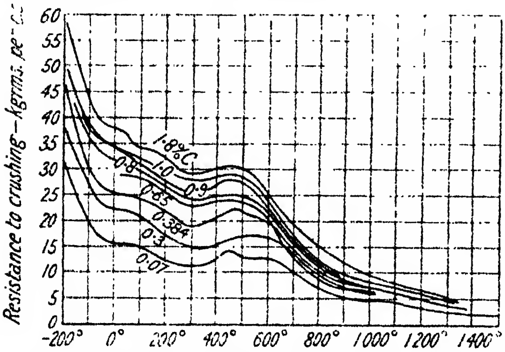


Fig. 230.—The Resistance of Carbon Steels to Crushing at Different Temperatures.

The presence of phosphorus greatly increases the resistance of steels to crushing. Thus the resistance of a steel containing 0·06 per cent. of carbon and 1 per cent. of phosphorus is equal to that of a rail steel containing 0·4 per cent. of carbon. The influence of phosphorus is to produce a rapid decrease in the resistance to crushing at a red-heat; its intensity may fall below that of other steels so long as the percentage of phosphorus is fairly considerable. The presence of sulphur appears to harden the steel somewhat at about 700° and at a higher temp. Burnt steel (steel contaminated with oxide) revealed no anomalies in the curve of resistance to crushing. The presence of silicon or of manganese in small percentages in carbon steels does not appear to exert much influence on the appearance of the curves.

Cast iron cannot be regarded as forgeable, and the investigations relating to this part of the subject have been but few in number. Generally speaking, it was not possible to obtain a reduction of one-fifth in the depth of normal cylinders, so that the crush numbers had to be ascertained by interpolation from the results obtained with lesser degrees of crushing. The presence of phosphorus greatly increases the resistance of cast iron, and the appearance of the resistance curves differs from that of the steels. The fall in the resistance to crushing is very nearly uniform from 300° up to the temp. of fusion. Neither a maximum nor a minimum can be seen. Cast iron generally, and phosphoric pig iron in particular, crack on forging before the temp. of fusion, and have no cohesion. When the fusion point of the eutectic is reached, the elements separate in a granular form, and crushing "yields nothing but a shower of sparks." A. Pomp gave for the crushing strength of steel with 0·5 per cent. of carbon, 14·5 tons for rods 10 mm. diameter; and with 0·06 per cent. carbon steel, 12·7 tons.

In general, *pearlitic steels* undergo the same variations as carbon steels; variations in the resistance to crushing may be greatly reduced or even obliterated by the presence of a sufficient amount of an element in soln., such, for example, as chromium. *Martensitic steels* yield a decreasing curve which possesses neither maximum nor minimum; the greatest fall in resistance commences at 500°. *Austenitic steels* vary little in their resistance to crushing up to about 550° or 600°. The resistance to crushing increases considerably at liquid air temp. Starting from 0° the curve is in general practically rectilinear up to about 600°, where the most important fall in the resistance occurs. Special steels containing the free carbide and the high-speed steels behave similarly. Their resistance at ordinary temp., and particularly at about —190°, is, generally speaking, high. Some steels preserve a high degree of resistance to crushing at high temp., a resistance much greater than that of carbon steels. The presence of nickel favours this resistance at high temp.—*vide* the special elements.

P. Galy-Aché showed that for copper and iron the elastic limits under tensile stress and compression are the same. M. Koepke and E. Hartig, and R. Thurston, found that brittle metals showed a constant relation between the resistance to fracture under tensile stress, and under compression. F. Robin added that the resistances to fracture by tensile and compressive stresses are not comparable, but the elastic limits under tensile stress and compressive static stresses can be compared, and for pearlitic carbon steels, they are generally the same; but M. Rudeloff found that for nickel and manganese steels they are quite different. J. O. Arnold gave 40 to 60 tons per sq. in. for the crushing strength of cast iron. Observations were also reported by A. P. Carman and M. L. Carr, H. I. Coe, M. Denis, G. H. Gulliver, H. I. Hannover, S. H. Ingberg and P. D. Sale, R. L. Keynon, E. Kieft, F. Körber and H. Müller, M. Lorenz, P. Ludwik and E. Schen, W. Mason, H. Monden, S. Nadasan, F. B. Seely and W. J. Putnam, E. Siebel and A. Pomp, C. A. M. Smith, A. H. Strang and L. R. Strickenberg, W. C. Unwin, and A. Victorin; and H. A. Schwartz measured the effect with malleable cast iron.

Only in the case of metals like copper, silver, and aluminium does a variation of temp. cause the physical properties to vary in a continuous manner; with iron, the alloy steels, and many other alloys, the variations in the properties display sudden changes. These metals are known to undergo transformations, and there may be some relation between these transformations and the variations in the physical properties. M. Leblant and others have noticed that starting from 100°, the elongation may take place intermittently, and it may be accompanied by jerks and noises. Steels show characteristic properties at about 15° and 400°, and this is in agreement with F. Robin's results except for the hardness developed by mechanical deformation, and the notched-bar brittleness after cold-working, which indicate that steel is harder and more brittle after mechanical working at 400° than it is at 15°. M. Leblant also found that the resistance, and the proportional limit elongation are a minimum at about 100°, while from 200° to 400° there is a maximum resistance, and a minimum contraction and elongation. This explains the greater likelihood of breaking a test-piece while deforming it within the latter range of temp., than there is in testing it between 20° and 100°. The results with dynamic tests are different. The resistance to crushing under shock is a minimum at 300°, and the ductility shown by the median bulge is a maximum at this temp., whereas the tendency to fissure, and the crushing brittleness are here lower than at neighbouring temp. As F. Robin shows, it is difficult to draw any conclusions as to the constitution of iron from these results. Between 0° and 100°, the hardness, the elastic limit, the resistance to breaking, and the resistance to crushing decrease, and hence it might appear as if the elongation would be augmented, but it diminishes. Again, from 100° to 200° the elastic limit is low and there is but little elongation, while the resistance to stress, and hardness increase; the resistance to crushing is low, and the interstrain hardness due to deformation, and the median bulge increase. Hence, each physical property exhibits discontinuity at very different points, and the part played by the different states of iron has not been determined for each case.

According to F. Robin, from a visible red-heat upwards, it appears that all the properties resulting from static or dynamic effects agree, not perhaps numerically, but in their mode of variation. The rate of speed of the stresses applied act, therefore, uniformly on steel and on other hard metals, such as lead in the cold, in proportion as they lose their elasticity. It would appear that from this temp. onwards metals become pasty during their transition to the liquid state; the results of various tests collated resemble each other in a general way. A variation in the allotropic state, such as that of iron, appears, therefore, but little marked. Towards 700° the curves of steel have a bend which might be referred to the allotropic transformation point; but copper and nickel give similar results at neighbouring temp. The transformation of α-iron into β-iron may, however, betray itself in the curves representing the variation of the mechanical effects in terms of the temp. without the possibility of definitely affirming that it does so. The hardness curves and curves of the resistance to crushing show that the steels give curves which become very nearly horizontal at about 800°. Unlike the case of metals which do not possess transformation points, such as copper, the resistance of the metal decreases rapidly and uniformly at a cherry-red heat, there is with steel a break in the curve. M. Leblant found a similar break during the tensile testing of steels containing 0·2 to 0·4 per cent. of carbon. He even found a slight increase in the resistance to breakage for a dead-soft steel at about 800°. These remarks are not based upon decisive results, but they agree with the recent observation made by W. Rosenhain and J. C. W. Humfrey. They remarked that, when making tensile tests *in vacuo* on thin, polished, and heated discs of several metals, at about 800°, the temp. in the neighbourhood of the transformation of γ- to β-iron in a soft steel, the appearance of the deformed metal under tensile stress altered in a characteristic manner; the point of least resistance of the metal when heated unequally is found at the limit of α-iron shown by the deformation and by a more resistant zone; although at a temp. slightly higher and probably corresponding to the sphere of influence of β-iron. The diametrical bulge, which diminishes from 900° to 1000° upwards, indicates the commencement of the disintegration of the metal and the diminution of the cohesion of the grains. It does not indicate the return of the metal to its anterior condition, for the other properties belie this hypothesis.

J. E. Howard studied the cubic **compressibility,** the cold flow, and the crushing strength of iron and steel. The test cylinders were 2·5 diameters long; the compressions are expressed in lbs. per sq. in. The results are summarized in Table XXXIV. The specimens began to bulge laterally under the influence of free compressive stresses when the elastic limit was passed, and thereafter the stress per sq. in. increased for a time, whilst the shortening in length and increase in diameter continued. Whilst the gross load was gradually increased to the end of the test, a period was reached where the stresses per sq. in. on the sectional area, as it existed, ceased to increase, and for an interval the flow was continuous, with practically no increase of stress. This period marked the ultimate compressive resistance of the metal. No marked difference in tensile strength resulted from the cubic compression; neither was the ductility of the metal, as indicated by elongation and reduction of area, materially changed by the compression. Under ordinary free tests by tension or compression, certain stresses—below the elastic limit—do not cause any change in the physical properties; but stresses exceeding the elastic limit usually bring about a series of phenomena which culminate in rupture or disintegration. Under cubic compression, no press. were reached which gave evidence of such a tendency in the ultimate result as that caused when the flow of metal occurred. This means that whilst it is probable that there is a restricted molecular orbit represented by the elastic limits of tension and compression, and that these orbits may be disturbed and thrown into new positions by loads exceeding the elastic limit, in the case of cubic compression, sufficiently high press. to disturb them were not employed in the experiments—nor is it certain whether such a limit can be attained by the means employed. J. Bauschinger's results are indicated in Table XXXIV. Observations were made by J. G. Dagron, W. K. Hatt, A. Portevin and F. le Chatelier, and S. H. Ingberg and P. D. Sale.

TABLE XXXIV.—THE CUBIC COMPRESSION OF IRON AND STEEL.

Metal	Reduced length (inches)	Concurrent compressive resistance	Ultimate compressive resistance	Percentage maximum elongation of surface	Tensile stress of ruptured section
0·09 C steel	1·24–0·83	84,030–85,470	85,580	72·8	106,434
0·20 ,,	1·31–0·83	100,120–101,890	105,520	75·6	113,704
0·31 ,,	1·26–0·95	115,150–115,560	116,790	80·5	126,640
0·37 ,,	1·26–0·88	121,070–121,850	121,850	72·1	134,600
0·51 ,,	1·425–0·89	131,760–131,900	133,480	95·5	152,380
0·57 ,,	1·245–0·965	156,630–156,640	157,100	58·8	134,880
0·71 ,,	1·34–0·89	156,250–156,640	156,800	59·1	151,510
0·81 ,,	1·465–1·20	194,240–196,300	196,300	54·5	158,140
0·89 ,,	1·60–0·93	181,100–183,250	188,110	51·3	147 860
0·97 ,,	1·33–1·05	192 550–193,090	193,090	45·6	161,910
Cast iron	1·825	96,320	96,320	9·6	– –
Wrought iron not ann.	1·545–1·21	90,630 90,290	91,500	43·2	– –
Wrought iron ann.	1·555–1·18	91,600–93,610	93,610	51·4	—

J. O. Arnold holds that compression tests furnish by far the best mechanical means of measuring the molecular rigidity of metals, because the interfering effects of variations in intercrystalline cohesion are reduced to a minimum. The flow curve for normal steels falls off until the iron contains 0·89 per cent. of carbon when it is practically stationary to 1·5 per cent. of carbon, for the dotted line in the curve is taken to represent the true result—the downward flow of the observed curve being due to the undesired separation of some graphite and the consequent production of a little soft iron. The annealing curve up to 0·89 per cent. of carbon measures graphically the effect on the flow from diffused to crystallized cementite; when more than 0·89 per cent. of carbon is present, the curve passes downwards, until, at 1·47 per cent. of carbon (most of which exists as graphite), the flow is actually greater than that of iron alone. This is attributed to the loosely deposited graphite crystals being themselves capable of some compression. The curve for hardened steel shows that molecular flow ceases with 0·89 per cent. of carbon, whilst the curve is very steep in passing from 0·2 to 0·6 per cent. of carbon.

T. W. Richards[18] gave $\beta=0\cdot0_641$ for the coeff. of compressibility of α-iron at 20° with press. of 100 to 500 atm.; this datum was afterwards corrected to $0\cdot0_660$. E. Goens and E. Schmid gave $5\cdot8\times10^{-13}$ dyne per sq. cm., and P. W. Bridgman, $5\cdot9\times10^{-13}$ dyne per sq. cm.; E. Grüneisen gave $0\cdot0_662$ at —190° for press. of 10 to 150 atm.; $0\cdot0_665$ at 18°; $0\cdot0_668$ at 128°; and $0\cdot0_669$ at 165°; E. Madelung and R. Fuchs, $0\cdot0_661$ megabar per sq. cm.; and A. Mallock gave $0\cdot0_664$ at 20°. L. H. Adams gave $\beta=0\cdot0_660$; and for $d\beta/dp$, $-0\cdot0_{11}4$. R. F. Mehl and B. J. Mair calculated from the compressibility of invar-steel, with iron in the γ-form, that the compressibility of γ-iron is $0\cdot0_685$, a value which would make γ-iron to be more compressible than α-iron.

Observations on steel were made by H. V. Regnault. E. Amagat gave $0\cdot0_668$; and P. W. Bridgman, $0\cdot0_655$ at 6500° atm. and 20°; and at 10,000 atm. press., $0\cdot0_660$ at 10°, and $0\cdot0_662$ at 50°. E. Madelung and R. Fuchs gave for steel $0\cdot0_661$ megabar per sq. cm., L. H. Adams and co-workers gave $0\cdot0_6575$ for a 2 per cent. carbon Bessemer steel, and a 0·8 per cent. carbon tool-steel. R. F. Mehl gave for the internal press., 587 kilomegabars, and for the maximum disruption press., 1884 kgrms. per sq. mm. R. F. Mehl and B. J. Mair observed that a quenched, eutectoid steel, with 0·89 per cent. carbon, and highly martensitic, had a compressibility of $0\cdot0_661$, and the same result was obtained after the steel had been annealed. A quenched, hypereutectoid steel, with 1·36 per cent. carbon, had a compressibility of $0\cdot0_683$, and after annealing, $0\cdot0_685$. The normal sp. gr. of the hypereutectoid steel showed that the high compressibility is not due to pore-spaces in the metal. Though the compressibilities of iron and of eutectoid steel are the same, the Brinell's hardness are, respectively, 75 and 241. The results show that the hardness of steel produced by quenching is not caused by any change in the normal cohesive forces. The fact that a glass-hard steel suffers the same vol. decrease with an increase of press. as does an annealed steel, is explained by the slip interference theory of hardness on the assumption that no increase in the binding forces between the atoms occurs on hardening, for the hardness is supposed to be caused by the mechanical arrangement of the structural units. L. H. Adams and E. D. Williamson gave for wrought iron; $\beta\times10^6=0\cdot60$ to $0\cdot68$; and for cast iron, 0·89 to 1·45. Cast iron, at a press. p megabars, suffers the vol. change, $(3dv/v)\times10^6=2\cdot04(p-69)-6\cdot1(p-69)^210^{-4}-10$, and has $\beta\times10^6=2\cdot010-0\cdot152(p-2000)10^{-4}+0\cdot006e^{-0\cdot003(p-2000)}$. The compressibility of cast iron between 0 and 12,000 megabars is indicated in Fig. 231. P. W. Bridgman's experiments on the compressibility of rolled metals show that neither variations in grain-size, nor mechanical strain make any appreciable difference to the compressibility, so that an increase in hardness caused by either or both these effects can have no marked influence on the compressibility. If lattice distortion be a cause of hardness in steel, it will be produced by an alteration of the interatomic forces, and this should make an appreciable difference in the compressibility

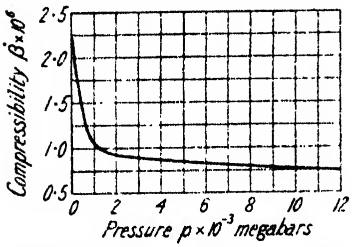


FIG. 231.—The Compressibility of Cast Iron.

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§ 19. Thermal Properties of Iron and Iron-Carbon Alloys.

The **thermal expansion** of iron has to be taken into consideration in the construction of iron bridges, in fixing buckstays of furnaces, etc. Under the influence of the sun's rays, the Eiffel Tower twists from east to west, its point forming an arc with a diameter of about 4 inches. After sunset, the tower slowly untwists. The twisting is greater in summer than it is in winter. There are many records of measurements of the coeff. of thermal expansion of iron and steel, made usually upon commercial samples, where the composition is not usually stated. This, of course, makes the results of less general importance. A. L. Lavoisier and P. S. Laplace[1] gave $0{\cdot}0_4122045$ for wrought iron, and $0{\cdot}0_4123504$ for soft iron drawn into wire; and E. Troughton, $0{\cdot}0_4144010$ for iron wire. J. Smeaton gave $0{\cdot}0_4125833$ for soft iron; M. G. von Paucker, $0{\cdot}0_411612$; H. Kopp, $0{\cdot}0_4125$; H. Rudolph, $0{\cdot}0_41197$; J. F. Daniell, $0{\cdot}0_411808$; A. Gray and co-workers, $0{\cdot}0_4124$ for soft iron; and H. Fizeau, $0{\cdot}0_41210$ for electromagnet iron at 40°, and $0{\cdot}0_41228$ at 50°. P. L. Dulong and A. T. Petit gave $0{\cdot}0_41182$ for iron between 0° and 100°, and $0{\cdot}0_41469$ between 0° and 300°; P. Glatzel, $0{\cdot}0_41387$ between 16° and 100°; and for wrought iron between −45° and 100°, T. Andrews gave $0{\cdot}0_586$; between −18° and 100°, $0{\cdot}0_4114$; and between 100° and 300°, $0{\cdot}0_4133$. I. von Zakrzewsky gave $0{\cdot}0_41092$ between −103° and 25°; $0{\cdot}0_41110$ between −78° and 25°; $0{\cdot}0_41252$ between 25° and 100°. E. Grüneisen gave $\alpha=0{\cdot}0_5907$ between −190° and 17°;

and $0{\cdot}0_4 1189$ between 17° and 100°. H. G. Dorsey gave $0{\cdot}0_5 930$ between -180° and 20° for purified iron, and $0{\cdot}0_5 840$ for iron with 1·4 per cent. of carbon. For iron with 0·057 per cent. of carbon, 0·13 manganese, and 0·05 silicon, H. le Chatelier gave $0{\cdot}0_4 11$ between 0° and 100°; $0{\cdot}0_4 16$ between 500° and 600°; $0{\cdot}0_4 165$ between 600° and 700°; and $0{\cdot}0_4 15$ between 700° and 800°. F. Henning gave for wrought iron with 0·1 per cent. of carbon, $0{\cdot}0_5 919$ between —191° and 16°. Observations were also reported by F. C. Calvert and co-workers, R. Roberts, R. S. Woodward and co-workers, W. Broniewsky, A. Börsch, C. Markham, J. Seigle, etc. K. Honda observed 0·000013 for iron at 100°; 0·0000149 at 300°; 0·0000158 at 500°; and 0·0000154 at 600°; whilst S. Sato obtained 0·0000212 between 906° and 1400°; and 0·0000125 between 1400° and 1535°. S. Sato gave 0·000016, but O. C. Ralston showed that 0·0000125 agrees better with the observed data. The best representative data are plotted in Fig. 232. The curve shows clearly how the coeff. of expansion of γ-iron exceeds that of α-iron; and that it is probable that the curve for δ-iron is a continuation of that for α-iron. O. C. Ralston calculated from these and the sp. gr. data, the average changes in vol. as purified iron is heated from 0° to 1670°:

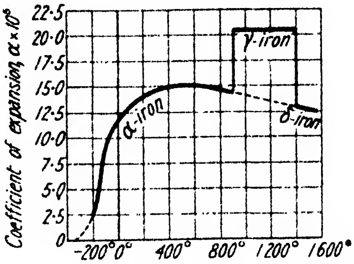


FIG. 232.—The Coefficients of Thermal Expansion of Purified Iron.

Form of iron	Temperature range	Change in volume per unit volume, or dv/v
α-iron	0° to 906°	0·000014 per degree
$\alpha \rightarrow \gamma$-iron	906°	$dv/v = -00846$
γ-iron	906° to 1400°	0·000021 per degree
$\gamma \rightarrow \delta$-iron	1400°	$dv/v = +0{\cdot}002553$
α-iron	1400° to 1535°	0·0000125 per degree
Melting-point	1535°	$dv/v = +0{\cdot}036$
Molten iron	1535° to 1670°	0·000483 per degree

R. Bach was not satisfied that his thermal expansion, and X-radiograms agreed with the assumption that the α-state of iron is distinguished uniquely from the β-state by magnetic differences. H. Quinney found that the change from single crystals to polycrystals reduces the contraction at the Ac_3-arrest where α-Fe passes to γ-Fe.

A. L. Lavoisier and P. S. Laplace gave $0{\cdot}0_4 107880$ for unhardened steel, $0{\cdot}0_4 107960$ for hardened steel, and $0{\cdot}0_4 123956$ for hardened steel tempered at 65°. W. Roy gave $0{\cdot}0_4 111000$ for unhardened steel; E. Troughton, $0{\cdot}0_4 118990$; J. Eliccot, $0{\cdot}0_4 10750$; M. Vandervyver, $0{\cdot}0_4 1101$; W. Struve, $0{\cdot}0_4 11301$; and J. K. Hörner, $0{\cdot}0_4 1150$ for Styrian, $0{\cdot}0_4 11120$ for Schaffhausen steel, and $0{\cdot}0_4 1070$ for Huntsman's steel. J. Smeaton gave $0{\cdot}0_4 115000$ for unhardened steel, and $0{\cdot}0_4 122500$ for hardened steel; F. Berthoud, $0{\cdot}0_4 10040$ for unhardened steel, and $0{\cdot}0_4 13715$ for hardened steel. W. Dittenberger gave for $\alpha \times 10^8$ for iron with 0·16 per cent. of carbon, for wrought iron with 0·14 per cent. of carbon, steel with 0·55 per cent. of carbon, and cast iron with 3·22 per cent. of carbon:

	0°–250°	0°–375°	0°–500°	0°–625°	0°–750°
Wrought iron .	1286	1354	1406	1461	1488
Iron . . .	1272	1358	1405	1454	1470
Steel . . .	1248	1317	1379	1437	1329
Cast iron . .	1118	1198	1258	1393	--

or $\alpha \times 10^9 = 16777\theta + 4{\cdot}64\theta^2$ for wrought iron; $11392\theta + 5{\cdot}42\theta^2$ for iron; $11181\theta + 5{\cdot}26\theta^2$ for steel; and $9794\theta + 5{\cdot}66\theta^2$ for cast iron. J. A. N. Friend and R. H. Vallance gave $0{\cdot}0_4 123$ for the coeff. of expansion of armco iron, and for wrought iron between 10° and 100°—the former metal had 0·025 per cent. of carbon, and the latter metal 0·06 per cent. H. Fizeau gave for Huntsman's steel, $0{\cdot}0_4 1018$

at 20°, $0{\cdot}0_41038$ at 30°, and $0{\cdot}0_41077$ at 50°; T. Andrews gave for hardened Bessemer steel, $0{\cdot}0_585$ between −45° and 100°; $0{\cdot}0_4101$ between −18° and 100°; and $0{\cdot}0_4133$ between 100° and 300°; and for annealed Bessemer steel, $0{\cdot}0_593$ between −45° and 100°; $0{\cdot}0_4117$ between −18° and 100°; and $0{\cdot}0_4159$ between 100° and 300°. He also gave:

			Coefficients of thermal expansion		
			−45° to 100°	−18° to 100°	100° to 300°
Rolled bars	Wrought iron		0·0000086	0·0000114	0·0000133
	Bessemer steel	Soft	0·0000093	0·0000117	0·0000159
		Hard	0·0000085	0·0000101	0·0000133
	Siemens-Martin steel	Soft	0·0000088	0·0000116	0·0000144
		Hard	0·0000079	0·0000100	0·0000139
	Cast steel	Soft	0·0000086	0·0000112	0·0000150
		Hard	0·0000084	0·0000101	0·0000130
Hammered forgings	Wrought iron		0·0000096	0·0000117	0·0000131
	Bessemer steel		0·0000099	0·0000107	0·0000137
	Siemens-Martin steel		0·0000093	0·0000113	0·0000142

J. E. Howard found for the coeff. of expansion of weld iron, 0·00001211; for steel with 0·09 to 0·51 per cent. of carbon and 0·11 to 0·58 per cent. of manganese, 0·00001194; for steel with 0·57 to 0·97 per cent. of carbon and 0·93 to 0·80 per cent. of manganese, 0·00001133; and for cast iron, 0·00001067. H. le Chatelier gave for hard steel at 1000°, $0{\cdot}0_4140$. H. Fizeau found for annealed cast steel $0{\cdot}0_41101$ at 40°, and $0{\cdot}0_41113$ at 50°; and when hardened, $0{\cdot}0_41322$ at 40°, and $0{\cdot}0_41363$ at 50°; and for grey cast iron, $0{\cdot}0_41061$ at 40°, and $0{\cdot}0_41075$ at 50°; while H. le Chatelier gave $0{\cdot}0_41175$ at 100°; and for steel with 14 per cent. of manganese, $0{\cdot}0_4245$ at 1000°. For cast iron with 3·5 per cent. of carbon, F. Henning gave $0{\cdot}0_5886$ between −191° and 16°; for steel with 0·1 per cent. of carbon, $0{\cdot}0_5915$; and with 0·5 per cent. of carbon, $0{\cdot}0_5896$. G. Charpy and L. Grenet gave for hardened steel with 1·5 per cent. of carbon, $0{\cdot}0_41000$ between 0° and 100°, and when annealed $0{\cdot}0_41115$. W. Souder and P. Hidnert gave for electrolytic iron which had been melted in vacuo, $\alpha=0{\cdot}0_412$ between 25° and 100°; the average for steels was $0{\cdot}0_4112$ between 25° and 100°; and $0{\cdot}0_4142$ between 25° and 600°; and for ordinary steels above the critical range, $0{\cdot}0_423$. R. von Dallwitz-Wegner gave $0{\cdot}0_4351$ for the cubic coeff. at 0°, and $0{\cdot}0_4383$ at 100°. Observations were also reported by O. Bauer and H. Sieglerschmidt, E. Bernardon, F. C. Calvert and co-workers, E. G. Coker, H. J. French, A. W. Gray, H. C. Knerr, C. Markham, R. Roberts, A. Schulze, E. Straube, R. S. Woodward and co-workers, etc.

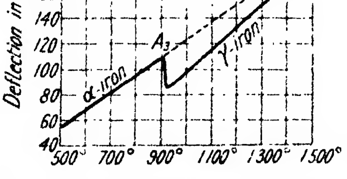


FIG. 233.—The Effect of Temperature on the Expansion of Purified Iron.

G. Gore, R. Norris, and W. F. Barrett made observations on the changes which occur during the recalescence of cooling iron. C. Benedicks measured the coeff. for iron of a high degree of purity—99·967 per cent. Fe. The corresponding curve by S. Sato is shown in Fig. 233. A. Mallock found no discontinuity in the coeff. of thermal expansion between 1400° and 1500°. As also observed by G. Charpy and L. Grenet, and J. Driesen, there is a discontinuity at the A_3-arrest, and the change is reversible, but there is some hysteresis. According to E. Maurer, the maximum observed by J. Driesen at 755°, is not connected with the A_2-arrest; but C. Benedick's curve, and also that of P. Chevenard, showed that it is connected with the appearance of the magnetic properties of iron. Observations were made by H. Esser, H. S. Rawdon and co-workers, H. E. Publow and co-workers, and H. Ebert. F. C. Powell estimated that the mean increase in length, l, of iron on passing from the non-magnetic to the magnetic state is $dl/l=1{\cdot}2\times10^{-4}$. With nickel there is an anomalous contraction in the magnetized state. The calculation is based on W. Heisenberg's theory of ferromagnetism which assumes that magnetization is accompanied by a change in the strength of the bond between the atoms. W. P. Davey discussed the expansion of crystals from the point of view of the space-lattice theory as the temp. passed from the absolute zero to the m.p. F. L. Uffelmann observed that the curve for the coeff. of thermal expansion of steel is a little different if taken on heating and cooling curves.

A. Gray and co-workers gave $0{\cdot}0_4136$ for the coeff. of thermal expansion of mild steel. H. G. Dorsey observed that the effect of carbon on the coeff. of thermal expansion is approximately linear. H. le Chatelier found the values of $a \times 10^7$ for temp. between the limits indicated, starting from 0° for steel with 0·13 to 0·24 per cent. manganese, and 0·05 to 0·14 per cent. of silicon, and

Carbon		0·057	0·205	0·49	0·75	0·80	0·84	1·21 per cent.
$a \times 10^7$	100°	110	110	110	110	110	110	105
	200°	120	110	110	110	110	110	110
	300°	130	120	118	118	118	118	118
	400°	140	125	101	101	101	101	125
	500°	150	130	130	130	130	130	130
	600°	160	135	135	135	139	135	133
	700°	165	139	139	139	135	139	137
	800°	130	—	—	—	—	—	—

Consequently, all sorts of iron and steel at ordinary temp. have a coeff. of linear thermal expansion of 0·000011; and at 758°, approximately 0·000017; or the mean value, between 0° and 758°, is 0·000014; or the true coeff. of expansion at temp., θ°, between 0° and 758°, is $da/d\theta = 0{\cdot}000011 + 0{\cdot}0_8 8\theta$. Above the critical zone, 758°, the coeff. increases with the proportion of carbon so that

Carbon	0·05	0·2	0·8	1·2 per cent.
$da/d\theta$	$0{\cdot}0_4 15$	$0{\cdot}0_4 17$	$0{\cdot}0_4 22$	$0{\cdot}0_4 29$

Consequently, there is a kind of shrinkage with increasing proportions of carbon, and this attains a minimum with about 0·8 per cent. of carbon:

Carbon	0·05	0·2	0·5	0·8	1·2 per cent.
Transformation temp.	840°	768°	728°	730°	725°
Shrinkage	0·26	0·23	0·21	0·08	0·10 per cent.

H. le Chatelier showed that steel with about 0·8 per cent. of carbon expands regularly up to about 700°, and above that temp. it suddenly decreases in vol. about 0·1 per cent. Thus follows a gradual, or at 50° higher temp., an abrupt expansion, so that the vol. is nearly the same as before the contraction occurred. Beyond this temp., the expansion is regular. These changes are reversed on cooling. When the sudden contraction occurs, the metal consists of pearlite, and when the sudden expansion occurs, of martensite, and in between, of troostite. At the critical point A_1, there is not only a simple volume change corresponding with the melting or dissolution of a substance, but there are also two opposing volume changes which are approximately compensated with steel containing 0·9 per cent. of carbon. Thus, the expansions, δl mm. per 100 mm., were:

	315°	500°	600°	760°	800°	830°	860°	900°	950°
δl	0·35	0·63	0·82	0·05	1·00	1·12	1·20	1·25	1·34

The maximum is here twice as much as the value obtained by G. E. Svedelius, who heated his samples very rapidly, while H. le Chatelier heated them very slowly. No sudden vol. change, above 0·01 mm. per 100 mm., was observed at the A_2-arrest. There are some anomalies at the A_3-arrest, which seem to be connected with the presence of hydrogen or sulphur, because, working with iron with 0·05 per cent. carbon, the results varied with the nature of the atm. Thus:

Atmosphere	Transformation temperature	Change in length
Hydrogen	840° to 860°	0·26 mm.
Hydrogen	900° to 1000°	0·25 ,,
Air	950° to 1025°	0·20 ,,
Hydrogen	925° to 975°	0·14 ,,

F. Sauerwald and co-workers found for pig-iron an expansion which increased from a sp. vol. of 0·1460 to a maximum 0·1484 at 840°, and then decreased steadily as the m.p. was approached—*vide supra*, sp. gr. H. Sieglerschmidt observed a marked increase in the thermal expansion of high- and low-carbon steels as they passed through the transition temp.—approximately 700°. J. Seigle studied the subject. K. Honda and co-workers found for the coeff. of linear expansion, α, of cementite steels:

Carbon . . .	1·5	1·8	2·0	2·5	2·9 per cent.
α	$0\cdot0_4208$	$0\cdot0_4202$	$0\cdot0_4194$	$0\cdot0_4186$	$0\cdot0_4179$

and for cementite between 0° and 1130°, 0·0000315. K. Honda's results with Swedish iron, and carbon steels are summarized in Fig. 234. The A_1- and A_3-transformations can be easily detected by the abnormal change in length in the ranges of these transformations. The coefficients of expansion of these steels, below the A_1-arrest, increase rapidly with temp., the coeff. of expansion-temp. curve being slightly concave towards the temp. axis. The contrary is the case with low-tungsten steels. According to G. Sirovich, at 370°, the A_0-arrest, where $\alpha_1\text{-Fe} \rightleftharpoons \alpha_2\text{-Fe}$, the coeff. of thermal expansion of the two forms of α-iron are different. W. Broniewsky found three critical points in the expansion curves of purified iron, one for α-iron stable below 730°, another for β-iron stable at 950°, and a third with γ-iron at 1020°. The observations of J. H. Andrew and co-workers are summarized in Table XXXV. J. H. Andrew and co-workers found that with the slow cooling of steel, at the $Ar_{3,2}$-arrest there is an increase in vol. which is continuous with the Ar_1-arrest. At the Ar_1-arrest there is a sudden expansion depending on the carbon-content, and initial temp. At 150° to 60° there is a large expansion independent of the carbon-content. On tempering, at 100°, there is a contraction when the carbon-content is greater than 0·6 per cent. when quenched above the Ac_3-, $_2$-, $_1$-arrest; between 150° to 300°, there is no change; between 300° and 330°, the contraction is neutralized by the γ-iron present; and at 500°, there is no change. The changes in volume and expansion which occur when austenite is transformed into martensite were discussed by E. Scheil, G. Tammann and E. Scheil, J. H. Whitehead, S. Sato, F. Stäblein, A. Schulze, B. D. Enlund, F. Wever and P. Rütten, L. E. Daweke, F. A. Fahrenwald, Z. Jeffries, W. Fränkel and E. Heymann, H. Hanemann and L. Träger, S. Konno, T. Kase, F. Ribbeck, and A. M. Portevin and P. Chevenard—*vide supra*, tempering. F. Roll studied the thermal expansion of cast iron. M. A. Grossmann studied the changes in length from 606° to room temp. when a high-speed steel—0·72, C; 18·0, W; 4·0 Cr; 1·0, V—is being cooled from its hardening temp., and found that when the quenching temp. is low, 938°, the transformation to such martensite as is formed is sudden and complete, but the amount of martensite formed is comparatively small. As the quenching temp. is raised, there are two effects:—(i) the austenite cools further before transforming to martensite, the austenite being more stable because it has dissolved more alloy and carbon; and (ii) the transformation to martensite takes place over a wider range of temp. At the highest quenching temp., the expansion, once begun, proceeds during the whole cooling period to room temp., and, indeed, the expansion continues at room temp.—with the 1321° curve, at room temp. an expansion of 0·00003 in. occurred during the next 12 hrs. The results show how difficult it is to locate transformation points by

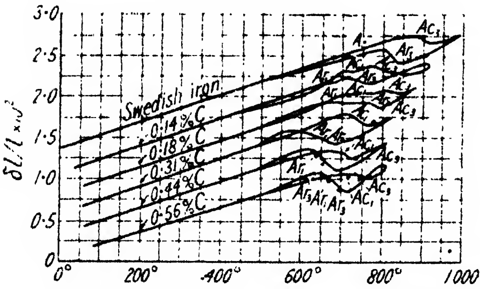


FIG. 234.—Thermal Expansion of Iron and Steel.

cooling curves, and also that martensite continues to form over a long period of time down to room temp. Some measurements were also made by E. C. Bain and W. S. N. Waring, H. Scott, and S. L. Hoyt. A. Werner found that with hardened soft steels, the coeff. of thermal expansion was 7 to 21 per cent. greater than the same alloy in the soft state; the actual values were $10{\cdot}4\times10^{-6}$ to $12{\cdot}6\times10^{-6}$ for soft steels, and $11{\cdot}1\times10^{-6}$ to $14{\cdot}7\times10^{-6}$ for hardened steel at 20°. At the temp. of liquid air, say −160°, the minimum values fell to $6{\cdot}3\times10^{-6}$ and $7{\cdot}1\times10^{-6}$ respectively, and at 150°, they varied between $12{\cdot}1\times10^{-6}$ and $14{\cdot}6\times10^{-6}$ respectively. The introduction of manganese raised the coeff. of thermal expansion. The effect of cold-work was studied by W. Jubitz, who observed that the rolling or hammering of cast iron produced no change greater than 1 per cent. in the coeff. of thermal expansion.

TABLE XXXV.—THE EFFECT OF INITIAL TEMPERATURE ON THE PHYSICAL PROPERTIES OF STEEL.

Critical point	Thermal capacity	Thermal expansion	Resistivity	Magnetic properties
		1. *Slow Cooling*		
$Ar_{3,2}$	Evolution of heat	Increase in vol. continuous with Ar_1	Fall in resistivity continuous with Ar_1	Slight change.
Ar_1	Evolution of heat	Sudden expansion depending on carbon-content and initial temp.	Sudden decrease in resistance	Sudden increase in permeability.
400° - point in Ni-Cr steels	,,	,,	,,	,,
Low point at 150° to 60°	Small evolution of heat	Large expansion independent of carbon-content	Decrease in resistance	Increase in permeability.
		2. *Tempering*		
Point at 100°	No change noted	Contraction with carbon greater than 0·6 per cent. when quenched above $Ac_{3,2,1}$	Decrease in resistance	Slight increase in permeability.
150°–300°	Evolution of heat	No change	Above change continues	Above change continues.
300°–250°	Evolution of heat if gamma iron be present	Contraction neutralized by γ-iron present	Sudden decrease in resistance if γ-iron present	Sudden increase in permeability if γ-iron present.
500°	None	None	None	Increase in permeability.

O. Weigel gave for the true linear coeff. of expansion of steel:

	0°	100°	200°	300°	400°
Linear coeff. $\times10^6$ . .	9·193	10·388	11·563	12·748	13·933

and he represented the length at θ° by $l_0(1+0{\cdot}0_59193\theta+0{\cdot}0_85925\theta^2)$. For the two coeff. α and β, L. Holborn and A. Day gave, respectively, $0{\cdot}0_59173$ and $0{\cdot}0_8336$ between 0° and 300°. W. Wimmer gave $\beta=0{\cdot}000011$ at 20°, and 0·0000093 at −180°. According to L. Holborn and A. Day, the expansion with wrought iron can be represented by $(11{,}705\theta+5{\cdot}254\theta^2)\times10^{-9}$, and with a high-carbon steel, $(9173\theta+8{\cdot}336\theta^2)\times10^{-9}$. J. R. Benoit found the expansion of a slowly cooled steel to be $1+\alpha\theta+\beta\theta^2$, where α is $0{\cdot}0_410354$ to $0{\cdot}0_410457$, and β is $0{\cdot}0_8523$ to $0{\cdot}0_8520$. W. Voigt gave for steel $\alpha=\{11{\cdot}47+0{\cdot}0519(\theta-30)\}\times10^{-6}$ between 26° and 58°;

and for iron, $a=\{11{\cdot}58+0{\cdot}048(\theta-30)\}\times10^{-6}$ between 24° and 68°. E. Grüneisen observed for temp. between :

	−190° to 16°	16° to 250°	250° to 375°	375° to 500°	500° to 625°	625° to 750°
δl . . .	1·87	3·04	1·88	1·98	2·02	2·02

for a metre rod at 0°, and $\delta l=1000\times0{\cdot}0_6679\ (T_2^{1{\cdot}43}-T_1^{1{\cdot}43})$ mm., or $\delta l=1000\{0{\cdot}0_611557(\theta_2-\theta_1)+0{\cdot}0_8517(\theta_2^2-\theta_1^2)\}$.

J. Driesen's results for $a\times10^8$ are summarized in Table XXXVI. The A_1- and A_3-arrests appear as minima ; the A_1-minimum remains constant, but the A_3-minimum falls with increasing proportions of carbon. The results for higher proportions of carbon are shown in Table XXXVI. Cast iron is a mixture of graphite, the phosphide eutectic, cementite, and ferrite, and each of these constituents has its own thermal expansion. C. Benedicks and H. Löfquist also observed that when 1 per cent. of combined carbon is changed into graphite, the volume of the casting increases 2·04 per cent. Consequently the thermal expansion of cast iron depends on a number of secondary effects, and is quite a complicated phenomenon. Thus, E. Morgan showed that a cast iron with 3·5 per cent. of carbon and 2 per cent. of silicon will expand uniformly up to 550° when it is heated at the rate of 30° per minute. Above 550°, in addition to the ordinary thermal expansion, graphitization occurs and this causes an increase in vol. dependent on the degree of graphitization. At the Ac_1-critical point, there is (*a*) a contraction due to the change of *a*- into *γ*-iron ; and (*b*) the dissolution of some carbide not decomposed below the Ac_1-point, and this involves an expansion. As a rule, all the undecomposed carbide does not dissolve at the Ac_1-point, because the heating it has received at the lower temp. causes the grains to become coarser, and to dissolve less rapidly in the austenite. The rate of expansion of austenite with temp. is different from that of iron below the Ac_1-arrest. This expansion is also modified by the dis-

TABLE XXXVI.—COEFFICIENTS OF THERMAL EXPANSION FOR CARBON STEELS.

Temperature range	Percentage of carbon								
	0·06	0·22	0·33	0·40	0·65	0·81	1·25	1·45	1·67
20°–100°	1166	1166	1108	1129	1104	1104	1087	1013	1044
100°–200°	1293	1252	1254	1235	1203	1194	1124	1100	1012
200°–300°	1423	1396	1413	1374	1358	1400	1328	1366	1333
300°–400°	1534	1506	1534	1546	1516	1513	1510	1541	1513
400°–500°	1627	1592	1618	1622	1596	1622	1608	1646	1555
500°–600°	1664	1647	1641	1647	1655	1673	1643	1664	1643
600°–700°	1703	1703	1647	1685	1713	1645	1671	1655	1728
700°–800°	+1212	+8	−1176	−871	−74	+1097	+1708	+1985	+2014
800°–900°	−589	+882	+1287	+1709	+2295	+2169	+3105	+3674	+3720
900°–1000°	+2218	+2100	+2100	+2086	+2138	+2104	+2390	+3150	+3710

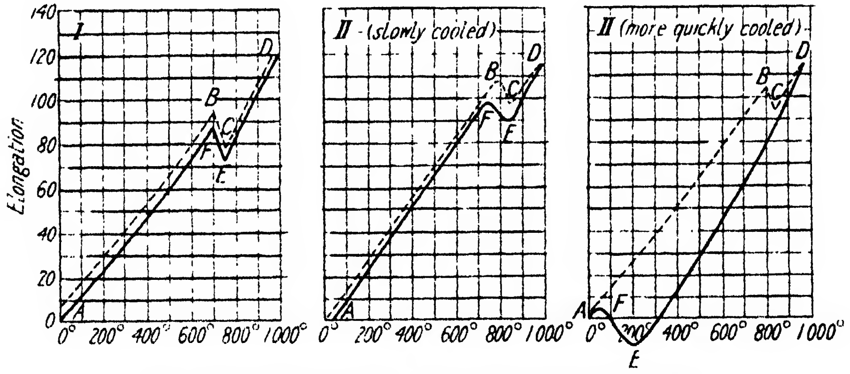
TABLE XXXVII.—COEFFICIENT OF THERMAL EXPANSION OF CAST IRON.

Temperature range	Percentage of carbon			
	1·97	2·24	3·66	3·80
20°–100°	994	961	851	871
120°–200°	997	967	794	793
200°–300°	1325	1336	1277	1298
300°–400°	1519	1541	1543	1548
400°–500°	1644	1697	1679	1679

solution of iron carbide in austenite as the temp. is raised. At still higher temp., some of the temper-carbon deposited at the lower temp. is re-absorbed. In the low-silicon cast irons, the carbide remains stable almost to the Ac_1-critical point; mottled irons are stable, but show a discontinuity at about 250° owing to a magnetic change; whilst the chromium cast irons at about 400° show a change in the expansion curve from about $0\cdot0_4130$ to $0\cdot0_4150$. The average thermal expansion of cast irons can be taken to be $0\cdot0_4140$. H. A. Schwartz found the coeff. of expansion of molten cast iron to be constant between 1375° and 1500°.

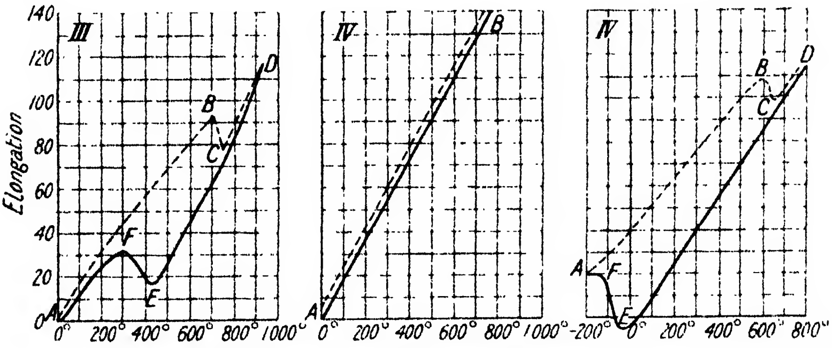
According to H. Esser, the thermal expansion curve of pure iron that has been de-gassed by repeated heating at 700° to 800° in vacuo, places the Ar_3-point at 898° and the Ac_3 at 904°; the Ac_1-arrest is detectable only when at least 0·06 per cent. of carbon is present in a steel, and the Ar_1-arrest when there is 0·20 per cent. With 0·86 per cent. of carbon, both the A_1- and A_3-arrests coincide, the Ar-arrests at 708°, and the Ac-arrests at 736°. The line joining the Ac_1-arrests of iron-carbon alloys containing up to 0·86 per cent. is horizontal at 736°, whereas that joining the Ar_1-arrests rise in a smooth curve from 685° with 0·1 per cent. to 708° with 0·86 per cent. The Ar_3- and Ac_3-lines fall steeply in smooth curves to join the A_1-lines at the eutectoid point.

G. Charpy and L. Grenet measured the elongation of various alloy steels at different temp., and the results are plotted in Figs. 235 to 240. *AB* represents the stable condition on heating from the ordinary temp., and it corresponds with the thermal expansion; *BC* represents a transformation which is accompanied by a contraction; *CD* represents the stable condition above the transformation temp., and it represents the thermal expansion; *DE* represents the contraction of the steel on cooling from, say, 950°; *EF* represents the transformation on cooling, and it is accompanied by an expansion; and *FA* represents the contraction as the steel cools from the transformation to ordinary temp. The alloy steels arrange themselves approximately into four groups: *Group I*, Fig. 235. These steels exhibit very nearly the same transformation temp. on heating and on cooling. The hysteresis effect with slow cooling is less than 150°. Examples are the carbon steels, and the majority of alloy steels used for structural purposes where the proportion of alloying metal is small. *Group II*, Figs. 236 and 237. These steels have nearly the same transformation temp. on slow cooling as on heating, but with moderately rapid rates of cooling the transformation on cooling is much lower than with heating. The interval of temp. depends on the maximum temp. attained, and on the time the steel is kept at this temp. Examples are the high-speed tool steels—the Cr-W, Cr-Mo, Cr-W-V, and Cr-W-V-Co steels. If these steels are not heated above a certain temp., the transformations are reversible; but if this temp. is exceeded, the transformation temp., with ordinary rates of cooling, generally drops from about 600° to 300°, or even to atm. temp., and there is no transforma-



FIGS. 235, 236, and 237.—Thermal Expansion Curves.

tion between these temp. By suitably selecting the temp., a portion of the transformation can be made to occur at 600°, and the remainder at 300°. *Group III*, Fig. 238. In these steels the transformation temp. with very slow rates of cooling differ from those on the heating curves. Examples are the nickel-chromium steels with from 3·5 to 6·0 per cent. of nickel, 1 to 2 per cent. of chromium, and less than 0·65 per cent. of carbon. The steels exhibit the same behaviour if the chromium is wholly or partly replaced by manganese, tungsten, or molybdenum. The lowering of the transformation temp. is not proportional to the amount of added metal. A small addition—say 5 to 6 per cent.—may depress the transformation temp. on cooling from, say, 600° to 200°, and further additions may produce only a slight effect. The transformation point of these steels is always lowered by cooling, and since any heating of the steel above the transformation temp. produces a hardening effect, these steels are softened by subjecting them to a form of tempering below the transformation temp. on heating. *Group IV*, Figs. 239 and 240. The transformation temp. of these steels is below the ordinary temp., and the steels between 0° and 950° show linear curves both on heating and on cooling. High-nickel, high-manganese, and high-nickel-manganese steels come under this category. In some cases the transformation may occur on cooling below atm. temp.



FIGS. 238, 239, and 240.—Thermal Expansion Curves.

E. Grüneisen found that for pressures, p kgrms. per sq. cm., the coeff. of expansion varies so that:

	$p=1$		$p=1000$	
	$-190°$ to $17°$	$17°$ to $100°$	$-190°$ to $17°$	$17°$ to $100°$
a	$0{\cdot}0_5907$	$0{\cdot}0_41189$	$0{\cdot}0_5903$	$0{\cdot}0_41182$

G. R. Dahlander studied the influence of a tension, p kgrms., on the coefficient of linear expansion, a, between 0° and 100°. He found for an iron wire of 0·878 mm. diameter, and with loads:

p	1·250	2·500	3·750	5·000
a	$0{\cdot}0_411902$	$0{\cdot}0_411956$	$0{\cdot}0_412074$	$0{\cdot}0_412253$

and for steel wire 1·249 mm. diameter, and loads 3·750, 6·250, and 10·0000 kgrms. at 17°, the values of a were respectively $0{\cdot}0_411296$, $0{\cdot}0_411409$, and $0{\cdot}0_411508$. For elastic limits E_1 and E_2 at the respective temp. θ_1 and θ_2 when the loads are respectively p_1 and p_2, and the coeff. of thermal expansion a_1 and a_2, the relations for a wire of cross-section a, are summarized by:

$$a_2-a_1=\frac{P_2-P_1}{a(\theta_2-\theta_1)}\left(\frac{1}{E_2}-\frac{1}{E_1}\right)$$

R. Mallet's observations on the sp. gr. of molten iron have been already discussed. He said that at the moment of solidification, molten iron does not expand, but rather contracts, so that the sp. gr. of liquid cast iron is 6·65, when that of the solid is 7·17, and that the coeff. of cubical expansion between 15° and 1315° is 0·00005994. F. Nies and A. Winkelmann made observations on this subject. T. Wrightson found that with grey Cleveland iron, the volume expands as the temp. rises until it is in the plastic state, when it has the sp. gr. 6·5, the cold iron having a sp. gr. 6·95. After this, a contraction occurs until the mass becomes liquid, when its sp. gr. is 6·88. Hence, if the vol. of liquid iron be taken as 100, that of plastic iron is 105·85, and that of solid iron at atm. temp., 98·98—*vide supra*, the sp. gr. of molten iron.

In preparing castings of cast iron, it is part of the moulder's craft, discussed by A. McWilliam and P. Longmuir,[2] and others, to deal with the **casting or cooling shrinkage** which renders necessary an allowance for the difference in size between pattern and casting. H. Moissan showed that whilst iron contracts on solidification, a sat. soln. of carbon in iron expands on solidification. E. Flachat said that the contraction with grey pig-iron is nearly 1 per cent.; and with white pig-iron, 2 to 2·5 per cent. The formation of pipe cavities in steel ingots, etc., is an example of liquid shrinkage. The *Hütte* gave a linear decrease of $\frac{1}{55}$th, with a low-carbon steel on cooling from the m.p. to ordinary temp. So far as the size of the casting goes, the net result is determined (i) by the change in vol. which occurs during the solidification of the liquid, (ii) by the thermal contraction of the metal during cooling, and (iii) by the changes attending the chemical and physical transformations which occur as the metal cools down from its f.p. Whatever condition affects the state of the cementite, etc., will naturally influence the shrinkage. Thus, the hotter the casting temp. of the metal, the greater the shrinkage. R. A. F. de Réaumur stated that cast iron expands on solidifying, but B. Kerl said that cast iron contracts in such a way that at the commencement of its solidification it first expands so as to fill up the smallest depressions and cavities of a mould, but after solidification, it contracts. R. Mallet opposed the view that cast iron expands during solidification, and although his curve showed a distinct expansion, corresponding with that shown by phosphoric, grey cast iron, he argued that the expansion was a freak result, or rather an experimental error, and thus missed a true phenomenon. W. C. Roberts-Austen and T. Wrightson, compared the sp. gr. of a number of metals during solidification, and found that a contraction occurred with cast iron. On the contrary, A. Ledebur said that there is a slight expansion at the moment of solidification. E. J. Ash and C. M. Saeger observed an expansion of 1·65 per cent. with grey cast iron, and a contraction of 5·85 per cent. with a low-carbon, low-silicon type of iron. F. Erbreich, T. Turner, S. G. Smith, F. Körber and G. Schitzkowsky, P. A. Russell, C. M. Saeger and E. J. Ash, R. Moldenke, and F. Busse made observations on this subject. T. D. West found that the harder grades of cast iron contract least on solidification owing to the segregation of graphite. W. J. Keep showed that iron alone contracts normally without showing any expansions; but when sufficient carbon is present to furnish tool steel, there is a considerable arrest in the contraction curve at a red-heat, and a distinct expansion occurs before the normal rate of contraction is resumed. With cast iron low in silicon, a slight expansion occurred immediately after solidification, this was succeeded by a normal contraction until, at a red-heat, another expansion occurred, and this was followed by a normal rate of contraction down to ordinary temp. With a cast iron containing 3·10 per cent. of carbon, and 3·85 per cent. of silicon, three expansions appeared in the curve. F. Osmond suggested that the first expansion may be at about 1100°, where the bulk of the graphite segregation occurs; that the second, probably at about 900°, is due to the presence of phosphorus; and that the third, probably at 700°, corresponds with the recalescence temp. T. Turner found that the volume changes on the cooling curves with iron containing:

	Carbon only	C and Si	C, Si, and P
First expansion . . .	Nearly absent	1135°	1060°
Second expansion . . .	Absent	Absent	900°
Third expansion . . .	665°	695°	730°

W. J. Keep also studied the effect of silicon. The first arrest observed by T. Turner is apparently raised by the presence of an increasing percentage of silicon, and lowered by the presence of phosphorus. The results confirm F. Osmond's hypotheses. The second expansion corresponds with the breaking down of the ternary eutectic of the system Fe–P–C, observed by J. E. Stead. The first expansion is negligibly small except when carbon is present; in that case, the separation of cementite from austenite accounts for the observed effect. The third expansion is connected with the transformation of the solid soln. or hardenite into pearlite. W. J. Keep also observed that some carbon segregates in this zone, and this would accentuate the expansion attending the pearlitic transformation. The effects produced by foreign elements are mainly due to their effects on the carbon segregation—thus, silicon increases the shrinkage; sulphur, and manganese increase the shrinkage; while phosphorus has very little influence. G. Hailstone showed that liquid contraction is accompanied by a lowering of the sp. gr. or density. If the metal is cast with iron hotter than will conduce to liquid contraction—say, between 1386° and 1428°—solid, dense castings result; liquid contraction occurs when the metal is cast at a medium heat; and if the temp. of the iron is too low, blow-holes appear. Conditions favouring a maximum solid contraction favour a maximum liquid contraction. A cast iron poured at its casting temp. shows a closer microstructure than otherwise, and the phosphide eutectic will collect in the network formation. Occluded gases appear to be held more tenaciously in cast iron poured at a high temp., and therefore a more solid casting is produced. Observations were also made by P. Bardenheuer and C. Ebbefeld, E. Bauer, O. Bauer, O. Bauer and K. Sipp, R. Buchanan, J. W. Donaldson, F. C. Edwards, H. Endo, H. O. Evans, J. E. Fletcher, J. Gray, A. Hanszel, F. Körber and G. Schitzkowsky, J. Longden, G. Masing, A. Messerschmitt, C. W. Meyer, A. L. Norbury, C. Pack, N. B. Pilling and T. E. Kihlgren, W. H. Pretty, R. T. Rolfe, R. T. Rolfe and J. Laing, C. M. Saeger and E. J. Ash, F. Sauerwald, F. Sauerwald and co-workers, H. A. Schwartz, O. Smalley, R. Stotz, D. J. Thomas, F. Wüst, and F. Wüst and G. Schitzkowsky. The general results show that the shrinkage which occurs on casting cast iron is conditioned by the chemical composition, the condition of the carbon, the casting temp., the rate of cooling, and the temp. gradient within the casting. The shrinkage of grey cast iron is less than that of white cast iron. K. Tanimura studied the effect of the melting temp. on low-carbon cast iron; and P. Bardenheuer and W. Bottenberg, the effect of the gas-content. H. I. Coe observed that there is an expansion during the solidification of white cast irons containing manganese. The curve shows minima corresponding with Fe_3C and no manganese; $8Fe_3C.Mn_3C$, or 5 per cent. Mn; $2Fe_3C.Mn_3C$, or 15·3 per cent. Mn; and $3Fe_3C.2Mn_3C$, or 19 per cent. Mn. There is also a depression corresponding with $4Fe_3C.Mn_3C$. The expansion with grey cast irons reaches a maximum with 10 per cent. Mn.

J. H. Andrew and co-workers observed that with steels during slow cooling, there are an evolution of heat and an increase in vol. at the $A_{3,2}$-arrest continuous with the Ar_1-arrest; and there is a sudden expansion with the evolution of heat at the Ar_1-arrest. The expansion depends on the carbon-content and the initial temp. Similar remarks apply to the arrest at 400° which occurs with nickel-chromium steels. The arrest between 150° and 160° in consequence of a small evolution of heat is attended by a large expansion, independent of the carbon-content. In tempering at 100°, there is a contraction, without the evolution of heat, when the proportion of carbon is greater than 0·6 per cent., and the steel has been quenched from above the Ac_3-,$_2$-,$_1$-arrest. No change in vol. occurs when heat is evolved at 150° to 300°. At 300° to 350°, heat is evolved if γ-iron be present, and a contraction is neutralized by the γ-iron present. No thermal change or abnormal change in vol. was observed at 500°. J. H. Andrew and co-workers concluded from their observations on the dilation of steels:

The change in vol. which occurs at the normal transformation points, is the resultant of two changes working in opposition—(*a*) an allotropic change, and (*b*) a change due to carbide. The latter change in steels of high carbon-content is not completed at the ferrite, carbide, or *SE*-line, but continues to a temp. depending on its composition—particularly on the carbon-content—it increases with the carbon-content. The dilation is a measure of the mol. conc. of the carbide in soln., and controls the temp. at which the allotropic transformation takes place. Quenching merely stereotypes the condition of the carbide, which, in its turn, controls the allotropic change. This variation in the mol. conc. is explained by assuming that carbide dissociates at and above the temp. of the normal transformation point. Nickel-chromium steels behave in much the same way as carbon steels, excepting that in the latter the time factor necessary to produce the same changes in the carbide is of a much lower order. Martensite is a product formed when the allotropic change has been depressed by dissociated carbide, to a temp. at which the latter is able to exist as such in the α-iron formed. At the temp. of the normal transformation point martensite is not formed as an intermediate phase between austenite and pearlite. When the mol. conc. of the carbide is such that the allotropic change is depressed below atm. temp., the resulting product will be austenite, *i.e.* the iron is retained in the γ-state. By tempering austenite in such a way that the carbide becomes partially associated, the allotropic change is able to take place on re-cooling, forming martensite, and the phenomenon of secondary hardening results. Dilation measurements enable the proportions of α- and γ-iron in the quenched product of any steel to be determined. In carbon steels quenched at 1000°, the iron in the product is in the α-state. In alloy steels γ-iron is present in various proportions, particularly with high carbon-content. In extreme cases, α-iron is entirely absent.

L. Aitchison and G. R. Woodvine observed that with nickel-chromium steels, the expansion that should be produced at the critical range during the cooling from the hardening temp. is not completed during the slow cooling in air; re-heating to quite low temp. induces a further expansion; further re-heating to low temp. brings about a contraction; prolonged heating at low temp. induces still further contraction; re-heating to intermediate temp. (300° to 500°) induces a similar initial expansion and then a contraction; re-heating to 600° induces a contraction; the smaller initial expansion at the intermediate temp. is likely to be the resultant of the expansion and contraction proceeding simultaneously; the total contraction brought about at temp. up to 200° by repeated heating and cooling is less than that similarly produced at higher temp.; and the maximum contraction brought about in any way, at all the different temp., is the same in amount. They found that the longitudinal and lateral expansions are the same. The exposure of steel to a higher temp. for a long time produces a metal which expands less on cooling, quickly or slowly. The expansion depends on the production of a stable austenite, which changes to martensite reluctantly and hence produces a smaller expansion. Air-hardened nickel-chromium steels when heat-treated in the ordinary way, are not in a stable volume condition. The tempering for volume stability requires a long time. For the changes in vol. during the ageing of steel, *vide supra*. The change in length of steels during tempering is a combined effect of tempering and temp.; K. Tamura eliminated the effect of temp. by measuring the increase in length of the cold specimen. The results show that the length decreases at first rapidly, then slightly, and afterwards there is a gradual decrease in length as the tempering interval increases; and also that for a constant interval of tempering, 1 hour, there is a decrease in length from room temp. to 200°, owing to the transformation of α- into β-martensite, and also to a slow decomposition of the martensite to form cementite; the maximum, lying between 230° and 300°, is due to the transformation of residual austenite to β-martensite; and the rapid contraction between 260° and 340° is due to the decomposition of β-martensite. The decrease in length above 340° is very slow. G. M. Eaton discussed the dilation of steel by the formation of martensite during quenching. The changes in vol. which occur during the quenching of steel were discussed by A. A. Blue, F. Berger, D. K. Bullens, H. Brearley, P. J. Haler, A. Portevin and P. Chévenard, J. Seigle, A. Heller, J. F. Keller, O. E. Harder and co-workers, R. S. MacPherran and R. H. Krueger, J. W. Donaldson, D. Hattori, and C. U. Scott. I. Jaederström discussed the effects of carbon, silicon, sulphur, manganese, phosphorus, nickel, and chromium on the casting shrinkage of cast iron. O. Bauer and H. Sieglerschmidt observed that the addition of about half per cent of copper or of nickel to cast iron had no perceptible effect on the growth of the metal. A. Portevin discussed the deformation of steel during heat-treatment.

A. Bramley and co-workers found that in gaseous cementation, samples of iron increased in diameter but generally decreased in length. If the original specimen contained a high proportion of carbon, or if the carburization was conducted below 900°, the changes in dimensions were comparatively small.

In 1791, T. Beddoes[3] reported: "In annealing crude iron with or without charcoal, it is known to increase in all its dimensions. I have seen bars, originally straight, bent like an S when long exposed to heat in circumstances where they could not extend themselves." It is a common thing to find the **growth of cast iron** with grate bars, stove-pipes, kiln-bats, oven-plates, etc., on exposure to high temp. J. Prinsep noticed that the capacity of an iron retort increased with successive heatings. Observations were also reported by A. Guettier, P. W. Brix, A. Erman and P. Herter, and J. Percy on the permanent expansion of cast iron by exposure to long-continued heat at or above redness. A. E. Outerbridge showed that grey cast iron expands more rapidly than white cast iron; that the deposition of carbon owing to the dissociation of the carbide does not account for the change in vol.; and that wrought iron and steel contract slightly when subjected to the same treatment. C. H. Wingfield also observed that wrought iron contracts permanently with the same treatment.

C. Benedicks and H. Löfquist analyzed the phenomenon by showing that permanent changes in vol. can occur in metals in three ways: (i) *Changes due to internal, irreversible or monotropic reactions* like that involved in the transformation of cementite into ferrite and annealing or temper carbon, or graphite. T. Kikuta thought that this change might develop internal cracks, but C. Benedicks and H. Löfquist, and H. F. Rugan and H. C. H. Carpenter showed that the theoretical expansion so caused is in agreement with the calculated value, and the change is not accompanied by internal cracks. Another monotropic reaction is the increase in vol. attending the oxidation of silicon, manganese, and iron by the entry of oxygen through cracks in the metal—*vide infra.*

(ii) *Permanent changes of shape resulting from normal expansion and contraction.* J. H. Whiteley, and J. F. Keller showed that a homogeneous metal cylinder when repeatedly quenched in water from a glowing state undergoes a permanent shortening. C. Benedicks and H. Löfquist said:

> On immersing a hot cylinder in the water, the outer layer is, of course, quickly cooled, and is consequently subjected to a sudden contraction. This will exert a considerable contraction stress on the inner, still warm layers—provided the tensile strength of the metal be sufficient—which will be noticeable especially in the direction of the cylinder axis; the plasticity of the inner layers being considerable on account of their higher temp., these will partly yield, and the length of the cylinder after completely cooling will be somewhat less than before treatment. The length thus successively decreasing by sudden coolings, it is a necessary consequence that the diameter should simultaneously increase, as otherwise a successive increase in the sp. gr. of the metal would occur. The result will be a growth of the middle part of the cylinder, together with a simultaneous shortening of its length; after repeated quenchings the cylinder will thus finally approach to a spherical form. That this must be the case is easily understood in the following way: A sudden cooling of the peripheric portions produces a high hydrostatic press. in the inner portions of the cylinder; this must cause a deformation tending towards a spherical form, in the same way as the blowing up of a heated, irregularly formed, closed glass tube will give a more or less spherical ball. If, instead, the homogeneous cylinder is subjected to a very sudden heating, as, for instance, by immersion in a molten salt bath, the outer parts must exert a certain stretching influence on the underlying portions, with a tendency permanently to elongate the cylinder (and lessen the diameter of the middle part). As in this case the inner portions have a lower temp., it is evident that the resulting elongation of the cylinder will be less than the shortening on sudden cooling. On the other hand, if the metal contains embedded particles which reduce its tensile strength, the possibility of the *formation of cracks* must be taken into consideration. Accordingly, in the case of a material in which cracks are easily formed, the following will occur: On account of the tensile stress exerted by the outer portions on the inner ones, on sudden heating, cracks may arise in the interior. On sudden cooling, however, cracks will arise, especially in the outer portions

of the cylinder, on account of the stresses appearing there. As a matter of fact, the interior —even if already containing cracks—will offer a considerable resistance to compression, as explained above. Consequently, a series of sudden coolings will cause an increasing internal bursting or porosity, proceeding throughout the cylinder, and accompanied by an increase in volume. As this action is caused by the difference in expansion of adjacent layers of the specimen, it will, however, not be of any appreciable magnitude, except when the temp. change takes place very suddenly; the velocity of temp. change—and consequently of expansion—which may be attained by ordinary heating and cooling being rather insignificant, the phenomenon will be difficult to observe.

(iii) *Permanent increase resulting from anomalous expansion and contraction.* When a metal has an allotropic phase transformation point, at which a considerable anomalous change in length occurs, this is equivalent to an extremely high speed of normal expansion and contraction. From the above, it follows that in a heterogeneous material possessing an anomalous dilation point, and in which internal bursting may occur, repeated heatings with subsequent coolings will cause a sensible and permanent increase in vol., and this even if the changes in temp. are made very slowly. The expansion of iron at the Ar-transition temp. was studied by G. Charpy and L. Grenet, A. M. Portevin and P. Chévenard. For pure iron, the reversible contraction at the Ac-arrest amounts to about 0·3 per cent. of the length at room temp. corresponding to a vol. contraction of 0·9 per cent. when α-iron changes into γ-iron. Its intensity diminishes with increasing carbon-content, so that with 0·7 per cent. carbon, the vol. contraction is 0·45 per cent. This decrease is due to the fact that a given amount of carbon has a greater vol. when dissolved in γ-iron above the Ac-arrest than when combined with iron in cementite, below Ac. If, instead, the carbon below Ac is present as graphite, the vol. change must be even greater than for pure iron. Actually, when 0·7 per cent. of carbon passes from cementite into graphite, an increase of 1·43 per cent. occurs. Consequently, in an iron containing 0·7 per cent. of carbon in graphite, if this is entirely dissolved at the Ac-change, a decrease in vol. of 1·9 per cent. will occur. Again, if 0·7 per cent. of carbon is dissolved in γ-iron above Ar_1 and the carbon entirely precipitated as graphite, an increase in vol. of 1·9 per cent. will occur, and this corresponds to an increase in length of 0·63 per cent. This represents the maximum anomalous expansion which can occur in grey cast iron at Ar. If the silicon-content be high, the percentage of carbon passing into γ-soln. will presumably be less than 0·7 per cent.; further, the carbon may not all be precipitated as graphite, for part may be precipitated as cementite. In both cases, the vol. or length changes at Ar will be less than the maximum value.

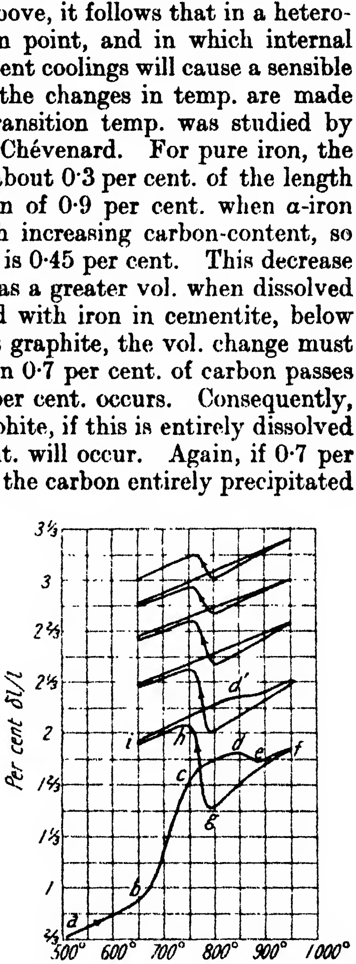


FIG. 241.—Curve showing the Permanent Increase in Length of Cast Iron during Repeated Heatings and Coolings.

Basing their hypothesis on the above considerations, C. Benedicks and H. Löfquist interpreted the phenomenon by a diagram, Fig. 241, resembling those obtained by T. Kikuta. The increase in the length, *l*, of a cylinder of cast iron will then be represented by a curve, *ab*, defined by the expansion coeff. of α-iron, namely, 12×10^{-6}, which increases slowly with temp. The coeff. of expansion of graphite cannot sensibly affect the result because the quantity present is so small. When the cementite begins to decompose, the vol. increases faster than is defined by the coeff. of thermal expansion. If 0·9 per cent. of combined carbon be present, the increase in vol. will be about 0·6 per cent., and the resultant expansion is represented by the curve *cd*, and the intermediate stage *bc*. T. Kikuta found that *b* is approximately at 700°. The formation of temper-carbon is complete at *c*.

The expansion proceeds along *cd* until Ac is attained, and if the proportion of silicon is high, the temp. is 850°. The transformation of the α- to the γ-state begins in the outer zone of the cylinder, and a linear contraction of about 0·63 per cent. occurs. This contraction will be opposed by the layer immediately below, which, like the whole of the interior, is still in the α-state. The metal here offers a great resistance to compression, so that the outer layer will be subjected to a severe strain giving rise to an internal bursting of the metal, which, on account of the contained graphite, possesses a very low tensile strength, and this results in a permanent lengthening. If thereby the tensile strength of the outer layer be very slight in comparison with the compression strength of the inner part, the outer layer, γ, would lengthen to exactly the same length still held by the inner part, α. The transformation having proceeded is this way until all is in the γ-state, no perceptible contraction of the cylinder would be observed. The metal, however, originally assumed to be devoid of cracks, possesses a certain tensile strength, so that on the first heating of the cylinder, a slight decrease in the resultant length may occur. If a quarter of the specific contraction takes place in this way, the resultant contraction, 0·16 per cent., will be that represented in Fig. 241 by the jump from *cd* to *ef* at 850°. The slope of *ef* is rather greater than that of *cd*, corresponding with the fact that γ-iron has a greater coeff. of expansion than α-iron. Since the graphite requires time to dissolve in the iron, a sudden jump will not occur, and *de* extending over an interval of, say, 50°, represents the region where the graphite is dissolving. The heating may now be continued up to 950°, represented by *f* in the diagram. On cooling, the contraction would follow the curve *fe*, but a certain dissolution of graphite would occur at this high temp., since a surplus of graphite is present, and this makes the backward curve *fg* slightly below *ef*.

The Ar-arrest is reached at about 800°. The transformation first occurs in the outer layer of the cylinder, which undergoes a strong anomalous expansion which, as indicated, attains a maximum of about 0·63 per cent. before the expansion of the underlying parts has begun. The outer layer is thus subjected to severe compression, and the inner part to strain. As a result, either the dilated outer layer is unable to produce any bursting of the interior layers, or the expansion of the outer layer will cause a certain bursting of the underlying layers. In the former case, the underlying layer will successively undergo the same expansion as the outer layer, and in the latter case, the underlying layers, after the transformation has taken place, will possess a somewhat larger vol. than that corresponding with the anomalous expansion itself. The latter case is the less probable, even if the tensile strength of the material be low, since the surface-layer, being very thin to begin with, cannot exert any considerable lengthening stress on the inner parts. In any case the resultant effect will be an expansion of the cylinder as a whole. Consequently, the expansion on the first passing of Ar may be assumed to amount to the theoretical maximum of 0·63 per cent. This increase in length corresponds with the passing of the curve from the point *g* to the curve *hi*. The change from *g* to *hi* does not take place suddenly, because the reaction cannot take place instantly; the precipitation of graphite occupies a certain time, especially as it is possible that a certain amount of cementite is formed primarily, and only later decomposed into graphite. The change, therefore, proceeds along the curve *gh* covering an interval of, say, 50°. The change in length during the subsequent cooling of the cylinder is represented by *hi*, and may continue until the point *i* is attained, say, 650°, when the cylinder is re-heated. The expansion may then proceed along *ih*, or rather along *id'*, because a slight continued precipitation of graphite may occur.

When the Ac-arrest is reached for the second time at *d'*, the prevailing circumstances are the same as before, with the difference that an internal bursting of the cylinder remains as a result of the previous heating. Making the necessary modifications for the residual effects of previous heatings and coolings, a series of loops is obtained as indicated in the diagram. The primary cause of the growth of cast iron is attributed to the fact that on account of internal bursting around the graphite lamellæ, the anomalous contraction at Ac decreases much more rapidly than the anomalous expansion at Ar. Every heating cycle consequently gives rise to a residual expansion. The repeated heating of the iron through Ac results in a continuous growth with an increased internal bursting. This bursting implies a lessened probability of the dissolution of graphite at Ac, etc. When heated in air, the cracks which are developed render possible a strong oxidation proceeding successively inwards. This phase of the subject was studied by H. F. Rugan and H. C. H. Carpenter, H. F. Rugan, J. H. Andrew and co-workers, J. E. Stead, C. E. Pearson, M. Horikiri and K. Uyeno, E. Richards, T. Terao, J. E. Hurst, H. Stäger, T. Wrightson, J. E. Fletcher, E. Honeggar, E. Scheil, J. Seigle, P. Bardenheuer, and F. K. Neath.

H. F. Rugan and H. C. H. Carpenter found that growth proper begins at about 650°, and it increases eightfold at 675°; it appears to reach a maximum at about 730°, and at 900° a further increase in volume was only just perceptible. They showed that alloys free from graphite do not grow, and that under suitable conditions, alloys containing graphite are capable of growing. With approximately constant carbon, the ultimate growth after repeated heating is approximately proportional to the percentage of silicon up to 6 per cent. The growth is far in excess of that caused by the transformation of combined into free carbon, and, in fact, growth was greatest in high-silicon alloys containing no carbon combined with iron. Two agencies thus appear at work: The internal press. of gas which the alloys contain in their original cast condition, and which is probably physical in character; the effect of external gas in contact with the alloys during their heat-treatment, which is probably partly physical and partly chemical in its nature. It was shown that the silicon is mainly responsible for the expansion, and that the expansion due to the precipitation of free carbon is relatively insignificant. There is an increase in weight which is approximately equal to the increase in the weight of iron and silicon oxidized minus the loss in weight due to the oxidation of carbon. The oxidation of silicon combined as FeSi is not sufficient to account for the gain in weight, and hence iron itself must also be oxidized. The carbon is oxidized to a greater extent in alloys containing least silicon; and in irons with least combined carbon, the oxidation of this element is at a minimum. It was inferred that when the metal is cooling, furnace gases penetrate to a certain depth in the metal, possibly along slits existing between the plates of carbon and the solid soln. of iron silicide, and through holes which exist here and there. The carbon oxides are assumed to oxidize the iron silicide, and during this period, growth and incipient disintegration occur. J. W. Donaldson found that the presence of chromium retards the growth of cast iron. The main cause of growth is the oxidation of the iron silicide. E. H. Saniter added that every time the metal is annealed and expanded, whether by the oxidation of the silicon or of the iron, the presence of the oxidation products prevent the metal from contracting to its original size when cooled. The process is repeated when the iron is again stretched by heating. H. F. Rugan and H. C. H. Carpenter were unable to expand iron-silicon alloys containing more than 0·20 per cent. of carbon; free carbon is necessary for the phenomenon. One specimen of metal shrank, if anything, when heated to 900° in vacuo, but when heated in furnace gases it expanded 67 per cent. Each time the metal is heated and cooled, the furnace gases penetrate a little deeper owing to the opening up of fresh avenues by the reactions just indicated. Each time the metal is heated and cooled the reactions are repeated, the iron is more and more disintegrated, and a further growth takes place. At the end of the process, the metal has lost the properties of cast iron; it has no mechanical strength, and may be sawn like chalk. H. C. H. Carpenter found that for grey cast iron the approximate percentage growths, with increasing proportions of silicon, were:

Si . .	1·0	1·50	2·0	2·5	3·0	3·5 per cent.
Growth .	15·0	21·5	27·0	31·0	34·0	37·0

Phosphorus tends to diminish the growth, since the growth was lessened about 3 per cent. by the presence of 0·3 per cent. of phosphorus, and still more with a higher percentage of phosphorus; the small amount of sulphur in commercial cast irons has but a slight influence in the direction of retardation; manganese retards the growth in all cases. Thus, alloys with 2·25 to 2·40 per cent. of carbon and 0·40 to 0·48 per cent. of silicon, as well as 0·510, 0·735, and 0·935 per cent. of manganese, after 151 heats, had respectively growths of 7·49, 6·06, and 3·09 per cent. Dissolved gases have no influence on the growth of an iron containing more than 3 per cent. of silicon; with between 1·75 and 3·00 per cent. silicon they may cause a growth of 1 to 2 per cent. Their most potent influence occurs when silicon does not exceed 1 per cent., and in such cases may be responsible for a growth of at least 10 per cent. An iron alloy with 2·66 per cent. of carbon, 0·587 per cent. of silicon, 1·64 per cent. of manganese showed no signs of growth after 150 heats, but rather about 0·13 per cent. contraction. The factors which lessen the growth sometimes act by lessening the intensity of the transformation—*e.g.* hydrogen, and nitrogen, observed by F. Wüst and O. Leihener, F. Osmond, W. C. Roberts-Austen, J. H. Andrew, H. S. Rawdon and co-workers; or by the stabilizing influence of different substances on cementite—*e.g.* phosphorus, observed by F. Wüst and co-workers, O. Bauer and K. Sipp, P. Oberhoffer, E. Schüz, H. C. H. Carpenter, J. H. Andrew and R. Higgins, etc., a subject discussed by W. H. Hatfield, and J. E. Hurst; sulphur, discussed by E. Schüz; chromium, by P. Goerens and A. Stadeler, and O. Bauer and K. Sipp. The case of aluminium was discussed by C. Benedicks and H. Löfquist, C. Geiger, and E. G. Odelstierna; of sulphur, by O. Bauer and K. Sipp; of nickel, by O. Bauer and K. Sipp; and of titanium, by B. Freise, and R. R. Kennedy and G. J. Oswald. In some cases the effect is due to the production of more finely-divided graphite which, as W. E. Remmers, and H. Hanemann have shown, increases the tensile strength of iron, and retards growth.

W. E. Remmers found that the alloying elements, silicon, aluminium, and, under certain conditions, titanium, and nickel, which favour the precipitation of carbon, tend to increase the growth, while such elements as chromium and manganese, which exert a stabilizing effect on the carbon, tend to decrease the growth. An increase in the total carbon increases the growth.

The general result is to show that the growth of cast iron when repeatedly heated is due to the physical changes at the Ac_1- and Ar_1-arrests, accompanied by bursting and cracking; as a result of the opening up of the iron, oxygen enters and produces the changes indicated by H. F. Rugan and H. C. H. Carpenter. T. Kikuta observed no sensible growth when the maximum temp. does not exceed the critical temp., though a considerable growth occurs on exceeding that region. Several instances of the growth of cast iron have been reported at temp., not exceeding Ac_1, and C. Benedicks and H. Löfquist added that the observed effect must be due to the formation of temper-carbon from cementite. F. Wüst and O. Leihener concluded that the influence of chemical composition on the growth of cast iron is obscured by other factors; that the growth in a neutral atm. cannot be explained by the decomposition of cementite; that the finer the state of subdivision of the graphite, the smaller the growth; that the growth in the middle zone is faster than in the border zone; and that the gas-content of the cast iron has an important influence on growth.

A. E. Outerbridge thought that the growth of cast iron is "an inherent quality of the metal, and has existed for all time. . . . The astonishing change in vol. is a molecular not a chemical process." H. F. Rugan and H. C. H. Carpenter showed that the phenomenon is a consequence of the oxidation of iron silicide. E. H. Saniter said that the phenomenon must have some relation to the thermal expansion of the metal because it is necessary to heat and cool the iron to make it increase so much in volume. T. Kikuta believed that the first growth on heating through 700° to 800° is partly due to the decomposition of the cementite, but the continued expansion of grey cast iron in vacuo during repeated heating and cooling is due to the differential expansion of the various constituents which produce numerous fissures or cavities in the neighbourhood of the plates of graphite. If the metal be now heated in air, these cavities serve as avenues for the entry of oxidizing gases in accord with the theory of H. F. Rugan and H. C. H. Carpenter. H. C. H. Carpenter did not obtain a growth in vacuo. C. E. Pearson suggested that any observed growth in vacuo is due to the influence of occluded gases; he found that the growth in hydrogen is inconsiderable. A. E. Outerbridge, J. E. Fletcher, and M. Okochi and N. Sato consider that the growth of cast iron by repeated heating and cooling through the Ar_1-range is caused by the press. of occluded gas. T. Kikuta said:

> The growth of grey cast iron during the first heating through 700° to 800°, is partly attributable to the decomposition of cementite. The continuous growth of grey cast iron in a vacuum during repeated heating and cooling through the A_1-range is the effect of the differential expansion at different microportions of the same specimen, numerous fissures or cavities being thus formed in the region of graphite flakes. In an oxidizing atmosphere, the growth is accelerated by oxides formed and filling the fissures or cavities during Ar_1-transformation. Thus the effect of oxidation on the growth of cast iron is indirect. The growth of white cast iron is almost completed in the first heating to 800°. About one-third of the whole expansion is due to the decomposition of eutectic and pearlitic cementites, and the other two-thirds to the minute fissures or cavities formed by the irreversible expansion in different microportions of the same specimen. The elongation observable at higher temperatures than the A_1-point is due to the pressure of occluded gases.

A. Campion and J. W. Donaldson observed an expansion up to 0·3 per cent. after 25 heatings at 450°; a definite growth was also observed at 550°. Observations on the subject were made by J. H. Andrew and R. Higgins, J. H. Andrew and H. Hyman, P. Bardenheuer and co-workers, O. Bauer and co-workers, W. H. Blackburn and J. W. Cobb, W. C. Bogenschutz, J. W. Cobb, J. W. Donaldson, J. S. Durn, J. Durand, W. Freytag, J. W. Gardom, W. H. Hatfield, H. M. Howe, T. E. Hull, F. H. Hurren, J. E. Hurst, D. H. Ingall and H. Field, R. L. Keynon, T. Kikuta, O. Leihener, A. Levi, O. Lellep, G. C. McCormick, R. S. MacPherran and R. H. Krueger, R. Mitsche, J. H. G. Monypenny, E. Morgan, A. L. Norbury and E. Morgan, P. Oberhoffer and E. Piwowarsky, M. Okochi and N. Sato, C. E. Pearson, E. Piwowarsky and O. Bornhofer, E. Piwowarsky and co-workers, W. H. Poole, W. E. Remmers, F. Roll, W. Schreck, W. Schwinning and H. Flössner, K. Sipp and F. Roll, R. Stumper, V. N. Svechnikoff, Y. Utida and M. Saito, T. Wrightson, F. Wüst and co-workers, and F. Wüst and O. Leihener studied the growth of cast iron under tension. According to J. Percy:

> Advantage has been taken of the permanent increase in volume which cast iron acquires by long exposure to a high temperature, in rendering cannon-shot serviceable which had been cast too small. The shot was heated in a charcoal fire, well embedded in the charcoal, and allowed to cool under charcoal dust. Their surface was bluish-grey, and did not require any cleaning to fit the shot for use; whereas in previously attempting to employ a hot-blast oven for the same purposes, the surface became coated with firmly adherent red oxide, so difficult to detach that it was found preferable to re-cast the shot than incur the labour and expense of cleaning them.

The observations of H. F. Rugan and H. C. H. Carpenter, W. H. Hatfield, and J. E. Stead show that the method of making over-shrunk castings grow to their proper size by re-heating, recommended by A. E. Outerbridge and others, can be employed only at the cost of some deterioration of the metal.

G. Wiedemann and R. Franz[4] said that if the **thermal conductivity** of silver is 100, that of iron is 11·6; L. Holborn and W. Wien said that if the conductivity of copper is 0·918, that of iron is 0·156, and steel 0·062 to 0·111. F. E. Neumann found the thermal conductivity of iron to be $k=0·1638$ cal. per cm. per second per degree; A. Berget gave 0·1587 above 0°; K. Angström, 0·1988 at 0°, and 0·1417 at 100°; L. R. Ingersoll, 0·1428 between 20° and 100°; L. Lorenz, 0·1665 at 0°, and 0·1627 at 100°; and H. Weber, 0·1485 at 39°. H. Masumoto extrapolated

0·1741 for the thermal conductivity of pure iron. J. D. Forbes obtained for wrought iron:

	0°	50°	100°	130°	200°	275°
k	0·2070	0·1772	0·1567	0·1447	0·1357	0·1240

R. W. Stewart gave for the thermal conductivity of iron, at 0°, $k=0{\cdot}172(1-0{\cdot}0011\theta)$. C. H. Lees gave 0·147 at 18°, and 0·152 at −160°. T. C. Baillie, P. G. Tait, P. Straneo, T. S. Taylor, and L. Ott made observations on this subject. For wrought iron, W. Jaeger and H. Diesselhorst gave 0·1436 at 18°, and 0·1420 at 100°; E. Grüneisen gave 0·171 at 18°; W. Beglinger, 0·111 to 0·150 at 8°; and E. H. Hall, 0·1528 at 28°. M. Jakob gave 0·135 for the best representative value of wrought iron. For cast iron, W. Beglinger gave 0·093 to 0·153 at 8°; and E. H. Hall and C. H. Ayres gave 0·1490 at 30°. M. Jakob gave 0·12 for the best representative value of cast iron. G. Kirchhoff and G. Hansemann gave 0·0964 at 15° for Bessemer steel with 0·52 per cent. C; and W. Beglinger, 0·0985 to 0·104 at 8°; and for Siemens-Martens steel, 0·133; while E. H. Hall, for similar steel with 0·1 per cent. of carbon, gave 0·1325 at 27·2°, and 0·1300 at 59·2°. G. Kirchhoff and G. Hansemann gave 0·1418 at 15° for puddled steel with 0·13 per cent. of carbon, and 0·1375 at 15° when 0·25 per cent. of carbon was present. W. Beglinger gave 0·123 at 8° for hard Thomas' steel, and 0·122 at 8° when the steel was softened; hard crucible steel has the value 0·108 at 8°; and the soft steel, 0·105 at 8°. F. Kohlrausch gave 0·062 for hard steel, and 0·111 for soft steel. E. Grüneisen gave 0·124 at 18° for steel with 0·57 per cent. of carbon, 0·123 for steel with 0·99 per cent. of carbon, and 0·119 for steel with 1·50 per cent. of carbon. W. Jaeger and H. Diesselhorst gave 0·1085 at 18° and 0·1076 at 100° for steel with 0·1 per cent. of carbon; and C. H. Lees, 0·115 at 18° and 0·113 at −160° for steel with 0·1 per cent. of carbon. Observations were also made by J. Mercier and P. Michoulier, H. J. French and O. Z. Klopsch, E. M. Bryant, G. Halliday, J. Hirsch, A. C. Kirk, M. Zittenberg, A. J. Durston, W. F. Barrett and co-workers, T. M. Barlow, J. W. Bolton, E. J. Janitzky, G. Graf, N. M. H. Lightfoot, A. L. Feild, P. Lejeune, J. W. Donaldson, T. J. Ess, H. Schmick, H. Thyssen and co-workers, J. Thoulet, R. C. Carpenter, D. Royce, A. Blechynden, J. G. Hudson, and W. Beglinger.

H. Masumoto found that in the case of cast iron, and steels, the thermal conductivity decreases rapidly at first, and then slowly as the proportion of carbon increases. The annealing of the cast iron raises the conductivity, but a subsequent annealing produces no change provided no graphitization occurs. Thus, with chill-cast and annealed (at 1000°) cast iron, the conductivities were:

	Carbon .	2·41	2·67	3·17	3·64	4·13	4·40	4·61 per cent.
k	Chill-cast .	0·0763	0·0702	0·0607	0·0513	0·0435	0·0350	0·0309
	Annealed .	0·0801	0·0760	0·0633	0·0540	0·0477	0·0390	0·0370

Graphitization decreases the thermal resistivity by about 3.99 for 1 per cent. of graphite. Thus, a sample with 4·35 per cent. of carbon with no graphite had a conductivity of 0·0347, and with 3·89 per cent. of the carbon as graphite, 0·1346; and a sample with 4·63 per cent. of carbon and no graphite had a conductivity of 0·0297, and with 4·55 per cent. of the carbon as graphite, 0·1332. By extrapolation, the thermal conductivity of cementite is 0·017 cal. per degree per cm. per second, when the corresponding value for iron is 0·1741 at 34°. C. Benedicks and co-workers represented the thermal resistivity, k^{-1}, the reciprocal of the thermal conductivity, by $k^{-1}=4{\cdot}4+8{\cdot}7\Sigma C$, where ΣC denotes the carbon value of a dissolved element, and it is obtained by multiplying the percentage proportion of the element by the ratio of the at. wt. of carbon to that of the element. H. Masumoto gave $k^{-1}=5{\cdot}744+2{\cdot}432[\mathrm{C}]+5{\cdot}081[\mathrm{Si}]+2{\cdot}461[\mathrm{Mn}]$.

J. W. Donaldson found that the thermal conductivity of grey cast iron varies from 0·11 to 0·137 cal. per sq. cm. per sec., and decreases as the temp. rises; *e.g.* one sample, with 0·65 per cent. Si, had a conductivity of 0·135 at 100° and 0·114 at 400°, and when the silicon was raised to 1·24 per cent., the corresponding values were 0·127 and 0·109. Silicon, nickel, vanadium, and manganese lower the conductivity—*vide infra*, the special steels—the influence of phosphorus is negligible; and chromium and tungsten raise the conductivity. Structure is of less importance than composition, though ferrite is a better conductor than eutectoidal pearlite. K. Honda and T. Simidu obtained the following results for Swedish iron, and for steels with different proportions of carbon, between the temp. named:

Swedish iron	30°	137°	234°	375°	516°	613°	710°	834°
	0·134	0·128	0·119	0·109	0·095	0·086	0·084	0·078
0·18 per cent. C	30°	123°	214°	325°	504°	639°	768°	926°
	0·108	0·108	0·108	0·101	0·089	0·085	0·072	0·075
0·44 per cent. C	30°	156°	230°	392°	540°	643°	773°	862°
	0·081	0·080	0·081	0·079	0·072	0·070	0·060	0·062
0·64 per cent. C	30°	118°	248°	368°	523°	639°	771°	926°
	0·105	0·105	0·103	0·098	0·088	0·086	0·069	0·076
0·80 per cent. C	30°	179°	242°	369°	508°	629°	757°	897°
	0·101	0·101	0·101	0·095	0·092	0·082	0·073	0·077
1·02 per cent. C	30°	116°	254°	360°	544°	625°	758°	886°
	0·103	0·101	0·103	0·100	0·095	0·089	0·074	0·077
1·30 per cent. C	30°	110°	214°	322°	530°	637°	749°	874°
	0·086	0·086	0·087	0·088	0·078	0·074	0·066	0·067
1·50 per cent. C	30°	129°	219°	303°	418°	527°	631°	775°
	0·086	0·086	0·087	0·085	0·083	0·074	0·074	0·066

K. Honda and T. Simidu observed that G. Wiedemann and R. Franz's law—**3**. 31, 5—holds for temp. up to about 900°; and L. Lorenz's law—**3**. 21, 5—applies for Swedish iron; but for steels, the conductivity-resistance curve does not pass through the absolute zero. The subject was discussed by A. Eucken and K. Dittrich. T. Simidu observed that for forged, quenched, and annealed steels, the products of the thermal and electrical conductivities are approximately constant, the mean value is 0·185 or $7{\cdot}75 \times 10^{10}$ in c.g.s. units. This is greater than the theoretical value $6{\cdot}5 \times 10^{10}$, and the discrepancy is attributed to a special molecular condition of the steels which is distinguished from that of other metals by their ferromagnetism. H. Masumoto found that the product of the electrical resistance and thermal conductivity of iron is a little greater than the theoretical; with increasing impurities the product increases slightly. With steels and cast iron, the products increase slightly with increasing carbon-content. Graphitization causes a large increase in the product. Extrapolation gives 0·24 for the product with cementite. The subject was discussed by G. Kirchhoff and G. Hansemann, F. Kohlrausch, A. C. Mitchell, E. Grüneisen, F. A. Schulze, E. D. Campbell and W. C. Dowd, E. Grüneisen and E. Goens, W. G. Kannuluik, R. Kikuchi, and F. A. Fahrenwald.

The "temperature" conductivity, represented by $a^2 = k/Dc$, where D denotes the sp. gr., and c the sp. ht., was found by G. Kirchhoff and G. Hansemann to be for puddled steel with 0·13 per cent. of carbon, $a^2 = 0{\cdot}1694 - 0{\cdot}00034\,(\theta - 15)$, and with 0·25 per cent. of carbon, $a^2 = 0{\cdot}1637 - 0{\cdot}00027\,(\theta - 15)$; and for Bessemer steel, $a^2 = 0{\cdot}1148 - 0{\cdot}00019\,(\theta - 15)$.

P. W. Bridgman found the press. coeff. for the thermal conductivity to be $-0{\cdot}0_63$ for press. between 0° and 12,000 kgrms. per sq. cm. For pressures up to 12,000 kgrms. per sq. cm., P. W. Bridgman found a 0·3 per cent. reduction in the thermal conductivity, so that the press. coeff. for the conductivity is $-0{\cdot}0_63$. For loads in tension of 2050 and 1025 kgrms. per sq. cm., P. W. Bridgman found the percentage change of thermal conductivity to be respectively $-0{\cdot}534$ and $-0{\cdot}32$; the proportional change of thermal conductivity, respectively $-2{\cdot}61 \times 10^{-6}$ and $-3{\cdot}08 \times 10^{-6}$; and the proportional change of sp. thermal conductivity, respectively $-1{\cdot}90 \times 10^{-6}$ and $2{\cdot}37 \times 10^{-6}$. A. Johnstone found that stretching increased the thermal conductivity about 0·5 per cent. for a tension of about 0·7 of the elastic limit, and when the tension was withdrawn the conductivity returned to its original value. H. M. Brown found that a longitudinal magnetic field of 10,000 gausses decreased the thermal conductivity 1·14 per cent., and a transverse field of 4000 gausses decreased it 0·4 per cent.—*vide infra*, magnetic properties of iron. C. Schwarz, A. M. Kuhlmann and A. D. Spillman, S. Saito, E. J. Janitzky, C. Benedicks and co-workers, and F. Riedel investigated the distribution of the temp. in the interior of masses of cooling steel.

The **specific heat** of iron was found by H. Tomlinson [5] to be 0·11302 between 0° and 100°; J. C. Wilcke gave 0·126; A. Crawford, 0·1269; W. Irvine, 0·143; P. L. Dulong and A. T. Petit, 0·1098 between 0° and 100°; 0·1150 between 0° and 200°; 0·1218 between 0° and 300°; and 0·1255 between 0° and 350°; H. V. Regnault gave 0·11352 between 19° and 98°, and 0·11380 at a red-heat. E. Bède gave 0·1123 between 15° and 100°; 0·1153 between 16° and 142°; and 0·1233 between 20° and 274°. L. Lorenz gave 0·1050 at 0°, 0·1107 at 50°, and 0·1136 at 75°; A. Naccari, 0·1091 at 15°, 0·1151 at 100°, 0·1249 at 200°, and 0·1376 at 300°. J. Pionchon gave 0·17654 at 500°, 0·32431 at 700°, 0·218 between 720° and 1000°, and 0·19887 between 1000° and 2000°. E. Grüneisen gave c_p=0·0851 between −190° and 17°, and c_p=0·112 between 17° and 100°. The sp. ht. of iron increases rapidly with a rise of temp.; and the metal undergoes a change between 660° and 720°, since the sp. ht. at 700° is greater than it is at 720°. W. N. Hartley gave 0·213 for the sp. ht. between 750° and 1000°, 0·218 between 954° and 1006°, and 0·19887 between 1050° and 1700°. P. Oberhoffer said that the mean sp. ht. of iron increases from 0·1221 at 250° to 0·1675 at 750° and then remains practically constant up to 500°. O. Byrström gave for the sp. ht. of purified iron:

	0°	50°	100°	150°	200°	250°	300°
Iron .	0·111641	0·112359	0·113795	0·115950	0·118821	0·122410	0·126719

P. L. Dulong and A. T. Petit represented the effect of temp. on the true sp. ht. by $0\cdot1062+0\cdot0_{4}56\theta+0\cdot0_{6}24\theta^{2}$, and on the mean sp. ht. by $0\cdot1062+0\cdot0_{4}28\theta+0\cdot0_{7}8\theta^{2}$. O. Byrström, on the true sp. ht. by $0\cdot11164+0\cdot0_{5}718\theta+0\cdot0_{6}1436\theta^{2}$, and on the mean sp. ht. between 0° and 660°, J. Pionchon gave $0\cdot11012+0\cdot0_{4}25\theta+0\cdot0_{7}547\theta^{2}$; between 660° and 720°, $0\cdot57803-0\cdot001436\theta+0\cdot0_{5}1195\theta^{2}$; between 720° and 1000°, $0\cdot218-39\theta^{-1}$; and between 1050° and 1160°, $0\cdot19887-23\cdot44\theta^{-1}$. W. A. Roth and W. Bertram gave for the sp. ht., c, of α-iron up to 720°, $c=0\cdot1060+0\cdot0_{4}6003(\theta-20)$; and for the true at. ht.:

	100°	200°	300°	400°	500°	600°	700°
c .	6·46	7·13	7·80	8·47	9·14	9·81	10·48

J. A. Harker found the mean sp. ht. of iron—containing 0·01 per cent. of carbon, 0·02 per cent. silicon, 0·03 per cent. sulphur, and 0·04 per cent. phosphorus—between 0° and

	200°	500°	750°	850°	900°	1050°	1100°
c .	0·1175	0·1338	0·1537	0·1647	0·1644	0·1512	0·1534
C .	—	7·47	8·58	9·20	9·18	8·44	8·57

W. Jaeger and H. Diesselhorst gave 0·1054 for the sp. ht. of iron at 18°, and 0·1185 at 100°; P. Schübel, 0·1096 between 18° and 100°, 0·1201 between 18° and 300°, and 0·1351 between 18° and 600°; and W. A. Tilden, 0·10983 between 17° and 100°; and H. Schimpff, 0·1098 between 17° and 100°.

H. A. Jones and co-workers represented the at. ht. at T° K. by $C_p=4\cdot39+0\cdot00405T$. W. H. Dearden found the sp. ht. of iron—with 0·04 per cent. of carbon; 0·006, S; 0·006, Si; and 0·069, P—to rise from 0·0852 at 17° to a maximum of 0·1942 at 108°, and then to fall to about 0·12 in the range of 150° to 200°, and it then rises again. This has not been confirmed. The high value at about 110° is said to correspond with other abnormalities, sonorousness, resistance, and mechanical properties. E. Lecher reported a maximum at about 740°. H. Klinkhardt found the A_2-arrest approximates to 760° with a step-down of rather more than 8 cals. per gram-atom per degree. He gave for the minimum value approximately 10·3 cals. per gram-atom per degree for β-iron, and 8·6 for γ-iron. Observations were made by J. B. Austin, F. K. Bailey, L. F. Bates, A. I. Brodsky, H. Klinkhardt, F. Morawe, J. F. Shadgen, N. Stücker, and M. Stupakoff. For W. Gerlach's curve of the temp. coeff. of the sp. ht., *vide infra*, the electrical resistance of iron.

P. Weiss and co-workers investigated the heat changes which occur through the ranges where iron is losing its magnetization, and they found that the sp. ht. increased to a maximum as the substance approached the Curie point; there was then an abrupt drop in the curve to a low value characteristic of paramagnetic substances. The magnetic transformation is thus associated with a comparatively large change in the internal energy, which is manifested by the excess of sp. ht. over what was normally expected. This excess falls off with diminishing temp. below the Curie point, but it is still sensible at room temp. so that it alters the shape of the sp. ht. curve. P. Weiss and P. N. Beck gave:

	170°	202·7°	453°	598°	711°	753°	777·7°	806°	844·3°	873·7°
c .	0·1012	0·1168	0·1458	0·1756	0·2185	0·3136	0·2280	0·2179	0·2206	0·2503

F. Wüst and co-workers obtained confirmatory results, but they smoothed their curve so that the deviations were either eliminated or averaged. F. Wüst and co-workers gave for the mean sp. ht. of purified iron, $0·10545+0·0_4 5684\theta$ between 0° and 725°; $0·1592-1·63\theta^{-1}$ between 785° and 919°; $0·14472+18·31\theta^{-1}+0·0_7 5\theta$ between 919° and 1404·5°; $0·21416-77·18\theta^{-1}$ between 1404·5° and 1528°; and $0·15012+70·03\theta^{-1}$ between 1528° and 1600°. For the sp. ht., they also gave $0·10545+0·00011368\theta$ between 0° and 725°; and $0·14472+0·0_6 10\theta$ between 919° and 1404·5. R. Durrer gave the sp. ht., *c*, and the at. ht., *C*, of electrolytic iron, between 0° and

	Solid							Molten	
	725°	785°	918°	920°	1404°	1405°	1528°	1528°	1600°
c .	0·1467	0·1571	0·1574	0·1647	0·1578	0·1592	0·1637	0·1959	0·1939
C .	8·19	8·77	8·79	9·20	8·81	8·89	9·14	10·94	10·83

Discontinuities in the curve at 1404° and 919° correspond with the A_4- and A_3-arrests, respectively. The character of the curve at the A_2-arrest between 725° and 785° is different from the others, and it is attributed to the reversible transformation α-Fe$\rightleftharpoons\beta$-Fe. S. Umino found the mean and true sp. hts. of iron with 0·04 per cent. of carbon to be:

	100°	200°	400°	600°	700°	750°	800°	850°
Mean .	0·1102	0·1133	0·1226	0·1347	0·1436	0·1494	0·1578	0·1645
True .	0·113	0·121	0·144	0·178	0·215	0·251	0·273	0·262
	900°	1100°	1200°	1300°	1400°	1500°	1570°	1630°
Mean .	0·1682	0·1699	0·1696	0·1698	0·1725	0·1726	0·1570	0·1630
True .	0·170	0·176	0·180	0·182	0·186	0·188	0·222	0·222

The abnormal values for the true sp. ht., in the range of the ferromagnetic change, are shown up by the curves. The sp. ht. of the molten metal does not change in the range of temp. examined. S. Umino measured the sp. ht. of electrolytic iron, and obtained for the true sp. ht., *c*:

	850°	900°	950°	1000°	1200°	1350°	1450°	1500°	1560°
c .	0·185	0·185	0·161	0·163	0·172	0·179	0·185	0·185	0·194

The results are plotted in Fig. 242, along with values for the mean sp. ht. There are abrupt changes at the A_3- and A_4-arrests, and at the m.p. In the other ranges of temp., the sp. ht. increases linearly with temp. Above the A_2-point, the sp. ht. remains constant until the A_3-point is reached, when there is a discontinuous decrease, but afterwards, an increase with rise of temp. up to the A_4-point, where a discontinuous increase again occurs, and then remains constant. During fusion there is a marked increase. The two portions of the true sp. ht. curve, lying above and below the curve for γ-iron, probably fall on the same straight line. A. Mallock observed no discontinuity in the sp. ht. between 1400° and 1500°, but the sp. ht. at ordinary temp. is about three times as great as it is above the recalescence point.

J. Maydel gave for the at. ht., $A=8\cdot803-938\cdot9(\theta+330)^{-1}$. A. Eucken and H. Werth gave for the at. hts. at constant vol. and constant press., and for Θ, the characteristic temp. in Debye's function—**1.** 13, 15—for electrolytic iron:

$T°$ K.	16·90°	26·80°	40·00°	84·00°	109·90°	148·52°	189·64°	205·59°
C_p .	0·03732	0·1125	0·3673	2·182	3·200	4·312	5·015	5·245
C_v .	0·03732	0·1125	0·3673	2·178	3·189	4·286	4·970	5·182
Θ .	392	431	430	420	417	395	368	350

F. M. Jäger gave 5·89 Cals. for the at. ht. of α-iron at 0°; 21·0 Cals. at 756°; 8·89 Cals. at 790° (β-iron), and it remains constant at 8·086 Cals. between 919° and 1200°; at 1404·5° it becomes about 12 Cals., and quickly falls to 8·382 Cals. (δ-iron), which value it retains up to the m.p.

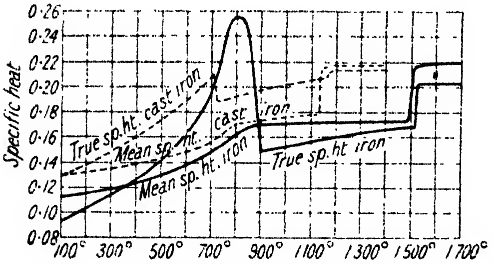


FIG. 242.—The Specific Heats of Iron (0·04 per cent. of Carbon) and of Cast Iron (4·12 per cent. of Carbon).

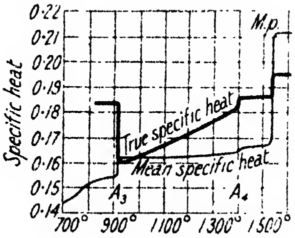


FIG. 243.—The Effect of Temperature on the Specific Heat of Iron.

For temp. below atmospheric, U. Behn gave 0·0721 between −186° and −79°, and 0·0999 between −79° and 18°; P. Ewald, 0·0697 at −135°, 0·1001 at −38°, and 0·1062 at 28°; P. Nordmeyer and A. L. Bernoulli, 0·095 between −185° and 20°; T. W. Richards and F. G. Jackson, 0·0859 between 20° and −188°; and J. Dewar, 0·0175 between −253° and −196°. E. H. and E. Griffiths' results down to −223°, and P. Günther's for still lower temp., are as follow:

	97·5°	20·5°	0°	−63°	−163°	−223°	−231·1°	−237·9°	−241·1°
c .	0·1137	0·1078	0·1046	0·0960	0·0621	0·0176	0·0058	0·0043	0·0027
C .	6·35	6·02	5·84	5·36	3·47	0·98	0·325	0·244	0·152

W. H. Rodebush and J. C. Michalek gave 0·0326 at −200·2°; 0·0491 at −182·7°; and 0·096 at −75·1°; and M. Kawakami, 0·1133 between 30° and 172·3°; 0·1148 between 30° and 205·8°; and 0·1170 between 30° and 250°. Observations on sp. ht. were also made by F. A. Fahrenwald, J. W. Richards, H. Klinkhardt, H. E. Schmitz, and M. Pirani.

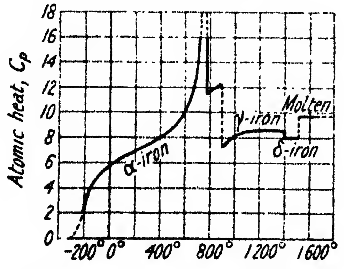


FIG. 244.—The True Specific Heat of Iron.

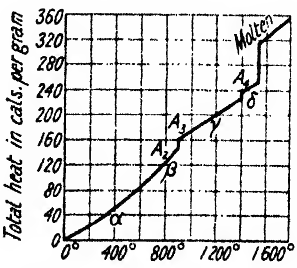


FIG. 245.—The Thermal Capacity of Iron.

The data were collected by O. C. Ralston, and the results for the sp. ht. and the thermal capacity of iron are summarized in Figs. 244, 245. The sp. ht. rises from absolute zero and, as ordinary temp. is approached, it turns off to a horizontal asymptote as in the case of most substances. The effect of the magnetic component of the sp. ht. now appears bending the sp. ht. curve upward until a peak is reached where the magnetic change proceeds for test. After the Curie point, A_2, is reached, the sp. ht. of paramagnetic α-iron, *i.e.* β-iron, is nearly constant, and then abruptly changes at the A_3-arrest and remains nearly constant in the range of stability of γ-iron. There is another break at the A_4-arrest as δ-iron is formed, and, according to P. Oberhoffer and W. Grosse, the value for δ-iron is a continuation of the curve for normal α-iron. There is another break at the m.p., and the sp. ht. of molten iron then remains constant. The thermal capacity curve, Fig. 245, explains itself. A gram of cold iron requires 252·3 cals. to bring it to the m.p., and 317·2 cals. to produce a gram of liquid iron from cold iron; and it also follows that at the b.p. of iron, it requires 613·6 cals. to produce a gram of liquid iron at the b.p., or 2403·6 cals. to produce a gram of iron gas at its b.p. It is assumed that the sp. ht. of molten iron is constant 0·176, and that the latent heat of vaporization is near 100 Cals. per gram-atom. The thermal capacity curve for ferromagnetic α-iron is not a straight line, but rather a curve of increasing slope which culminates in the A_2-arrest. The energy required to raise the temp. is expended in increasing the thermal motions of atoms or groups of atoms in the space-lattice, in increasing the distance between the atoms in the space-lattice, in overcoming the tendency of the atoms to orient themselves magnetically, and in electronic displacements.

P. Weiss, on the basis of his theory of an internal field, showed that a ferromagnetic substance should exhibit characteristic changes in the neighbourhood of its magnetic critical point. The argument runs somewhat as follows:

The magnetic energy per c.c. of a ferromagnetic substance is $W=-\frac{1}{2}HI$, where I is the intensity of magnetization, and H is the molecular field. It is assumed that $H=nI$, where n is a constant dependent on the nature of the material. Hence, $W=-\frac{1}{2}nI^2$, and $dW/dt=-\frac{1}{2}nd(I^2)/dT$, where T is the temp. dW/dt will contribute to the sp. heat of the substance which will become equal to $S=s+(1/\rho J)(dW/dI)$, where s denotes the sp. ht. neglecting the magnetic contribution; S, the total sp. ht.; ρ, the density; and J, the mechanical eq. of heat. Consequently, $S=s-(n/2\rho J)d(I^2)/dT$.

From the shape of the magnetization-temperature curves, P. Weiss concluded that the sp. ht. should rise to a maximum at the critical temp., and then decrease discontinuously owing to the disappearance of the magnetic term. The results of observations with iron found by P. Weiss and co-workers, A. Piccard and A. Carrard, were not wholly in agreement with the theory. The best results were obtained with nickel, but the observations of W. Sucksmith and H. H. Potter with Heusler's alloy and with nickel were not in agreement with P. Weiss' theory of the sp. ht. of ferromagnetic substances. Similarly with L. F. Bates' observations with manganese arsenide.

A. Weinhold gave for the sp. ht. of wrought iron, between θ°_2 and θ°_1, $c=0{\cdot}105907+0{\cdot}00003269(\theta_2-\theta_1)+0{\cdot}0_722159(\theta_2-\theta_1)^2+0{\cdot}0_3110795(\theta_2-\theta_1)^3$; A. Naccari, $c=0{\cdot}10440+0{\cdot}0001075\theta$; and E. Bède, $c=0{\cdot}1053+0{\cdot}000071\theta$. H. V. Regnault found for hardened steel of sp. gr. 7·7982, 0·1175 between ordinary temp. and 100°, and for annealed steel of sp. gr. 7·8609, 0·1165. C. Chappell and M. Levin observed no difference, within the limits of experimental error, between the sp. ht. of cold-drawn metals, before and after annealing. The sp. ht. of mild steel was 0·1117 to 0·1120, and that of hard steel 0·1132 to 0·1134 in the two conditions respectively. O. Byrström's values for the sp. hts. of cast iron and of cast steel are:

	0°	50°	100°	150°	200°	250°	300°
Cast steel .	0·11782	0·11850	0·11986	0·12190	0·12462	0·12802	0·13211
Cast iron .	0·12768	0·12830	0·12954	0·13140	0·13388	0·13698	0·14070

O. Petterson and E. Hedelius gave for wrought iron 0·108079 between 4° and 27°. H. V. Regnault gave 0·12983 for white cast iron, 0·12728 for cast iron, and 0·11848 for cast steel. W. Schmidt found the sp. ht. of pig-iron with approximately the eutectic proportion, 4·35 per cent. of carbon, was 0·3136 between 1175° and 1275°, and 0·3216 from 1275° to 1375°. S. Umino found the mean and true sp. hts. of cast iron with 4·12 per cent. of carbon to have the values:

	100°	200°	400°	500°	600°	700°	800°	900°
Mean . .	0·1308	0·1341	0·1400	0·1417	0·1482	0·1542	0·1679	0·1712
True . .	0·131	0·139	0·159	0·172	0·187	0·207	0·194	0·198

	1000°	1050°	1100°	1150°	1200°	1250°	1300°	1350°
Mean . .	0·1748	0·1773	0·1776	0·1791	0·2191	0·2188	0·2185	0·2185
True . .	0·202	—	0·207	—	0·215	0·215	—	0·215

W. Brown found an increase in the sp. ht. of iron with 0·0089 per cent. of carbon; and for steels with about 0·1 per cent. of silicon, 0·14 to 0·32 per cent. of manganese, and

Carbon . . .	0·028	0·05	0·14	0·89	1·23 per cent.
Sp. ht. . . .	0·1134	0·1136	0·1144	0·1192	0·1234

whilst for steels with about 0·48 per cent. of silicon, 0·58 per cent. of manganese, and 0·58, 1·00, and 1·25 per cent. of carbon, the sp. hts. were respectively 0·1170, 0·1220, and 0·1225. While A. Meuthen found breaks at 1·0 per cent. of carbon in the curves for the sp. ht. of steels with different proportions of carbon, M. Levin and H. Schottky obtained only a linear relation. K. Honda gave for forged and annealed steels between 20° and 150°:

Carbon .	0·00	0·10	0·20	0·50	0·70	0·89	1·11	1·29	1·48 per cent.
Forged .	0·1126	0·1135	0·1145	0·1179	0·1195	0·1219	0·1225	0·1230	0·1233
Annealed	—	0·1131	0·1129	0·1144	0·1167	0·1187	0·1190	0·1197	0·1212

for quenched steel, 0·1188; and when annealed, 0·1176; and for cast iron, 0·1371 when cast; annealed at 670° for 5 mins., 0·1345; for 10 mins., 0·1316; and for 60 mins., 0·1158.

The sp. ht. of steel should be the sum of the sp. hts. of the contained ferrite and cementite, so that the relation between the percentage of carbon and the sp. ht. should be linear. A. Meuthen, however, found that the curve between 0° and 700° consists of two straight lines intersecting at the eutectoid composition. G. Tammann said that this peculiarity is due to a difference in the size of the cementite grains. M. Levin and H. Schottky observed that with annealed steels there is a linear relation between the sp. ht. and the carbon concentration at room temp. as well as at temp. below the A_1-point. K. Honda showed that the sp. ht. of iron is not a linear function of the proportion of carbon, but is modified by the presence of stresses. The decrease in the sp. ht. of quenched steels produced by a prolonged annealing at 650° is partly due to the release of the strain, and partly to the decomposition of the cementite during the annealing. A high degree of strain in a metal is accompanied by an internal or a molecular disorder, which is equivalent to a small degree of freedom, and hence causes an increase in the sp. ht.

The sp. ht. of cementite has been worked out by S. Umino, who found the true sp. ht., c_p, and the mol. ht., C_p, to be

	0°	200°	220°	300°	500°	600°	700°	800°	900°
c_p	0·1475	0·1495	0·1497	0·1225	0·1660	0·1785	0·1925	0·2100	0·2264
C_p	26·9	51·5	100·4(17·9)	21·1	29·6	35·9	37·7	—	—

The results were plotted as a smoothed curve by S. Umino, but O. C. Ralston showed that the curve has the form shown in Fig. 246, where the break is the A_0-arrest, that is, the temp. of magnetic transformation, or the Curie point of cementite. Obviously, in determining the sp. ht. of steels at elevated temp. by quenching, the hot metal in the liquid of the calorimeter may alter the nature of the constituents. If quenched from below 720°, the thermal capacity will be a function of the carbon-content, but if quenched in the calorimeter from higher temp. the thermal capacity will be a function of the proportion of austenite, martensite, troostite, sorbite, or pearlite. The energy changes involved in passing from austenite to martensite, and from martensite to pearlite have been studied by N. Yamada, S. Umino, and A. Meuthen—*vide infra.* S. Umino's values for the sp. ht. of electrolytic iron and different steels are shown in Fig. 247.

E. Grüneisen found the effect of pressure, p, on the sp. ht., c_p, of iron to be $dc_p/c_pdp=-0{\cdot}0_641$; and $dv/vdp=0{\cdot}0_660$. J. Russner, B. V. Hill, and J. R. Ashworth discussed the relation between the thermal and magnetic constants of iron; E. Grüneisen and E. Goens, the sp. ht. and sp. resistance—*vide infra,* electrical resistance; and J. Russner, and A. H. Stuart, the relation between the sp. ht. and the mechanical constants. According to J. Stefan, and A. Wassmuth, the sp. ht. of magnetized iron is greater than that of unmagnetized iron. J. W. Richards, and J. Maydel discussed some relationships of the sp. ht.; and K. Försterling, the relationship between the lattice energy and the sp. ht. E. D. Eastman and co-workers calculated $C_p-C_v=0{\cdot}10$ Cal. per degree per mol.

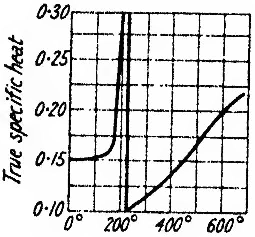


FIG. 246.—The Specific Heat of Cementite.

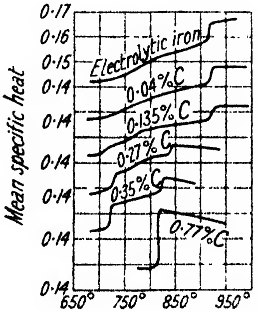


FIG. 247.—Mean Specific Heat Curves of Iron and Steel at Different Temperatures.

Amongst the older determinations of the **melting-point** of iron there is one by L. B. G. de Morveau [6] at 175° on the Wedgwood scale, and one by G. S. Mackenzie at 158° on the same scale. J. F. Daniell gave 1587°; C. S. M. Pouillet, 1500°; T. Carnelley, 1804°; R. Pictet, 1600°; F. Osmond, 1520°; and W. C. Roberts-Austen, 1600°. W. R. Mott gave 1507° for the m.p. of iron; C. Brisker, 1500°; F. Wüst and co-workers, 1528°; S. Umino, 1535°; P. Oberhoffer and W. Grosse, 1528°; H. C. H. Carpenter and B. F. E. Keeling, 1505°; A. Müller, 1485° to 1525° on the heating curve, and 1505° to 1485° on the cooling curve. For purified iron, B. Saklatwalla gave 1510°; H. Harkort, 1501°, and 1504°; D. Hanson and J. R. Freeman, and E. M. Terry, 1530°; R. Sahmen, 1532°; A. G. C. Gwyer, 1515°; R. Ruer and E. Schütz, 1502°; E. Isaac and G. Tammann, 1524° to 1527°; W. Guertler and G. Tammann, 1492°; C. Benedicks and co-workers, 1525°; and when 0·1 per cent. of carbon is present, 1480°; R. Ruer and R. Klesper, and R. Ruer and F. Goerens, 1528°; J. H. Andrew and D. Binnie, 1537°; F. S. Tritton and D. Hanson, 1535°±5°; K. Honda and H. Endo, 1530°; W. Gontermann, 1525°; N. S. Konstantinoff, 1514°; G. K. Burgess, 1507°; G. K. Burgess and R. G. Waltenberg, 1533°, for electrolytic iron with 0·012 per cent. of carbon, 0·072, H; 0·013, Si; and 0·004, P. C. H. M. Jenkins and M. L. V. Gayler gave 1527±3° for the m.p. of 99·98 to 99·99 per cent. iron; this value is based on the assumption that the m.p. of palladium is 1555°, and that of gold, 1063°. The observation of H. C. H. Carpenter and B. F. E. Keeling is based on the m.p. of platinum, 1710°; more recent determinations place the m.p. of platinum 45° to 65° above this value, and hence H. C. H. Carpenter and B. F. E. Keeling's value should probably be 20° to 30° above 1505°. L. I. Dana and P. D. Foote, and W. Guertler and M. Pirani gave for the best representative value, 1530°; H. C. H. Carpenter, 1505°; and

O. C. Ralston, 1537°. A. Mallock studied this subject. T. Carnelley discussed the relation between the m.p. and the coeff. of thermal expansion; W. Crossley, the relation between the m.p. and the at. vol.; K. Honda and H. Masumoto, and L. P. Sieg, the relation between the elastic constants and the m.p.; and G. Moressée, the relation between the m.p., the at. wt., and the latent heat of fusion.

The liquidus and solidus curves for iron and carbon alloys were measured by H. C. H. Carpenter and B. F. E. Keeling, R. Ruer and R. Klesper, S. Kaya, R. Moldenke, J. H. Andrew and D. Binnie, and K. Honda and H. Endo—*vide supra*, the equilibrium diagrams. R. A. Hadfield gave 1135° for the m.p. of Swedish iron with 4 per cent. of carbon; 1220° for grey foundry iron with 3·5 per cent. of carbon (1·75 per cent. Si, and 0·5 per cent. P); 1410° for steel with 0·90 per cent. of carbon; 1453° for steel with 0·30 per cent. of carbon; and 1475° for steel with 0·10 per cent. of carbon. E. Widawsky and F. Sauerwald gave for the liquidus temp. of the iron-carbon alloys:

Carbon .	0·0	0·5	1·0	1·5	2·0	2·5	3·0	3·5	4·0	4·5 per cent.
Liquidus .	1533°	1480°	1458°	1422°	1382°	1341°	1290°	1232°	1170°	1150°

W. Schmidt said that temp. discontinuities at T° K. in the various physical properties of iron conform with the relation $T=nT_m/m$, where T_m, the m.p. of iron, is taken as 1803° K., $m=14$, and n is an integer less than 14. The effect of press. on the m.p. obtained by Clapeyron's equation—1. 6, 4—for $dv=0{\cdot}2735$ c.c., and one atm. press., is $dT=0{\cdot}00330$, meaning that the change in the m.p. is 0·0033° per atm., or 1° per 300 atm. The effect of press. on the A_3- and A_4-arrests has been previously discussed. Z. Herrmann studied the energy at the m.p.; and E. Kordes gave 1·52 for the entropy change on melting.

Most metals pass abruptly from the solid to the liquid state, and are in some cases brittle and easily pulverized near the temp. of incipient fusion, and even if there is a temp. at which the metal becomes viscid before melting, the range between that temp. and the m.p. is very narrow. Ordinary iron is remarkable in developing a viscid character through a considerable range of temp. below its m.p. Thus, at a bright red-heat, the iron is soft enough to be forged; and at a white-heat, it is so pasty that two pieces when pressed together unite intimately and firmly, as also in the operation of *welding*. Platinum, like iron, is a weldable metal. T. Scheerer said that if the iron be quite free from carbon, or nearly so, it can only be imperfectly welded, and even that with great difficulty; he considered that the carbon is necessary to prevent the formation of a layer of oxide on the surface, which prevents adhesion. J. Percy questions the fact and the explanation. The welding may be effected by the extrusion of the melted scale, but if the scale be not liquid the iron will not weld. T. Wrightson compared the phenomenon of welding in iron to the regelation of ice. Wrought iron at a welding temp. possesses the same property of cooling under pressure as exists with freezing water, and on which the accepted theory of regelation depends. The process of melting together, and the process of welding differ in that the latter occurs at a temp. much below the m.p. As in the case of the regelation of ice, the property of welding in iron depends upon a critical condition existing over a limited range of temp. between the molten and the plastic state. T. Turner discussed the semi-fluid state of iron. F. J. R. Carulla noted that the interior of a block of mild steel may be raised to the fusing point whilst the exterior remains solid, and if the surface be pierced the molten interior can be drained off leaving an empty shell. G. J. Snelus thought that the surface had become decarburized by air. R. Wright and R. C. Smith, and R. C. Smith found that reduced iron sinters at 750° to 850°, and precipitated iron at 750°; and B. Garre showed that at about 700° the metal diffuses from particle to particle in the solid state so that the tensile strength of iron powder, compressed at 3000 kgrms. per sq. cm., is raised from 10 to 19·4 kgrms. per sq. mm. after being heated to 700°. The sintering of powdered iron was studied by L. Schlecht and co-workers.

According to R. Hare,[7] if an electric current be passed by means of charcoal points through iron, in vacuo, there is formed a quantity of the vapour of iron which burns with a flash on admitting air, and deposits a yellow film on the glass. H. Pellat said that steel acts on a photographic plate even when separated by a sheet of cardboard, but not when separated by a sheet of glass; the action is attributed to the **volatilization** of the metal at ordinary temp. R. Colson obtained negative results with iron. Possibly the effect was due to the escape of occluded reducing gases. W. Crookes said that the comparative volatility of electrically heated wires of iron is 5·50 when that of gold is 100. According to A. Knocke, the volatilization of iron is sufficiently great to be detected at 755° in vacuo. G. W. C. Kaye and D. Ewen found that when iron is heated to 950° in an inert atm., particles are emitted at right-angles to the surface, leaving the surface etched and pitted. The effect is distinct from volatilization. E. Botolfsen found that iron can be sublimed in a high vacuum at temp. below its m.p. The effect is independent of the origin of the iron and of the presence of certain substances likely to act as catalysts, and at 1300° its rate is of the order of 0·07 per cent. per hr. The sublimate takes the form of a thick deposit of metallic crystals, and is almost pure. J. W. Mellor has noticed a similar effect on the surface of glass and vitreous porcelain if heated rapidly; in this case the effect is probably a mechanical disintegration produced by occluded gases. O. Ruff and W. Bormann gave 2450° for the **boiling-point** of iron; H. A. Jones and co-workers, 3202°; O. P. Watts, 2600°; H. C. Greenwood, 2723° to 2925°; E. Mack and co-workers, 2723°; and W. R. Mott, 3000°. H. Moissan found that iron can be readily volatilized in the electric arc furnace. A sublimate or distillate of iron can be obtained as a grey powder mixed with brilliant malleable scales. The distillation of iron by this process is difficult owing to the violent frothing produced by occluded gases. O. Ruff and co-workers studied the b.p. of soln. saturated with carbon. H. A. Jones and co-workers gave for the **rate of evaporation,** m, of iron, $\log_{10}m=40{\cdot}231/4{\cdot}577-(86350+240)/4{\cdot}577T-(0{\cdot}971/4{\cdot}577)\log_{10}T-0{\cdot}00203T/4{\cdot}577-2675/(4{\cdot}577\times3475)$; and for the **vapour pressure,** p mm., $\log_{10}p=40{\cdot}231/4{\cdot}977+3{\cdot}486-2675/(4{\cdot}577\times1808)-(86350+240)/4{\cdot}577T-(0{\cdot}971-0{\cdot}5)\log_{10}T-0{\cdot}00203T/4{\cdot}577$; or

$T°$ K. .	600°	1000°	1500°	2000°	2600°	3000°	3600°
p. .	$2{\cdot}48\times10^{-20}$	$1{\cdot}76\times10^{-7}$	$3{\cdot}60\times10^{-1}$	$3{\cdot}9\times10^{2}$	$3{\cdot}5\times10^{4}$	$2{\cdot}2\times10^{5}$	$1{\cdot}0\times10^{6}$

H. C. Greenwood estimated a vap. press. of 760 mm. at 2450°. J. Johnston gave for the vap. press. $\log p=-17000T^{-1}+9{\cdot}10$; and R. W. Millar, p mm., of liquid iron, $\log p=1{\cdot}7151\log T-18440T^{-1}+14{\cdot}221$; and for the b.p. at different press.:

p . .	760	500	300	100	50	10	1	0·1 mm.
B.p. .	3235	3097	2930	2670	2520	2225	1900	1655

L. E. Gruner[8] gave for the **heat of fusion** of white cast iron 32 to 34 cals. per gram, or 1·8 to 1·9 Cals. per gram-atom; and for grey cast iron, 23 cals. per gram, or 1·3 Cals. per gram-atom. For purified iron, at 1528°, F. Wüst and co-workers gave 49·4 cals. per gram, or 2·75 Cals. per gram-atom; R. Durrer, 49·35 cals. per gram; Y. Chu-Phay, 66·4 cals.; W. Schmidt, 59 cals. per gram, or 3·3 Cals. per gram-atom; S. Umino, 65·65 cals.; and P. Oberhoffer and W. Grosse, 64·38 cals. C. Brisker based a calculation on assumptions as to the state of carbon in soln., and from the equation for the lowering of the f.p., obtained 31·6 cals. per gram, or 1·765 cals. per gram-atom, or when re-calculated by O. C. Ralston, 57·50 cals. per gram, or 3·210 cals. per gram-atom—the results are poor. C. P. Yap calculated 64·4 cals. per gram for the heat of fusion of α-iron, and 66·4 cals. per gram for that of γ-iron. The subject was discussed by E. Kordes. E. Rabinowitsch and E. Thilo gave for the heat of fusion, 0·12 volt; for the heat of vaporization, 4·09 volts; and for the heat of sublimation at the m.p., 4·21 volts when 1 volt=23 Cals. N. M. H. Lightfoot discussed the effect of the latent heat on the solidification of steel ingots; W. Herz discussed the relation between the heat of fusion and the vibration frequency; and G. Moressée, the thermodynamics of the latent heat of fusion. If L denotes the m.p. at T_m° K.; and A, the at. wt., then $L=3T_m°/A$.

J. Johnston gave 77,800 cals. per mol. for the **heat of vaporization.** H. C. Greenwood gave 88,900 to 94,300 cals. per gram-atom, and E. Mack and co-workers, 71,400 cals. per gram-atom. O. C. Ralston calculated 100,000 cals. per gram-atom, and obtained from Trouton's rule, 77,000 cals. per gram-atom. H. A. Jones and co-workers gave for the latent heat of vaporization, 89,025 cals. at about 1000°. They gave $LT^{-1}=40{\cdot}231-0{\cdot}971 \log_{10}T-4{\cdot}577 \log_{10}m-0{\cdot}00203T-240T^{-1}$.

The **transformation points** of iron are discussed elsewhere. G. Sirovich [9] found an arrest occurs at 370° where the supposed α_1-Fe changes into α_2-Fe—*vide supra*, allotropes of iron. For the A_2-arrest where $\beta\text{-Fe}\rightleftharpoons\alpha\text{-Fe}$, W. C. Roberts-Austen gave 770° on the heating curve; H. Harkort, 764° to 759° on the cooling curve, and 691° to 763° on the heating curve; A. Müller, 765° to 774° on the heating curve, and 766° and 759° on the cooling curve; G. Charpy, 730° on the cooling curve, and 740° on the heating curve; F. Osmond, 780° on the cooling curve, and 800° on the heating curve; H. C. H. Carpenter and B. F. E. Keeling, 790° on the cooling curve; R. Sahmen, 840° on the heating, and 800° on the cooling curves; R. Ruer and E. Schütz, 780° on the heating, and 773° on the cooling curves; E. Isaac and G. Tammann, 740° on the cooling curve; W. Gontermann, 770° on the cooling curve; R. Ruer and R. Klesper, 769° on the cooling and heating curves; A. Westgren and G. Phragmen, 770°; and G. K. Burgess and J. J. Crowe gave 768° on the heating and cooling curves. P. Weiss and P. N. Beck gave 753°; P. Weiss and co-workers, 784°; F. Wüst and co-workers, 755°; P. Oberhoffer and W. Grosse, 785°; S. Umino, 820° to 825°; F. Wever, and R. Ruer and K. Bode, 763°. Observations were made by R. Averdieck, A. Mallock, and C. H. M. Jenkins and M. L. V. Gayler.

W. C. Roberts-Austen placed the *A_3-point* where $\gamma\text{-Fe}\rightleftharpoons\beta\text{-Fe}$ at 895° on the cooling curve; A. Müller gave 894° on the cooling curve, and 917° on the heating curve; H. C. H. Carpenter and B. F. E. Keeling, 900° on the cooling curve; H. Harkort, 888° to 875° on the cooling curve, and 910° to 917° on the heating curve; G. Charpy, 840° on the cooling curve, and 865° on the heating curve; F. Osmond, 880° on the cooling curve, and 905° on the heating curve; R. Sahmen, 888° on the cooling curve; E. Isaac and G. Tammann, 832° on the cooling curve; W. Gontermann, 852° on the cooling curve; F. Wever, 900°; G. K. Burgess and J. J. Crowe, 909° on the heating curve, and 898° on the cooling curve; and R. Ruer and R. Klesper, 898° on the cooling, and 906° on the heating curves. F. Wüst and co-workers gave 919°; P. Oberhoffer and W. Grosse, 906°; S. Umino, 906°; E. M. Terry, 903°; T. Ishiwara, 890°; and K. Honda and H. Takagi, 889° to 898°. Observations were made by C. H. M. Jenkins and M. L. V. Gayler. H. Quinney found that the time-temp. curve of single crystals falls about 4° below that for polycrystals, but the Ac_3-arrest is the same in both cases. According to W. Rosenhain, of the work performed during the plastic deformation of a mild steel under tensile stresses, 10 per cent. is dissipated as heat, and the remainder is expended in doing internal work; this work is assumed to involve a change of phase from the crystalline to the plastic state.

For the A_4-arrest, where $\delta\text{-Fe}\rightleftharpoons\gamma\text{-Fe}$, R. Ruer and R. Klesper gave 1401°, F. Wever, and W. Gontermann, 1411°, on the heating and cooling curves. R. Ruer and K. Kaneko gave 1420°; D. Hanson and J. R. Freeman, 1400°; P. Weiss and G. Foëx, 1395°; T. Ishiwara, 1390°; and E. M. Terry, 1406°. Observations were made by C. H. M. Jenkins and M. L. V. Gayler.

R. Ruer and F. Goerens, G. K. Burgess and J. J. Crowe, E. Maurer, and H. le Chatelier discussed the effect of the *speed of heating and cooling* on the transition points, and the effect of other influences have been previously described. G. Tammann said that at 770°, α-iron passes into the β-form, which at 890° is transformed with contraction into the γ-form. These transformations are reversible, and the influence of press. on the transition temp. may be calculated by aid of the formula,

$dT/dp=\delta T/Rp$. In the transformation of the α- into the β-form, the value $dT/dp=0$, that is, the temp. of the transformation, is independent of the press. At 770°, under a press. of 12,000 kgrms. per sq. cm., the transition curves of the α- into the β-form and of the β- into γ-form cut one another at a triple point, where α-, β-, and γ-iron are in equilibrium. Observations were made by H. Hort, and F. K. Bailey.

Lord Kelvin (W. Thomson) pointed out that the theory of the mutual convertibility of heat and mechanical work in reversible operations when applied to these phenomena proves (i) that a piece of soft iron at a moderate or low red-heat, when drawn gently away from a magnet experiences a cooling effect, and when allowed to approach a magnet experiences a heating effect; that nickel and cobalt at high temp., within some definite range below that of melting copper, experience the same kind of effects when subjected to similar magnetic operations. (ii) That cobalt at ordinary atm. temp., and at all temp. upwards to its temp. of maximum inductive capacity, experiences a cooling effect when allowed to approach a magnet slowly, and a heating effect when drawn away.

W. C. Roberts-Austen estimated 2·86 cals. for the **heat of transformation** of γ-iron into β-iron; and 1·00 Cal. for β-iron into α-iron; P. N. Laschtschenko gave 5 cals. per gram, or 0·28 Cal. per gram-atom, for the former, and 6·1 cals. per gram, or 0·38 Cal. per gram-atom, for the latter. W. Schneider gave 13·2 cals. per gram for the heat of transformation of γ-iron into α-iron, and said that the value decreases linearly with increasing proportions of carbon up to 6·68 per cent., when it disappears. S. Evershed calculated for a change at 700° an absorption of 4·5 cals. per gram; at 770° to 810°, when α-iron changes to β-iron with the loss of magnetism, an absorption of 1·4 cals. per gram; at 919°, when β-iron changes to γ-iron, an absorption of 6·7 cals. per gram; at 1405°, when γ-iron changes to δ-iron, an absorption of 1·9 cals. per gram; and at 1528°, when solid iron becomes liquid, an absorption of 49·3 cals. per gram.

C. P. Yap calculated 2·0 cals. per gram for the heat of transformation of γ-iron to δ-iron; and Y. Chu-Phay, 2·2 cals. per gram, and for α-iron to γ-iron, 5·5 cals. per gram. R. Durrer found 6·56 cals. per gram for the heat of transformation at the A_2-arrest. W. A. Roth and W. Bertram gave 0·324 Cal. per gram-atom for the heat of the transformation at 750°. Estimates of the heat of transformation at the A_2-arrest were made by F. Osmond, 1·3 cals. per gram; A. S. Stansfield gave 1·0 cal.; J. Pionchön, 5·3 cals.; F. Wüst and co-workers, and S. Umino, 3·65 cals. S. Umino gave 3·1 to 5·60 cals. per gram for the heat of transformation at the A_3-point. F. Osmond gave 3·8 cals.; A. S. Stansfield, 2·86 cals.; F. Wüst and co-workers, 6·56 cals.; P. Oberhoffer and W. Grosse, 5·6 to 6·765 cals. R. Durrer, 6·67 cals.; and A. Meuthen, 3·0 cals. W. Bertram gave 0·324 Cal. per gram-atom at 750°. S. Umino gave 2·53 cals. per gram for the heat of the A_4-transformation; F. Wüst and co-workers, 1·94 cals.; P. Oberhoffer and W. Grosse, 2·531, and R. Durrer, 1·94 cals.

S. Umino gave for the heat of fusion of the eutectic, at 1135° with 4·25 per cent. of carbon, 46·63 to 47·0 cals. per gram of alloy. W. Schmidt gave 59 cals. per gram for 4·35 per cent. carbon. The other heats of transformation are not unique. S. Umino's value for the Curie point, at A_0, is 9·72 cals. per gram of cementite at 150° to 220°. The following may tentatively be taken as the best representative values for the heats of transformation, Q cals. per gram, of iron:

	A_2	A_3	A_4	M.p.	B.p.
Q	3·65	5·0	2·5	65·0	1660

The thermal changes during the transformations of the constituents of the iron-carbon alloys.—N. Yamada, and S. Umino studied the rapid quenching of steels in order to obtain the maximum amount of martensite with as little undecomposed austenite as possible. The thermal capacity of the result represents the normal thermal capacity together with the energy involved in passing across the

A_1-line from austenite to martensite. The quenching prevents the formation of pearlite, so that the result is definite and is represented by the *austenite-martensite* curve, Fig. 248. The *martensite-pearlite* curve—*vide supra,* martensite—was obtained by quenching samples from the austenite field, tempering one at 500° whilst the other remained in the martensite condition, and heating them separately in a calorimeter at 350° to 400°. The difference represented the heat of transformation of martensite to pearlite—excepting that hypereutectoid steels also contained austenite. The hypereutectoid samples on the martensite-pearlite line were quenched from temp. below the cementite solubility line, whilst the hypereutectoid samples quenched from within the austenite field form an upward continuation of the hypoeutectoid martensite-pearlite line. The difference is supposed to represent the heat of precipitation of cementite from austenite; it is represented in Fig. 248 by the *austenite-cementite* above the A_1 curve. The total thermal capacity curves in passing from A_3 down to A_1, represent the heat involved in passing these points, which correspond with the A_3+A_2+*austenite-martensite* curve in the diagram. By extrapolation to zero carbon, the A_3-heat is 12 cals. per gram. For hypereutectoid steels it corresponds with the austenite-martensite transformation alone. S. Umino also arranged for the austenite to be transformed into pearlite instead of martensite, and so obtained the *austenite-pearlite* curve—*vide supra,* martensite. Subtracting the martensite-pearlite heats from the austenite-pearlite heats gives the heats indicated in the *austenite-martensite* curve — *vide supra,* martensite. Eutectoidal steel, having 0·9 per cent. of carbon, furnishes only one thermal anomaly as the austenite passes into 100 per cent. pearlite. At this temp. the heat involved represents the transformation of austenite to α-iron and cementite from the supersaturated solid soln. of α-iron plus the heat of the A_3-transformation. By arranging for the γ-iron to have been transformed into α-iron, the heat of the austenite-martensite transformation is eliminated, and for hypoeutectoid steels, the heat involved is proportional to the carbon or cementite content, and it represents the heat of precipitation of cementite from its soln. in α-iron, or, conversely, the heat of dissolution of cementite in α-iron—N. Yamada gave 75·3 cals. per gram of cementite, and S. Umino, 75·9 cals. The austenite-pearlite curve also enables the heat of precipitation of cementite from γ-iron to be calculated—A. Meuthen gave 118·5 cals. per gram of cementite, and S. Umino, 120 cals. N. Yamada obtained 83·6 cals. for the heat of precipitation of cementite in hypereutectoid steels above the A_1-arrest. This datum is intermediate between the values for α- and γ-iron, and it is taken to mean that, in quenching, from temp. intermediate between A_1 and the cementite solubility curve, some austenite survived, and only part was converted into martensite. The heat effects involved in the mild tempering of martensite to furnish atomically-displaced carbon—troostite—or, on further tempering, to furnish dispersed cementite—sorbite—and on further tempering, crystallized cementite—pearlite — are probably summated in the difference between the heats of the austenite-martensite and the austenite-pearlite transformations. According to M. Kawakami, the heat of precipitation of cementite from α-martensite is 3·7 cals. per gram, and it is about half as large as is that from β-martensite.

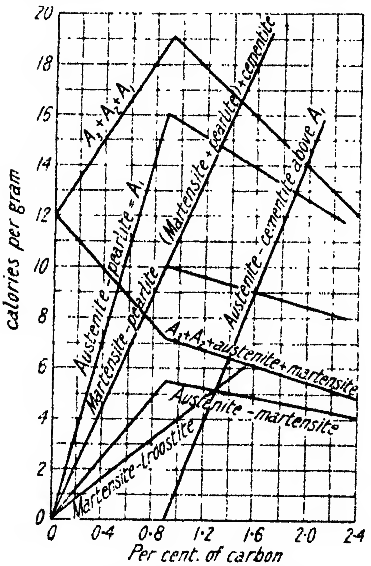


FIG. 248.—Heat Changes in the Transformations of Steels.

M. Kawakami, assuming that there are two forms of martensite, α and β—*vide supra*—and that heating to 200° decomposes only the α-form, leaving the β-form which requires for decomposition a temp. of 370°, measured the heat involved, and obtained the results indicated in the *martensite-troostite* curve, Fig. 248. The heat involved in tempering eutectoid steel at 200° is 3·7 cals. per gram. If troostite is formed by the conversion of a super-saturated solid soln. of cementite in α-iron into atomically-dispersed carbon in α-iron, the heat effect is 410 cals. per gram of carbon, or 4920 cals. per gram-atom; but if troostite is cementite precipitated from a supersaturated solid soln. in α-iron, the heat effect is 27·4 cals. per gram of cementite, or 4920 cals. per mol. O. C. Ralston summarized, in Table XXXVIII, the heat changes in eutectoidal steels with 0·9 per cent. of carbon.

TABLE XXXVIII.—THE THERMAL VALUES OF THE TRANSFORMATION IN EUTECTOID STEELS.

Metallographic change	Supposed chemical change	Heat liberated (in calories)		
		per gram of pearlite	per gram of cementite	per mol. of cementite
Austenite→martensite	Solution α-Fe→solution α-Fe	5·9	43·8	7,870
Martensite→troostite	Solution α-Fe→α-Fe+carbon	3·7	27·4	4,920
Troostite→pearlite	α-Fe+carbon→α-Fe+Fe_3C	6·2	46·0	8,260
Martensite→pearlite	Solution α-Fe→α-Fe+Fe_3C	9·9	73·0	13,170
Austenite→pearlite	Solution γ-Fe→α-Fe+Fe_3C	15·8	117·2	21,040

H. Esser and W. Grass gave for the austenite→pearlite transformation, 21·22 cals. per gram, and R. Averdieck, 22·54 cals. A. Meuthen's value, 3·0 cals., for the pearlite transformation is rather low. S. Umino also calculated thermal values, in calories, for the A_1-, A_2-, and A_3-arrests, and obtained:

	Electrolytic iron	Percentage of carbon in steel				
		0·040	0·135	0·270	0·350	0·770
A_1 . .	0·00	0·67	2·40	4·70	6·00	13·60
A_2 . .	3·63	3·55	3·50	3·36	3·23	3·18
A_3 . .	5·35	5·00	5·48	3·66	3·50	0·80

A. Meuthen obtained for iron alone, A_2=5·60 cals. and A_3=3·0 cals.; and the results are nearly equivalent to a reversal of S. Umino's results. S. Umino traced the A_2 transformation as far as 0·770 per cent. of carbon; and he traced the effects of the magnetic component of the sp. ht. as low as 130° below the A_2-transformation, and a slight disturbance probably occurs very much below this. The extrapolation of the A_3-arrest to 0·9 per cent. carbon, 100 per cent. pearlite, gives zero for the thermal value of the A_3-transformation, whilst the A_1-transformation takes 15·95 cals. The thermal value of the A_2-transformation is not added to that of the A_1-transformation, because the A_2-change is not a discontinuity in the thermal capacity curve, Fig. 249, but only a change of direction, for the sp. ht. is the change in the thermal capacity, Q, with temp. θ, namely, $dQ/d\theta$. According to A. McCance, Q=3·2 cals. is the mean value of the A_3-transformation. Where the A_2- and A_3-arrests are merged into one, and Q_m denotes the energy of demagnetization, and A. McCance calculated:

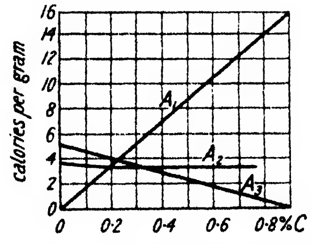


FIG. 249.—The Thermal Values of the A_1-, A_2-, and A_3-Transformations.

	752°	742°	732°	716°	700°
Q_m . . .	0·23	0·93	2·10	3·74	4·95 cals.
Q' . . .	3·4	4·1	5·3	6·9	8·1 ,,

The A_2-point for the steel with 0·77 per cent. carbon is higher than the A_3-point, because the A_3S-line, Fig. 249, crosses the A_2-line at about 0·6 per cent. of carbon. These results may all be regarded as first approximations to the truth in a very difficult quest. The subject was studied by F. Stäblein and H. Jäger.

According to N. Yamada, the heat of dissolution of carbon in iron, measured by the difference of the heat of dissolution of quenched and tempered carbon steels in molten alkali nitrate, is as follows :

Carbon . .	0·38	0·52	0·65	0·70	1·30	1·7 per cent.
Heat dissolution.	4·3	6·2	8·0	8·2	14·4	19·5 cals.

and for the two last hypereutectoid steels, quenched at 750°, the values were respectively 9·3 and 8·8 cals.—*vide* Fig. 250. This shows that the heat of dissolution of carbon in iron increases linearly with the contents of carbon in the steel, and amounts to 1130 cals. per gram of carbon, or 75·3 cals. per gram of cementite ; and the mol. ht. of dissolution of carbon or cementite is then 13·6 Cals. W. Schneider gave 33·2 cals. per gram for the heat of solid soln. of Fe_3C in α-iron.

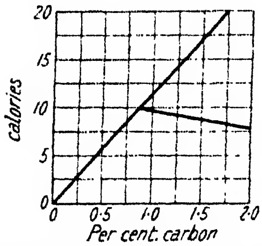


Fig. 250.—Heats of Dissolution of Carbon in Iron.

E. D. Eastman,[10] and G. N. Lewis and co-workers calculated the **entropy** of iron atoms by two different methods to be 6·5 to 7·0 cals. per degree at 25°. The subject was discussed by W. Herz, K. K. Kelley, R. D. Kleeman, B. Bruzs, and W. M. Latimer. Some results calculated by W. H. Rodebush and J. C. Michalek, and O. C. Ralston from the results of plotting the true at. ht. against the natural logarithms of the absolute temp., gave for the entropy, in cals. per gram :

	0°	25°	100°	200°	400°	600°	720°	800°	900°
Entropy .	6·36	6·87	8·24	9·78	12·45	14·74	16·00	17·41	18·47
	906°	906°	1000°	1200°	1400°	1400°	1535°	1535°	1600°
Entropy .	18·63	18·86	19·39	20·68	21·71	21·77	22·41	24·00	24·39

O. C. Ralston calculated 66·74 units for the absolute entropy of cementite at 700°, and 31·94 units at 25°, he also gave for the relative entropy of cementite :

	0°	100°	200°	220°	300°	400°	600°	700°	720°
Entropy .	0	5·79	12·92	16·90	18·94	23·40	31·01	34·8	35·68

J. B. Austin gave for the entropy, S ; heat capacity, Q Cals. for gram-atom ; and free energy, F, of α-iron :

	−273·1°	−123·1°	0°	100°	500°	1000°	1535°
S .	0	2·83	6·10	8·10	13·72	19·27	22·88
Q .	0	290	950	1566	4689	10280	15945
F .	0	−134	−715	−1455	−5911	−14251	−25400

and for γ-iron :

	−273·1°	−100°	0°	100°	500°	1000°	1500°
S .	0	4·98	7·90	9·94	15·60	19·86	22·92
Q .	0	538	1185	1880	5016	9411	14048
F .	960	636	−12	−867	−6083	−14911	−25630

A. Eucken and H. Werth calculated for the entropy at the transition point $\alpha \rightleftharpoons \gamma$ at 1181° K., 19·35 cals. per gram-atom for α-iron, and 18·59 cals. per gram-atom for γ-iron ; and W. M. Latimer and R. M. Buffington, values for the relative entropy of $Fe^{\cdots}$-ions. R. Dallwitz-Wegener discussed the **free energy** of the element.

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§ 20. Optical Properties of Iron and Iron-Carbon Alloys.

Powdered iron obtained by reducing the heated oxide in hydrogen at a comparatively low temp., is a powder which is dull grey or black in **colour**, and it acquires a silver-white lustre under the burnisher ; according to G. Magnus,[1] if reduced at a higher temp., the powder is greyish-white. J. L. C. Schroeder van der Kolk found that the streak of iron on a biscuit tile is brownish, like that of graphite. M. Faraday said that thin films are dark brown by transparent light, and steel-grey by reflected light. B. Dessau obtained thin films which were grey in transmitted light; and G. T. Beilby, blue by reflected light. A. W. Wright observed that a thin film of iron in transmitted light appears of a neutral tint with a faint brownish tinge, and E. van Aubel, and L. Houllevigue added that thin films deposited on glass by cathode spluttering, or electrolysis, are transparent, and brown. For layers 31 to $72\mu\mu$ thick, L. Houllevigue found the transparency to be an exponential function of the thickness. G. le Bon observed that ordinary light contains waves, which he called *la lumière noire*, which will traverse thin sheet iron and produce photographic effects. G. Govi found that films of red-hot iron up to 0·4 mm. thickness are opaque. C. A. Skinner and A. Q. Tool said that films obtained by rapid cathode spluttering appear deep black by reflected light, and yellowish-brown by transmitted light; whereas those obtained more slowly have a metallic lustre, and are opaque. G B. Rizzo, and P. Secchi discussed the colour of thin films; W. C. Sabine discussed the selective absorption of films of steel for ultra-violet light. W. L. Dudley found that the incandescent vapour is greenish-blue. E. M. Péligot observed that the iron obtained by reducing the chloride in hydrogen is filamentous, compact, malleable, and is almost as white as silver. J. J. Berzelius observed that wrought-iron filings melted under ferrous oxide, in a luted fireclay crucible, furnish a button with crystalline fracture, greyish-white in colour. Electrodeposited iron, by E. A. Jacquin's or R. Böttger's processes, has a bright lustre, and, according to E. Lenz, it has the colour of platinum after it has been heated in vacuo. E. F. Dürre discussed the colour and lustre of different varieties of iron, and also the fracture, and texture of the metal. W. Ramsay said that it seemed as if it were possible to see objects through a regular stream of the molten cast iron, and they appeared to be of a yellow colour, but the transparency of molten cast iron was denied by T. Turner.

M. White and F. W. Taylor gave for the colours of iron at high temperatures: 532°, dark blood-red, black-red, incipient red, and *rouge naissant*; 566°, dark red, blood-red, low red, and *rouge sombre*; 635°, dark cherry-red, incipient cherry-red, and *cerise naissant*; 682°, medium cherry-red; 746°, cherry-red, full red, and *cerise*; 835°, light cherry, bright cherry, scaling heat, light red, and *cerise clair*; 899°, orange, salmon, free scaling heat, and *orange foncée*; 941°, light orange, light salmon, and *orange clair*; 996°, yellow; 1079°, light yellow; and 1205°, white, and *blanc*. The results agree with those of H. M. Howe, but they differ from those C. S. M. Pouillet obtained in 1836.

The crystalline characteristics have been previously described. T. Turner discussed the colour of the tarnish films of iron—*vide infra*, temper colours—and W. Biltz, and J. Meisenheimer, the colour of iron compounds.

H. E. J. G. du Bois and H. Rubens[2] found the **index of refraction,** μ, of precipitated iron to be for wave-length, λ:

λ . . .	4310	4860	5893	6440	6700
μ . . .	2·05	2·43	2·72	3·06	3·12

P. A. Ross gave 1·48 for $\lambda=4500$; 1·85 for $\lambda=5893$; and 2·1 for $\lambda=6200$, with electrolytic iron; and C. Statescu, 2·182 for $\lambda=5880$. Observations on the refractive index were also made by A. Beer, A. L. Bernoulli, H. E. J. G. du Bois and H. Rubens, P. Drude, L. R. Ingersoll, H. Knoblauch, A. Kundt, W. Meier, R. S. Minor, A. Pflüger, D. Shea, C. A. Skinner and A. Q. Tool, J. T. Tate, A. Q. Tool, and W. Voigt. The refractive index for the X-rays was measured by R. L. Doan, A. Gouy, J. A. Prins, and A. Winkelmann and R. Straubel. A. Kundt found that for red-light at 18°, 20°, 102°, and 106°, the refractive indices were respectively 0·66, 1·92, 2·54, and 3·69. W. Linnik and W. Laschkareff measured the refractive index of steel and iron for X-rays. C. V. Raman and K. S. Krishnan discussed the colour, intensity, and polarization of light diffracted through large angles by steel wedges and screens with polished edges. A. J. Ferreira da Silva found that with iron salts, the **atomic refraction** of bivalent iron is 11·6, and of tervalent iron, 20·1; for long waves, A. Heydweiller gave 5·07 and 7·97 respectively for bi- and ter-valent iron; and A. Hauke gave for the **refraction equivalents,** calculated from the refractive indices of aq. soln. of iron salts by the μ-formula, and for bivalent and tervalent iron respectively 11·6 and 20·6, and by the μ^2-formula, 4·75 and 5·83 respectively. W. J. Pope gave 13·38 for the refraction equivalent of bivalent iron, and 23·03 for tervalent iron; and J. H. Gladstone, respectively 11·6 and 19·4. The **anomalous dispersion** of iron was studied by S. Albrecht, P. Drude, H. Giesler, A. S. King, J. A. Prins, L. Puccianti, and W. Voigt. The double refraction of iron was discussed by H. Behrens, and S. Procopiu. M. Cau observed that thin films of iron, formed by the condensation of iron vapour, exhibit a **birefringence** accompanied by **dichroism,** the principal directions of which are parallel and perpendicular, respectively, to that of the original wire. The effect ceases when the deposit is removed, and is due to the magnetic field of the heating current, in which the atoms of vapour tend to orient themselves in positions which are retained after deposition and are unaffected by a magnetic field placed parallel to the deposit. The component of the vibration parallel to the axis is less absorbed than the normal component by the birefringent dichroic layers of iron. In the middle of the spectrum, the dispersion is normal for the ellipticity, and abnormal for the rotation of the emergent vibration. C. Statescu gave for the **extinction coefficient** of electrolytic iron, k=2·716; A. Kundt, μ=1·52 for blue-light, μ=1·73 for white-light, and μ=1·81 for red-light; whilst A. Pflüger gave μ=3·66 for red-light. W. Meier found for electrolytic iron, the following values for the index of refraction, μ, the extinction coeff., k, and the percentage **reflecting power,** R:

λ	2573	2749	2981	3255	3611	3982	4413	4678	6080	5893	6680
μ	1·01	0·95	0·92	0·99	1·04	1·17	1·28	1·34	1·38	1·51	1·70
k	0·88	0·80	0·83	0·91	1·10	1·29	1·37	1·45	1·50	1·63	1·84
R	16·2	14·4	16·0	17·4	22·4	26·7	27·7	29·2	30·2	32·6	36·2

P. Drude found for massive iron, λ=5890, k=320, μ=2·36, and R=56·1; and W. W. Coblentz gave for the reflecting power of massive iron for λ=5000, 6000, 7000, and 8000, R=55·0, 57·5, 59·5, and 61·5 respectively. He also gave:

λ	0·5	1·0	2·0	3·0	5·0	7·0	8·0	9·0 μ
R	55·0	65·0	78·0	84·5	91·5	94·0	94·0	93·0

I. C. Gardner, and F. von Fragstein measured the reflecting power in the ultraviolet. Observations on the optical constants of steel were made by A. L. Bernoulli, G. Breithaupt, J. Clavier, P. Drude, F. A. Fahrenwald, P. Glan, E. Hagen and H. Rubens, S. Haughton, H. Hauschild, R. Hennig, E. O. Hulbert, L. R. Ingersoll, J. Jamin, J. T. Littleton, M. Luckiesh, W. Meier, R. S. Minor, G. Pfestorf, G. Quincke, J. T. Tate, A. Q. Tool, and V. S. M. van der Willigen. The following is a selection from the results:

λ	1880	2265	3255	4000	5000	6200	7000	8700
k	—	1·64	2·09	1·73	3·15	3·30	3·47	4·08
μ	—	1·30	1·37	1·68	2·09	2·58	2·73	3·02
R	22	34·8	44·8	53·9	56·9	56·8	58·0	63·2

λ	1·0	1·25	1·50	1·75	2·00	2·25	8·80	14·0μ
k	4·43	5·08	5·75	6·32	6·88	7·41	—	—
μ	3·19	3·45	3·71	3·88	4·02	4·14	—	—
R	65·5	69·7	73·1	75·6	77·7	79·7	93·0	96·0

M. Chikaschige and D. Uno measured the reflecting power of the iron-carbon alloys. For alloys with the pearlitic structure—normalized at 1000°, and annealed at 700°—the reflecting powers with different spectral lines are indicated in Fig. 251. The fact that the curves are nearly parallel shows that the colour is independent of the proportion of carbon. The dotted lines, which merge into the continuous lines of Fig. 251, refer to martensite—normalized at 1000° and quenched in water from 800°. Fig. 252 shows the reflecting powers of a 0·9 per cent. carbon steel normalized at 1000°; quenched at 800° in water at 20°; and then annealed at the temp. indicated—350° for troostite; 550° for sorbite; and 700° for pearlite. The results show that the reflecting powers of the constituents decrease in the order: martensite, troostite, sorbite, ferrite, and pearlite. W. Arkadieff studied the reflection of electromagnetic waves; E. Gerold, the lustre of iron; and E. Rupp, the optical properties of iron before and after exposure to hydrogen, nitrogen, and hydrogen sulphide; and W. Bruch found that the optical properties indicated that cast iron is isotropic.

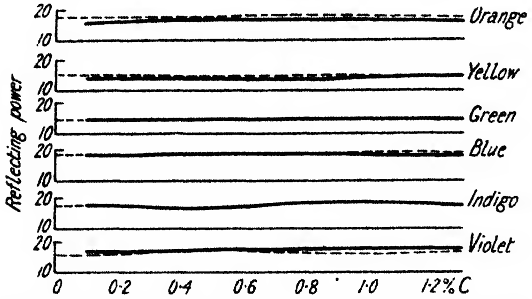

Fig. 251.—Reflecting Powers of Martensite (dotted) and Pearlitic Iron-Carbon Alloys.

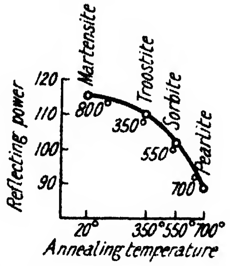

Fig. 252.—The Effect of Annealing Temperature on the Reflecting Power of Steel.

W. Meier, and G. Jaffé calculated values for the optical constants based on the theory of electrons: S. Nakamura studied the relation between the optical constants and the permanent mechanical expansion of steel; J. T. Littleton, the relation between the optical constants and the carbon-content and heat-treatment of steel; L. R. Ingersoll and J. T. Littleton, the optical constants of steel in the ultra-red; and G. Jung, W. H. J. Vernon, and H. Freundlich and co-workers, the relation between the optical constants and the tarnish colours.

Observations on the reflecting power of the visible rays were made by A. L. Bernoulli, P. Drude, E. O. Hulbert, L. R. Ingersoll, J. Jamin, S. Rösch, R. S. Minor, G. Quincke, J. T. Tate, and A. Q. Tool; on the reflecting power of the ultra-violet rays, by R. Hamer; on the reflecting power for the heat rays, by H. Rubens and E. F. Nichols, and A. Trowbridge; on the reflecting power for the ultra-red rays, by H. Rubens and co-workers, and L. R. Ingersoll and J. T. Littleton; the effect of temp. on the reflecting power, by W. R. Grove, E. Hagen and H. Rubens, and R. Sissingh; on the reflecting power of iron under water, by J. Conroy, and P. Drude; and on the reflecting power of the active and passive forms of iron—*vide infra*, passive iron—by F. Haber and F. Goldschmidt, P. Krassa, F. J. Micheli, and W. J. Müller and J. Königsberger. A. Gouy, W. Wien, and C. V. Raman and K. S. Krishnan studied the reflection and diffraction colours of iron.

E. Hagen and H. Rubens measured the **emissivity** of steel for long waves, and they also measured the effect of temp. on the emissivity. According to H. F. Weber, heated iron begins to emit greyish light when the temp. has risen to 377° or 378°; and for polished iron, R. Emden gave 405°. G. Malander said that even at ordinary temp., hardened steel emits weak ultra-violet rays. C. C. Bidwell compared the apparent temp. with the true black body temp. of iron surfaces, and found that the relative emissivity of bright, clean iron, radiating freely into air, varied from as low as 28 per cent. of that of a black body at 700°, through 30 per cent. at 1300°, to 48 per cent. at 1700°. M. Möller and co-workers found that the relative emissivity is 43·5 per cent. for polished iron, and 80 per cent. for an oxidized surface at 700° to 1100°. G. K. Burgess and P. D. Foote also obtained a relative emissivity of 80 to 85 per cent. for an oxidized surface of iron at 700° to 1100°. Optical and total radiation pyrometers thus require corrections according as bright or oxidized surfaces of iron are involved. Observations were made by E. R. Binkley, G. R. Greenslade, K. Lubowsky, and A. L. Helfgott. G. Naeser, and R. Hase measured the emissivity of liquid iron; H. T. Wensel and W. F. Röser found in measuring the temp. of molten cast iron that there is a change in the emissivity in the neighbourhood of 1375° from 0·7 to 0·4, and this is attributed to the formation of a film of oxide which renders a correction necessary in reading the temp. with an optical pyrometer.

V. A. Suydam measured the total radiation energy of iron, and found, for $T°$ K., the following values of the energy E, in watts per sq. cm.:

Temp. °K.	696°	805°	915°	1083°	1180°	1233°	1303°
E	0·2230	0·4362	0·7952	2·1810	3·3628	4·7000	7·880

He represented the results by Wien's law, $E=cT^5$, where the constant c ranged from $2{\cdot}99\times10^{-17}$ to $3{\cdot}99\times10^{-17}$. The press. was 0·0002 mm. The wave-length of the maximum energy, E, emitted from smooth, solid iron is shifted in the direction of the shorter wave-length as the absolute temp. rises in accord with Wien's law. Matt, slag-free iron, emits the grey radiation approaching the black body condition as the temp. rises. The heat spectrum of liquid iron closely resembles that of the smooth metal with respect to energy and spectral distribution. R. Hase's results are summarized in Fig. 253. G. R. Greenslade studied the radiation energy between 782° and 1312°. The subject has been discussed by C. B. Thwing, M. Kahanowicz, I. Langmuir, G. Moressée, F. Wamsler, A. R. Meyer, K. Lubowsky, F. Paschen, C. P. Randolph and M. J. Overholser, V. Polak, E. Schmidt, E. Furthmann, C. C. Bidwell, and M. Möller and co-workers. E. Hagen and H. Rubens measured the relation between the emissivity and the electrical conductivity; M. Kahanowicz, the effect of a magnetic field, and of oxidation films on the emissivity; and H. P. Gurney, the relation between the emission and absorption of heat rays for different kinds of iron.

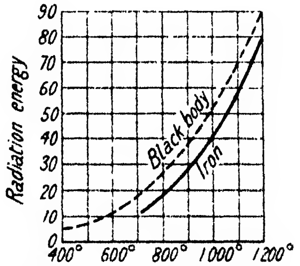

FIG. 253.—The Radiant Energy from Iron.

K. Endell and H. Hanemann[3] studied the polarization of light reflected from iron. The magnetic rotation of the plane of polarized light by iron was discovered by J. Kerr, and it is called the **Kerr effect.** The phenomenon was studied by E. van Aubel, S. G. Barker, H. Behrens, H. E. J. G. du Bois, M. Cau, P. D. Foote, L. Houllevigue and co-workers, L. R. Ingersoll, A. Kundt, J. G. Leathem, W. Lobach, P. Martin, H. Ollivier, B. Pogany, and C. Snow. The gyromagnetic value of iron was studied by S. J. Barnett. The so-called **Faraday effect,** that is, the rotation and elliptical polarization of light by passage through thin films of iron in a magnetic field, was studied by J. Becquerel and W. J. de Haas, H. Behrens, M. Cau, J. Dorfman, C. J. Gorter, W. D. Harris, E. Hirsch, H. R. Hulme, L. R. Ingersoll, H. Poritsky, R. W. Roberts and co-workers, C. A. Skinner and A. Q. Tool, C. Snow, and W. Voigt. Luminescent iron vapour, or a precipitated film of iron on glass produced in a magnetic field, emits polarized rays, and the phenomenon is called the **Thomson effect.** It was studied by E. Thomson,[4] O. J. Lodge, and R. Whytlaw-Gray and J. B. Speakman.

Neither ferrous nor ferric salts show a **flame spectrum** which is sufficiently characteristic for recognition tests. There are lines which are feeble in the oxy-hydrogen flame, but which appear strengthened in the Bunsen flame. G. A. Hemsalech and C. de Watteville,[5] and C. de Watteville found that the flame spectrum extends far into the ultra-violet. J. N. Lockyer observed that in the oxy-coal gas flame there are present a line and fluted band spectrum. G. A. Hemsalech and C. de Watteville observed that in the oxy-acetylene flame, there are present lines which appear in the oxy-hydrogen flame, and the strengthened lines of the Bunsen flame. W. N. Hartley observed a series of lines, and a band between 554 and 593$\mu\mu$ in the oxy-hydrogen flame, and J. N. Lockyer and H. E. Goodson, and J. Meunier observed that the lines in the oxy-hydrogen flame can be arranged in three classes according as they are stronger, weaker, or of the same intensity as the lines of the arc-spectrum. G. A. Hemsalech, and A. de Gramont found that in the mantle of the flame there are lines at 3860, 4119, 4957 A., and in the cone there are the lines 3936, 4119, and 4957 A., whilst there are triplets at 4046 and 4384 A. which are intense in the cone and feeble in the mantle. The subject was studied by A. Gouy, R. Eisenschitz and A. Reis, and A. Hagenbach and H. Konen. H. Auerbach observed numerous lines in the Bunsen flame, and in the oxy-coal gas flame, but not in the coal gas flame with a blast of air; and M. Adam, in the hydrogen flame. J. M. Eder and E. Valenta observed a band at 4400 A. in the flame spectrum of ferric chloride. E. N. da C. Andrade studied the spectra of iron in the flame of chlorine, bromine, and iodine. The flame with chlorine is coloured yellow, due, it is supposed, to the presence of undissociated ferric chloride which is able to maintain its existence in the presence of an excess of chlorine. A. Mitscherlich examined the spectra produced by the vapours of ferric chloride and iodide in the hydrogen flame. E. L. Nichols and H. S. Howes observed the spectrum of iron when a ferruginous bead of sodium pyrophosphate, or borax, is heated in hydrogen; and G. D. Liveing and J. Dewar, T. Hori, and S. Kalandyk and co-workers, when detonating gas is exploded in an iron tube. A. S. King studied the spectrum of iron heated in the electric furnace and found that the result at 2400° agrees with the flame spectrum; but above 2400°, the spectrum resembles that of the low-voltage arc. H. Schüler observed that the vapour electrically excited shows lines resembling that of the arc spectrum. Observations were also made by E. Carter and A. S. King, and by G. A. Hemsalech.

When soln. of the iron salts are sparked by the aid of a condenser, they give a complicated **spark spectrum** containing thousands of lines. A. Masson, D. Alter, and G. Kirchhoff were among the first to study the spark spectrum of iron. E. Formanek regarded the following as the more important lines in the simple spark spectrum of iron: in the orange-yellow, 6462, 6400, 6350, 6095, and 5916; in the yellow, 5762, 5714, 5708, and 5614; in the green, 5601, 5594, 5586, 5571, 5455, 5444, 5429, 5370 (ϵ, Fig. 254), the triple lines 5326, 5266, and 5232 (α, Fig. 254), the pale green lines 5192, 5168, 5139, and 5004 (δ, Fig. 254), and the stronger green lines 4959, and 4923 (β, Fig. 254); the blue lines 4891, and 4874 (ζ, Fig. 254), 4531, 4404, and 4382 (γ, Fig. 254), 4325 and 4307 (η Fig. 254), and, finally, 4271, and 4251. The sets α (5326, 5266, and 5232), β (4959, and 4923), ζ (4891, and 4874), and γ (4404, and 4383) are said to be characteristic in the spectral detection of iron. A. de Gramont gave as characteristic of iron and ferruginous minerals the lines 4960 in the green; 4415 in the blue; and 4404, 4383, 4271, 4260, and 4071 in the indigo.

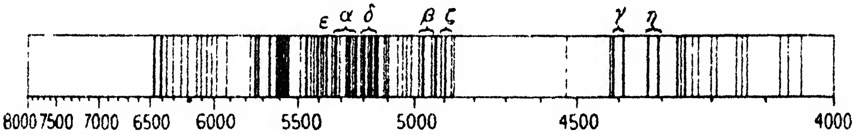

FIG. 254.—The Spark Spectrum of Iron.

Observations on the spark spectrum of iron were also made by W. A. Miller, H. D. Babcock, E. O. Hulbert, E. Carter and A. S. King, L. and E. Bloch, D. Alter, A. Masson, G. Kirchhoff, T. R. Robinson, W. E. Adeney, J. L. Schönn, T. Takamine and S. Nitta, R. A. Millikan and co-workers, T. R. Robinson, W. Finkelnburg, W. Huggins, R. Thalén, L. de Boisbaudran, A. Gouy, R. Capron, E. Carter, E. Carter and A. S. King, F. Müller, G. S. Monk, O. Stuhlman, J. B. van Milaan, G. Ciamician, J. Parry and A. E. Tucker, W. N. Hartley and co-workers, G. D. Liveing and J. Dewar, F. McClean, J. M. Eder, J. M. Eder and E. Valenta, F. Papenfus, J. H. Pollok, A. S. King, J. Wilsing, F. Exner and E. Haschek, H. Konen, A. Hagenbach and H. Konen, J. N. Lockyer, G. E. Hale and N. A. Kent, G. E. Hale, G. A. Hemsalech and C. de Watteville, H. W. Morse, O. Lohse, and H. Finger.

W. B. Anderson discussed the effect of variations in the experimental conditions on the spark spectrum; H. R. von Traubenberg, the effect of the surrounding gaseous atmosphere: (i) oxidizing—oxygen, carbon dioxide, nitrous oxide, or sulphur dioxide; (ii) reducing—hydrogen, methane, acetylene, and carbon monoxide. The spectrum of wires exploded by the disruptive discharge was examined by J. A. Anderson, S. Smith, R. Déchène, A. C. Menzies, A. S. King, T. Hori, and H. Nagaoka and co-workers; and the spectrum of the disruptive discharge, by H. Nagaoka and co-workers. The spark discharge in a capillary tube filled with gas was found by J. Trowbridge to show no iron lines. J. H. Pollok found that the discharge in the vacuum tube with ferric chloride has an iron spectrum corresponding with the spark spectrum. P. E. Robinson, F. Grünbaum, L. Janicki, L. Janicki and R. Seeliger, and K. L. Wolf studied the spectrum of the spark discharge in the vacuum tube. According to G. A. Hemsalech, the velocity with which luminous particles are emitted by the iron electrode is 27·2 metres per sec.; the duration of the luminosity in the spark discharge is between 40×10^{-3} and 282×10^{-3} sec.—it increases with the capacity; it is proportional to the intensity of the lines; and it decreases in a magnetic field. The spark spectrum of the discharge in water was observed by E. von Angerer and G. Joos, L. and E. Bloch, L. de Boisbaudran, G. Ciamician, H. Finger, W. H. Fulweiler and J. Barnes, G. E. Hale, G. E. Hale and N. A. Kent, E. O. Hulbert, H. Konen, H. Konen and H. Finger, J. N. Lockyer, W. F. Meggers and F. M. Walters, A. L. Narayan and K. R. Rao, J. Parry and A. E. Tucker, B. Setna, H. Stücklen, N. K. Sur, and J. Wilsing. T. Tucholsky, and H. Nagaoka and co-workers observed the change in the wave-length and intensity of iron lines by the disruptive discharge. A portion of the **arc spectrum** by A. S. King is shown in Fig. 254.

The arc spectrum was examined by K. Behner, E. G. Bilham, Lord Blythswood and W. A. Scoble, P. H. Broderson, H. Buisson and C. Fabry, K. Burns, K. Burns and F. M. Walters, R. Capron, W. Clarkson, A. Cornu, H. Crew, H. Crew and B. J. Spence, W. G. Duffield, J. M. Eder and E. Valenta, E. J. Evans, F. Exner and E. Haschek, C. Fabry and co-workers, F. Goos, A. Hagenbach and H. Konen, A. Hagenbach and K. Langbein, S. Hamm, J. Hartmann, G. A. Hemsalech and C. de Watteville, H. Hertenstein, A. Hilger, W. J. Humphreys, C. V. Jackson, L. Janicki, C. E. St. John and H. D. Babcock, H. Kayser and C. Runge, A. S. King, W. Kleinewefers, E. A. Kochen, J. Lang, G. D. Liveing and J. Dewar, J. N. Lockyer, P. Maring, W. F. Meggers and C. C. Kiess, P. W. Merrill, J. B. van Milaan, G. S. Monk, C. E. Moore and H. N. Russell, J. E. Petavel and R. S. Hutton, M. Pirani and R. Rompe, R. A. Porter, H. Pressentin, S. P. de Rubies, H. Schumacher, A. Secchi, A. Sellerio, R. Thalén, and H. Viefhaus.

The so-called *normal spectrum* was discussed by W. E. Adeney, S. Albrecht, H. D. Babcock, F. L. Brown, H. Buisson and C. Fabry, K. Burns and co-workers, J. M. Eder, J. M. Eder and E. Valenta, P. Eversheim, C. Fabry and A. Pérot, L. Glaser, F. Goos, J. Hartmann, S. Hoeltzenbein, L. Janicki, C. E. St. John and co-workers, H. Kayser, H. Kayser and co-workers, C. C. Kiess, J. Lang, F. McClean, W. F. Meggers and co-workers, K. W. Meissner, G. S. Monk, F. Müller, H. Nagaoka, F. Papenfus, A. H. Pfund, H. Pickhan, H. A. Rowland, H. Schumacher, H. Viefhaus, P. Wallerath, and H. Werner.

The *intensity* of the spectral lines was studied by P. H. Broderson, R. Frerichs, O. Laporte, J. B. van Milaan, and L. S. Ornstein; the relative intensity of arc and spark lines, by G. Nakamura; and the *selective reflection* of the lines in the arc spectrum, by R. W. Wood. H. Crew and B. J. Spence studied the effect of different phases of an *alternating current arc* on the spectrum; C. Fabry and H. Buisson, the effect of the potential difference between the electrodes; H. Crew, and G. D. Liveing and J. Dewar, the effect of an atmosphere of hydrogen; R. A. Porter, the effect of an atmosphere of hydrogen, oxygen, or ammonia; M. la Rosa, and E. Donek, the effect of an atmosphere of oxygen; H. Nagaoka, the displacement of the lines as a result of press., potential difference, and speeds of ions and electrons - the so-called *pole effect;* P. W. Merrill, the strengthening of the lines at the positive pole; H. Konen, the arc spectrum under water; M. Pierucci, the spraying of iron salts in the carbon arc light; E. G. Bilham, K. Burns, W. G. Cady, W. R. Mott, H. Nagaoka and Y. Sugiura, Siemens-Schuckertwerke, the effect of electrodes containing various other metals, carbon, oxides, etc.; and A. Hagenbach and K. Langbein, and H. Buisson and C. Fabry, the temp. of the arc. The effect of *pressure* was discussed by W. S. Adams, H. D. Babcock, H. Buisson and C. Fabry, M. A. Catalan, W. G. Duffield, G. E. Hale and W. S. Adams, W. J. Humphreys, C. Keller, A. S. King, P. Maring, J. F. Mohler, A. Pérot, J. E. Petavel and R. S. Hutton, and R. Rossi; and the *magnetic field*—**Zeeman effect**—by J. S. Ames and co-workers, H. D. Babcock, A. E. Becker, H. Becquerel and H. Deslandres, H. B. van Bilderbeek van Meurs, A. Dufour, J. M. Graftdyk, G. E. Hale, W. Hartmann, G. A. Hemsalech, N. A. Kent, A. S. King, O. Lüttig, A. A. Michelson, H. Nagaoka, H. Nagaoka and Y. Sugiura, T. Preston, H. M. Reese, Y. Takahashi, J. H. van Vleck and A. Frank, K. Yamada, and P. Zeeman. Using a magnetic field equivalent to 37,000 gauss., H. Nagaoka, and Y. Takahashi observed that of the nine strong violet lines seven were found to give separations proportional to the field, while two gave larger separations in stronger fields. Of the weaker lines some give larger separations than usual, which are not proportional to the field. The effect of an *electric field*—the **Stark effect**—on the spectrum of iron was examined by M. Adam, J. A. Anderson, H. Nagaoka and Y. Sugiura, and T. Takamine; the *self-induction*, by G. A. Hemsalech, B. Eginitis, E. Néculcéa, P. E. Robinson, and G. Berndt; *reversed lines*, by G. D. Liveing and J. Dewar; *anomalous dispersion*, by H. Ebert, L. Puccianti, and H. Geisler; *enhanced lines*, by J. N. Lockyer, J. N. Lockyer and F. E. Baxandall, F. E. Baxandall, W. G. Duffield, P. W. Merrill, G. E. Hale and W. S. Adams, C. Fabry and H. Buisson, and A. Fowler. *Les raies ultimes*, the *ultimate or residual rays*, and the *sensitiveness* of the spectrum of iron were studied by E. Bayle and L. Amy, F. Brasack, A. de Gramont, W. N. Hartley and H. W. Moss, W. Kraemer, J. H. Pollok, J. H. Pollok and A. G. G. Leonard, and D. M. Smith. A. de Gramont said that the last lines to be visible are in the group 2767·6 to 2737·0, and also 3020·8; with ocular observations, 4404 and 4383; and with photographic observations, 4045, 3820, 3737, 3570, 3565, 2755, 2749, 2739, 2395, and 2382. The lines 2395·7, and 2382·2 are visible with a dilution of 1 : 1,000,000; 2755·8, 2749·4, 2739·6, 2599·5, and 2598·5, with a dilution of 1 : 100,000; and 3737·5, and 3735·0, with a dilution of 1 : 10,000. W. N. Hartley and H. W. Moss gave 3886·4, 3860·0, 3824·5, 3749·6, 3745·7, 3735·0, 3733·4, 3722·6, and 3720·0 for the ultimate lines of iron in the oxy-hydrogen flame; 2753·4, 2749·4, 2747·1, 2746·6, 2743·2, 2739·6, 2825·8, 2628·4, 2599·5, and 2598·5 for the ultimate lines of the spark spectrum between iron electrodes. F. Twyman and co-workers, T. Negresco, W. Kraemer, A. Schleicher, and J. R. Green discussed the spectral analyses of metals in quantitative and qualitative analyses.

The **ultra-violet spectrum** was examined by J. L. Schönn, G. D. Liveing and J. Dewar, F. Exner and E. Haschek, J. Thibaud, V. Schumann, R. J. Lang, T. Royds, T. Takamine and S. Nitta, S. Hamm, J. C. McLennan and co-workers, P. Maring, S. P. de Rubies, O. Stuhlman, C. C. Kiess, R. A. Millikan and co-workers, and L. and E. Bloch; and the **ultra-red spectrum,** by H. Becquerel, J. Querbach, H. Lehmann, W. W. Coblentz, K. W. Meissner, W. F. Meggers and C. C. Kiess, W. de W. Abney, E. A. Kochen, E. J. Evans, L. Geiger, H. M. Randall and E. F. Barker, and J. C. McLennan and co-workers. The electrodic **luminescence spectrum** was studied by W. von Bolton; the luminescence spectrum produced by the action of cathode rays on the vapour of iron, by E. Carter and A. S. King; and the spectrum of the luminescence of iron vapour in nitrogen, by P. Lewis. The existence of iron lines in the **solar spectrum** was discussed by J. von Fraunhofer, S. A. Mitchell, H. von Klüber, A. Cornu, J. Wilsing, H. Ebert, J. N. Lockyer and F. E. Baxandall, J. N. Lockyer, A. S. King, C. Fabry and co-workers, R. Woolley,

S. Albrecht, H. A. Rowland, H. Deslandres, A. de Gramont, C. E. Moore and H. N. Russell, and H. W. Vogel; and in **stellar spectra,** by A. de Gramont, G. P. Merrill, P. W. Merrill, W. W. Morgan and co-workers, O. Struve, O. Struve and P. Swings, and G. P. Merrill and C. G. Burwell, S. Albrecht, J. N. Lockyer and F. E. Baxandall, R. Furnhjelm, and H. Ludendorff; and the spectra of meteorites, by W. Crookes—*vide supra,* the occurrence of iron. R. Gans studied the absorption spectrum of a *colloidal* soln. of iron; and J. N. Lockyer, and J. Parry, the possible dissociation of iron at high temp.

The **absorption spectrum** of the *vapour* of iron was discussed by K. L. Wolf, H. Gieseler and W. Grotrian, A. S. King, J. C. McLennan and A. B. McLay, W. F. Meggers, J. N. Lockyer and W. C. Roberts-Austen, G. D. Liveing and J. Dewar, J. A. Anderson, and E. von Angerer and G. Joos. A. S. King's results with the vapour at different temp. are indicated in Fig. 255.

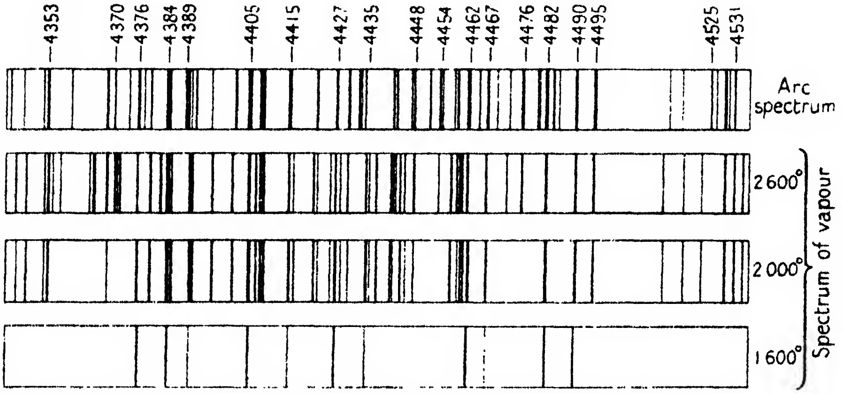

FIG. 255.—The Spectra of Iron Vapour at Different Temperatures.

According to J. Formanek, coloured solutions of iron salts do not furnish absorption spectra suitable for analytical purposes. The ferrous salts absorb more or less red rays, and the ferric salts, blue or violet rays —*vide infra,* the special salts. The absorption spectrum of ferric thiocyanate in amyl alcohol is shown in Fig. 256. Soln. of ferric salts react with alkanna tincture, and with neutral aq. soln. the liquid first becomes bluish-grey, and afterwards dirty green. This liquid has a strip at 4955, and a band in the blue. The addition of a drop of ammonia to the liquor precipitates the iron compound, and the absorption spectrum disappears; but if a trace only of ammonia be added, the liquor becomes grass-green, and a strong absorption appears at 6645, and a feeble one at 6030. Alkanna tincture acts similarly on soln. of ferrous salts, but the colour is bluish-violet. If ammonia be added as before, the colour becomes reddish-brown, and shows bands in the green and blue, and two strips at 5895 and 5475. After the liquid has stood for some time it becomes dirty green, and turbid, and the spectrum disappears. Observations were made by J. Plotnikoff and M. Karschulin, R. Samuel, and H. I. Schlesinger and H. B. van Valkenburgh. M. Luckiesh, and T. Dreisch studied the special transmission of glasses coloured with iron.

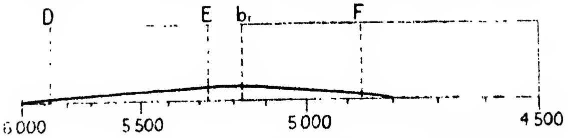

FIG. 256.—The Absorption Spectrum of Solutions of Ferric Thiocyanate.

Regularities in the spectra and **series spectra** of iron were examined by A. Schuster, and W. N. Hartley. A. S. King arranged the lines in different classes, according to their behaviour with respect to temp., one class was well developed at 1600°, another at 2000°, and another at 2300°; and G. E. Hale and W. S. Adams also found that the lines could be arranged in classes according to their behaviour with respect to press. The subject was also discussed by M. A. Catalan, E. Gehrcke, A. de Gramont, A. Hagenbach and H. Schumacher, G. A. Hemsalech, J. N. Lockyer and co-workers, and J. Meunier. H. D. Babcock discussed the changes of energy involved in the passage from one class to another. The multiplets—doublets, triplets, quartets, and sextets—were examined by E. von Angerer and G. Joos, N. Bohr and D. Coster, W. M. Cady, M. A. Catalan and co-workers, W. Clarkson, D. Coster, R. Frerichs, E. Gehrcke, R. C. Gibbs and H. E. White, H. Gieseler and W. Grotrian, S. Goudsmit and co-workers, A. de Gramont, W. Grotrian, S. Hoeltzenbein, F. Hund, C. E. St. John, M. Kahanowicz, P. K. Kichlu, C. C. Kiess and O. Laporte, M. Kimura and G. Nakamura, O. Laporte, E. M. Lindsay, J. C. McLennan and A. B. McLay, W. F. Meggers, W. F. Meggers and O. Laporte, J. B. van Milaan, H. Nagaoka and Y. Sugiura, A. L. Narayan and K. R. Rao, P. G. Nutting, L. S. Ornstein and H. C. Burger, E. Paulson, A. Rubinowicz, R. Rudy, H. N. Russell, M. Sawada, N. K. Sur, F. M. Walters, H. E. White, and A. T. Williams.

There are supposed to be rings or shells of electrons connected respectively with the emission and absorption of the K-, L-, M-, and N-series of the X-rays; while with the heavier atoms like uranium and thorium, there may be six such shells—denominated K, L, M, N, O, and P groups, beginning with the innermost—the K-group has 1 member; the L-group, 3; the M-group, 5; the N-group, 7; the O-group, 5; and the P-group 3. According to N. Bohr's theory,[6] the electrons in any given shell move in orbits more or less elliptical, and spatially arranged so as not to be co-planar. Owing to variations in the eccentricity, the orbits of the electrons in different shells are interpenetrating so that electrons in the exterior shells may approach closely to the nucleus at perihelion of the highly elliptical orbits. Consequently, the force acting on an electron in an elliptical orbit may undergo enormous variations in each revolution, so that the inverse square rule is approached only in the exterior parts of the orbits. In certain cases, the binding force on the electrons in exterior shells may be greater than that acting on the electrons in the interior shells. With the more simple pictures of the Bohr atom, the K-rays are due to electrons whose quantum number, n, decreases to 1, and such an electron drops into the K-ring, orbit, or shell; when the quantum number of the electron has dropped to 2, it gives off L-rays, and the electron is said to have dropped into the L-ring, shell, or orbit. J. Palacios and M. Velasco studied the fine structure of the X-ray absorption spectrum.

J. Laub assumed that hard X-rays furnish a *J-series* of **X-ray spectra,** but M. Siegbahn could not confirm this. The *K-series* of X-ray spectra were found by H. G. J. Moseley, and E. Wagner to furnish $\alpha=1{\cdot}946$, and $\beta=1{\cdot}765$. A. Larsson gave $\alpha_1=1{\cdot}932066$, $\alpha_2=1{\cdot}935987$, $\alpha_{3:4}=1{\cdot}92330$; there are also $\beta'=1{\cdot}75646$, and $\beta'''=1{\cdot}7371$, as well as $\beta_1=1{\cdot}753013$, $\beta_2=1{\cdot}74076$. Measurements were made by U. Andrewes and co-workers, M. Balderston, J. A. Bearden, H. Beuthe, S. Björek, D. M. Bose, W. Bothe and co-workers, M. de Broglie, C. T. Chu, D. Coster and co-workers, A. Dauvillier, A. C. Davies and F. Horton, B. Davis and H. Purks, G. B. Deodhar, V. Dolejsek, V. Dolejsek and co-workers, M. J. Druyvesteyn, W. Duane and co-workers, S. Eriksson, J. D. Hanawalt, E. Hjalmar, S. Idei, A. Karlsson, S. Kawata, G. Kettmann, B. Kievit and G. A. Lindsay, E. H. Kurth, K. Lang, A. Larsson, A. E. Lindh, G. A. Lindsay and H. R. Voorhees, H. Mark and L. Szilard, L. H. Martin, H. T. Meyer, F. L. Mohler and P. D. Foote, B. C. Mukherjee and B. B. Ray, G. Ortner, T. H. Osgood, S. Pastorello, R. L. Petry, M. Privault, B. B. Ray, O. W. Richardson and F. C. Chalklin, M. Sawada, N. Seljakoff and co-workers, M. Siegbahn, M. Siegbahn and co-workers, M. Siegbahn and B. B. Ray, M. Siegbahn and W. Stenström, M. Siegbahn and M. Zacek, N. Stensson, E. C. Stoner, R. Thoraeus, J. Valasek, A. P. R. Wadlund, B. Walter, F. Wever, F. J. von Wisniewsky, Y. H. Woo, and S. Yoshida. The limit of absorption of the K-series was placed by V. Dolejsek at 1·7395; by W. Duane and co-workers at 1·7396; and by E. Wagner at 1·7377. The absorption of the

K-series was also studied by W. Duane, W. Duane and H. Fricke, J. L. Glasson, and R. Thoraeus. A. E. Lindh found for the absorption limit with elemental iron, 1·7405; for Fe_2O_3, 1·7373; for $Fe(OH)_3$, 1·7371; for $FeCl_3$, 1·7372; for $(NH_4)_2Fe(SO_4)_2$, 1·7371; for FeS, 1·7389; for $FeSO_4$, 1·7383; for $Fe_2(SO_4)_3$, 1·7371; and for $FeSO_4$, 1·7371. The relation between the electronic structure and the K-series was discussed by G. A. Lindsay and H. R. Voorhees, and B. B. Ray; and the electronic energy, by R. Whiddington, and G. W. C. Kaye. The *L-series* includes the lines α=17·66, $\alpha_{1,2}$=17·58, β=17·33, β_1=1722, $\beta_{4,3}$=15·61, ϵ=20·12, and η=19·63. The *L-series* was studied by S. Björek, N. Bohr and D. Coster, A. Dauvillier, M. J. Druyvesteyn, H. Hirata, C. E. Howe, F. L. Hunt, A. Karlsson, G. Kellström, E. H. Kurth, B. C. Mukherjee and B. B. Ray, F. P. Mulder, O. W. Richardson and F. C. Chalklin, G. K. Rollefson, M. Siegbahn and co-workers, A. Sommerfeld, E. C. Stoner, J. Thibaud and A. Soltan, C. H. Thomas, R. Thoraeus, B. Walter, and R. B. Witmer and J. M. Cook. The *M-series* was studied by U. Andrewes and co-workers, F. L. Mohler and P. D. Foote, B. C. Mukherjee and B. B. Ray, J. A. Prins and A. J. Takens, R. L. Petry, B. B. Ray and R. C. Mazumdar, O. W. Richardson and F. C. Chalklin, G. K. Rollefson, O. Stuhlman, and C. H. Thomas. The *N-series* was studied by E. H. Kurth. H. Stintzing, and O. Eisenhut and E. Kaupp attempted the analysis of iron by X-ray spectra.

The **absorption coefficients**, μ, for the K-series of X-rays was found by C. G. Barkla and V. Collier to be 0·0202 for air; 0·204 for H_2S; 0·24 for SO_2; 0·112 for ethyl chloride; and 0·384 for ethyl bromide; and E. A. Owen gave μ=0·0254 for air; 0·0456 for CO_2; and 0·2673 for SO_2. C. W. Hewlett gave for the relative mass absorption coeff. for wave-lengths λ A.:

λ . .	0·130	0·210	0·324	0·471	0·666	0·861	1·006
μ/D .	0·437	1 16	3·76	11·22	31·05	60·60	91·70

and C. G. Barkla and C. A. Sadler, and C. A. Sadler and A. J. Steven gave for the absorption of the K-series of radiations from

	Cu	Ag	Zn	Tl	As	Se	Cr	Fe	Co	Ni
μ/D .	268	17·4	221	173	134	116·3	103·8	66·1	67·2	314

J. A. Becker found that the absorption coeff. of iron for X-rays of short wave-length were very little affected by a magnetic field of 18,000 gauss. Observations were made by S. J. M. Allen, T. E. Aurén, C. G. Barkla and co-workers, H. R. Voorhees and G. A. Lindsay, R. A. Houstoun, L. H. Martin and K. C. Lang, L. M. Alexander, J. A. Prins, N. Ahmad, L. Bastings, J. A. Bearden, W. H. Bragg and co-workers, F. Dessauer and B. Winawer, W. Duane and H. Fricke, C. W. Hewlett, J. A. Becker, H. Hädicke, H. S. Read, J. Palacios and M. Velasco, A. H. Compton, M. Ishino and S. Kawata, G. W. C. Kaye, J. Laub, L. H. Martin, F. K. Richtmyer and co-workers, M. Siegbahn, O. Stelling, and K. A. Wingardh. W. Kossel discussed the relation between the absorption coeff. of Cu, Zn, Fe, and Ni; J. Veldkamp, the effect of lattice structure on the X-radiograms; J. A. Becker, the effect of magnetization on the absorption of X-rays; and B. Rossi, the absorption and diffusion of penetrating corpuscular radiation in iron.

C. H. Thomas, U. Nakaya, F. C. Chalklin, H. Kulenkampff, G. Shearer, and C. T. Chu studied the emission of soft X-rays; O. W. Richardson and F. S. Robertson, L. P. Davies, and U. Nakaya, the effect of oxidation on the emission of soft X-rays; R. Whiddington, the velocity of the X-rays; L. H. Martin, the efficiency of the emission of the K-series of Z-rays; and H. S. Read, the effect of temp. on the absorption of X-rays; W. Arkadieff, the magnetic absorption spectrum. The absorption of polarized X-rays in a magnetic field was examined by J. A. Becker, J. C. Chapman, A. H. Forman. P. H. Brodersen studied the intensity of X-rays; R. W. G. Wyckoff, E. N. Coade, S. J. M. Allen, A. A. Claassen, A. J. Bradley and R. A. H. Hope, R. W. James and G. W. Brindley, C. W. Hewlett, E. N. Coade, and

R. J. Havighurst, and E. A. Owen, the scattering of X-rays; A. H. Armstrong, the diffraction of X-rays; R. Glocker and K. Schäfer, the dispersion of X-rays; P. Günther and G. Wilcke, the analysis of mixtures of iron and cobalt by X-radiograms; E. Rupp, the diffraction of electrons; S. Pastorello, iron as a deflection lattice for X-rays; R. L. Doan, W. Ehrenberg and F. Jentzsch, J. E. Henderson and E. R. Laird, and R. W. G. Wyckoff, the reflections of X-rays; and H. Haas detected no polarization of the K-rays with a voltage of 7·4 to 12·6 kilovolts. C. E. Eddy and T. H. Laby, and O. Eisenhut and E. Kaupp studied the analysis of iron by means of the Lenard rays; and G. R. Fonda and G. B. Collins, by means of the X-ray spectrum. W. A. Wood observed that manganese deposited on aluminium will remove the β-rays by selective absorption from the characteristic radiation of iron. The production of the K-series of X-rays by α-rays was studied by W. Bothe and co-workers. The secondary X-rays of iron were studied by C. G. Barkla, C. D. Cooksey, W. Kaufmann, and C. A. Sadler. The production of X-ray fluorescence was studied by M. Balderston, W. Bothe and co-workers, M. I. Harms, W. Kossel, L. H. Martin, and V. Posejpal. C. G. Barkla and A. J. Philpot, and E. A. Owen, measured the ionization coeff. of the $K\alpha$-rays in their passage through hydrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen sulphide, sulphur dioxide, hydrogen selenide, and ethyl bromide and iodide. M. von Laue and G. Siljeholm found that near the A_3-arrest, the changes in the thermal electron emission are related with those occurring in the thermal energy; and E. Rupp and E. Schmid found maxima for V 20, 110, 175, and 230 in the voltage-intensity of the electronic reflexion curve. W. Arkadieff studied the magnetic and electric spectra of electromagnetic waves. G. Fournier, and E. Rupp studied the **absorption of electrons**; J. Thibaud and F. D. la Tour, and P. Auger, the **absorption of neutron rays**; W. Espe, S. R. Rao, H. Hase, and H. E. Farnsworth, the distribution of energy and the **emission of electrons** from iron; H. E. Farnsworth, and G. A. Carse and D. Jark, the emission of electrons from magnetized and unmagnetized iron when no appreciable difference could be detected; E. Rupp, and E. Rupp and E. Schmid, the **diffraction of electrons**; and W. Boas and E. Rupp, the diffraction of electrons by purified and passive iron. W. Ehrenberg and F. Jentzsch, the **reflection of electrons**; C. H. Kunsman, M. N. Davis, H. B. Wahlin, F. Simon, A. Goetz, L. R. L. Barnes, G. Siljeholm, F. M. Penning, and M. von Laue, the **emission of positive ions** from heated iron; A. K. Brewer, the effect of ammonia; and, according to A. Goetz, there is no displacement, but there is a change in the direction of the curve of electronic emission at different temp. on passing through the transition points of iron; F. E. Myers and R. T. Cox tried to detect the polarization of electrons passing through magnetized iron-foil, and G. A. Carse and D. Jark observed no difference in the emission of electrons from magnetized and unmagnetized iron excited by the X-rays. A. Nodon observed the permeability of iron to the penetrating ultra-radiations of the sun. R. Robl observed no luminescence in ultra-violet light. B. Rossi measured the absorption of corpuscular radiations. H. R. von Traubenberg found the range of the α-particles in iron to be $18{\cdot}7\times10^{-4}$ cm. G. P. Thomson discussed the diffraction of the **cathode rays.** R. Holoubek studied the tracks of the H-particles from iron bombarded by α-**rays**; A. Wegerich studied the effect of bombarding iron with α-particles—*vide infra*, the atomic disintegration of iron. H. Robinson and W. F. Rawlinson investigated the emission of β-**rays** from iron; K. W. F. Kohlrausch, E. Stahel and H. Ketelaar, H. Herszfinkiel, L. H. Gray and G. T. P. Tarrant, and A. H. Compton, the absorption of the γ-**rays** of radium; and E. J. Workman, and H. Herszfinkiel, secondary ionization by hard γ-rays. According to R. F. Mehl and C. S. Barrett, the penetration limit of the γ-rays through steel is about twice as great as that of the X-rays. H. Schindler studied the effects of ultra-penetrating radiation. N. Piltschikoff observed that iron emits the so-called Moser rays which are capable of passing through thin layers of paper, celluloid, gelatin, or aluminium; and which can decompose silver bromide.

J. Lifschitz studied the Becquerel effect. W. G. Guy, and I. I. Borgman observed no evidence of the **radioactivity of iron.** N. R. Campbell calculated from the ionization of air by iron that the radioactivity, if present, is but $1\cdot7\times10^{-12}$ times as strong as is that of radium. Y. H. Woo studied the Compton effect.

The **critical potentials** found by U. Andrewes and co-workers were 73 and 166 volts; H. N. Russell gave 7·83 and 16·5 volts respectively for the series and ionization potentials of iron. A. V. Douglas gave 6·6 volts for the ionization potential of iron deduced from astronomical data; and G. B. Kistiakowsky, 11 to 13 volts. O. Laporte gave 5·9 volts for the ionization potential, and 3·20 volts for the first excitation potential. R. Hamer and S. Singh found critical potentials with 3·7, 7·15, 11·2, 16·3, 19·4, 24·5, 29·0, 33·9, 38·8, 42·1, 45·7, 48·4, 51·4, 54·8, 61·6, 72·7, 89·6, 103·1, 111·6, and 125·8 volts. G. K. Rollefson found that in the range 40 to 175 volts, the critical radiation potentials of the M-series are 3·46, 6·03, 7·05, 8·21, 9·63, 10·40, 10·88, 11·33, and 11·83 volts; and the values for the L-series in the range 60 to 70 volts are 45·5, 47·0, and 51·5 volts. In the range from 600 to 700 volts, O. W. Richardson and F. C. Chalklin found critical voltages at 608·1, 640·0, and 689·7 volts; C. H. Thomas, 639 and 704·3 volts; and G. K. Rollefson, 618, 637, and 697 volts. R. L. Petry observed critical potentials for the secondary electron emission of iron at 6·7, 9·0, 13·5, 26, 34, 39, 42·8, 48·3, 54·6, 66·7, 80·5, 92·7, 740, 810, and 1010 volts. There is a long range of voltages below 200 volts observed by O. W. Richardson and F. C. Chalklin, G. K. Rollefson, A. V. Douglas, M. de Broglie, S. C. Roy, D. R. Hartree, C. H. Thomas, S. C. Biswas, R. N. Ghosh, E. H. Kurth, U. Andrewes and co-workers, and C. T. Chu; the critical voltages follow the series $V=180-2420n^2$, where $n=4, 5, 6, 7, 8, 9, 10, 11, 12$. Observations on the series and critical potentials were also made by S. C. Biswas, A. C. Davies and co-workers, E. H. Hall, U. Andrewes and co-workers, F. Hund, O. Laporte, R. L. Petry, B. B. Ray and R. C. Mazumdar, O. Stuhlman, C. H. Thomas, and F. M. Walters. W. Grotrian represented graphically the energy stages, volts, for atoms of iron for different groups of spectral lines by Fig. 257. W. Herz gave $8\cdot25\times10^{-12}$, and J. E. P. Wagstaff, $0\cdot67\times10^{-12}$ for the **vibration frequency** of iron—*vide* 1. 13, 19. J. B. Austin gave between $7\cdot0\times10^{-12}$ and $9\cdot7\times10^{-12}$.

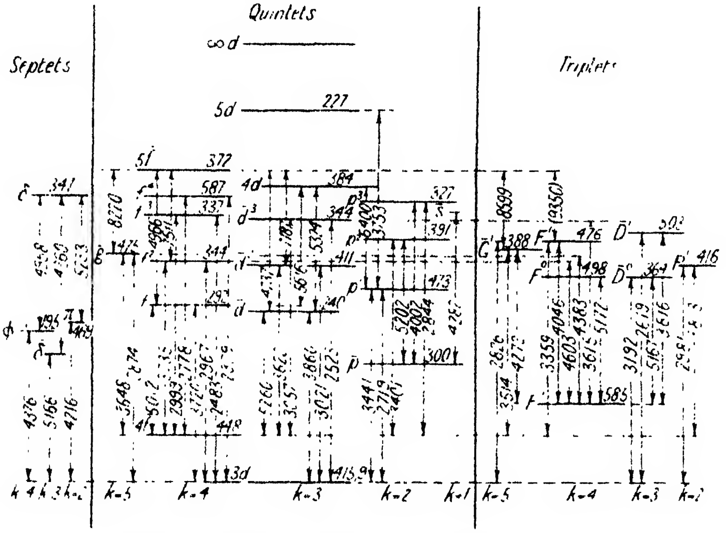

FIG. 257.—Energy Stages in the Spectra of Iron.

The **photoelectric effect** with iron was studied by G. B. Bandopadhyaya, A. K. Brewer, A. B. Cardwell, L. P. Davies, G. N. Glasoe, G. L. Locher, R. Hamer, G. B. Kistiakowsky, T. H. Osgood, T. Pavolini, G. Reboul, O. W. Richardson and

F. S. Robertson, and J. J. Weigle. According to G. B. Welch, the photoelectric effect is in the threshold of 3155 A.; R. Hamer gave 3425 A. A. K. Brewer, and U. Nakaya discussed the influence of adsorbed gas on the photoelectric effect. A. B. Cardwell observed the effect of removing the occluded gas on the photoelectric effect, and found that a thoroughly outgassed specimen showed no fatigue for 12 hrs. after treatment. When this state was reached, the strength of the photoelectric current depended on the rate of cooling of the iron filament. The photoelectric sensitiveness thus increases if the specimen be annealed in vacuo. There was a decrease in the photoelectric sensitivity if a filament heated above 910° was suddenly cooled, this being due to the retention of part of the γ-iron. The variation of the photoelectric current with temp. of the filament was investigated for iron which had been outgassed by heat-treatment for 150 hrs. The variation is complex. Between about 475° and 768° there is a decrease in photoelectric current due to a pure temp. effect. At 768° (where there is a transition of α- to β-iron) the sensitivity remains constant or increases slightly. Near 910° (transition of β- to γ-iron) there is an abrupt decrease in the sensitivity. The thermionic current was also measured and plotted against heating current. There is an abrupt change in the curve at 910°. The long wave-length limit for thoroughly outgassed iron lies between 2580 and 2652 A. The work function, obtained by substituting these values in Einstein's photoelectric equation, is $4{\cdot}72 \pm 0{\cdot}07$ volts. S. Chandrasekhar studied the photoelectric absorption by iron. The subject was studied by W. Frese; the effect of magnetization, by G. Polvani; and the effect of polishing with iron the metals copper, silver, gold, and platinum, by R. F. Hanstock; the effect of gases, by R. Dümpelmann; and the effect of magnetization, by J. H. J. Poole. F. Ehrenhaft found that iron particles show positive and negative **photophoresis** in that they move both with and against the direction of an incident beam of light.

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§ 21. Electrical Properties of Iron and Iron-Carbon Alloys.

P. E. Shaw and C. S. Jex,[1] A. Coehn and A. Lotz, A. Lafay, J. B. Seth and co-workers, H. F. Richards, and P. A. Mainstone studied the **triboelectricity** or friction electricity produced when iron is rubbed against glass, etc. R. F. Hanstock studied the effect of cold-work on the triboelectric effect.

Many observations on the **electrical conductivity** of iron and steel have been reported. Thus, A. Matthiessen and C. Vogt gave for the electrical conductivity, K, of electrolytic iron ignited in hydrogen, $K=16{\cdot}810-0{\cdot}519\theta+0{\cdot}00134\theta^2$; and ignited in air, $K=16{\cdot}810-0{\cdot}509\theta+0{\cdot}00127\theta^2$ when the value for K_0 for silver is 100; they also found for pianoforte wire, $K=13{\cdot}293-0{\cdot}425\theta+0{\cdot}00092\theta^2$; and for commercial iron, $K=18{\cdot}774-0{\cdot}428\theta+0{\cdot}000090\theta^2$. C. W. Siemens gave for iron, 8·3401 at 0° when the conductivity of mercury is unity; R. Benoit, 7·861; A. Berget, 7·88; L. Lorenz, 9·685 at 0°, and 6·189 at 100°; W. Kohlrausch, 8·405 at room temp. for electrolytic iron, 0·8913 at a red-heat, 0·8196 at a yellow-heat, and 0·7949 when the iron is non-magnetic. Observations were also made by A. Arndtsen, C. Barus, E. Becquerel, T. Berglund and A. Johansson, L. Cailletet and E. Bouty, J. A. Capp, O. Chwolson, A. Emo, J. A. Fleming, P. Fournel, C. A. Hering, W. H. Johnson, G. C. Knott, A. Macfarlane, A. Matthiessen and C. Vogt, A. R. Meyer, J. R. A. Mousson, J. Müller, A. Oberbeck and J. Bergmann, J. H. Partridge, M. Pirani, W. H. Preece, P. T. Riess, C. M. Smith and co-workers, H. Tomlinson, C. Villiers, A. von Waltenhofen, H. Wedding, etc. J. Dewar and J. A. Fleming, and E. Dickson gave for the electrical conductivity in mhos of purified, and annealed iron:

	−205·3°	−78°	0°	98·5°	196·1°
Mhos × 10^{-4} .	153·40	18·80	11·30	5·62	4·65

W. Meissner and B. Voigt also made observations between −271·8° and 0°; and found for the ratio, r, of the resistance, R, at the given temp. to the resistance, R_0, at 0°, for a sample, I, of electrolytic iron, and a sample, II, of iron with 0·001 per cent. Mn, 0·004 per cent. of copper, 0·0049 per cent. of nickel, etc., and tempered, when the resistance of I was $R_0=0{\cdot}0067$ ohm at 0°, and that of II, $R_0=0{\cdot}160$, and the calculated values of the ratios for the pure metals, r_{red}:

		0·16°	−185·58°	−194·15°	−252·60°	−268·79°	−271·62°
I	r . . .	1	0·1169	0·09194	0·02282	0·02160	0·02156
	r_{red} . .	1	0·09745	0·07194	0·00130	0·00005	0·00001
II	r . . .	1	—	0·0756	0·00892	0·00818	—
	r_{red} . .	1	—	0·06797	0·00075	0·00000	—

L. Guillet found the electrical resistance of annealed electrolytic iron to be 10·22 microhms per cm. cube at 20°, and since the only measurable impurities were 0·025 per cent. of phosphorus, and 0·011 per cent. of arsenic, A. L. Norbury estimated that by allowing for an increased resistivity of 0·32 microhm from these sources, the corrected value is 9·90 microhms per cm. cube at 20°. F. C. Thompson and co-workers gave 7·3 microhms for the sp. resistance of pure iron. T. D. Yensen gave 9·96 microhms per cm. cube for the resistance at 20° of annealed, doubly refined electrolytic iron, melted in vacuo. The only impurities were carbon, 0·006 per cent., and silicon, 0·01 per cent. Allowing for these, A. L. Norbury estimated the resistance to be 9·81 microhms, and F. Ribbeck, 9·62 microhms, per cm. cube at 20°. E. Gumlich and P. Goerens gave 9·94 microhms for the electrical resistance of purified iron at 20°. F. Stäblein gave 10 microhms for the sp. resistance of pure iron; 14·7 microhms for that of the eutectoid with 0·9 per cent. of carbon, and 70 microhms for cementite. G. Niccolai, and L. Holborn obtained 10 microhms per cm. cube for the resistance of iron near 0°; H. Masumoto, 10·44 microhms; and G. K. Burgess and I. N. Kellberg, 9·713 microhms per cm. cube. These investigators also obtained for the resistance of iron in ohms × 10^{-5} per cm. cube:

	−253°	−192°	−78°	0°	100°	200°	300°	400°
R . .	—	0·237	0·691	1·000	1·557	2·240	3·069	4·058
H . .	0·0113	0·0878	0·5794	1·000	1·6476	(2·4726)	3·4738	(4·6536)
B and *K* .	—	·	...	0·9713	1·5880	—	3·40	4·61

	500°	600°	700°	750°	800°	900°	900°	950°
B and *K* .	6·05	7·61	9·51	10·67	11·60	12·16	12·24	12·41

Measurements were made by P. Saldau; E. Grüneisen and E. Goens, and W. Rohn. J. C. McLennan and co-workers gave 8·85 for the sp. resistance of iron at 0°, and 0·101 for the value at 252·4°, whilst W. Meissner gave:

	0·20°	−185·57°	−194·14°	−252·60°	−268·79°	−271·66°
R	1	0·1169	0·09194	0·02282	0·02160	0·02156

or, by extrapolation, 0·02155 at −273°. W. Tuijn and H. K. Onnes found that iron did not show superconductivity at low temp.; and V. A. Suydam gave for the resistance, *R*, at *T*° K., taking the value at 0° or 273° as unity:

	273°	411°	588°	694°	851°	983°	1177°	1290°	1363°
R .	1·000	1·777	2·945	3·871	5·491	7·322	9·361	9·937	10·632

The observations of K. Honda and Y. Ogura, summarized by the light curve, Fig. 258, show a marked change in direction at 798°, or the A_2-arrest. G. K. Burgess and I. N. Kellberg observed no such change, but rather obtained a continuous curve in which the greatest change in the resistance, per degree rise of temp., occurred in the vicinity of the A_2-arrest. W. Broniewsky also observed perceptible singularities in the resistance curve at about 750°, 850°, and 950°, but W. Heraeus showed that the method of measurement was unsatisfactory, and the results improbable. The resistance of non-magnetic *α*- or *β*-iron is a continuous function of that of the ferromagnetic variety without exhibiting any sharp change. G. K. Burgess and I. N. Kellberg took observations at intervals of 2° or 3°, and found that the curves on a rising and on a falling temp. did not quite coincide, especially near the A_3-point. The observations of L. Holborn at low temp. fall on the curve, and indicate that the resistance approaches zero at about −253°. The resistance data of A. R. Meyer fall on or near the curve of G. K. Burgess and I. N. Kellberg. W. Conrad found that the electrical conductivity of molten steel is two hundred times worse than that of the same steel at ordinary temp. W. Jaeger and H. Diesselhorst obtained for iron with 0·1 per cent. carbon, $8·36 \times 10^4$ mhos at 18°, and $5·95 \times 10^4$ mhos at 100°; and for iron with 0·1 per cent. carbon, 0·2, Si, and 0·1, Mn, $7·17 \times 10^4$ mhos at 18°, and $5·31 \times 10^4$ mhos at 100°. V. Strouhal and C. Barus gave at 0°, $8·30 \times 10^4$ mhos for iron; $1·02 \times 10^4$ mhos for hard cast iron; $1·34 \times 10^4$ mhos for soft cast iron; forgeable cast iron in its original state—$4·10 \times 10^4$ mhos, hard, and $3·06 \times 10^4$ mhos, soft—$4·35 \times 10^4$ mhos for piano wire; $8·47 \times 10^4$ mhos for glass-hard steel; $3·46 \times 10^4$ mhos for that steel tempered at a yellow-heat; and $4·88 \times 10^4$ mhos when tempered at a blue-heat. H. Pécheux gave for very soft steel, with a little silicon, $8·50 \times 10^4$ mhos, and with more silicon, $7·40 \times 10^4$ mhos, while for semi-hard steel he gave $8·39 \times 10^4$ mhos, and for hard steel with a little silicon, $6·48 \times 10^4$ mhos; G. Kirchhoff and G. Hansemann, $7·11 \times 10^4$ mhos for puddled steel, and $4·31 \times 10^4$ mhos for Bessemer steel. W. Jaeger and H. Diesselhorst gave for steel with 1 per cent. of carbon, $5·02 \times 10^4$ mhos at 18°, and $3·91 \times 10^4$ mhos at 100°; J. Hopkinson, for magnetic steel with 25 per cent. of nickel, $1·92 \times 10^4$ mhos at 20°, and when non-magnetic, $1·39 \times 10^4$ mhos; and H. le Chatelier, for steel at 15° with 13 per cent. of manganese, $0·78 \times 10^4$ mhos when magnetic, and $0·61 \times 10^4$ mhos when non-magnetic. M. Mathieu studied the resistance of iron to an alternating current of 50 cycles.

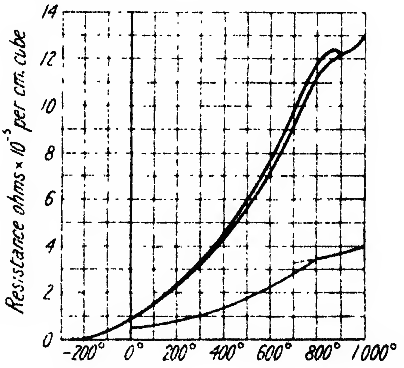


Fig. 258.—The Electrical Resistance of Iron.

The use of iron in place of copper conductors for electrical cables was discussed by W. T. Ryan, L. P. Perry, M. D. Leslie, H. B. Dwight, C. H. Risdale, W. Peukert, H. Pinsl, T. A. Worcester, W. Esch, and A. E. Kennelly. According to L. W. W. Morrow, the resistance rapidly increases with the current owing to the skin effect. The comparative resistances, R, in ohms per mile of single wire were :

Current	5	15	25 amperes
R Copper	1·172	1·172	1·172
R Iron (steel)	8·12	9·96	13·40
	9·35	9·96	11·10

The temp. coeff., a, of the resistance, was found by L. Cailletet and E. Bouty to correspond with $R=R_0(1+0\cdot004900\theta)$ between $-100°$ and $0°$. J. Dewar and J. A. Fleming gave for the resistance of soft, annealed iron, $R=R_0(1-0\cdot005310\theta)$ between $-100°$ and $0°$, and $R=R_0(1+0\cdot006250\theta)$ between $0°$ and $100°$, whilst for iron with 0·25 per cent. of manganese, and 0·01 per cent. of silicon, $R=R_0(1-0\cdot005440\theta)$ between $0°$ and $100°$. W. Jaeger and H. Diesselhorst gave $R=0\cdot0_410512(1-0\cdot005440\theta)$ for annealed iron with 0·25 per cent. manganese, and 0·01 per cent. of sulphur, between $-197°$ and $0°$, and for the hot-drawn metal, $R=0\cdot0_59065(1-0\cdot006250\theta)$. In the latter case :

	−39·2°	−81·9°	−197·1°	−217°	−222·2°
R	$0\cdot0_57168$	$0\cdot0_55318$	$0\cdot0_51220$	$0\cdot0_6725$	$0\cdot0_6660$

For iron with 0·1 per cent. of carbon, $R=R_0(1-0\cdot004610\theta)$, and for iron with 1·0 per cent. of carbon, $R=R_0(1-0\cdot0051310\theta)$. G. Niccolai gave $R=R_0(1-0\cdot0055700\theta)$ for the temp. coeff. between $0°$ and $100°$; P. W. Bridgman, $R=R_0(1-0\cdot0062060\theta)$ for iron with 0·03 per cent. of impurity, and at temp. between $0°$ and $100°$; L. Holborn, and A. R. Meyer gave $R=R_0(1-0\cdot006570\theta)$; G. K. Burgess and I. N. Kellberg, $R=R_0(1-0\cdot006350\theta)$; and E. P. Harrison gave for the resistance of iron up to $500°$, $R=0\cdot3318+0\cdot0012300\theta+0\cdot0_52209\theta^2$. A. Arndtsen gave $R=R_0(1-0\cdot0041300\theta+0\cdot0_411788\theta^2)$ between $5°$ and $156°$; H. F. Lenz, $R=R_0(1-0\cdot0017200\theta+0\cdot0_584670\theta^2)$ between $0°$ and $200°$; H. Tomlinson, $R=R_0(1-0\cdot0051310\theta+0\cdot0_581520\theta^2)$ for iron between $18°$ and $100°$; J. Hopkinson, $R=R_0(1-0\cdot00480\theta)$ at ordinary temp., $R=R_0(1-0\cdot00180\theta)$ at $855°$, and $R=R_0(1-0\cdot00670\theta)$ above $855°$; and R. Benoit, $R=R_0(1-0\cdot004516\theta+0\cdot0_51457\theta^2)$ between $100°$ and $860°$. A. A. Somerville gave for the purified metal, $R=R_0(1-a\theta)$:

	25°	100°	200°	400°	600°	750°	800°	1000°
$a\times10^4$	52	68	90	133	170	250	120	05

H. Pécheux found for very soft steel with a little silicon, $R=R_0(1-0\cdot00650\theta+0\cdot0_543\theta^2)$, steel with a little more silicon, $R=R_0(1-0\cdot00870\theta+0\cdot0_574\theta^2)$, for semi-hard steel, $R=R_0(1-0\cdot00490\theta+0\cdot0_589\theta^2)$, and for hard steel with silicon, $R=R_0(1-0\cdot00400\theta+0\cdot0_554\theta^2)$. V. Strouhal and C. Barus found for steel between $10°$ and $35°$, $R=R_0(1-0\cdot001610\theta)$ when glass-hard, $R=R_0(1-0\cdot002440\theta)$ when tempered at a pale yellow-heat, $R=R_0(1-0\cdot003300\theta)$ when tempered at a blue-heat, $R=R_0(1-0\cdot004230\theta)$ for soft steel, and $R=R_0(1-0\cdot00420\theta)$ for piano wire ; R. Benoit gave $R=0\cdot1149(1-0\cdot0049780\theta+0\cdot0_57430\theta^2)$ for soft steel between $100°$ and $860°$, and for soft iron, $R=0\cdot1272(1+0\cdot004520\theta+0\cdot0_5580\theta^2)$. J. A. Fleming gave $R=R_0(1-0\cdot001320\theta)$ for 24 per cent. nickel steel at $20°$, and $R=R_0(1-0\cdot0040\theta)$ at $600°$, whilst for manganese steel, he gave $R=R_0(1-0\cdot00120\theta)$.

T. Kase studied the change of electrical resistance of cast iron in the vicinity of the eutectic temp., and the results for white pig-iron with 3·52 per cent. of carbon, cooled from 1380°, are summarized in Fig. 259 ; analogous results were obtained with grey pig-iron. He found that the electrical resistance of the molten cast iron gradually decreases from 1380° down to the liquidus temp., 1210°, *AB*, and the slope of the curve then changes down to the eutectic temp., 1130°, *BC*, when the eutectic begins to separate ; the electrical resistance decreases abruptly at this temp., CD_2, and then decreases slowly, *DE*, Fig. 259. The ordinates at *D* and *C* are respectively 2·23 and 2·76, showing that at the eutectic temp., the resistance decreases by 19 per cent. of that of the melt. There is no evidence of a two-step transformation, one for cementite and one for graphite. H. Shimank estimated the resistance of unannealed iron to be 2·614 ohms at 0° K., and for the ratio $R_r : R_0$ at 273·09°, 198·3°, and 20·4° K., the respective values 1·0000, 0·6148, 0·1088, and 0·0330. Similarly, for annealed iron, $R_0 = 3·342$ ohms, and the ratio $R_r : R_0$ at 273·09°, 197·8°, 80·6°, and 20·4° K. becomes respectively 1·0000, 0·6130, 0·1033, and 0·0280. J. T. MacGregor-Morris and R. P. Hunt, A. R. Meyer, and J. W. Donaldson studied the conductivity of iron.

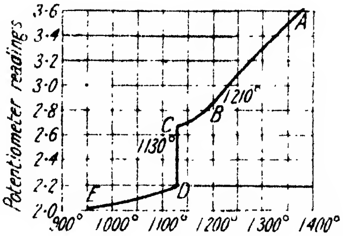
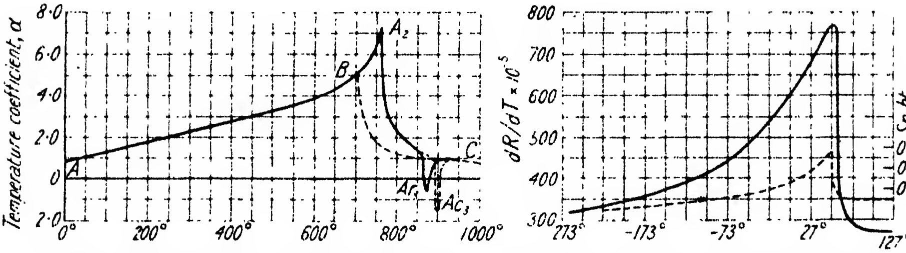


FIG. 259.—The Change of the Electrical Resistance of Cast Iron near the Eutectic Temperature.

G. K. Burgess and I. N. Kellberg measured the variations in the electrical resistance of electrolytic iron with variations of temp., *i.e.* the temp. coeff. of the resistance, $a = (R_{100} - R_0)/100R_0$, between 0° and 950°, and found that the value of a increases at a gradually increasing rate until the neighbourhood of the first critical region (A_2) is reached—Fig. 260. This region is characterized by a point of inflexion on the curve at 757°. As the temp. is further increased, there is an abrupt fall in the value of a at about 894°, and the reverse change occurs at approximately the same temp. when the temp. is allowed to fall. This second critical region (A_3) extends over an interval of 25°. Whilst the change A_2 is reversible and does not appear to be associated with any alteration in crystalline structure, the change A_3 seems to be progressive and (thermoelectrically) non-reversible, and furthermore it is associated with a change in crystalline form. A. R. Meyer's results are represented by the dotted line, *ABC*, Fig. 260, where the transition temp. is 710°. K. Tamaru gave $32·7 \times 10^{-6}$ ohm for the sp. electrical resistance of austenite in a 0·5 per cent. carbon austenitic steel; and K. Honda gave $20·8 \times 10^{-6}$ for the resistance of β-martensite. W. Gerlach's values for the relation between the temp. coeff. of the resistance, dR/dT, are given in Fig. 261, and, for comparison, the dotted line represents the sp. ht.



FIGS. 260 and 261.—The Change in the Temperature Coefficient of the Electrical Resistance of Electrolytic Iron with Temperature.

W. Kohlrausch, and J. Hopkinson also observed that there is an abrupt change in the electrical resistance of iron at the critical temp. A. Goffey and F. C. Thompson, and F. C. Thompson and E. Whitehead observed discontinuities in the resistance of mild steel at approximately 60°, 120°, 170°, 260°, 320°, 360°, and occasionally at 90°, 200°, and 230°. These values vary according to the rate of heating. With high-carbon steels, there are well defined points at 50°, 90°, 120°, 160° (often a double point), 200° to 190°, 220°, 250°, 300°, and 350°. Electrolytic iron gave peaks at 70°, 120°, 170°, 230°, 290°, 310°, and 350° (usually a double peak). There are also indications of breaks at 200° and 300°—*vide supra*. P. Fournel observed singularities in the temperature-resistance curves for steels with :

Carbon . . .	0·08	0·11	0·22	0·37	1·05 per cent.
A_1	—	670°	695°	730° to 770°	730° to 750°
A_2	775°	780°	740°		
A_3	880°	890°	790°		

In addition to the observations of G. K. Burgess and I. N. Kellberg on the breaks in the electrical resistance of iron as the temp. passes through the critical points, discontinuities were also observed by W. Broniewsky, E. Hall, B. V. Hill, and O. Boudouard. A. von Hippel and O. Stierstadt studied the conductivity in the vicinity of the γ–β transition temp. K. Bornemann and K. Wagemann measured the conductivity of molten iron; F. Skaupy and O. Kantorowicz, and O. Jaamaa and Y. E. G. Leinberg, the resistance of finely-powdered iron; H. Kamura, of hydrogen-reduced iron; F. Sauerwald and S. Kubik, and F. Skaupy and O. Kantorowicz, the resistance of powdered iron under pressure; and H. B. Peacock, and J. Kramer and H. Zahn, the resistance of thin films.

According to C. Benedicks, if an electric current passes through a homogeneous metallic conductor, with originally a uniform temp. throughout, it generally exerts a transport of heat in its own direction, or else in the reverse direction, according to the nature of the material. If the transport of heat is positive as in the case of copper, and some kinds of carbon steel, the temp. decreases, in the direction of the current, but if the transport is negative, the temp. increases in the direction of the current.

L. Campredon observed that the conductivity of steel diminishes with increasing proportions of impurities, manganese being specially deleterious. H. le Chatelier concluded from his observations on the effect of additions of carbon that in annealed carbon steels, the progressive addition of cementite caused a linear increase in the resistance of iron corresponding with 7·0 microhms per cm. cube per 1 per cent. of cementite, and, by extrapolation, he concluded that the sp. resistance of cementite is 45·0 microhms, and that of ferrite, 9·5 microhms. E. Gumlich plotted the results of his own observations, and also those of J. Hopkinson, and H. le Chatelier, and concluded that the values for the electrical resistances lie on a straight line for proportions of carbon increasing up to 1 per cent. at the rate of 6 microhms per cm. cube. Above 1 per cent. of carbon, the slope of the curve is less steep. F. Stäblein said that the sp. resistance of the carbon steels is a linear function of the proportion of carbon, with a break at 0·9 per cent. E. Gumlich's later results for the resistance R, and the temp. coeff. α, for steels cooled slowly from 930°, and for the resistance R', and the temp. coeff. α', for steels quenched from 850°, give curves which have a break at about 0·9 or 1·0 per cent. of carbon. E. Gumlich gave for the resistance of purified iron, $R=0·0994$, and for alloys with p per cent. of carbon, $R=0·105+0·03p+0·02p^2$ for alloys slowly cooled from 930°, and $R=0·103+0·016p+0·236p^2$ for alloys quenched from 850°. The break in the curve for the hardened alloy is dependent on the quenching temp. With higher quenching temp., when the whole of the carbon as well as hypereutectoidal cementite is in solid soln., the resistance curve is said to be a straight line. P. Saldau found an average increase of 9·0 microhms per cm. cube for 1 per cent. of carbon; and he observed a small peak at the eutectoidal composition. His steels were heated up to and cooled down from 1000°, so that they do not represent normal annealed steels. K. Honda and T. Simidu's observations indicate an increase of about 4 or 5 microhms per 1 per cent. of carbon. The slope of E. D. Campbell's curves correspond with an increase of about 4·5 microhms per cm. cube for 1 per cent. of carbon. The variable results here indicated for annealed steels are possibly connected with different conditions of annealing. A. L. Norbury represented E. D. Campbell's values for carbon steels, water-quenched from 900° and 1100°, and showed that the resistances do not lie on a straight line, but rather on a curved line. This is also in agreement with P. Saldau's, and E. Gumlich's results for water-quenched steels. A. Michels, and E. L. Dupuy found that cold-work—*e.g.* drawing into wire—decreases the resistance, and L. Guillet and M. Ballay found that the percentage increase in the resistance of iron due to cold-work is 0·50. G. Tammann and M. Straumanis studied the effect of cold-work on the resistance. E. D. Campbell found that at 1100°, 1 per cent. of carbon increases the resistance of iron by about 34 microhms.

B. D. Enlund found the sp. electrical resistance, *R*, microhms, of annealed and quenched steels:

Carbon . .	1·56	1·22	0·88	0·83	0·58	0·35	0·21 per cent.
Annealed . .	25·2	20·3	19·1	17·8	16·7	17·0	17·8
Quenched . .	56·0	45·0	37·0	34·3	26·4	21·0	17·6

and the effect of annealing temp. is summarized in Fig. 262. This shows that in all cases there are two breaks, one between 110° and 120°, and another between 250° and 260°. The breaks correspond with the precipitation of cementite accompanied by an increased conductivity. The first break is assumed to be due to the transformation of martensite into austenite, and the second to the splitting of austenite into α-iron and cementite. The second bend with mild steels is quite distinct, showing that these steels are not free from γ-iron. The subject was studied by L. Grenet, A. Schulze, and G. Dillner and A. F. Enström; the effect of repeated heating and cooling on the resistance of iron, by H. Tomlinson; the resistance of plates, by G. Haufe; and the resistance of thin films, by J. C. Steinberg, and J. Kramer and H. Zahn. W. Geiss and J. A. M. van Liempt found that the variations in the electrical conductivity produced by cold-work cannot be adequately explained by changes in the atomic distances, but they assume that a kind of anistropy is induced at the surface of the crystallites.

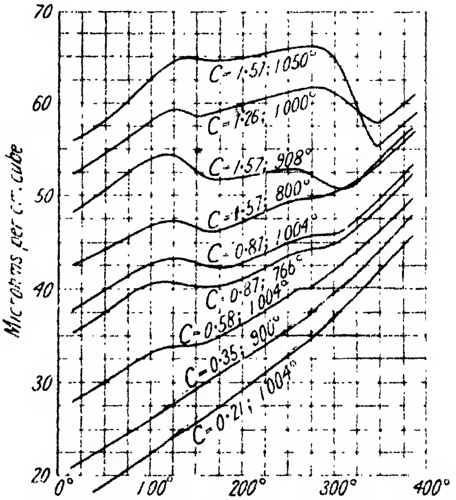


FIG. 262.—The Effect of the Annealing Temperature on the Resistance of Steels.

E. D. Campbell obtained the results indicated in Table XXXIX, for steels quenched from 892° and tempered at different temp. The calculated values for

TABLE XXXIX.—THE EFFECT OF HEAT-TREATMENT ON THE SPECIFIC RESISTANCE OF CARBON STEELS.

Carbon (per cent.)	Quenched from 892°	Re-heated to							
		105°	105°	295°	400°	492°	600°	700°	800°
0·04	11·12	10·94	10·81	10·83	10·78	10·75	10·69	10·78	10·70
0·30	16·13	15·56	14·96	13·86	13.55	13·04	12·84	12·64	13·20
0·35	17·59	16·67	16·05	15·11	14·86	14·37	14·25	14·27	14·51
0·41	18·91	17·79	16·94	15·69	15·13	14·82	14·51	14·47	14·98
0·57	22·31	19·92	17·08	16·24	15·60	15·02	14·71	14·67	15·11
0·94	35·95	27·97	22·40	19·42	18·37	17·60	16·65	16·19	17·23
1·04	41·92	33·02	25·73	21·82	20·62	19·92	19·60	19·03	19·08
2·71	52·59	42·65	32·49	27·41	26·17	24·94	24·21	22·57	20·82

the annealed steels are made on the assumption that in the second and third cases, it is assumed that 0·07 per cent. of carbon remains in solid soln., and in all those containing more than 0·45 per cent. of carbon, 0·27 per cent. remains in solid soln.:

Carbon	0·04	0·35	0·41	0·57	0·76	0·945	1·05 per cent.
ΣC	0·076	0·461	0·521	0·678	0·901	1·063	1·174
R Obs.	11·10	17·63	18·46	21·41	30·95	36·82	40·07
R Calc.	9·63	19·96	21·56	25·78	31·75	36·09	39·06
R'' Obs.	10·66	14·38	14·45	14·78	17·26	17·23	17·50
R'' Calc.	9·63	12·45	12·45	17·72	18·61	18·00	18·16

The results are taken to mean that it is not the atomic concentration of the carbon which determines the effect of the solute on the sp. resistance. Equimolar concentrations of carbides in soln. exert an equal influence on the sp. resistance. A comparison of the values for the sp. resistances, *R*, of steels quenched from 907° and tempered at 105°, and the sp. resistance, *R′*, of steels annealed at 880° :

Carbon	0·04	0·35	0·41	0·57	0·76	0·945	1·05 per cent.
R 25°	10·90	16·83	17·89	19·87	25·75	27·31	29·19
R 95°	15·11	21·12	22·25	24·23	30·35	31·98	33·83
R' 25°	10·66	14·38	14·45	14·78	17·26	17·23	17·56
R' 95°	14·65	18·42	18·48	18·82	21·51	21·51	21·82

shows that the increase in the sp. resistance between 20° and 95° ranges in all cases between 0·057 and 0·067 per degree, and the deviation from the value with almost pure iron is very small. This is taken to mean that the increase in the sp. resistance with the rise of temp. is almost wholly due to the increase in the sp. resistance of the solvent, while that component of the total sp. resistance due to the solute in solid soln. is only slightly affected by the rise of temp.

The influence of the heat-treatment on steels was examined by C. Benedicks, O. Boudouard, H. le Chatelier, L. Campredon, H. A. Dickie, K. Honda, J. Hopkinson, W. H. Johnson, W. Köster and H. Tiemann, A. Martens and co-workers, E. Maurer, F. Osmond, W. Rohn, R. Schneider, T. Swinden, and G. Tammann and co-workers. V. Strouhal and C. Barus gave for the resistance, *R* microhms, and the temp. coeff., *a*, of steels :

		Annealed				
	Glass-hard	Light yellow (220°)	Yellow (250°)	Blue (300°)	Light blue (320°)	Soft
R	45·7	28·9	26·3	20·5	18·4	15·9
a	0·00161	0·00244	0·00280	0·00330	0·00360	0·00423

I. Iitaka studied the electric conductivity changes which accompany the cementite transformation. E. D. Campbell found the data of Table XXXIX for the sp. resistance, in microhms per cm. cube at 20°, of steels quenched from 892°, and tempered or annealed at the indicated temp. The result shows a close relationship between the concentration of the carbides in solid soln. and the sp. resistance. The divergence at 800° is attributed to the segregation of the carbides into relatively large masses, and although the precipitation would be nearly complete, the separated cementite consists of carbides saturated with iron in solid soln., and this causes an increase in the sp. resistance. H. le Chatelier, C. Benedicks, E. Maurer, E. D. Campbell, and A. McCance also showed that the electrical resistance of hypoeutectoidal steels increases with the temp. of quenching.

O. von Auwers and G. J. Sizoo measured the effect of *grain-size* on the sp. electrical resistance of iron, but obtained no appreciable difference. J. R. A. Mousson, and O. Chwolson found that the sp. resistance of drawn wire is smaller in the hard tempered state than that of the same wire in the soft state. P. Goerens observed that the change in the electrical conductivity of various steels induced by cold-working is too small to be detected ; and that the effect of the temp. of annealing is to produce a fall in the sp. conductivity from 12·25 to 11·90 corresponding with a 2·8 per cent. reduction in the conductivity in the neighbourhood of 520°. E. Maurer's observations on the percentage change in the resistance of austenite with variations in the annealing or tempering temp ; and the observations of J. H. Andrew and co-workers, and others are summarized in Table XXXIX. The effect of annealing was studied by I. P. Parkhurst ; and the effect of the duration of the period of heating before quenching, by A. M. Portevin. H. Kleine found that the electrical resistance of iron annealed in vacuo increases linearly if it be allowed to stand in air over a period of 5 days. The effect is due to the absorption of gases. Similarly, if the gassed metal is re-heated in vacuo, the resistance falls.

K. Honda and T. Simidu obtained for the sp. resistance, *R*, in 10^{-5} ohms per cm. cube at 30°, of iron with the following proportions of carbon, silicon and manganese, as forged, and as annealed at 900°, and quenched at 900° :

Carbon . . .	0·14	0·18	0·44	0·64	0·80	0·94	1·30	1·50	per cent.
[Mn + Si] . .	1·01	0·54	1·35	0·39	0·50	0·61	0·57	0·47	at. per cent.
R Forged . .	1·91	1·75	2·32	1·78	1·91	1·99	2·09	2·18	
R Annealed . .	1·91	1·75	2·14	1·77	1·92	1·99	2·18	2·18	
R Quenched . .	1·93	1·77	2·41	1·82	2·02	2·30	2·23	2·50	

J. H. Andrew and co-workers measured the sp. resistance of a number of steels quenched and tempered at different temp., and the results with carbon steels show that the sp. resistance of hypereutectoid steels is increased by raising the quenching temp., and that with hypoeutectoid steels, the sp. resistance is decreased by raising the quenching temp. E. D. Campbell, and P. Saldau reported that in hypoeutectoid steels, the raising of the quenching temp. increased the sp. resistance ; H. le Chatelier, C. Benedicks, and A. McCance, that this treatment made no change in the sp. resistance ; whilst J. H. Andrew and co-workers observed this treatment depressed the sp. resistance. The annealed carbon steels show a break at the eutectoid concentration, and beyond this percentage of carbon, the resistance increases less rapidly with the proportion of carbon. The amount of carbon dissolved in α-iron increases with the carbon-content up to 0·9 per cent. when further additions produce only free cementite. The sp. resistance of carbon steels, tempered for 6 hrs. at 240°, shows that some carbon steel remained in soln. in the tempered steels, although tempering was practically completed for that particular temp. To compare these results with those obtained by others, J. H. Andrew and co-workers recommended using the correction of G. K. Burgess and co-workers, E. Gumlich, and H. le Chatelier for silicon, where 1 per cent. silicon raises the resistance 13·5 microhms ; that of E. d'Amico, where 1 per cent. of phosphorus raises the resistance 11·0 microhms ; and that of W. F. Barrett and co-workers, G. Lang, and T. Matsushita, where 1 per cent. of manganese raises the resistance 5·5 microhms. C. Benedicks' corrections apply for carbon steels, but not for alloy steels. The resistance curves of the annealed steels are similar ; there is first a rapid increase and then a slow fall, or almost a constant value. In the curve for 1·6 per cent. carbon some austenite was retained after the quenching, and the other curves are typical of the tempering of martensitic steels. W. Fraenkel and E. Heymann measured the electrical resistance, *R*, of a steel containing 0·80 per cent. carbon, and 0·50 per cent. manganese, and quenched from 800°, at different stages of the annealing process. C. Barus, and L. C. Brant observed that glass-hard steel gradually softens at ordinary temp. when kept for prolonged periods. Thus, the curve, Fig. 263, represents the sp. resistance of two glass-hard, steel wires over a period of 30 years.

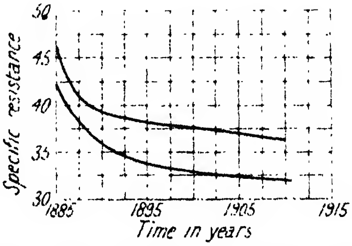


Fig. 263.—The Effect of Time on the Electrical Resistance of Hard Steel.

K. Takahasi observed minima in the changes in the electrical resistance of electrolytic iron, armco iron, and 0·1 and 0·3 per cent. carbon steels at different temperatures. The minimum for electrolytic iron is at 750° ; for armco iron, at 680° ; for 0·1 and 0·3 per cent. carbon steels, respectively, at 650° and 620°. The change of electrical resistance of a metal produced by cold-working has been attributed to the orientation of the minute crystals of which the metal consists. That is, by drawing, the minute crystals of the metal arrange themselves in a certain direction parallel to each other and also to that of the cold-drawing. The electrical resistance of the crystals is assumed to be greater in this direction than in all others, and hence the resistance of the metal increases in the direction of the cold-working. If, however, the metal is recrystallized by annealing, the orientation of the crystals has no longer a definite direction and the electrical resistance decreases. Against this view, K. Takahasi said that the anisotropic nature of the electric resistance of crystals belonging to the cubic system is not in agreement with observation. Besides, the change of resistance of a cold-worked metal by annealing has no intimate relation with the recrystallization of the metal. According to G. Tammann and co-workers, the change is not due to the internal stresses produced by cold-working because, in a metal severely cold-drawn, there is tension in the outer portion of it, and compression in the inner, and the equilibrium is maintained elastically. In this case, the change of resistance due to elastic tension and compression is equal in magnitude and opposite in sign, and these two effects cancel each other. It is not reasonable therefore to attribute the cause of the change of resistance to the internal stress. K. Takahasi bases his explanation on the fact that a severely cold-worked metal generally consists of a large number of minute groups of crystals, in each of which one portion undergoes a tension and the other portion a compression, these two balancing each other, so that the lattice expands in one portion and contracts in the other. Now, according to the ordinary law of atomic force, the expansion of the lattice is somewhat greater than the contraction for the same strength of tension and compression. Hence, the lattice expands as a whole, cold-working thus causing a diminution of density. Again, each atom of a metal consists of a nucleus and bound electrons revolving around it; the mutual distance of these atoms is very small, but comparable with the diameter of the orbit of outer electrons; hence, some of these electrons may stray off from the atom, to which they were originally bound, through the attraction of the nuclei of other atoms, and play the rôle of free electrons, thus conducting electricity through the metal. When the distance of these atoms is increased by cold-working, some of the free electrons may be caught again by an atom and the number of free electrons be diminished, an increase of electrical resistance being thus caused by cold-drawing. As the decrease of density caused by cold-drawing does not increase beyond a certain limit, the increase of resistance also cannot exceed a certain limit. Again, the electrical resistance is affected by the fibrous structure; as mentioned above, a metal which has undergone a severe cold-working has a fibrous structure; the crystals are broken up into small pieces which are elongated in the direction of the drawing. Hence, in this direction, the number of crystal boundaries is much less than that in the perpendicular direction, so that the specific resistance will be less in the direction of the drawing than in all other directions. As the degree of cold-drawing increases, the crystals become more and more elongated in the direction of the drawing, and thus the specific resistance in this direction always diminishes. Besides, insoluble impurities which have been segregated in a thin layer in the crystal boundaries and have prevented the flow of electricity, are broken up by cold-drawing and thus diminish the electrical resistance on the crystal boundaries. These two effects of the fibrous structure of metals are thus the cause of diminishing the electrical resistance in the severely cold-drawn metals. Hence, the cold-drawing produces, on one hand, an increase of resistance by internal strain, and, on the other hand, a decrease of it owing to the fibrous structure; as the result of these two opposite effects, the electrical resistance first increases and reaches a maximum, as the degree of cold-working increases, and afterwards begins to decrease. For C. Nusbaum and W. L. Cheney's observations on the effect of cooling an eutectoid carbon steel at different rates, *vide* Table XLI, magnetism.

H. Kleine observed that the resistance of iron decreased when the metal was tested under reduced press., and the phenomenon was traced to the effect of absorbed gases. T. Skutta studied the effect of high gas press. W. F. Barrett found that the conductivity of iron is diminished by alloying it with another metal, even though that metal be a much better conductor than iron. This reduction of conductivity is not related to the resistivity of the added metal; on the contrary, an alloy of very high sp. resistance can be produced by adding to iron an element of much lower sp. resistance than the iron itself; for instance, aluminium is more than three times a better conductor than iron, yet the addition of 5 per cent. of aluminium to iron makes the conductivity of the alloy five times worse than that of iron. The greatest reduction in conductivity in a given alloy is produced by the first increments of the added elements. A relationship appears to exist between the sp. ht. of the added element and the resistance of the alloy formed with the iron. Thus, the sp. resistance of an alloy of 5·5 per cent. of aluminium with iron is 70 microhms; the same amount of silicon with iron gives an alloy with a resistance of 65 microhms; of manganese with iron, 38 microhms; of nickel, 27 microhms; and of tungsten, 18 microhms. Now, the sp. ht. of these elements are: aluminium 0·212, silicon 0·183, manganese 0·122, nickel 1·109, and tungsten 0·035. Consequently, those elements having high sp. ht., and therefore small at. masses, produce the greatest increase in the electrical resistance of the corresponding alloy with iron.

H. le Chatelier observed that equi-atomic proportions of carbon and silicon in soln. raise the resistance of iron by the same amount. He showed that in A. Matthiessen's resistance curves for alloys, showing the effect of composition on the resistance, indicates that the constituents are mechanically admixed, but a drop in the curves corresponds with the formation of solid soln. W. F. Barrett and co-workers found that the effect produced on the resistance of iron by 1 per cent. of added element is inversely proportional to the at. wt. of the latter, and that the increase in sp. resistance follows the same order as the increase in sp. ht. C. Benedicks suggested that equivalent quantities of foreign elements dissolved in iron cause the same increase in resistance. The rule is based on the assumption that equi-atomic solutions in iron possess equal resistances; the subject was discussed by E. D. Campbell. If ΣC denotes the summated values of all the elements dissolved in the iron expressed in terms of carbon, and if 25·8 represents the increase in resistance caused by the presence of 1 per cent. of carbon, then, if 7·6 microhms per cm. cube represents the resistance of iron alone, the resistance of the alloy will be represented by *Benedicks' rule*: $R=7{\cdot}6+25{\cdot}8\Sigma C$. The carbon value is obtained by dividing the percentage proportion of the element, here represented by the chemical symbol in brackets, by its at. wt., and multiplying the result by 12, the at. wt. of carbon, *e.g.* $\Sigma C=[C]+0{\cdot}4200[Si]+0{\cdot}2184[Mn]+\ldots$ The rule was found to apply fairly closely for solid soln. containing C, Al, Si, P, Cr, Mn, Co, Ni, As, Mo, and W. C. Benedicks said that it is difficult to fix the upper limit of the validity of the rule. It applies to dil. soln. Probably ΣC will exceed 2 per cent., but not 3 per cent. He also observed that iron carbide or cementite does not appear to exert any influence on the resistance so long as it is isolated within the mass of the iron, but A. M. Portevin found that the structure has a considerable influence on the nature of the variations in resistance due to the addition of elements to iron—*vide infra*. Again, C. Benedicks' extrapolated value, 7·6 microhms per cm. cube, for the resistance of iron is much lower than the observed value about 10·0 microhms per cm. cube. C. Benedicks said that the difference can be explained by remembering that the higher value would be lowered to the extrapolation result by admitting the presence of only 0·004 per cent. of hydrogen in solid soln. A. Sieverts, however, heated iron wire in hydrogen between 20° and 920°, but could not detect any appreciable alteration in the electrical resistance. H. Jellinek found that the electrical resistance of iron shows an 8·9 per cent. increase when the press. of the hydrogen rises from 0 to 35 atm.; and in nitrogen, a decrease of 4·5 per cent. between 0 and 15 atm. press., and an increase of 13·3 per cent. between 15 and 20 atm. press. T. Sexl studied the effect of adsorbed gas on the resistance of iron. T. Skutta observed that the resistance of steel, in atm. of hydrogen and nitrogen, at press. up to 30 atm., is augmented, and that with hydrogen a stable soln. is formed. The extrapolation is based on the assumption that the resistance curve is a straight line, but this assumption is not quite correct. H. Masumoto's observations extrapolated for cementite, Fe_3C, gave $R=0{\cdot}0_314$ ohm per cm. cube; and F. Stäblein's observations, $0{\cdot}0_47$ ohm per cm. cube.

Other methods of calculating the electrical resistance of steels from the chemical composition, were discussed by P. Mahler, J. H. Partridge, F. Stäblein, M. A. Hunter and A. Jones, L. Guillet, E. D. Campbell and W. C. Dowd, C. H. Risdale, C. H. and N. D. Risdale, K. Honda and T. Simidu, and O. Boudouard. H. Masumoto gave $R=1{\cdot}044+0{\cdot}548[C]+1{\cdot}527[Si]+0{\cdot}718[Mn]+\ldots$ T. D. Yensen gave $R=9{\cdot}6+82{\cdot}5[C]+4{\cdot}5([C_1]-0{\cdot}02)$, where [C] denotes the excess of carbon under

TABLE XL.—THE EFFECT OF ADDED ELEMENTS ON THE ELECTRICAL RESISTANCE OF IRON.

Element	Atomic weight	Increase in the resistance in microhms per cm. cube, due to the presence of 1 per cent. of added element	Temperature	Product of at. wt. and resistance	Increase in the sp. resistance due to the presence of one gram-atom added element in 100 gram-atoms of alloy	Authority
Nitrogen	14·0	14·6	20°	204	3·6	H. Braune
Aluminium	27·1	11·1	18°			W. F. Barrett, etc.
,,	—	11·7	23°			A. M. Portevin
,,		12·0	20°	325	5·8	T. D. Yensen
,,	—	12·0	20°			E. Gumlich
Silicon	28·3	14·0	—			H. le Chatelier
,,		10·3	18°			W. F. Barrett, etc.
,,	—	12·0	—			G. K. Burgess, etc.
,,		13·0	15°			P. Paglianti
,,		13·0	20°			T. D. Yensen
,,		14·0	20°		—	E. Gumlich
,,		13·5	—	382	6·9	A. L. Norbury
Phosphorus	31·0	11·0		341	6·1	E. d'Amico
Vanadium	51·1	5·0	—	255	4·6	A. M. Portevin
Chromium	52·0	5·4	12°	281	5·0	A. M. Portevin
Manganese	54·9	5·0 magnetic	—	—	—	H. le Chatelier
,,	—	3·5 non-magnetic	—	—	—	W. F. Barrett
,,		5·0	18°			G. Lang
,,	—	5·5	20°	302	5·4	T. Matsushita
,,	—	5·5	30°			
,,		5·0	20°	275	4·9	E. Gumlich
Nickel	58·7	1·5	—	—	—	A. M. Portevin
,,	—	1·5	30°	88	1·5	K. Honda
Cobalt	59·0	1·0	30	59	1·0	K. Honda
Copper	63·6	3·0 or 4·0	—			G. K. Burgess, etc.
,,	—	4·0		254	4·5	R. Ruer, etc.
Molybdenum	96·0	3·4 (approx.)	17°	326	5·8	A. M. Portevin
Tungsten	184·0	1·1	18°			W. F. Barrett, etc.
,,	—	1·5	15°	276	4·9	A. M. Portevin
Gold	197·2	1·1	—	217	3·9	W. Guertler

0·02 per cent., and $[C_1]$, the excess of carbon over 0·02 per cent.; and E. D. Campbell and H. W. Mohr, $R=10{\cdot}44+3{\cdot}7[C]$ for [C] up to 1·1 per cent., and $R=14{\cdot}51+7{\cdot}8([C_1]-1{\cdot}1)$ for $[C_1]$ between 1·1 and 1·5 per cent. The results of a number of observations on the effect of additions of various elements on the electrical resistance of iron, compiled by A. L. Norbury, are given in Table XL, and the summary in Fig. 264 shows that equi-atomic proportions of the different elements in solid soln. in iron do not increase the electrical resistance to the amount required by C. Benedicks' rule. A factor dependent on the atomic properties of the particular elements in solution seems to determine the increase in the atomic resistance. E. D. Campbell pointed out that C. Benedicks' rule that equi-atomic concentrations in iron possess equal resistances, assumes that the elements other than iron are wholly in soln., and that each atom exerts an equal influence on the resistance. He compared the sp. resistances of steels hardened by quenching and when annealed, and added that in order that the elements may be in soln. as completely as possible, the sp. resistance under consideration must be that of steels in the hardened condition. Even then, however, there are such wide differences between the observed and calculated values that he said "the formula of C. Benedicks cannot be considered as being of any particular significance."

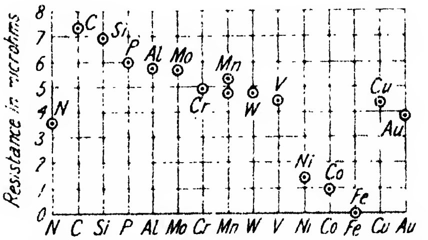


Fig. 264.—The Increase in the Specific Resistance of Iron by the Addition of 1 Gram-atom of Element in 100 Gram-atoms of Alloy.

K. Honda and T. Simidu, E. Grüneisen and E. Goens, and H. Masumoto compared the electrical and thermal conductivities from the point of view of G. Wiedemann and R. Franz's rule—*vide supra,* thermal conductivity. W. Broniewsky compared the sp. vol. and resistance of metals.

A. M. Portevin found that the electrical resistance of alloy steels varies with the nature of the added elements, and with the microstructure produced by quenching. As a result, the following types can be distinguished :

1. *Pearlitic steels.*—The resistance increases steadily with an increase in the percentage of the added element, and may be represented in terms of the latter factor, by a linear formula, or by a parabolic formula the coeff. of the squared term of which is small (aluminium steels). On quenching the steels, the resistance increases corresponding with the passage into solid soln. of the available carbon of the carbide. It was possible, in most instances, to verify the fact stated by C. Benedicks, that steels with about 0·8 per cent. of carbon in the normal state contain about 0·27 per cent. of their carbon in a state of solid soln. The presence of certain elements, such, for instance, as molybdenum, appears to modify the latter figure.

2. *Martensitic steels.*—The increase in the electrical resistance with that in the percentage of the special element is smaller than in the case of the pearlitic steels. The variation in the resistance on hardening is practically *nil* for the steels containing a low percentage of carbon, as may be very clearly seen with pearlitic steels containing the same percentage of carbon. For the martensitic steels with 0·8 per cent. of carbon there is an increased electrical resistance on hardening, the magnitude of which decreases in proportion as the percentage of the special element becomes higher. Not all the carbon of the martensitic steels is therefore in soln. This fact corresponds, likewise, with the hardening which occurs on quenching the martensitic steels; this is seen, in particular, with those steels which border closely on the pearlitic steels.

3. *Polyhedral steels.*—The polyhedral steels are distinguished by a rapid rise in the electrical resistance, with the rise in the percentage of the added element. On hardening they undergo no variation, or only a slight diminution. This diminution corresponds with the appearance of martensite, in lanceolate crystals, and occurs in steels which border closely upon the martensitic class.

4. *Double carbide steels.*—Two conditions may be distinguished : (*a*) The addition of the special element betrays itself by an increase in the amount of carbide (chromium and tungsten steels and vanadium steels with 0·8 per cent. of carbon and less than 5 per cent. of vanadium), while the electrical resistance remains practically constant or undergoes but slight increase. (*b*) With increasing proportions of the special element the amount of carbide varies but slightly (vanadium steels with low percentages of carbon and vanadium, and steels with 0·8 per cent. of carbon and over 7 per cent. of vanadium), and there is then seen a notable increase in the electrical

resistance which corresponds with the increased conc. of the solid soln. surrounding the carbide. The variation in the resistance on hardening depends both on the nature of the constitution which surrounds the carbide, and on the solvent capacity of this carbide. The pearlitic steels and those containing the carbide undergo an increase in their electrical resistance on hardening, corresponding with that of the ordinary pearlitic steels, to which has, at times, to be added that which results from the soln. of the carbide (vanadium steels). Steels with a martensitic basis display a smaller increase in electrical resistance on hardening than those of the preceding category.

Steels consisting mainly of a solid soln. do not, generally speaking, undergo any change on hardening. It is necessary in this connection to point out that the soln. of carbon on hardening depends on all the phases of the heat-treatment: temperature of heating; duration of heating; rate of cooling; and rate of traversing the critical point. It is not possible, therefore, definitely to pronounce upon the influence of this treatment on the electrical resistance, except after experiments in which these different factors had been varied. From what has been said it will be seen that C. Benedicks' law which expresses linearly the variation of the electrical resistance in terms of the percentages of the elements in solid soln. in the iron, can only be applied in the case of low percentages of the special elements. The limits of its applicability may, in the case of steels containing low carbon percentages (0·2 per cent.), be fixed approximately as follows: nickel steels less than 2·0 per cent.; chromium steels less than 1·0 per cent.; tungsten steels 7·0 per cent.; aluminium steels 1·0 per cent.; molybdenum steels 5·0 per cent.; vanadium steels 3·0 per cent.; titanium steels less than 0·5 per cent.; and boron steels less than 0·2 per cent. Below these amounts the increase in the electrical resistance for each per cent. of the element added agrees in a satisfactory manner with that calculated from C. Benedicks' formula, which thus appears to be chiefly a limiting formula to which an approach is made whenever the percentage of the added element decreases. It is the equation of the tangent of the commencement of the curve representing the electrical resistance in terms of the percentage of the special element. Observations were made by B. V. Hill.

O. Chwolson discovered a minimum in the resistance curve of steel when tempered below 350°, and C. Fromme observed a maximum in the sp. gr. curve in the same region. There is a rough sort of proportionality between the sp. gr. or sp. vol. and the resistance. Thus, with C. Fromme's data, for steel:

	Commercial soft	Glass-hard	Annealed			
			Yellow (250°)	Blue (300°)	Grey (350°)	Soft
Sp. gr. . .	1·00000	1·00772	1·00347	1·00217	0·99957	--
Resistance .	---	46	26	20	18	16

V. Strouhal and C. Barus studied the relation between *specific gravity*, and electrical resistance, and failed to find an immediate relation; and they also showed that the temp. coeff. of the electrical resistance decreases in proportion as the electrical resistance decreases, or as its hardness increases at a rate which diminishes in passing from soft to hard steel—*vide supra.*

N. S. Kurnakoff and S. F. Schemtschuschny showed that in solid soln. of the metals, there is a relation between the electrical resistance and the *hardness*, since these two properties usually vary in the same proportion. Comparing the hardness of alloy steels observed by L. Guillet with the resistance curves, A. M. Portevin observed that in their general characters, the curves present an air of family likeness, notably in the case of chromium steels, and tungsten steels containing 0·8 per cent. of carbon, and aluminium steels with 0·2 per cent. of carbon. Notable points of difference occur with the nickel steels. It is therefore inferred that these two physical properties—electrical resistance and hardness—are functions of a large number of variable factors, and that amongst those variable factors, there are certain common ones whose influence, when not masked by that of others, reveals itself by a correspondence in the appearance of the curves of variations in resistance and hardness.

P. W. Bridgman examined the effect of temp. and *pressure* on the electrical resistance of iron with less than 0·03 per cent. of impurity, and consisting entirely of ferrite. The results show that for press., p kgrms. per sq. cm., the press. coeff. are:

		0°	25°	50°	75°	100°
R		1·0000	1·1416	1·2918	1·4519	1·6206
Press. Coeff.	$p=0$	$-0{\cdot}0_5 2405$	$-0{\cdot}0_5 2420$	$-0{\cdot}0_5 2436$	$-0{\cdot}0_5 2451$	$-0{\cdot}0_5 2468$
	$p=1{\cdot}2000$	$-0{\cdot}0_5 2119$	$-0{\cdot}0_5 2150$	$-0{\cdot}0_5 2180$	$-0{\cdot}0_5 2209$	$-0{\cdot}0_5 2238$
	Averago	$-0{\cdot}0_5 2262$	$-0{\cdot}0_5 2285$	$-0{\cdot}0_5 2308$	$-0{\cdot}0_5 2330$	$-0{\cdot}0_5 2353$

These results correspond with an average temp. coeff. of 0·006206 between 0° and 100°; and for the average press. coeff., $-0{\cdot}0_5 246$. The value of the press. coeff. of the resistance of iron, $R^{-1}(dR/dp)$, is related to the change in the conductivity and compressibility, dv/dp, by the expression $R^{-1}(dR/dp)=K^{-1}(dK/dp)+\frac{1}{3}v(dv/dp)$, where K denotes the conductivity; v, the volume; and p, the press. U. Fischer gave for the press. coeff., $-10^{-7}dR/Rdp=21{\cdot}6$ at 273·1° K.; 23·7 at 198° K., and 34·4 at 81° K. P. W. Bridgman obtained for the average press. coeff. at 0°, −7·84°, and −182·9°, at press. up to 7000 kgrms. per sq. cm., $-0{\cdot}0_5 234$, $-0{\cdot}0_5 227$, and $-0{\cdot}0_5 234$. B. Beckman observed $-0{\cdot}0_5 2405$ for the press. coeff. E. D. Williamson found the ratio of the resistances at 1 and 12,000 kgrms. per sq. cm. press. to be 0·9729. A. T. Waterman, and A. Schulze discussed the conductivity as a function of press. in accord with the electron theory. The effect of cold-work on the electrical resistance was studied by P. Bardenheuer and H. Schmidt. A. Campbell measured the Joule heating effect of currents. G. R. Wait and co-workers observed that exposure to radio-frequencies had no effect on the resistance.

H. Rolnick, R. S. Bedi, J. Russner, and W. H. Johnson studied the effect of tensile stresses on the electrical resistance of iron. H. Tomlinson observed that the temporary increase in the electrical resistance of an iron wire under *tensile stresses* where the wire is stretched in the same direction as the current, is exactly proportional to the stretching force. The percentage increase in the resistance which occurs when a cube of the material is stretched by the same weight is greater with iron than with steel wire, and this increase is nearly the same for different specimens of the same material. The percentage increase in the resistance which occurs when the material is stretched to the same extent is greater with iron than with steel wire. There is in each case a residual increase over and above that which would follow from a mere increase in length or sectional area which is greater with iron than with steel. H. Tomlinson gave 2111×10^{-12} for the increase of resistance per unit produced by a stress of a gram per sq. cm.; 4·180 for the increase per unit of resistance which would be caused by a stress sufficient to double the length of the wire, and 2·618 for the increase per unit of sp. resistance which would be caused by a stress sufficient to double the length of the wire. Otherwise expressed, the percentage increase in the sp. resistance by a stretching force of one kilogram per sq. cm. is $0{\cdot}0_5 1080$ for steel, and $0{\cdot}0_5 1258$ for iron. S. Fukuta found for steels with 0·3 to 1·5 per cent. of carbon, the average $0{\cdot}0_6 1139$. In general, the increase in sp. resistance is proportional to the applied stress; and the increase in the sp. resistance decreases slightly with an increase in the proportion of carbon. T. Uêda found that the sp. electrical resistance of iron and carbon steel, when stretched, increases as the tensile stress increases, and makes a discontinuous change at the yield-point, and afterwards increases. The discontinuity is at first positive, and as the carbon-content increases, it becomes negative. The rate of change of the sp. resistance decreases as the carbon-content increases. R. S. Bedi, and J. B. Seth and C. Anand observed no decrease such as occurs with nickel wires in the early stages of the stretching. A. Campbell found no change in the electrical resistance of iron, and iron-nickel wires when subjected to tensile stresses up to the breaking-point. A. Campbell also found that the conductivity of soft iron remained practically constant under the influence of tensile stresses, indicating that up to the breaking-point the metal stretches out as if it were a liquid. W. Brown measured the effect of an electric current on the subsidence of the torsional oscillations of an iron wire.

P. W. Bridgman showed that the percentage change of electrical conductivity with loads of 2050 and 1025 kgrms. per sq. cm. are respectively $-0{\cdot}518$ and $-0{\cdot}257$ while the proportional changes of conductivity per kgrm. per sq. cm. are respectively $-2{\cdot}53\times10^{-6}$ and $-2{\cdot}51\times10^{-6}$; the proportional changes of sp. conductivity per kgrm. per sq. cm. are respectively $-1{\cdot}82\times10^{-6}$ and $-1{\cdot}80\times10^{-6}$. The value of $(1+2\sigma)/E$ is $0{\cdot}71\times10^{-6}$. He also found that with iron, the longitudinal fractional change of resistance per kgrm. per sq. cm. is $2{\cdot}13\times10^{-6}$ when the tension is parallel and also perpendicular to the direction of rolling, and when corrected for distortion, the value is $1{\cdot}42\times10$. The geometrical mean of longitudinal and transverse fractional change of resistance per kgrm. per sq. cm. is $0{\cdot}99\times10^{-6}$, or corrected for distortion, $0{\cdot}86\times10^{-6}$, when the tension is parallel to the direction of rolling; and when perpendicular to the direction of rolling, $1{\cdot}33\times10^{-4}$, or, when corrected for distortion, $1{\cdot}20\times10^{-6}$. The calculated fractional change of transverse resistance per kgrm. per sq. cm. is $0{\cdot}30\times10^{-6}$ when taken parallel, and $0{\cdot}78\times10^{-6}$ when taken perpendicular to the direction of rolling. R. S. Bedi found that the resistance of iron or steel, under a stretching load, decreases up to the elastic limit, and the resistance minimum coincides with the elastic limit. F. Credner observed that the decrease in the resistance of wires under tension when heated, reaches a minimum with iron at 600°—*vide* nickel. T. Ionescu discussed the Joule effect; W. G. Kannuluik, R. Kikuchi, the relation between the electrical and thermal conductivities—*vide supra*; and S. Procopiu, the relation between the electrical resistance, the sp. ht., and the temp. of a metal wire.

W. K. Mitiaeff observed an anomalous change in the resistance of iron wire at radio-frequencies, but G. R. Wait and co-workers would not verify this. H. M. Brown found that a magnetic field of 10,000 gausses increased the electrical conductivity 0·2 per cent. G. Barlow, W. F. Barrett, H. Bethe, L. Bloch, G. Borelius, H. Braune, W. Brown, M. Dumermuth, J. Dorfman and co-workers, N. H. Frank, W. Gerlach and E. Englert, W. Gerlach and K. Schneiderhan, K. Ghosh, T. Gnesolto, A. Gray and E. T. Jones, P. Kapitza, G. Mahoux, J. A. Mathews, M. Medici, E. Merritt, A. Perrier, H. Sachse, K. Schneiderhan, O. Stierstadt, and H. Tomlinson studied the change of the electrical conductivity in strong magnetic fields *vide infra*. O. Stierstadt studied the change in the electrical conductivity of iron in a longitudinal magnetic field. H. H. Potter measured the effect of magnetization on the change of resistance and some results are summarized in Fig. 265. The temperatures are expressed in terms of the Curie temperature 1050° K. The dotted lines refer to the transverse and the continuous lines to the longitudinal effect. Near the Curie point, the value $\delta R/R$ changes less rapidly than the first power of H, but with rising temp. the curves gradually change in shape until, above the Curie point, the value of $\delta R/R$ varies as H^2. H. Walker, and R. Schenck made observations on the subject. O. Stierstadt observed that some of the anomalies observed with small fields are due to errors, mainly incomplete demagnetization. A. G. S. Gwyer, A. T. Waterman, K. Höjendahl, and K. F. Herzfeld discussed the theory of the conductivity of metals. A. Eucken defined a metal in terms of its electrical conductivity, which term is dependent on

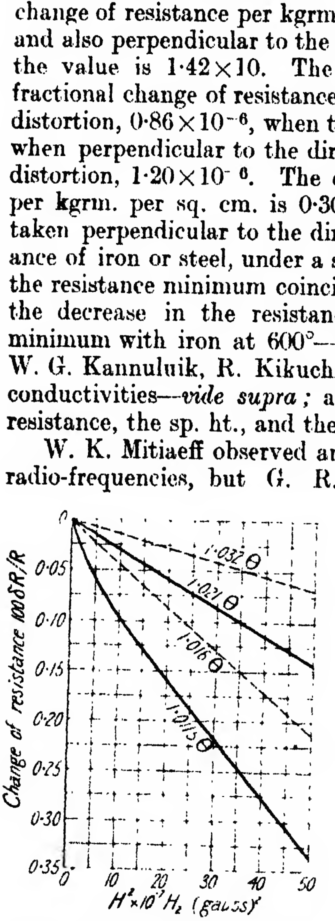


FIG. 265.—The Effect of Magnetization on the Resistance.

the presence of free electrons. Only a certain number of elements have these free electrons.

W. Ostwald[2] calculated for the **heat of ionization** of $Fe^{\cdot\cdot}$ from the metal, Fe, in dil. aq. soln., +93 kilojoule, when the heat of ionization of $H^{\cdot}$ from H_2 is zero; and for the formation of $Fe^{\cdot\cdot\cdot}$ from $Fe^{\cdot\cdot}$, +39 kilojoules. J. D. Bernal and R. H. Fowler calculated for the **ionization energy** of $Fe^{\cdot\cdot}$, 561 Cals. per gram-ion, and of $Fe^{\cdot\cdot\cdot}$, 1346 Cals. The **transport number** of $Fe^{\cdot\cdot}$-ions at 18° was found by K. Szalagyi to be 50; A. Heydweiller gave 45·2; G. von Hevesy, 48; and A. Stepniczka-Marinkovic, 46. For $Fe^{\cdot\cdot\cdot}$-ions, A. Heydweiller gave 61·2 at 18°; G. von Hevesy, 45; and K. Hopfgartner, 43.

E. Dubois[3] studied the **Volta effect** in water-vapour. M. Andauer attributed the potential difference between iron and air, of the order of 0·15 volt, to the formation of a conducting film of gas over the entire surface of the metal. M. Forro and E. Patai found the contact potential of iron and sodium to be 1·4 volts. S. J. French and L. Kahlenberg studied the gas-metal electrode of iron with oxygen, hydrogen, or nitrogen. J. Galibourg measured the contact potential of steels of various kinds against mercury at temp. between 20° and 320°. He found the results dependent on the composition of the metal, but were only slightly affected by the degree of tempering. He said that the steels can thus be classified without analyzing them. G. Mönch gave − 0·35 volt for the contact potential of iron and copper; G. N. Glasoe, 0·21 volt for gas-free iron and nickel; and F. Polednik gave 1·99 volts for the contact potential of iron and quartz, and 1·15 volt for iron and glass. W. Ende, and R. F. Hanstock studied the effect of cold-work on the contact potentials of metals. J. B. Seth and co-workers studied the e.m.f. developed by a rapidly rotating steel disc against aluminium magnesium, zinc, tin, cobalt, cadmium, lead, manganese, bismuth, nickel, platinum, antimony, arsenic, gold, tellurium, copper, and silver, and the values increase from —730 millivolt to 123 millivolts in the order stated. E. Perucca, O. Scarpa, A. Lafay, and H. F. Richards studied the subject. R. D. Kleeman and W. Fredrickson studied the electric charges of colloidal particles of iron in distilled water. R. T. Dufford studied the **photovoltaic effect** with iron in Grignard's soln.; and P. E. Shaw and co-workers, the **triboelectric effect**.

When iron dissolves in dil. hydrochloric acid, it forms a soln. of bivalent iron, ferrous chloride, and assuming that the salt, under these conditions, is ionized, the reaction is represented $Fe+2H^{\cdot}=Fe^{\cdot\cdot}+H_2$. Salts of univalent iron are unknown —*vide infra*. A unit charge is equivalent to $C=96,540$ coulombs, so that when iron passes into a bivalent charge ion, $Fe^{\cdot\cdot}$, it acquires a charge of 2×96,540 coulombs; and when bivalent iron passes into a tervalent ion, $Fe^{\cdot\cdot\cdot}$, it acquires a charge of 3×96,540 coulombs. From this point of view, iron, and the bivalent and tervalent charged ions, can almost be regarded as allotropic modifications of one substance. The electrical energy or work, W, involved in the reversible transformation $Fe\rightleftharpoons Fe^{\cdot\cdot}$ is the product of the quantity of electricity, C, and the pressure E, so that the work $W=2CE$ volt-coulombs. E can be determined by dipping iron in a soln. of a ferrous salt, and measuring the difference of potential of this combination against another electrode taken as zero. Observations show that the difference of potential, E, depends on the conc., $[Fe^{\cdot\cdot}]$, of the soln. such that $E=E_0+0{\cdot}02885 \log [Fe^{\cdot\cdot}]$ volt, where E_0 represents the value of E when the conc. $[Fe^{\cdot\cdot}]=1$. The **electrode potential** of iron in a soln. of a ferrous salt of conc. $[Fe^{\cdot\cdot}]=1$ is called the normal potential. Since E and E_0 represent differences of potential, their respective values depend on the electrode which is taken as zero. As shown by R. Abegg and co-workers, if the normal calomel electrode, Hg : HgCl : N-KCl be taken as zero, the potential is symbolized E_0; if the dropping electrode be zero, E is symbolized E_0; and if the normal hydrogen electrode be zero, E is symbolized E_H. Under these conditions $E_H=E_0-0{\cdot}277$; $E_c=E_0-0{\cdot}56$, so that $E_H=E_c+0{\cdot}283$.

R. Schenck and co-workers calculated from the equilibrium measurements of E. Baur and A. Glässner, and A. B. Lamb's observations on the heat of formation of ferrous oxide, that the **normal potential: $Fe \rightarrow Fe^{\cdot\cdot}$** is $E_H = -0{\cdot}47$ volt for iron in contact with a molar soln. of a ferrous salt. K. Jellinek and H. Gordon think this value is too strongly positive. W. H. Hampton gave −0·4413 volt; C. Drucker, −0·44 volt; and R. Abegg and co-workers considered −0·43 volt to be the best representative value for iron in contact with a normal soln. of a ferrous salt at 18°. This gives for the e.m.f. of the transformation $Fe \rightarrow Fe^{\cdot\cdot}$,

$$E_H = -0{\cdot}43 + \frac{0{\cdot}058}{2}\log[\mathrm{Fe}^{\cdot\cdot}] \text{ volt} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

For a normal soln. of ferrous chloride, B. Neumann gave −0·361 volt, and for a $2N$-soln., E. Petersen gave −0·337 volt. F. Förster found for the electrode potential of iron in a soln. with N-$FeCl_2$ and N-NH_4Cl, at the beginning, −0·492 volt at 20°, and −0·420 volt at 75°; and after an hour's time, respectively −0·463 and −0·420 volt. Numerous observations have been made with iron against soln. of ferrous sulphate. B. Neumann obtained −0·367 volt for the electrode potential of iron against N-$FeSO_4$; M. Mugdan, −0·34 volt for $0{\cdot}1N$-$FeSO_4$; E. Petersen, −0·337 volt for $2N$-$FeSO_4$. W. Muthmann and F. Fraunberger found that iron deposited electrolytically on iron or platinum gives $E_H = -0{\cdot}66$ volt. This value agrees with that obtained by F. W. Küster; and G. Coffetti and F. Förster showed that the high value applies not to iron, but rather to iron charged with hydrogen; if an allowance be made for this, the value for iron in N-$FeSO_4$ is −0·46 volt. High results for electrolytic iron were also obtained by C. E. Fawsitt. S. Glasstone gave for the cathode potential of iron in N-$FeSO_4$ at 15° for current densities of D amp. $\times 10^{-4}$ per sq. cm.:

D	$0{\cdot}02N$-H_2SO_4	$p_H = 2{\cdot}8$	$p_H = 4{\cdot}0$	$p_H = 5{\cdot}0$
0·14	−0·46	−0·47	−0·47	−0·47
4·2	−0·46	−0·49	−0·49	−0·53
8·4	−0·46	−0·52	−0·50	−0·58
20·0	−0·48	−0·57	−0·56	−0·60
40·0	−0·53	−0·68	−0·68	−0·68
80·0	−0·68	−0·70	−0·69	−0·70
100·0	−0·70	−0·78	−0·71	−0·71

The overvoltages are discussed below.

O. Bauer observed with electrolytic iron in a 1 per cent. soln. of sodium chloride a potential of −0·363 volt at the start; −0·479 volt in 1 hr.; −0·739 volt in 24 hrs.; and −0·755 volt in 120 hrs. For cast iron, the potential at the start was −0·628 volt; −0·740 volt after 2 hrs.; and −0·765, and −0·762 volt after 24 and 120 hrs. respectively. For mild steel, with 0·036 per cent. carbon, −0·575 volt at the start; −0·688 volt after 5 hrs.; and −0·755 volt after 120 hrs. For 0·86 per cent. carbon steel, −0·528 volt at the start; −0·626 volt after 1 hr.; −0·700 volt after 5 hrs.; and −0·744 volt after 120 hrs.

For an acidified soln. of N-$FeSO_4$, F. Haber and F. Goldschmidt gave −0·453, for cast or wrought iron. C. E. Fawsitt found that the proportion of carbon in iron had very little influence on the electrode potential; thus, with

Carbon	0	0·18	0·23	0·40	0·9 per cent.
E_H	−0·356	−0·352	−0·352	−0·351	−0·350 volt

T. W. Richards and G. E. Behr gave −0·72 to −0·74 volt; W. H. Hampton, −0·71 to −0·78 volt; K. Iwase and K. Miyazaki, −0·66 to 0·669 volt; and S. Sato, −0·68 volt. Observations on the electrode potential of iron in soln. of ferrous sulphate were also made by A. Finkelstein, T. W. and W. T. Richards, H. Endo and S. Kanazawa, K. Murata, E. Heyn and O. Bauer, E. Grave, B. Strauss, W. J. Sweeney, N. T. M. Wilsmore, S. Labendzinsky, and W. H. Walker and C. Dill. According to F. Förster, the effect of time on the electrode potential of iron in N-$FeSO_4$ containing 0·5 per cent. of boric acid is as follows:

Time		0	5	45	60	120 minutes
E_H	0°	−0·515	−0·479	—	−0·460	−0·460 volt
	20°	−0·480	−0·474	−0·460	−0·460	−0·460 „

C. A. Lobry de Bruyn also noted that with $0{\cdot}1N$-$FeSO_4$ in an atm. of hydrogen, the potential originally at —0·422 volt rises, when the soln. is exposed to air, and attains —0·387 volt in 24 hrs. G. Grube and H. Gmelin gave for a soln. of $0{\cdot}0242M$-Na_2FeO_2 in 40 per cent. sodium hydroxide, $E_H=-0{\cdot}855$ volt. A. Finkelstein gave —0·10 volt for iron against N-K_4FeCy_6; and W. van Wüllen-Scholten calculated from the solubility product of ferrous hydroxide, —0·569 volt for the electrode potential of iron against ferrous hydroxide. V. Nejedly gave for the e.m.f., $E=1{\cdot}320$ volt, and for the temp. coeff., $dE/d\theta=-0{\cdot}0011$, for iron and a soln. of $0{\cdot}001N$-$FeCl_2$ and $0{\cdot}01N$-KCl. According to W. H. Hampton, the potential of different varieties of iron against a $0{\cdot}1M$-soln. of ferrous chloride were for iron amalgam, 0·8090 volt; for finely-divided iron reduced from ferric oxide, 0·8088 volt. T. Mashimo observed that with iron electrodes in $0{\cdot}5M$-$FeCl_3$, and one electrode subjected to mechanical agitation and a magnetic field, the potential at the disturbed electrode was positive, and the other one, negative.

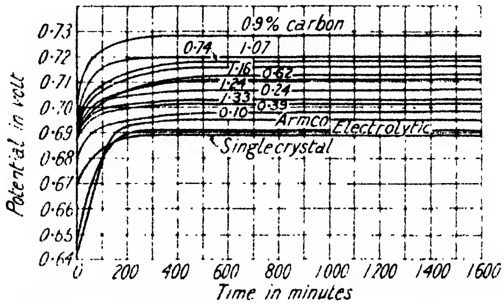


FIG. 266.—The Electrode Potentials of Iron and Steel.

H. Endo and S. Kanazawa measured the electrode potential of iron and steel with varying proportions of carbon, and the results are summarized in Fig. 266. The electrolyte was N-$FeSO_4$ against a normal calomel electrode. The electrolytic iron was re-melted. Forged iron gives the largest potential, cast iron comes next, and annealed iron gives the smallest potential. The effect of a roughened surface is greater than that of the carbon in steels. Thus, with electrolytic iron having the surface polished, with electrolytic iron unpolished, and with electrolytic iron heated for 15 hrs. at 250° to 300° in order to remove hydrogen and then polished:

	Electrolytic iron (polished)				Electrolytic iron (not polished)				Electrolytic iron (dehydrogenized and polished)			
Time .	2	62	222	3007	2	58	142	3143	5	79	372	3105
E.m.f.	0·647	0·705	0·734	0·738	0·656	0·740	0·755	0·750	0·696	0·729	0·732	0·733

The results with annealed and with fine globularized steel having 0·9 per cent. of carbon show that the annealed steel is at first a little more electropositive than the fine globularized steel, but it soon becomes electronegative, reaches a maximum, and then decreases to an asymptotic value 0·016 volt. With coarse globularized steel, the potential has an opposite sign to that of the fine globularized specimen. G. N. Glasoe studied the contact potential of iron and nickel.

The **normal potentials $Fe\rightarrow Fe^{\cdot\cdot\cdot}$** for iron in soln. of ferric salts, cannot be measured directly, because iron reduces soln. of ferric salts to the ferrous state. Applying R. Luther's study of the oxidation of iron in stages, K. Jellinek and H. Gordon, R. Abegg and co-workers, F. Auerbach, and C. Drucker found that the resultant of the operations $Fe\rightleftharpoons Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}$ is $Fe\rightleftharpoons Fe^{\cdot\cdot\cdot}$; so that the work, W, will be $W_{Fe\rightleftharpoons Fe^{\cdot\cdot}}+W_{Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}}$. If C denotes unit charge, $2CE_{Fe\rightleftharpoons Fe^{\cdot\cdot}}+CE_{Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}}=3CE_{Fe\rightleftharpoons Fe^{\cdot\cdot\cdot}}$, or $E_{Fe\rightleftharpoons Fe^{\cdot\cdot\cdot}}=\frac{1}{3}(2E_{Fe\rightleftharpoons Fe^{\cdot\cdot}}+E_{Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}})$. Again, for the reaction $Fe\rightleftharpoons Fe^{\cdot\cdot\cdot}$, $E=E_0+\frac{1}{3}0{\cdot}058\log[Fe^{\cdot\cdot\cdot}]$, on the assumption that the concentrations $[Fe^{\cdot\cdot}]$ and $[Fe^{\cdot\cdot\cdot}]$ are the same. By substituting the value of E for $Fe\rightleftharpoons Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}$, where $[Fe^{\cdot\cdot}]$ is the same, then, for $Fe\rightleftharpoons Fe^{\cdot\cdot\cdot}$ $E_0=\frac{1}{3}\{2(-0{\cdot}43)+0{\cdot}75\}=-0{\cdot}037$, that is, —0·04 nearly. G. Grube and H. Gmelin obtained $E_H=-0{\cdot}09$ volt. C. E. Fawsitt obtained values ranging from —0·128 to —0·234 volt for the electrode potential of different varieties of iron in N-$FeCl_3$; and A. Finkelstein, $E_H=-0{\cdot}09$ volt for iron in N-K_3FeCy_6. W. van Wüllen-Scholten calculated

$-0{\cdot}220$ volt for electrode potential of iron against ferric hydroxide from the solubility product of hydrated ferric oxide.

R. Peters studied the **normal potential : $Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}$,** where $E=E_0+0{\cdot}0577 \log [Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$, where $[Fe^{\cdot\cdot\cdot}]$ and $[Fe^{\cdot\cdot}]$ represent the respective ionic concentrations. The value of E_0 here works out to be $E_0=0{\cdot}0577 \log K$, where K is the equilibrium constant. By working with a normal mercury electrode, $Hg : HgCl . N\text{-}KCl : FeCl_2 . FeCl_3 : Pt$, where there is the reaction $Hg+Fe^{\cdot\cdot}+Cl'\rightleftharpoons Fe^{\cdot\cdot}+HgCl$. The current ceases when the free energy of the reaction : $Hg+Cl'\rightleftharpoons HgCl$ is equal to that of the reaction : $Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}$. For equilibrium, $[Fe^{\cdot\cdot}][HgCl]/[Hg][Fe^{\cdot\cdot\cdot}][Cl']$, or $K=[Fe^{\cdot\cdot}]/[Fe^{\cdot\cdot\cdot}]$ since the concentrations of the solids, and $[Cl']$ can be regarded as constant. Consequently, for the reaction $Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}$, $E=0{\cdot}0577 \log K+0{\cdot}058 \log [Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$. When $K=[Fe^{\cdot\cdot}]/[Fe^{\cdot\cdot\cdot}]$, E is zero, R. Peters measured E_c for soln. containing different proportions of ferrous and ferric salts, at 17°, and obtained :

$Fe^{\cdot\cdot}$.	0·5	1·0	10	20	40	60	80	99·5
$Fe^{\cdot\cdot\cdot}$.	99·5	99·0	90	80	60	40	20	0·5
E . .	0·296	0·312	0·375	0·391	0·419	0·436	0·462	0·545
E_0 . .	0·428	0·427	0·430	0·426	0·429	0·426	0·427	0·413

The best representative value of E_0 is 0·427 obtained from $E_0=E_c-0{\cdot}0577 \log [Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$, and since $E_0=0{\cdot}577 \log K$, $\log K=7{\cdot}45$, or $K=10^{7\cdot45}$. By the addition of potassium chloride, the value of K was diminished, the mean value obtained being $10^{7\cdot15}$. In neutral solutions, the potential was found to vary considerably with dilution, but this was not the case in acid soln. or in soln. containing potassium chloride. Solutions in a normal soln. of sodium nitrate gave values almost identical with those in pure water, so that ferric chloride and ferric nitrate are equally dissociated. In the case of mixtures of ferric and ferrous sulphates, the value of K was found to be $10^{6\cdot6}$, so that at equal concentrations ferric sulphate gives fewer ferric ions than the chloride. The addition of fluorine ions in all cases raises the reduction potential, and this effect was further examined. The conductivity of mixtures of iron salts with sodium fluoride is less than the sum of conductivities of the constituents, the difference being greatest with ferric compounds, in which case also it increases with dilution. The ferric salts, therefore, probably form complex compounds with the sodium fluoride, a view further supported by f.p. determinations. By the addition of sodium fluoride to the mixed iron salts the e.m.f. falls greatly ; thus, in the case of a mixture of $0{\cdot}1N$ ferrous and ferric salts the addition of an equal vol. of $0{\cdot}3N$-soln. of sodium fluoride caused the e.m.f. to become negative, or decreased the conc. of the ferric ions to 10^{-75} of its former amount. A white salt is also precipitated by the fluoride, and the composition was found to be $Na_3FeF_6\frac{1}{2}H_2O$. This was proved to be a complex salt in which the iron is present in the anion, as by electrolysis the percentage of iron increased at the anode and decreased at the cathode. It is probable that the reduction of the e.m.f. by addition of sodium fluoride is due to the formation, not only of the slightly dissociated ferric fluoride, but also of this salt. Confirmatory results were obtained by C. Fredenhagen ; he also found for the calomel electrode $E_0=0{\cdot}987$, or with the hydrogen electrode, in agreement with R. Peters, 0·710 volt. G. Grube found that with (i) a soln. of 250 c.c. of $0{\cdot}5M\text{-}K_3FeCy_6$ with 750 c.c. of $0{\cdot}5M\text{-}K_4FeCy_6$, and (ii) a soln. of 750 c.c. of the former and 250 c.c. of the latter :

	(i)			(ii)		
C . .	0	0·002	0·01	0·1	0·5	2·0
E_H . .	0·456	0·436	0·463	0·523	0·531	0·555 volt

W. Maitland obtained for the equilibrium constant, $K=10^{7\cdot8}$; and calculated for E_0, for the hydrogen electrode, 0·743 volt. R. Abegg and J. Neustadt gave 0·066 volt for E_0 in the reaction $Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}$ in pyridine soln. Observations were also made by C. Drucker, F. Auerbach, E. Müller and J. Janitzki, S. R. Carter and T. J. Glover, S. R. Carter and F. H. Clews, S. Popoff and co-workers, L. Michaelis and E. Friedheim, L. Michaelis and C. V. Smythe, K. Masaki and T. Ikkatai, T. J. Glover, and K. Jellinek and H. Gordon. R. Abegg and co-workers gave for the best representative value, with the hydrogen electrode, $E_0=0\cdot75$ volt, so that for the reaction $Fe^{\cdots}\rightleftharpoons Fe^{\cdot\cdot}$ at 18°:

$$E_H=0\cdot75+0\cdot058\log[Fe^{\cdots}]/[Fe^{\cdot\cdot}]\text{ volt} \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

R. Peters gave 0·296 volt for the e.m.f. of the cell Pt : $0\cdot0005N$-$FeCl_3.0\cdot0995N$-$FeCl_2$, $0\cdot1N$-HCl, $1\cdot0N$-KCl, Hg_2Cl_2 : Hg, at 17°; 0·522 volt at 17° for Pt : $0\cdot098N$-$FeCl_3$, $0\cdot002N$-$FeCl_2$, $0\cdot1N$-HCl, $1\cdot0N$-KCl, Hg_2Cl_2 : Hg; 0·429 volt at 17° for Pt : $0\cdot045N$-$Fe_2(SO_4)_3$, $0\cdot01N$-$FeSO_4$, $0\cdot1N$-H_2SO_4, $1\cdot0N$-KCl, Hg_2Cl_2 : Hg; 0·331 volt at 17° for Pt : $0\cdot005N$-$Fe_2(SO_4)_3$, $0\cdot09N$-$FeSO_4$, $0\cdot1N$-H_2SO_4, $1\cdot0N$-KCl, Hg_2Cl_2 : Hg. H. Schäfer gave 0·295 volt at 25° for Pt : $0\cdot01N$-$(NH_4)_2Fe(SO_4)_2$, $1\cdot0N$-$(NH_4)_2SO_4$, $1\cdot0N$-KCl, Hg_2Cl_2 : Hg; and 0·364 volt when $0\cdot09N$-$(NH_4)_2Fe(SO_4)_2$ is used. A. A. Noyes and B. F. Brann gave for Pt : xN-$Fe(NO_3)_3$, yN-$Fe(NO_3)_2$, $0\cdot05N$-HNO_3, 3·5 or $1\cdot75N$-KCl, $1\cdot0N$-KCl, Hg_2Cl_2 : Hg, at 25°, 0·04486 volt when $x=0\cdot05$ and $y=0\cdot05$; 0·4528 volt when $x=0\cdot0125$ and $y=0\cdot0125$; 0·4726 volt when $x=0\cdot0739$ and $y=0\cdot0293$; and 0·4643 volt when $x=0\cdot0112$ and $y=0\cdot0089$. C. Fredenhagen gave 0·133 volt at 17° for Pt : $0\cdot01N$-K_3FeCy_6, $0\cdot09N$-K_4FeCy_6, $1\cdot0N$-KCl, Hg_2Cl_2 : Hg; and 0·241 volt for Pt : $0\cdot09N$-K_3FeCy_6, $0\cdot01N$-K_4FeCy_6, $1\cdot0N$-KCl, Hg_2Cl_2 : Hg. For Pt : $0\cdot0245N$-K_3FeCy_6, $0\cdot00054N$-Na_4FeCy_6, $0\cdot1N$-KCl, Hg_2Cl_2 : Hg. K. Schaum and R. von der Linde gave −0·170 volt at 25° and −0·143 volt at 50°; and for Pt : $0\cdot00025N$-K_3FeCy_6, $0\cdot0270N$-Na_4FeCy_6, $0\cdot1N$-KCl, Hg_2Cl_2 : Hg, −0·039 volt at 25°, and −0·078 volt at 50°. E. Liebreich discussed the polarization of the cells Fe : Zn, Pb : Zn, and C : Fe, Hg : Fe.

S. Popoff and co-workers measured the oxidation-reduction potential with the ferric-ferrous electrode, $Pt.H_2 \mid HCl \mid HCl, FeCl_2.FeCl_3 \mid Pt$, with different concentrations of acid, and obtained the results shown in Fig. 267. The normal value is −0·7473 to −0·7476 volt. G. Grube represented the variation of the potential of the anode with current density by Fig. 268, and comparing the result with platinum, in neutral soln., it shows how very strong the polarization is with the iron anode which forms a surface film of oxide. Observations were made by W. J. Müller and co-workers, J. Hinnüber, and S. R. Carter and F. H. Clews. N. Isgarischeff and A. Turkovskaja studied the effect of various salts on the oxidation-reduction potentials of the $Fe^{\cdots}-Fe^{\cdot\cdot}$-system, and found that the e.m.f., E_H, is increased by the addition of cadmium chloride, and is diminished by the addition of various other chlorides in the following order: action of $LiCl<MgCl_2<CaCl_2<BaCl_2<NaCl<KCl<NH_4Cl$; zinc chloride lowers E_H at concentrations below normal and raises E_H at higher concentrations, whilst the action of the remaining chlorides increases with their concentration. Nitrates raise the E_H value proportionately to their concentration in the order: action of $NH_4NO_3<KNO_3<NaNO_3<Sr(NO_3)_2<Ca(NO_3)_2<LiNO_3<Mg(NO_3)_2<Cd(NO_3)_2$. The addition of sodium bromide

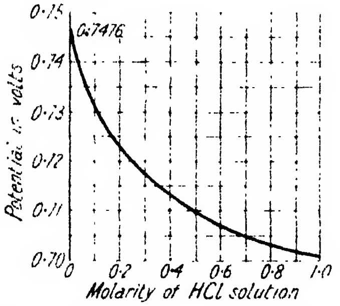


FIG. 267.—The Effect of Acid on the Oxidation-Reduction Potential of the Ferrous-Ferric Electrode.

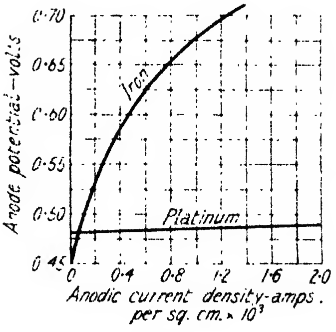


FIG. 268.—The Effect of Current Density on the Anode Potential of Iron.

raises E_H more than does sodium nitrate, and sodium sulphate depresses E_H to a greater extent than does sodium chloride. The above effects cannot be attributed to variations in p_H consequent on the addition of these salts, or to the formation of complex double salts with iron chlorides. S. Bodforss found that the potential of iron is a linear function of the H$^{\cdot}$-ion concentration of the soln. K. Murata, E. Liebreich, and J. Glover studied the subject. W. van Wüllen-Scholten found the potential of iron to ferrous hydroxide is —0·569 volt, and to ferric hydroxide, —0·220 volt, but in the presence of oxygen, a solid soln. of the two hydroxides occurs as a single phase where the ratio $Fe^{\cdot\cdot\cdot}/Fe^{\cdot\cdot}$ in the phase is dependent on the oxygen conc. of the soln.

K. Zang measured the oxidation of ferrous chloride soln., after the lapse of different intervals of time: $4Fe^{\cdot\cdot}+O_2+2H_2O\rightleftharpoons 4Fe^{\cdot\cdot\cdot}+4(OH)^1$, or $Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}+\ominus$. This represents the first phase of the reaction, and K. Zang assumed that in the second phase, the oxygen reacts with the electrons, and with this hypothesis deduced the equation $dx/dt=k_0(a-x)/x$. Let a denote the original conc. of the soln., and x the conc. of the ferric salt at the time t, then $k_1t=\log\{(a-x_0)/(a-x)\}$ represents the value of k_1 for a unimolecular reaction; let k_2 denote the constant for a bimolecular reaction; and k_0 the constant for the reaction whose speed is $dx/dt=k_0(a-x)/x$. The following is a selection from the observed results:

t	Potential	$x\times10^3$	$k_1\times10^4$	$k_2\times10^2$	$k_0\times10^6$
0	254·2	0·23	—	—	—
2	300·0	0·47	13·8	1·90	—
20·0	335·3	2·6	13·9	1·61	1·5
67·5	352·8	5·4	9·1	1·06	2·6
118·0	362·3	7·6	7·5	0·92	3·7
193·0	369·8	9·4	5·8	0·69	2·7
312·5	377·0	12·7	4·9	0·60	3·2
481·5	383·8	16·2	4·4	0·54	3·5

After a period of induction, the constancy of k_0 is taken to mean that the original hypothesis is confirmed.

According to C. Benedicks and R. Sundberg, the potential, E_H, of a metal in a soln. entirely devoid of oxygen—the hydrogen potential—and the potential, E_0, of a metal in a soln. containing oxygen—the oxygen potential—then, for quenched carbon steels, the H-potential is reduced irregularly from —0·745 volt down to —0·64 volt as the proportion of carbon increases, while the O-potential rises and also shows irregularities. For unquenched steels, the value for the H-potential falls as the proportion of carbon rises to 0·9 per cent., and then rises as the proportion of carbon increases still more. For steels with up to 0·9 per cent. of carbon, c, the value of $E_H=-0{\cdot}708+0{\cdot}010c$ volt. The O-potential rises from 0·311 volt as the carbon increases, and the results, though irregular, act like those with the H-potential but in the converse way.

For the **normal potential : Fe→Fe$^{\cdot\cdot\cdot\cdot\cdot\cdot}$**, G. Grube and H. Gmelin obtained $E_H=-0{\cdot}13$ volt; and with iron against 0·1M-Na_2FeO_4 in 40 per cent. sodium hydroxide, at 25°, the results were not constant, because the ferrate is reduced to ferrite in contact with iron.

Measurements of the electrode potential of iron against distilled *water*, and sea-water were made by T. Andrews, K. Arndt, F. Haber, F. Haber and P. Krassa, K. Hasegawa and S. Hori, E. Heyn and O. Bauer, A. de Méritens, W. Muthmann and F. Fraunberger, and F. H. Rhodes and E. B. Johnson. The electrode potential of iron against soln. of *ammonium hydroxide* was measured by A. Finkelstein, and M. Mugdan; against soln. of *sodium hydroxide*, by G. Grube and H. Gmelin, F. Haber and F. Goldschmidt, E. Heyn and O. Bauer, P. Krassa, M. Mugdan, and W. Pick; against soln. of *potassium hydroxide*, by J. Billiter, O. Faust, F. Förster and V. Herold, C. Fredenhagen, E. Grave, G. Grube and H. Gmelin, P. Krassa, M. Mugdan, W. Muthmann and F. Fraunberger, W. Pick, E. P. Schoch and C. P. Randolph, and J. Woost; and against a soln. of *calcium hydroxide*, by F. Haber and F. Goldschmidt, and E. Heyn and O. Bauer.

The electrode potential of iron in *hydrochloric acid* was measured by M. Centnerszwer and M. Straumanis, A. Thiel and K. Keller, and W. Muthmann and F. Fraunberger; of iron in a soln. of *potassium chloride*, by T. P. Hoar and U. R. Evans, and F. Vles and A. Ugo; and of iron in *sulphuric acid*, by T. Andrews, H. G. Byers and C. W. Thing, H. G. Byers and S. C. Langdon, M. Centnerszwer and M. Straumanis, C. Fredenhagen, E. Grave, W. J. Müller and O. Löwy, M. Mugdan, and A. Thiel and K. Keller. C. G. Fink and C. M. Decroly found the electrode potential of electrolytic iron in sulphuric acid of the percentage composition

H_2SO_4 .	0·45	2·40	5·14	9·92	17·54	32·03	54·69 per cent.
E . .	−0·941	−0·916	−0·928	−0·905	−0·872	−0·827	−0·715 volt

A. L. McAulay and G. L. White's results for the effect of the $H^{\cdot}$-ion concentration, represented by p_H, on the electrode potential of iron in air-free, 0·2*N*-KCl, are summarized in Fig. 269. The curve with a 0·2*M*-phosphate soln. is dotted in Fig. 269. H. G. Byers and S. C. Langdon, J. P. Hoar and U. R. Evans, and W. J. Müller and K. Konopicky measured the electrode potential of iron against sulphuric acid in the presence of hydrogen, and also oxygen; E. Grave, likewise against sulphuric acid in the presence of ozone, and also of hydrogen dioxide. C. Fredenhagen, W. J. Müller, and W. Muthmann and F. Fraunberger measured the electrode potential of iron against *nitric acid*—the passive state; E. Heyn and O. Bauer, against *arsenious acid*; E. Heyn and O. Bauer, W. Muthmann and F. Fraunberger, and G. C. Schmidt, against *dichromic acid*; and M. Mugdan, against *acetic acid*. Measurements of the potential are also discussed in connection with the passivity of iron.

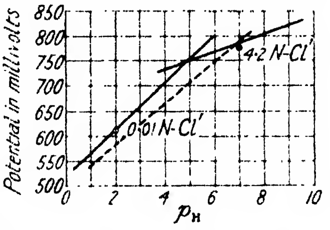


FIG. 269.—Equilibrium Potentials of Iron with Solutions of Different $H^{\cdot}$-ion Concentration.

J. H. Andrew and co-workers measured the electrode potentials of steels against a soln. of ferric chloride and a normal calomel electrode with the idea of finding the effect of heat-treatment, and the state of the carbon in the alloys. The results are indicated in Figs. 270 and 271. The electrode potential of quenched steels—with

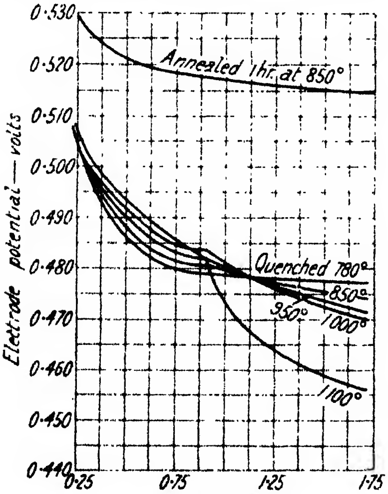


FIG. 270.—The Electrode Potentials of Carbon Steels Quenched at Different Temperatures.

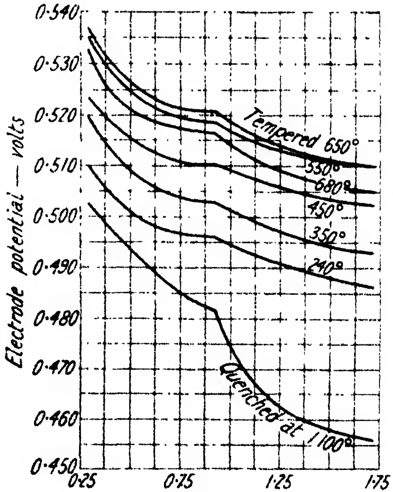


FIG. 271.—The Electrode Potentials of Carbon Steels Tempered at Different Temperatures.

α-iron—decreases as the proportion of carbon increases, so that the iron is rendered less active by dissolved carbon. The potential of hypoeutectoid steels is increased by raising the quenching temp., so that with an increase in the quenching temp., the least concentrated area of the solid soln. becomes less concentrated in carbon. J. H. Andrew and R. Hay found that carbide segregation occurs on soaking at a temp. above the Ac$_3$-arrest. The potential of hypereutectoid steels is lowered by an increase in the quenching temp. There is a marked deviation of the curve for hypereutectoid steels quenched at 1100° from that obtained for the same steel quenched at 1000°. Steels with over 1·2 per cent. of carbon, and quenched at 1100°, contain austenite, but since austenite is less active than martensite this does not explain the deviation of the curve at 1100°. The curves probably mean that the martensite obtained by quenching high-carbon steels from 1100° is much more concentrated than that obtained by quenching at 1000°. This may be due (i) to the cementite line being more curved than is generally assumed, so that the solubility of carbon in γ-iron at 1100° is much greater than it is at 1000°—this is not in accord with measurements of the electrical resistance; or (ii) that so long as particles of cementite in hypereutectoid steels remain undissolved before quenching, they may act as nuclei and cause a partial precipitation of the carbide even with rapid cooling.

The curves, Fig. 271, show that the electrode potential increases progressively with the raising of tempering temp., showing that the proportion of carbon in soln. is reduced by tempering. After tempering at any temp. up to, say, 450°, an appreciable amount of carbon remains in soln., and this proportion is reduced by raising the tempering temp. On heating quenched steels to a given temp., tempering proceeds until a limiting value is attained, after which it either stops or proceeds very slowly. A similar conclusion was inferred from measurements of the electrical resistance. The potential curve obtained after tempering at 680° lies below that obtained at 650°, indicating that carbon dissolves in α-iron below the Ac$_1$-arrest. C. F. Brush and R. A. Hadfield, and others have investigated the evolution of heat by a quenched steel at room temp.; and the effect of ageing on the potential of steel immediately after quenching, and after remaining at room temp. for different periods of time is indicated in Fig. 272. The potential decreases with time; this may be due to the relief of the strains caused by quenching. The electrode potentials at 18° of carbon steels quenched at 1100° and at 780°, and chromium steels at 1100°, did not change appreciably before and after immersion in liquid air. This indicates that austenite, unlike martensite, is not affected by liquid air. W. H. Walker and C. Dill discussed the electrode potential and the structure of iron.

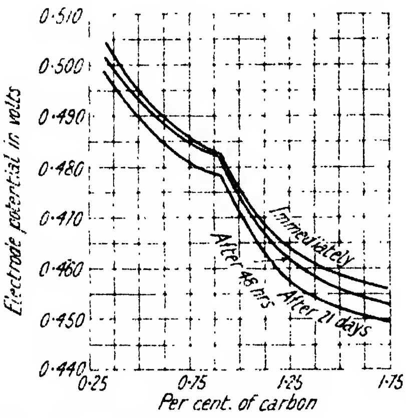


FIG. 272.—The Effect of Time on the Electrode Potential of Carbon Steels Quenched at 1100°.

M. Faraday studied the **electrochemical series,** and found that iron in nitric, hydrochloric, or sulphuric acid is negative towards bismuth, copper, and antimony, and positive towards tin, lead, cadmium, and zinc; in soln. of potassium hydroxide, iron is negative towards copper, silver, and nickel, and positive towards bismuth, lead, antimony, cadmium, tin, and zinc; and in yellow and colourless soln. of potassium sulphide, iron is positive towards many metals. According to J. C. Poggendorff, and S. B. Christy, iron in soln. of potassium cyanide is negative towards palladium, silver, carbon, and platinum, and positive towards nickel, bismuth, tin, antimony, copper, lead, cadmium, and zinc. S. B. Christy found that in distilled water, iron is positive towards zinc, and lead, and negative towards copper, silver, mercury, and gold. R. Abegg and co-workers gave for the electrochemical series —Li, K, Na, Mg, Zn, **Fe**, Cd, Co, Ni, Pb, Sn, H, Cu, Ag, Hg, Au+ ; F. Streintz gave for soln. of the metal in nitrate soln., —Mg, Zn, Cd, Sn, Al(Pb), Fe, Co, Bi, Ni, Cu, and Ag+ ; and in chloride soln., —Mg, Zn, Al, Cd, Fe, Sn, Bi, Co, Sb, and Cu+. C. B. Gates, and G. Gore studied the place of iron in the electrochemical series in molten salts, and in non-aqueous solvents ; and A. S. Russell found for iron in mercury, —Zn, Cd, Tl, Pb, Co, Mn, Fe, Bi, Co, Hg, Ni, and Pt+. T. Andrews studied the electrochemical series with different forms of iron and steel in sea-water, and in salt soln. ; whilst A. Schleicher found that the order with iron is + passive wrought iron, rusted cast iron, rusted wrought iron, wrought iron, passive cast iron, cast iron — ; and for steels, + nickel steel (25 : 75), nickel steel (5 : 95), chrome steel, tungsten steel, and cast steel (0·1 per cent. carbon). G. N. Glasoe gave 0·20 volt for the contact potential of nickel and iron.

The electrode potential of iron in *hydrofluoric acid* was examined by C. Bedel, and A. Travers and J. Aubert ; in an aq. soln. of *sodium fluoride*, by M. Mugdan ; in pyridine soln. of *lithium chloride*, by H. Eggert ; in acetone soln. of lithium chloride, by U. Sborgi and P. Marchetti ; in aq. soln. of *sodium chloride*, by T. Andrews, E. Heyn and O. Bauer, R. Lorenz, A. L. McAulay and F. P. Bowen, M. Mugdan, E. Petersen, and W. van Wüllen-Scholten ; *ammonium chloride*, by E. Heyn and O. Bauer ; in aq. soln. of *potassium chloride*, by K. Arndt, U. R. Evans, E. Heyn and O. Bauer, M. Mugdan, W. Muthmann and F. Fraunberger, G. C. Schmidt, W. H. Walker and co-workers ; in aq. soln. of different acidities, by F. Vles and A. Ugo ; in methyl alcohol soln. of potassium chloride, by H. Eggert ; in aq. soln. of *potassium bromide*, by M. Mugdan ; *potassium iodide*, by M. Mugdan, and G. C. Schmidt ; *potassium chlorate*, by M. Mugdan, E. Heyn and O. Bauer, and E. P. Schoch and C. P. Randolph ; *perchloric acid*, by A. Travers and J. Aubert ; *potassium perchlorate*, by M. Mugdan, and E. P. Schoch and C. P. Randolph ; *potassium bromate*, E. Heyn and O. Bauer, and E. P. Schoch and C. P. Randolph ; *potassium iodate*, by E. Heyn and O. Bauer, and E. P. Schoch and C. P. Randolph ; *calcium, barium, and magnesium chlorides*, by E. Heyn and O. Bauer ; in *sodium hydroxide*, by C. Bedel ; *stannous chloride* and hydrochloric acid, by A. Thiel and K. Keller ; *ammonium hydrosulphide*, by A. Finkelstein ; *sodium hydrosulphide*, by R. Zuppinger ; *sodium sulphate*, by H. G. Byers and C. W. Thing, and E. Heyn and O. Bauer ; *sulphuric acid*, by W. Wolff, A. Travers and J. Aubert, and C. Bedel ; *potassium sulphate*, by U. R. Evans, E. Heyn and O. Bauer, J. F. G. Hicks, A. L. McAulay and S. H. Bastow, M. Mugdan, and E. P. Schoch and C. P. Randolph ; and soln. of potassium sulphate mixed with sulphuric acid, potassium hydroxide, potassium fluoride, or potassium dichromate, by E. P. Schoch and C. P. Randolph ; *ammonium, magnesium and manganese sulphates*, by E. Heyn and O. Bauer ; acetone soln. of *silver nitrate*, by U. Sborgi and P. Marchetti ; ethyl alcohol soln. of *ammonium and calcium nitrates*, by U. Sborgi and G. Cappon ; *stannous sulphate* and sulphuric acid, by A. Thiel and K. Keller ; *sodium nitrate*, by E. Heyn and O. Bauer ; *potassium nitrate*, by M. Mugdan ; potassium nitrate with nitric acid or potassium hydroxide, by E. P. Schoch and C. P. Randolph ; *ammonium nitrate*, by E. Heyn and O. Bauer ; *silver nitrate*, by O. Kohlschütter and co-workers ; *ammonium, and sodium hydrophosphates*, by E. Heyn and O. Bauer ; *phosphoric acid*, by A. Travers and J. Aubert ; *sodium carbonate, and hydrocarbonate*, by F. Haber and F. Goldschmidt, and E. Heyn and O. Bauer ; *potassium carbonate*, and *calcium hydrocarbonate*, by E. Heyn and O. Bauer ; *sodium acetate*, by E. Heyn and O. Bauer, and M. Mugdan ; *ammonium acetate*, by E. Heyn and O. Bauer ; *potassium cyanide*, by A. Brochet and J. Petit, F. C. Frary and R. E. Porter, S. B. Christy, A. Finkelstein, C. B. Gates, E. Heyn and O. Bauer, W. Muthmann and F. Fraunberger, and A. van Oettingen ; *potassium thiocyanate*, by W. Muthmann and F. Fraunberger ; *sodium tetraborate*, by E. Heyn and O. Bauer ; *potassium chromate*, by E. Heyn and O. Bauer, and E. P. Schoch and C. P. Randolph ; *potassium dichromate*, by H. G. Byers and C. W. Thing, E. Heyn and O. Bauer, M. Mugdan, and E. P. Schoch and C. P. Randolph ; and *potassium permanganate*, by E. Heyn and O. Bauer, and M. Mugdan.

The **electromotive force** of a large variety of single, double, or more cells has been determined.

Single liquid cells.—In cells with one electrolyte and iron : Fe | solution | metal, C. Barus studied cells with water and steel annealed at different temp. R. B. Clifton observed that copper is positive and zinc negative with *water* as electrolyte. N. R. Dhar, that tin is positive ; C. A. Lobry de Bruyn, that aluminium is negative ; and F. Tödt, that platinum is positive. A. de la Rive observed that tin is positive and copper negative with a soln. of *ammonia* as electrolyte, and combinations with silver, platinum, copper, and tin were studied by J. C. Poggendorff ; F. F. Runge, and E. Branly found that with *potassium hydroxide* soln. zinc is negative, and J. C. Poggendorff studied the combinations with copper, silver, zinc, cadmium, mercury, tin antimony, or platinum. P. Bechtereff found that carbon with a 20 per cent. soln. of *sodium hydroxide* gives $E=0{\cdot}9$ volt at 95°; F. Tödt examined cells with sodium hydroxide soln. and platinum; and F. Jirza, with silver; J. C. Poggendorff also studied cells with *hydrochloric acid* and copper, silver, zinc, cadmium, mercury, tin, antimony, or platinum; C. L. Speyers, combinations with hydrochloric acid and mercury. M. Centnerszwer and M. Straumanis found that with hydrochloric acid of concentration 0·5, 0·25, and 0·1 eq. per litre against platinum at 25°, E was respectively 0·101, 0·116, and 0·152 volt. M. Centnerszwer found aluminium is negative in $0{\cdot}5N$-HCl. M. Centnerszwer and M. Straumanis found with a $0{\cdot}1N$-soln. of *hydrobromic acid* and platinum, $E=0{\cdot}109$ volt at 25°. K. W. G. Kastner studied combinations with a soln. of *sodium chloride* with zinc as the negative pole, and observations were also made by J. C. Poggendorff with the same soln. and copper, silver, zinc, cadmium, mercury, antimony or platinum; F. Tödt studied cells with $0{\cdot}01N$-NaCl and zinc. U. R. Evans studied a cell with $0{\cdot}5N$-NaCl and aerated and non-aerated electrodes. E. J. Micheli found copper is positive in a soln. of sodium chloride; R. Lorenz, that copper oxide is positive under similar conditions; and E. Liebreich measured the effect of coating the iron with red-lead, ferric oxide, zinc-white, white-lead, or varnish. W. van Wüllen-Scholten measured the e.m.f. of cells with rough and smooth iron in soln. of sodium chloride. N. R. Dhar found tin is positive with a soln. of *potassium chloride*, and C. A. Lobry de Bruyn, that aluminium is negative. N. R. Dhar studied the e.m.f. of iron against soln. of potassium chloride. E. Liebreich and co-workers found that with $0{\cdot}1N$-KCl at 20°, and ferric oxide, $E=0{\cdot}09$ volt, with zinc oxide, 0·150 volt, with lead carbonate, 0·095 volt, and with red-lead, 0·075 volt. U. R. Evans studied a cell with $0{\cdot}1N$-KCl and steel electrodes one of which was aerated. N. Vlacovich found that zinc is negative with a soln. of *ammonium chloride*. J. C. Poggendorff studied the combinations with a hydrochloric or sulphuric acid, or an aq. soln. of *potassium iodide*, or of *potassium bromide* and copper, silver, zinc, cadmium, mercury, tin, antimony, or platinum. M. Randall and M. Frandsen found that the cell Fe, $Fe(OH)_2$ against $0{\cdot}05M$-soln. of *barium hydroxide*, and HgO, Hg, had an e.m.f. of 0·973 volt at 25° with highly purified iron. E. L. Nichols and W. S. Franklin found that platinum is negative in a soln. of *ferrous chloride*; W. H. Hampton studied the cell with iron against $0{\cdot}1M$-$FeCl_2$ and HgCl, Hg, and gave 0·4413 for the electrode potential of iron. The cell was studied by M. Randall and M. Frandsen. E. Petersen found that the cell with carbon and $2N$-soln. of *ferric chloride* gives 0·90 volt; W. Spring, that with conc. ferric chloride, carbon or platinum is positive—the cell with carbon was also studied by A. A. Beadle, F. W. Küster, H. Pauling, and E. Petersen. E. Petersen found that zinc is negative with $2N$-$FeCl_2$ with 20 per cent. of sodium chloride, and $E=0{\cdot}537$ volt. W. H. Hampton obtained $E=0{\cdot}8088$ volt with a cell having $0{\cdot}2N$-$FeCl_2$ and a calomel electrode. Zinc is negative with a soln. of *zinc chloride*. E. L. Nichols and W. S. Franklin found that platinum is positive with a dil. hydrochloric acid soln. of potassium chlorate; M. J. Roberts, J. C. Poggendorff, and R. B. Clifton found that with dil. *sulphuric acid*, zinc is negative; M. J. Roberts, and C. Hockin and H. A. Taylor, that zinc amalgam is negative; E. Branly, that copper, platinum, and carbon are positive; P. Casamajor, iron-amalgam is negative. R. B. Clifton found that zinc is negative, and copper and mercury are positive with dil. sulphuric acid. J. C. Poggendorff studied cells with sulphuric acid and an electrode of copper, silver, zinc, cadmium, mercury, zinc amalgam, tin, antimony, or platinum; C. L. Speyers studied cells with sulphuric acid and mercury; and S. P. Thompson, sulphuric acid with an electrode of copper at different temp. A. L. McAulay and S. H. Bastow found that cells with $0{\cdot}5N$-soln. of *potassium sulphate* and a calomel electrode, had E between 0·75 and 0·80 volt. H. L. Heathcote found that iron is negative against passive iron in sulphuric acid (1 : 6); M. Centnerszwer and M. Straumanis gave for platinum against sulphuric acid of concentration C eq. per litre, at 25°:

C-H_2SO_4 . . .	1	0·5	0·25	0·1	0·05
E	0·161	0·163	0·171	0·169	0·171 volt.

A cell with $0{\cdot}5N$-H_2SO_4 and copper had $E=0{\cdot}024$ volt, and with silver, 0·060 volt. W. D. Bancroft studied cells with N- and $2N$-H_2SO_4 and iron electrodes one or both of which was treated with air, hydrogen, nitrogen, or coal gas. M. Centnerszwer examined cells with $0{\cdot}5N$- and $2N$-H_2SO_4 and aluminium. P. Goerens found that with cold-worked iron annealed at 520°, $0{\cdot}1N$-$FeSO_4$, and iron annealed at 520°, the voltage is practically zero. W. Broniewsky found that for soft steel, N-$FeSO_4$, and steel with

	Carbon	0·24	0·44	0·79	5·12 per cent.
E	Steel	0·014	0·017	0	0·016 volt
	Steel tempered . . .	0·021	0·027	0·014	0·038 ,,

C. A. Lobry de Bruyn studied cells with a calomel electrode having an electrolyte with a mixture of *ferrous and ferric sulphates*, against soft and hard steels. H. Wolff found that zinc is negative with a soln. of *zinc sulphate*; C. Hockin and H. A. Taylor, that zinc amalgam is negative with a soln. of zinc sulphate; J. C. Poggendorff, and R. T. Lattey and M. W. Perrin studied cells with a sulphuric acid soln. of zinc sulphate and copper, silver, tin, or platinum; and C. Barus and V. Strouhal studied cells with a soln. of zinc sulphate and steel annealed at different temp. G. Tammann and W. Wiederholt studied cells with N-$ZnSO_4$ and copper, silver, gold, zinc, tin, or lead; T. W. and W. T. Richards, ferrous sulphate of concentration C eq. per litre, and a normal calomel electrode at 25°:

C	1·02	0·366	0·327	0·039
E	0·741	0·753	0·759	0·778 volt
C-$FeSO_4$	0·365	0·393	0·366	0·390
C-H_2SO_4	0·001	0·100	0·25	0·50
E	0·753	0·724	0·669	0·634 volt
C-$FeSO_4$	0·329	0·329	0·327	—
C-$Fe_2(SO_4)_3$ . . .	0·003	0·017	0·088	—
E	0·719	0·687	0·630	— volt

F. F. Runge found that with *nitric acid*, mercury is positive; and the same cell was studied by C. L. Speyers. J. C. Poggendorff found that zinc is negative, and he also studied cells with nitric acid and copper, silver, zinc, cadmium, tin, antimony, and platinum; E. L. Nichols and W. S. Franklin showed that carbon is positive with nitric acid; and W. Hittorf, that platinum is negative. C. F. Schönbein studied a cell with dil. nitric acid and lead dioxide. M. Faraday showed that with conc. nitric acid, silver and copper are negative, but with dil. acid, positive; C. A. Lobry de Bruyn, that aluminium is negative with a soln. of *potassium nitrate*; and W. Wolff, that zinc is negative with a soln. of *zinc nitrate*. J. C. Poggendorff studied cells with a soln. of *sodium carbonate*, and copper, silver, zinc, cadmium, mercury, antimony, or platinum; and F. Tödt, cells with sodium carbonate soln. and platinum. S. P. Thompson found that with a soln. of *potassium cyanide*, carbon is positive, and J. C. Poggendorff studied cells with the same soln., and copper, silver, zinc, cadmium, mercury, tin, antimony, or platinum. C. L. Speyers studied cells with *acetic acid* and mercury. M. Dauvé found copper positive in a cell with a soln. of *copper acetate*. J. C. Poggendorff studied cells with *sodium tetraborate* and sulphuric acid and copper, silver, tin, or platinum; E. L. Nichols and W. S. Franklin, W. Kistiakowsky, and A. Naccari and M. Bellati, with *chromic acid* and a carbon positive electrode; and P. Bechtereff, cells with 20 per cent. soda-lye and *potassium permanganate* with a carbon negative electrode, and E. L. Nichols and W. S. Franklin, permanganate with platinum as positive electrode.

Double liquid cells.—M. Faraday observed that iron in a dil. soln. of *potassium hydroxide* is negative against iron in a conc. soln. of the alkali; J. C. Poggendorff, and J. P. Joule, that iron in potash-lye is negative against platinum in nitric acid; J. P. Joule, that iron in potash-lye is negative against platinum in nitric sulphuric acid and lead dioxide, or against copper in sulphuric acid; C. Fredenhagen gave 0·248 volt for iron in N-KOH against N-KCl, Hg_2Cl_2, and mercury. W. Hittorf found that iron in a soln. of *sodium hydroxide* is negative against platinum in chromic acid; and with iron in 0·1N-NaOH + 0·1N-KOH, M. Mugdan found the e.m.f. to be 0·303 to 0·403 volt, and with iron in 0·1N-NaOH against 0·1N-KCl Hg_2Cl_2, and mercury, F. Haber and F. Goldschmidt obtained an e.m.f. of 0·7 to 1·1 volt. W. Hittorf found that iron in a N-soln. of *ammonia* is negative against mercury in N-KCl with mercurous chloride, and with 0·1N-NH_4OH, M. Mugdan found that the e.m.f. is 0·103 volt; F. Haber and F. Goldschmidt found that iron in a soln. of *calcium hydroxide* against 0·1N-KCl, Hg_2Cl_2, and mercury, had an e.m.f. of 0·4 to 0·8 volt; and O. Faust, that iron in 20 per cent. potash-lye against zinc amalgam in 20 per cent. potash-lye containing 2 per cent. of zinc hydroxide had an e.m.f. of 0·446 volt. M. Mugdan found that with iron in a 0·1N-soln. of *sodium fluoride* against N-KCl, Hg_2Cl_2, and mercury the e.m.f. is 0·553 to 0·583 volt. M. Faraday found that iron in dil. *hydrochloric acid* is negative against iron and conc. hydrochloric acid; E. L. Nichols and W. S. Franklin, with platinum as positive electrode in a hydrochloric acid soln. of potassium chlorate; and with platinum as positive electrode in a soln. of ferrous chloride. J. Strachan found that iron in hydrochloric acid against carbon in a hydrochloric acid soln. of lead tetrachloride has an e.m.f. of 0·83 volt. L. Ponci, and J. Thomsen found that iron in a soln. of *ferrous chloride* is negative against carbon in a soln. of ferric chloride; S. Czapsky, negative against mercury in mercurous chloride; C. R. A. Wright and C. Thompson, negative against silver in silver chloride, and positive against amalgamated zinc in zinc chloride, or cadmium in cadmium chloride. R. Abegg and S. Labendzinsky found for iron in a mixed soln. of ferrous and potassium chlorides against N-KCl, Hg_2Cl_2, and mercury:

$FeCl_2$	1·0	1·0	0·1	0·1 eq. per litre
KCl	0	1·0	0	1·0 „
E	0·760	0·762	0·780	0·792 volt

A. F. W. von Escher, that iron in a soln. of *ferric chloride* is positive against zinc amalgam in sulphuric acid; T. Erhard, that iron in a soln. of ferric chloride is negative against indium in a soln. of indium trichloride; and T. W. Richards and G. E. Behr, that iron in a soln. of ferric chloride is negative against 0·1N-KCl, Hg_2Cl_2, and mercury; a similar cell was examined by C. A. Lobry de Bruyn; L. Kahlenberg, iron in 0·3N-$FeCl_3$ against mercury as positive electrode in N-KCl and mercurous chloride. A. Finkelstein found that iron is negative in a 0·01*N*-soln. of ferrous and ferric chlorides and 0·02*N*-HCl against *N*-KCl, Hg_2Cl_2 and mercury, and the e.m.ff. of the cell with the following percentage proportions of ferric chloride were:

$FeCl_3$.	0	10	20	40	60	80	100 per cent.
E . .	0·546	0·534	0·530	0·519	0·532	0·518	0·509 volt

C. R. A. Wright and C. Thompson found that iron in a soln. of *ferrous bromide* is positive against amalgamated zinc in zinc bromide, or cadmium in cadmium bromide. J. P. Joule found that iron in a soln. of *sodium chloride* is negative against platinum in nitric acid, or copper in copper sulphate; M. Mugdan gave 0·603 to 0·703 volt for the e.m.f. of a cell with iron in a 0·1*N*-soln. of *potassium chloride* with 0·1*N*-NaCl against *N*-KCl, Hg_2Cl_2, and mercury. W. H. Walker and co-workers studied the e.m.f. of the cell Fe : KCl : Pt : KCl : Fe. M. Mugdan found that against *N*-KCl, Hg_2Cl_2, and mercury, iron in a 0·1*N*-soln. of *potassium bromide* is 0·523 to 0·643 volt; with a 0·1*N*-soln. of potassium iodide, 0·473 to 0·553 volt; with a 0·1*N*-soln. of *potassium chlorate*, 0·203 to −0·353 volt; and with a 0·1*N*-soln. of *potassium perchlorate*, 0·703 volt. J. Strachan found that iron in a soln. of *ammonium chloride* against carbon in a hydrochloric acid soln. of lead tetrachloride has an e.m.f. of 0·95 volt; and if the ammonium chloride be replaced by *zinc chloride*, an e.m.f. of 0·73 volt.

M. Faraday observed that iron in dil. *sulphuric acid* is negative against iron in the conc. acid; J. P. Joule, that iron in dil. sulphuric acid is negative against platinum in nitric acid, copper in copper sulphate, or platinized silver in dil. sulphuric acid; E. L. Nichols and W. S. Franklin, with platinum as positive electrode in a dil. hydrochloric acid soln. of potassium chlorate; and with carbon as positive electrode in nitric acid; M. Mugdan, that with iron in 0·1*N*-H_2SO_4 against *N*-KCl, Hg_2Cl_2, and mercury, the e.m.f. is 0·553 to 0·603 volt—C. Fredenhagen gave 0·625 volt. R. Zuppinger studied the cell with iron in *sodium hydrosulphide* with zinc as negative electrode in a soln. of zinc sulphate; and A. Finkelstein, a cell with iron in a *N*-soln. of *ammonium sulphide* against mercury as positive electrode in *N*-KCl with mercurous chloride. F. Braun, and C. R. A. Wright and C. Thompson found that iron in a soln. of *ferrous sulphate* is positive against zinc in zinc sulphate or cadmium in cadmium sulphate; J. J. Coleman, C. R. A. Wright and C. Thompson, and F. Förster, negative against copper in copper sulphate; C. R. A. Wright and C. Thompson, iron in ferrous sulphate soln. is negative against silver in silver sulphate or lead in lead sulphate. H. W. Töpffer studied cells with iron in a soln. of ferrous sulphate with and without ammonium oxalate or sulphate against cobalt as positive electrode in a soln. of cobalt sulphate with or without ammonium oxalate or sulphate, and with nickel as positive electrode with a soln. of nickel sulphate with or without ammonium sulphate or oxalate; A. Finkelstein, iron as negative electrode in *N*-$FeSO_4$ against mercury in *N*-KCl with mercurous chloride, and M. Mugdan found with 0·1*N*-$FeSO_4$ the e.m.f. is 0·623 to 0·703 volt; H. Euler, iron in a soln. of ferrous sulphate against iron in a soln. of ferrous sulphate and sodium thiosulphate has an e.m.f. of 0·01 to 0·02 volt. T. W. Richards and G. E. Behr studied the e.m.f. of cells with iron, and of iron charged with hydrogen in *N*-$FeSO_4$ against 0·1*N*-KCl, Hg_2Cl_2, and mercury. A. H. Bucherer studied the case of iron in a sat. soln. of *ammonium ferrous sulphate* with a few drops of a soln. of ferric sulphate against iron as positive electrode in 1·5*N*-$Fe_2(SO_4)_3$ and a few drops of a soln. of ammonium ferrous sulphate. J. P. Joule found that iron in a soln. of *sodium sulphate* is negative against platinum in nitric acid, or copper in copper sulphate. W. Hittorf found that iron in a soln. of sodium sulphate is negative against platinum in a soln. of chromic acid; M. Berthelot, iron in a soln. of H_2SO_4+NaOH against iron in soda-lye has an e.m.f. of 0·295 volt; iron in a soln. of $NaOH+Na_2SO_4$ against iron in soda-lye, 0·185 volt; and in $Na_2SO_4+H_2SO_4$, 0·12 volt. M. Mugdan found that the e.m.f. of iron in a 0·1*N*-soln. of *potassium sulphate* against *N*-KCl, Hg_2Cl_2, and mercury, is 0·603 to 0·703 volt. E. Heyn and O. Bauer, and F. Förster found that a cell with iron in *N*-$FeSO_4$ against *N*-KCl, Hg_2Cl_2, and mercury, has an e.m.f. of 0·68 volt at 17·5°. R. Abegg and S. Labendzinsky found for iron in a mixed soln. of ferrous and sodium sulphates against *N*-KCl, Hg_2Cl_2, and mercury:

$FeSO_4$.	1·0	1·0	0·1	0·1	0·1	0·01	0·01	0·01 eq. per litre
Na_2SO_4 .	0	1·0	0	0·1	1·0	0	0·01	1·0 ,,
E . .	0·762	0·774	0·785	0·787	0·803	0·795	0·799	0·827 volt

C. A. Lobry de Bruyn found the e.m.f. of cells with passive iron in a 0·1*N*-soln. of mixed ferrous and ferric sulphates against *N*-KCl, Hg_2Cl_2, and mercury, to be:

$FeSO_4$ . . .	67·5	48·5	36·0	29·0	1·0 per cent.
E	0·335	0·357	0·370	0·380	0·460 volt

W. Broniewsky found that cells with steel in *N*-$FeSO_4$ against carbon in manganese dioxide had an e.m.f. of:

Steel . .	0·06	0·24	0·44	0·79	1·12 per cent. carbon
E . . .	1·112	1·099	1·097	1·110	1·091 volt

L. Kahlenberg found the e.m.f. of a cell with iron in 0·375*N*-$FeCl_3$ in ethyl alcohol against iron in 0·3N-$\mathrm{FeCl_3}$ in aq. soln. to be 0·273 volt; iron in a soln. of 1·4508 grms. of ferric chloride in 77·6 c.c. of nitrobenzene against iron in 0·375N-$\mathrm{FeCl_3}$ in ethyl alcohol $E=0{\cdot}909$ volt.

T. Hawkins studied the case of iron (positive) and *nitric acid* against sulphuric acid and zinc or iron; M. Faraday, iron (negative) and dil. nitric acid against iron and conc. nitric acid; J. P. Joule, that passive iron in nitric acid is positive against amalgamated zinc in potash-lye; and H. Buff that iron (passive, or superficially coated with oxide) is positive against zinc in sulphuric acid, or iron in sulphuric acid; F. Petruschefsky, that iron in nitric acid is positive against zinc amalgam in sulphuric acid; F. J. Micheli, that iron in fuming nitric acid is positive against copper in dil. sulphuric acid. W. Hittorf found that iron in a soln. of *sodium nitrate* is negative against platinum in nitric acid; M. Mugdan found that the e.m.f. of a cell with iron in a soln. of *potassium nitrate* against mercury in N-KCl and mercurous chloride falls rapidly to zero; and with 0·1N-$\mathrm{KNO_3}$, the e.m.f. is 0·443 to 0·583 volt.

W. Hittorf found that iron in a soln. of *potassium cyanide* is positive against platinum in chromic acid; S. B. Christy gave for soln. with 1, 0·1, and 0·001 eq. of KCy per litre against N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury, $E=0{\cdot}116$, 0·046, and 0·046 volt respectively; M. Mugdan gave for a cell with iron in 0·1N-KCy against a similar electrode, $E=0{\cdot}103$ to 0·263 volt; A. Finkelstein, that iron in N-KCy is positive against mercury in N-KCl and mercurous chloride, and that iron is negative in a N-soln. of *potassium ferrocyanide or ferricyanide* against mercury in N-KCl and mercurous chloride; and analogous cells were studied by E. Heyn and O. Bauer. M. Mugdan obtained $E=0{\cdot}543$ to 0·603 volt for a cell with iron in a 0·1N-soln. of *acetic acid* against N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury, and for iron in a 0·1N-soln. of *sodium acetate*, 0·103 to −0·303 volt. W. Hittorf found that iron is negative in a soln. of sodium acetate against platinum in chromic acid. W. Hittorf found that iron is negative in a soln. of *potassium dichromate* against platinum in chromic acid; M. Mugdan gave $E=0{\cdot}157$ volt for iron in 0·1N-potassium dichromate against N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury; and 0·577 volt for iron in a 0·1N-soln. of *potassium permanganate* against a similar electrode. P. Bechtereff also studied cells with iron in 20 per cent. soda-lye with potassium permanganate against iron in soda-lye.

Double liquid cells with an intermediate inert liquid.—N. R. Dhar examined cells with iron in distilled *water* against 0·1N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury, with 0·1N-KCl as intermediary and similar cells with iron in a 0·1N-soln. of *potassium chloride*; N. R. Dhar and G. Urbain studied similar cells with iron in a 0·1N-soln. of *ferric fluoride*. B. Rane studied cells with iron in a N-soln. of hydrochloric acid, in the presence of different proportions of brucine against N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury, with a sat. soln. of potassium chloride as intermediary. F. Streintz found that iron in a soln. of *ferrous chloride* is negative against copper in copper chloride with water as intermediary; and positive against zinc in zinc chloride with water as intermediary: F. Braun found that iron in ferrous chloride is negative against silver in silver chloride with hydrochloric acid as intermediary; B. Neumann, that iron in N-$\mathrm{FeCl_2}$ is negative against N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury, with a N-soln. of an indifferent electrolyte as intermediary; and similarly with a N-soln. of *ferric chloride*. N. R. Dhar and G. Urbain examined cells with iron in 0·1N-$\mathrm{FeCl_3}$, or in a 0·1N-soln. of *ammonium ferric chloride*, against 0·1N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury, with 0·1N-KCl as intermediary. F. Braun found that iron in a soln. of *ferrous sulphate*, is positive against cadmium in cadmium sulphate with and without nitric acid as intermediary; iron is negative in a soln. of ferrous sulphate against copper in copper sulphate, or platinum in hydrochloroplatinic acid, with sulphuric acid as intermediary, and also against silver in silver nitrate, or lead in lead acetate, with nitric acid as intermediary; B. Neumann, that iron is negative in N-$\mathrm{FeSO_4}$ against N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury, with a N-soln. of an indifferent electrolyte. F. Haber and F. Goldschmidt found that cast or wrought iron in acidified N-$\mathrm{FeSO_4}$ is negative against 0·1N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury, with a 1 per cent. soln. of potassium nitrate as intermediary. P. Krassa, W. Kistiakowsky, and N. R. Dhar and G. Urbain examined similar cells with a sat. soln. of potassium chloride as intermediary. F. Förster, and M. de Broglie examined similar cells with different varieties of iron; and B. Rane found that in these cells the e.m.f. is lowered by the addition of increasing proportions of brucine. N. R. Dhar and G. Urbain studied cells with iron in a 0·1N-soln. of *ammonium ferrous sulphate* against 0·1N-KCl, $\mathrm{Kg_2Cl_2}$, and mercury, with a soln. of potassium chloride as intermediary; S. Bodforss, a similar cell with N-KCl, $\mathrm{Hg_2Cl_2}$, and mercury; and K. Iwase and K. Miyazaki, cells with iron in ammonium ferrous sulphate against

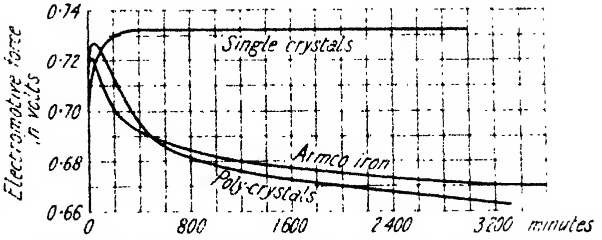


FIG. 273.—The Effect of Time on the Electromotive Force of Iron.

0·1N-KCl, Hg_2Cl_2, and mercury, with N-KCl as intermediary. The initial maximum, and end values of the e.m.f. were respectively with armco iron, 0·716, 0·722, and 0·669 volt, with polycrystals of iron, 0·718, 0·726, and 0·661 volt, and with single crystals of iron, 0·704, and 0·728 volt. The results are plotted in Fig. 273. N. R. Dhar examined cells with iron in a 0·1N-soln. of *potassium nitrate* against 0·1N-KCl, Hg_2Cl_2, and mercury, with 0·1N-KCl as intermediary. F. Streintz found that iron in a soln. of *ferric nitrate* is negative against copper in copper nitrate with water as intermediary; and positive against zinc in zinc sulphate with water as intermediary. G. Grube examined cells with iron in a mixture of *potassium ferrocyanide* and *potassium ferricyanide* with different proportions of potassium hydroxide against N-KCl, Hg_2Cl_2, and mercury, with a sat. soln. of potassium chloride as intermediary. N. R. Dhar and G. Urbain also examined similar cells with 0·1N-K_4FeCy_6, or 0·1N-K_3FeCy_6 against 0·1N-KCl, Hg_2Cl_2, and mercury, with a soln. of potassium chloride as intermediary; likewise also cells with iron in a 0·1N-soln. of *sodium nitroprusside*, or *potassium ferric oxalate*, or *ammonium ferric citrate* in place of the ferrocyanide.

Cells with fused oxides or salts as electrolytes.—W. W. Jacques constructed a cell with molten *sodium hydroxide* as electrolyte, an iron anode, and carbon cathode. The cell was studied by F. Haber and L. Bruner, A. C. Bradley, R. Lorenz, R. Lorenz and F. Kaufler, and P. Bechtereff. P. Bechtereff observed that the e.m.f. is a function of the temp., such that:

	337°	413°	456°	518°	551°	624°
E.m.f. .	0·623	0·683	0·728	0·784	0·804	0·830 volt

and the temp. coeff. between 400° and 580° is 0·00097 volt per degree. With a cell with passive iron as anode, fused sodium hydroxide, against 0·1N-KCl, Hg_2Cl_2, and mercury:

	337°	367°	418°	440°	552°	647°
E.m.f. .	0·288	0·308	0·363	0·378	0·478	0·583 volt

where the temp. coeff. between 400° and 580° is 0·00089 volt per degree. With active iron as anode:

	445°	501°	536°	564°	606°	618°
E.m.f. .	1·535	1·56	1·575	1·58	1·60	1·61 volt

E. Bauer found the e.m.f. of cells with molten sodium hydroxide, active iron as anode, and silver as cathode to be near 1·19 at 350° to 385°; and with passive iron as cathode, and active iron as anode, 1·19 volt at 350°. The e.m.f. of a cell with iron, molten sodium hydroxide and sodium was 2·16 to 2·26 volt at 380°. P. Bechtereff gave for a cell with carbon as cathode, passive iron as anode, molten sodium hydroxide and selenium as electrolyte, E=0·06 volt, with molten sodium hydroxide and tellurium as electrolyte, E is very small, using molten sodium hydroxide with 3 per cent. sodium chlorate, the e.m.f. was 0·65 volt at 395°; A. C. Bradley studied a cell with iron against carbon in molten sodium hydroxide and manganese dioxide and for a cell with passive iron, molten *lithium hydroxide* and potassium permanganate against carbon, the e.m.f. was 0·773 volt at 508°, and 0·822 volt at 616°. C. Liebenoff and L. Strasser found the e.m.f. of a cell with iron, molten *potassium hydroxide*, and carbon as cathode, to be $0·815+0·00105(\theta-500°)$ volt, and a cell with iron as cathode, molten potassium hydroxide, and N-KCl, Hg_2Cl_2, and mercury as anode, E=0·38 volt at 500°. R. von Hasslinger found that a cell with iron as cathode, platinum as anode, and molten *lithium or potassium chloride* as electrolyte:

	Lithium chloride				Potassium chloride			
	350°	800°	1000°	1100°	850°	950°	1200°	1500°
E .	0·68	1·07	0·88	0·77	0·54	0·75	0·81	0·85 volt

P. Bechtereff found for a cell with iron as anode, carbon as cathode, and molten *sodium and potassium carbonate* as electrolyte, E=0·32 volt at 1100°, and at higher temp. as the electrolyte begins to boil, the e.m.f. drops to zero. G. Gore studied a similar cell with a molten mixture of sodium carbonate, calcium oxide, and silica as electrolyte; C. P. Shrewsbury and co-workers, with molten *potassium nitrate* as electrolyte; G. Gore, with molten *lead chromate* as electrolyte; and P. Bechtereff, with molten *cryolite* and 10 per cent. alumina as electrolyte.

Cells with an iron electrode in the vapour of salts in flames.—These were studied by R. von Hasslinger. Iron is positive against platinum with 2N- and 4N-soln. of *lithium chloride* (E=0·37 and 0·43 volt), and positive against nickel with 2N-LiCl (E=0·11 volt):

	LiCl in flame			LiCl vapour in platinum tube	
	1550°	1400°	1000°	800°	500°
E	0·37	0·30	0·14	0·16	0·24 volt

Iron is positive against platinum with 2N- and 4N-soln. of *ammonium chloride* (E=0·29 and 0·33 volt), and against nickel with 2N-NH_4Cl (E=0·05 volt), and similarly with 2N-soln. of *ammonium bromide and iodide* (E=0·54 or 0·74 volt) against platinum. Iron is negative against platinum with $4N$-soln. of *sodium chloride* (E=0·16 volt), and $2N$-soln. of *potassium chloride, bromide, or iodide* (E=0·32, 0·37, and 0·26 volt). H. J. Bliksl ager studied the electrochemistry of iron electrodes in fused alkali chlorides. R. von Hasslinger observed that iron is positive against nickel with $4N$-*calcium chloride* (E=0·16 volt), and against platinum with $4N$- and $8N$-CaCl_2 (E=0·41 and 0·51 volt) with $4N$-soln. of *strontium chloride* (E=0·59 volt); with $2N$-soln. of *barium chloride* (E=0·30 volt); with $4N$-soln. of *ammonium sulphate* (E=0·43 volt); with a $2M$-soln. of *lithium salicylate* (E=0·10 volt); and with a $2M$-soln. of *aniline chloride* (E=0·28 volt).

S. J. French and L. Kahlenberg showed that the potential of iron in an electrolyte depends on the nature of the electrolyte and on the surrounding gas; W. Muthmann and F. Fraunberger, that the potential of the iron electrode is very sensitive to the presence of air; and J. Stapenhorst, that the longer the time iron is exposed to air, the more does the potential approach that of the noble metals. If two electrodes of iron dip in a soln. so that they are separated by a diaphragm, and if air be allowed to play about one electrode, the aerated electrode becomes the cathode and the other the anode. These aerated currents were studied by U. R. Evans, and F. Tödt. Observations were also made by T. W. Richards and G. E. Behr, by R. Kremann and H. Breymesser, and by W. Rathert. G. C. Schmidt observed that the presence of nitrogen has no perceptible effect on the electrode potential, but the potential is lowered by hydrogen and increased by oxygen, thus:

	Hydrogen				Oxygen	
Time . .	1	45	71	89	155	217 mins.
E_H . .	−0·535	−0·689	−0·721	−0·744	−0·730	−0·518 volt

T. Andrews observed that when opposite poles of two electrically connected magnets of approximately equal strength are immersed in various soln., the north pole becomes positive to the south pole. When the soln. were applied to the upper ends of the magnets, the north pole was still positive, but the e.m.f. was slightly less than before. In both cases the south pole becomes momentarily positive at the commencement of the experiment—*vide* passivity of iron for the effect of magnetism on the dissolution of iron in nitric acid. He also found that when couples consisting of magnetized and non-magnetized bars, simultaneously, were exposed to the action of a soln. of potassium chlorate with nitric acid or hydrochloric acid, also nitric, hydrochloric, and concentrated sulphuric acids, the magneto-chemical effects were very small. The magnetized rod was the positive element in every instance, except when dil. hydrochloric acid and conc. sulphuric acid were employed, when the electro-negative effect is possibly due to the presence of nascent hydrogen. D. Hurmuzescu observed that magnetized iron is always electropositive to non-magnetized iron; and that the e.m.f. depends on the strength of the magnetic field.

W. Muthmann and F. Fraunberger, and T. W. Richards and G. E. Behr agree that the presence of carbon has very little influence on the electrode potential of iron—*vide supra.* C. E. Fawsitt showed that the electrolytic soln. press. is raised by roughening the surface of the metal; and polishing the metal was found by W. Muthmann and F. Fraunberger, J. Stapenhorst, G. C. Schmidt, A. Speidel, H. Eggert, G. Tammann and C. Wilson, and H. Endo and S. Kanazawa—*vide supra*—to make the metal baser towards N-FeSO_4. According to T. W. Richards and G. E. Behr, the potential of iron towards soln. of its salts is not perceptibly influenced by raising the press. on the electrode to 350,000 kgrms. per sq. cm.; and likewise also an iron wire, 0·08 cm. in diameter, which had been subjected to a tension of 61 kgrms., suffered no perceptible change. T. Andrews, C. Hambuchen, and W. H. Walker and C. Dill also found that the effect of press. and torsion is very small; T. W. Richards and G. E. Behr, that iron reduced at a low temp. is baser than when the metal is reduced at a high temp., and E. Heyn and O. Bauer found that over-heated iron is nobler than it is when not over-heated. Hard, cold-drawn steel, low in carbon, in feebly acidified $0{\cdot}1N$-FeSO_4, is 0·040 volt nobler than the same metal in the annealed state; and P. Goerens found that the difference decreases as the annealing temp. is raised. H. Endo and S. Kanazawa found the effect of a slight strain on the potential of iron is masked by other influences, but with single crystals a strained electrode is more electropositive than is the case with an unstrained specimen. T. Andrews found that metal strained by tension, torsion, or flexion is electronegative to the unstrained metal, so that the strained metal, *per se*, is less liable to corrosion than the unstrained metal. I. Lifschitz and M. Reggiani studied the Becquerel effect—**10.** 58, 4.—with iron. T. F. Russell estimated that the cold-working of iron whereby 4·6 per cent. is converted into the vitreous phase, causes an increase of potential energy equivalent to 2·27 cals. per gram, or $9·49\times10^7$ ergs, on the assumption that the sp. ht. of crystalline and vitreous iron are the same. This means that the e.m.f. generated when cold-worked steel is one electrode and unworked steel the other, will be 0·000275 volt, or $0·000275\times10^8$ ergs—*vide supra*, cold-working. G. Tammann and C. Wilson found that hard iron is baser than soft metal; G. Tammann, that the rate of deposition of radium-F is greater for the hard metal than for the soft metal; and the rate of dissolution of iron in acids is augmented by cold-working.

According to R. Ruer, the cell Fe (passive) : HNO_3 (sp. gr. 1·4) : H_2SO_4 (66 per cent.) : Zn has an e.m.f. of 1·62 volts; and if an alternating current be applied, the e.m.f. rises to 1·95 volts, and if the alternating current be raised to 3 amp., no other change occurs. The original potential is restored by removing the applied alternating current. The cell Fe (passive) : H_2SO_4 (10 per cent.) : H_2SO_4 (66 per cent.) : Zn has the iron passivated by a direct current of 0·5 amp., and the cell gives an e.m.f. of 2·85 volt, and by the simultaneous application of an alternating current of 1 ampère, the iron is activated, and the e.m.f. falls to 0·67 volt. J. C. Ghosh found that an alternating current does not change the potential of iron in the cells Fe : $ZnSO_4$: Hg, Fe : $ZnSO_4$: Pt, and Fe : $CdSO_4$: Hg. P. Vaillant observed that an alternating current acting on the cell +Fe (small electrode) : NaCl; Fe (large electrode), makes the small electrode positive and the large electrode negative, and increasing the strength of the current makes the e.m.f. pass from a positive to a negative value. A. J. Allmand and R. H. D. Barklie compared the corrosion of iron by direct and alternating currents. The *moto-electric effect*, that is, the current produced in a short-circuited cell, consisting of two similar electrodes, in the same electrolyte, by the movement of one of them was discussed by A. H. Bucherer, W. Kistiakowsky, H. C. Regnart, and W. J. Müller and K. Konopicky. S. Procopiu measured the e.m.f. of a moving electrode of iron in water, $0·2N$-H_2SO_4, and $0·2N$-HNO_3, and found respectively 0·052, 0·062, and 0·072 volt. According to E. Bouty, if one of two electrodes in a ferrous or ferric salt soln. be heated, an e.m.f. is developed—0·000002 volt per degree with the former, and 0·00156 volt per degree with the latter—which is smaller with the ferrous than with the ferric salt soln. C. E. Mendenhall and L. R. Ingersoll found that small globules of iron in Nernst's glower move against the current.

When two similar electrodes are placed in a salt soln., and one electrode is placed in a magnetic field, an e.m.f. is developed. A. H. Bucherer, W. Rathert, and T. W. and W. T. Richards attributed the phenomenon to changes produced in the concentration of the electrolyte. T. Gross showed that with conc. soln. of ferric chloride or nitrate, or an acidified soln. of ferrous chloride or sulphate, an e.m.f. is developed if magnetized and non-magnetized iron electrodes are employed, and the e.m.f. and direction of the current re the same whether the north or the south pole of the magnetized rod of iron dips in the soln. E. L. Nichols and W. S. Franklin showed that if both electrodes be magnetized, one more intensely than the other, a current flows from the more strongly magnetized, electrode to the other electrode. Observations were also made by G. O. Squier. T. Andrews found that the direction of the current is different with different soln. The magnetized pole is positive with soln. of cupric sulphate, nitrate, acetate, chloride or bromide, nickel chloride, ferrous sulphate or chloride, mixtures of nitric acid with ferric chloride alone or mixed with potassium dichromate with or without ferric chloride, mixtures of potassium chlorate with nitric or hydrochloric acid, aqua regia, a mixture of a soln. of potassium bromide and bromine; the current flows from the non-magnetized to the magnetized electrode, and with sulphuric or hydrochloric acid, the current flows in the reverse direction. D. Hurmuzescu said that with oxalic acid, the magnetized electrode is positive. A. H. Bucherer found that with magnetized and non-magnetized iron electrodes the e.m.f. at 18° with $18N$-$Fe_2(SO_4)_3$ was 0·068 volt; with $1{\cdot}5N$-$FeCl_3$, 0·005 volt; with $5N$-HNO_3, 0·028 volt; with N-$KClO_3$ and $2N$-HNO_3, 0·002 volt; with $0{\cdot}2N$-H_2SO_4, 0·0008 to 0·001 volt; and $0{\cdot}2N$-$CuSO_4$, 0·014 volt. T. Gross observed a current of short duration first flowing from the non-magnetized to the magnetized electrode; H. A. Rowland and L. Bell called this the primary current, and A. H. Bucherer thought it was due to the shaking of the electrode. E. L. Nichols and W. S. Franklin found that the e.m.f. of the cell Fe (magnetized) : $(K_2Cr_2O_7+H_2SO_4)$: Pt increases with increasing field strength, *H* gauss :

H .	2,000	3,600	7,770	8,400	12,750	16,300	19,700
E.m.f.	0·0008	0·0045	0·0386	0·0424	0·0487	0·0510	0·0680 volt

Observations were also made by D. Hurmuzescu, and P. Janet, and E. Staicu. E. Staicu also showed that the e.m.f. is greater, the smaller the concentration of the iron salt soln. used as electrolyte; thus, with field strengths of 4700 and 5750 gauss, the e.m.ff. developed with 9·88 grms. of $FeCl_3$ per 100 c.c. of water are respectively 0·0276 and 0·0302 volt, and with a soln. of 0·988 grm. per 100 c.c. of water, respectively 0·03609 and 0·04059 volt. T. W. and W. T. Richards found that with the application of a magnetic field for 20 secs., the e.m.f. of the cell −Fe : $1{\cdot}02N$-$FeSO_4$: N-KCl, Hg_2Cl_2 : Hg+ falls about 0·001 volt; and if the iron is charged with hydrogen, the fall of the e.m.f. is greater, and is nearly proportional to the intensity of the magnetic field. The phenomenon was discussed by A. H. Bucherer, P. Duhem, D. Hurmuzescu, W. Rathert, and T. W. and W. T. Richards. C. Maurain discussed the magnetic properties of iron in the act of deposition; and O. M. Corbino, the polarization of colloidal iron in a magnetic field.

From W. Nernst's formula, $E=-(RT/n)\log(P/p)$, where p is the osmotic press. of the metal ions, and P is the **solution pressure**—1. 16, 3—if E is zero, $p=P$. For a concentration $[Fe^{\cdot\cdot}]=1$, and if the osmotic press. $p=22$ atm., and $E=0{\cdot}153$ volt, then $0{\cdot}153=\frac{1}{2}\times0{\cdot}059\log(P/22)$ for $Fe=Fe^{\cdot\cdot}$, or, at 18° the soln. press. is $3{\cdot}3\times10^6$ atm.; and similarly for $Fe\rightleftharpoons Fe^{\cdot\cdot\cdot}$, at 18°, the soln. press. is about 1·4 atm. Metallic iron thus behaves as if it were an alloy of ferrous and ferric iron with soln. press. in the ratio $1:10^{-6}$. The soln. press. can also be regarded as a measure of the tendency of the two ions to give up their charges. This tendency is very much greater with ferric than it is with ferrous ions. It can also be regarded as representing a tendency of the ferrous ions to acquire an additional charge. R. Abegg and G. Bodländer discussed the affinity of these ions for electric charges, and observed that the **electroaffinity** of ferrous ions is far greater than that of ferric ions; and K. Schaum said that of the two forms of ions, ferrous ions are the stronger.

The work involved in the production of the different stages of oxidation of iron can be calculated from the preceding formulæ. In an electrolytic cell, both ferrous and ferric ions can lose their charges at the cathode, or the ferric ions can be reduced to ferrous ions; and at the anode, $Fe^{\cdot\cdot}$-ions can be oxidized to $Fe^{\cdot\cdot\cdot}$-ions, or with an anode of iron, iron can produce $Fe^{\cdot\cdot}$-ions, or $Fe^{\cdot\cdot\cdot}$-ions. In order that these changes may occur, the electrode must not only be charged with a definite quantity of electricity, but it must be also charged to a minimum potential. If an iron wire dips into a soln. of ferrous ions of unit concentration, the electrode $E_H=-0{\cdot}43$ volt when the system is in a state of equilibrium; but if the wire is polarized by a positive potential, it follows from $E_H=-0{\cdot}43+\frac{1}{2}\times0{\cdot}058\log[Fe^{\cdot\cdot}]$ volt, that this corresponds with a higher conc. of the $Fe^{\cdot\cdot}$-ions for equilibrium, and accordingly $Fe^{\cdot\cdot}$-ions pass into soln.; and conversely, if the iron receives an additional negative potential, $Fe^{\cdot\cdot}$-ions will be discharged to form metallic iron. Consequently, if iron is to be deposited from a soln. of a ferrous salt, the potential of the cathode must exceed that value below which iron passes into soln. This subject was discussed by F. Förster, and H. Lee. Remembering also that the potential for the change $Fe \rightleftharpoons Fe^{\cdot\cdot}$ is $-0{\cdot}43$ volt, and for $Fe \rightleftharpoons Fe^{\cdot\cdot\cdot}$, $-0{\cdot}04$ volt, it follows that ferric ions have a greater tendency than ferric ions to form iron. Hence, in a mixture of ferric and ferrous ions it might, at first sight, be assumed that on electrolysis, the first change to occur will be $Fe^{\cdot\cdot\cdot} \rightarrow Fe$. Actually, it is easier to reduce ferric to ferrous salt: $Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$, because less work is required for the "distribution" of the positive charges. When the process has continued long enough, and the ratio $[Fe^{\cdot\cdot\cdot}]:[Fe^{\cdot\cdot}]$ corresponds with $0{\cdot}75+0{\cdot}058 \log [Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]=-0{\cdot}04+\frac{1}{3}0{\cdot}058 \log [Fe^{\cdot\cdot\cdot}]$, the work required for both changes is the same. This condition is satisfied when nearly all the ferric ions have been converted into ferrous ions. When the cathodic reaction $Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$ is about completed, and the ratio $[Fe^{\cdot\cdot\cdot}]:[Fe^{\cdot\cdot}]$ is favourable for the discharge of the $Fe^{\cdot\cdot}$-ions, it is necessary to raise the cathode potential in order to keep the process continuous, and it thereby attains a value which also favours the direct reduction of the ferric ions to the metal. Hence, all three reactions—$Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot} \rightarrow Fe$, and $Fe^{\cdot\cdot\cdot} \rightarrow Fe$—can take place simultaneously; but since the concentration of the $Fe^{\cdot\cdot\cdot}$-ions is very small, the work done at the cathode is virtually all expended in reducing the ferrous ions to the metal. Consequently, in the electrolytic deposition of iron it is best to work with a soln. of a ferrous salt. V. Kohlschütter and H. Stäger studied the anode reactions; and A. P. Rollet, the electrode reactions of iron in sulphuric acid, and alkali-lye under the influence of an alternating current, and noted that the electrodes are alternately covered with oxide and with powdery metal.

According to R. S. Lillie and S. E. Pond, an electric current corresponding with a potential of 10 volts flowing across a caoutchouc membrane of thickness 40μ interposed between two electrolyte soln., one of which is a mixture of ferrous chloride and potassium thiocyanate, causes oxidation of ferrous to ferric iron at the surface of the membrane facing the cathode.

According to E. J. Mills, when iron is deposited electrolytically on the bulb of a thermometer, a pressure, which has been called *electrostriction* is exerted, so that the bulb of the thermometer contracts. The phenomenon was studied by E. Bouty, who found that when first deposited, the film of metal may have a higher temp. than the electrolyte, and as the metal cools, it will contract and exert a pressure. In some cases there is a cooling effect, so that the metal immediately after deposition is heated, and expands. This subject was discussed by V. Kohlschütter and E. Vuilleumier, V. Kohlschütter and A. Nägeli, V. Kohlschütter, G. G. Stoney, R. H. D. Barklie and H. J. Davies, and H. Stäger—*vide* nickel.

The minimum cathode potential for the electrodeposition of iron is not the same with different soln. In the presence of other metal ions, the result depends on the conc. of the $Fe^{\cdot\cdot}$-ions, and on that of the $H^{\cdot}$-ions. Complex salts may be formed in the soln. which, when neutral, produce so small a proportion of ferrous ions that there is no electrodeposition. Thus the iron may not necessarily be cathodically precipitated from normal acidic molar soln. of ferrous chloride. The electrode potentials of the reactions $Fe^{\cdot\cdot} \rightarrow Fe$ and $2H^{\cdot} \rightarrow H_2$ are, respectively, $-0{\cdot}43$ and $0{\cdot}0$ volt. So little work is required for the separation of gaseous hydrogen that it is given off at once from the cathode, the conc. of the $H^{\cdot}$-ions is not much impoverished, and with high current densities it is scarcely possible to make the cathode potential as negative as is required for the deposition of iron: $Fe^{\cdot\cdot} \rightarrow Fe_2$. From the relation $-0{\cdot}43+\frac{1}{2}\times 0{\cdot}058 \log [Fe^{\cdot\cdot}]=0{\cdot}0+\frac{1}{2}\times 0{\cdot}048 \log [H^{\cdot}]^2$, it follows that when the same work is involved in the separation of iron and hydrogen from molar soln., $[H^{\cdot}]=3{\cdot}8\times 10^{-8}$. H. F. Haworth discussed the resistance of soln. of ferric chloride with an alternating current. S. Glasstone found the deposition potential of iron from normal soln. to be:

	15°	36°	55°	70°	90°
Potential . .	−0·68	−0·55	−0·49	−0·46	−0·46
Overvoltage . .	0·22	0·09	0·03	*nil*	*nil*

The reversible potential of iron in N-soln. of a ferrous salt is probably -0·46, as found by W. H. Hampton, so that at temp. of about 70° iron may be deposited almost reversibly.

The **hydrogen overvoltage** of iron was discussed by J. N. Pring and J. R. Curzon, and C. W. Bennett and J. G. Thompson. As with most metals, electrolytic hydrogen does not develop with the potential of $H^{\cdot}=H_2$. because there is an overvoltage effect, which W. A. Caspari found to be $E_H=-0·08$ volt for smooth iron in a soln. of sodium hydroxide. If the overvoltage effect is independent of the electrolyte and the current density, the above relation becomes $0·43+\frac{1}{2}\times0·058 \log [Fe^{\cdot\cdot}]=0·0+\frac{1}{2}\times0·058 \log [H^{\cdot}]^2-0·08$, so that the same work is required for the separation of iron and hydrogen from a molar soln. of ferrous chloride with a $H^{\cdot}$-ion concentration of $0·9\times10^{-7}$. This is nearly the same as for a neutral soln. which approximates to $0·74\times10^{-7}$, and this means that hydrogen is also given off when a neutral soln. of ferrous chloride is electrolyzed. A. Coehn and K. Dannenberg gave $E_H=-0·03$ volt for the overvoltage of hydrogen in N-KOH. H. G. Möller obtained −0·23 volt; G. Carrara, −0·21 volt; M. Centnerszwer and M. Straumanis gave −0·28 volt at 20°; E. Newbery, −0·30; and A. Thiel and W. Hammerschmidt, −0·17. F. Förster, and O. Mustad studied the effect of the $H^{\cdot}$-ion concentration in hydrochloric and sulphuric acid soln., and of additions of ammonium chloride, sodium hydrocarbonate, and boric acid. A. Thiel and E. Breuning gave for iron etched with sulphuric acid at 25°, and in

	N-KOH	N-NaOH	1·3N-LiOH	N-KH_2PO_4	5N-$KC_2H_3O_2$	5N-$NaC_2H_3O_2$
Overvoltage .	0·075	0·087	0·056	0·121	0·176	0·127

The two alkali acetate soln. were mixed with 2N-acetic acid. E. Newbery obtained the cathodic overvoltages E_H milliamps. in N-H_2SO_4, and N-NaOH at 15° with a current density D:

	D . . .	2	6	10	50	100	400	1000	2000
E_H	N-H_2SO_4 .	0·24	0·26	0·26	0·27	0·27	0·28	0·27	0·26
	N-NaOH .	0·28	0·32	0·33	0·34	0·35	0·35	0·34	0·34
	N-$FeSO_4$.	0·30	0·30	0·30	0·32	0·34	0·33		
	N-$FeCl_2$.	0·35	0·34	0·34	0·36	0·36	0·41		

The cathodic overvoltages in N-H_2SO_4 of iron of a high degree of purity; steel with 0·5 per cent. of carbon; and chrome steel with 10 per cent. of chromium, were:

Current density .	2	6	10	50	100	1000	2000
Iron . . .	0·27	0·27	0·27	0·29	0·30	0·29	0·27
Steel . . .	0·26	0·28	0·28	0·28	0·27	0·25	0·23
Chrome steel .	0·26	0·27	0·28	0·28	0·29	0·30	0·29

U. C. Tainton found that a high current density increases the hydrogen overvoltage of the iron cathode. A. L. McAulay and co-workers found that when there is no sensible concentration of the ions of an iron electrode in a soln., and when the electrode is not covered by an oxide film, its potential is determined by the $H^{\cdot}$-ion concentration if its hydrogen overvoltage is positive to the deposition potential which it would have in a soln. of the order of 0·001N of its own ions. When this is not the case, the potential is controlled by the concentration of the anions, probably acting through a film of electrolyte in contact with the metal and with a concentration of the iron-ions of the order 0·0001N. G. R. Hood and F. C. Krauskopf studied the hydrogen overvoltage in connection with the efficiency of the electrolyte reduction of aq. soln. of potassium chlorate.

M. Knobel and co-workers found for 2N-H_2SO_4 at 25°:

D . . .	0	1	5	10	100	200	500	1500
E_H . . .	0·2026	0·4036	0·5024	0·5571	0·8184	0·9854	1·2561	1·2908

M. Centnerszwer and M. Straumanis found that with a current density of 0·075 amp. per sq. cm., the overvoltage is independent of the current density. Observations on the overvoltage, and the iron cathode were also made by S. Glasstone,

N. Koboseff and N. I. Nebrassoff, H. L. Lochte, H. L. Lochte and R. E. Paul, E. Newbery, and M. Bodenstein. S. Glasstone found that when an alternating current of 0·10 max. amp. is superposed on a direct current of 0·12 amp., the overvoltage in N-NaOH is 0·64 to 0·66 volt, and in N-H_2SO_4, 0·67 to 0·71 volt. The overvoltage may be augmented in the presence of some organic substances. A. Sieverts and P. Lueg observed that the overvoltage of iron in acid is very little affected by the presence of α-naphthaquinone; the ether-soluble, basic constituent of crude anthracene increases the overvoltage. No connection was observed between the retardation of the rate of dissolution in acid, and the overvoltage, but it is assumed that the " poison " is adsorbed on the metal surface, and reduces the amount of metal accessible to the acid. L. G. Knowlton found the overvoltage in $2N$-H_2SO_4 sat. with aniline is 0·05 volt higher than with the acid alone; E. L. Chappell and co-workers observed the overvoltage with different kinds of iron in N-H_2SO_4 is augmented by the addition of quinoline ethiodide—*vide* Figs. 275 and 276, corrosion; and J. C. Warner found that the addition of gelatin raises the overvoltage. U. Sborgi and G. Cappon, and G. Carrara found that in an alcoholic soln. of N-KOH the overvoltage is 0·23 volt, and with a methyl alcohol soln., 0·26 volt at 19° to 20°.

According to A. Coehn and Y. Osaka, an iron wire dipping in N-KOH gives a current-voltage curve corresponding with an **oxygen overvoltage** of 0·24 volt. E. Newbery found that with a current density, D, in N-H_2SO_4 and N-NaOH, at 15°, the oxygen or anodic overvoltages are :

	D . .	2	6	10	50	100	400	1000	2000
E_H	N-H_2SO_4 .	0·75	0·76	0·75	0·74	0·73	0·70	0·67	0·63
	N-NaOH .	0·44	0·48	0·49	0·51	0·51	0·52	0·52	0·51
	N-$FeSO_4$.	0·02	0·06	0·06	0·08	0·09	1·85*	..	..
	N-$FeCl_2$.	0·05	0·07	0·08	0·10	0·10	0·11	..	..

The asterisk means that the metal became passive. Observations were also made by S. Glasstone, and F. Meunier. If a direct current of 0·12 amp. has superposed an alternating current of 0·07 to 0·10 amp., the oxygen overvoltage in N-NaOH is 0·52 to 0·54 volt, and in N-H_2SO_4, 0·62 to 0·74 volt. L. W. Haase found that the oxygen depolarization current varies with the illumination of the system iron-platinum with water or a dil. soln. of potassium chloride. U. Sborgi and G. Cappon found that the anodic behaviour in ethyl alcohol soln. of ammonium and calcium nitrates show that it is passive at all temp. and current densities employed. R. A. Dengg and H. J. Donker measured, with inconclusive results, the polarization of different types of iron and steel in $0{\cdot}1N$-KCl and $0{\cdot}1M$-K_2CO_3. W. M. Thornton and J. A. Harle, and K. Georgi studied the anodic corrosion of iron; and A. J. Allmand and R. H. D. Barklie, the effect of alternating currents on the electrolytic corrosion of iron. J. W. Shipley and C. F. Goodeve found that in the electrolysis of a soln. of sodium hydroxide with iron electrodes and an alternating current the critical density of 3·8 amp. per sq. cm. must be exceeded before gas is evolved; with steel electrodes, the critical density is 4·5 amp. per sq. cm. A. P. Rollet studied the anodic behaviour of iron in acidic or alkaline soln.; and R. T. Dufford, the photovoltaic effect with cells containing an ethereal soln. of Grignard's reagent and iron.

A. Günther-Schulze studied the **electrolytic valve action** of iron in fuming sulphuric acid. With an anodic current density of 0·003 amp. per sq. cm., and 60 per cent. sulphuric acid, the valve action appears, and with 75 per cent. sulphuric acid the valve action gradually changes into passivity; and with higher concentrations, the valve action is stable. Alternating currents are rectified by the iron under these conditions. A layer of oxide is formed. The rectification in 89 per cent. sulphuric acid at 0° is equal to that with aluminium. W. Winter observed that the rectification occurs in dil. soln. of sulphuric acid, and potassium hydroxide; it is only slight in hydrochloric acid, and does not occur in nitric acid. One per cent. sulphuric acid was found by W. Holtz to exert a small valve action.

According to A. Günther-Schulze, with polarizing iron anodes and a constant current, and with sulphuric acid of less conc. than 50 per cent. the iron is only rendered passive, but above 60 per cent. and a current of 3 milliamp. per sq. cm., valve action occurs before the metal becomes passive. The electrolytic valve action below 75 per cent. concentration of acid is unstable and slowly changes to passivity, but at higher concentrations is stable. The maximum potential varies according to the concentration of the acid between 40 and 70 volts. Below the maximum potential the residual current which flows through the cell is very small. Iron, both in conc. and in fuming sulphuric acid, has, like aluminium, the property of partially transforming an alternating current into a direct current. The electrostatic capacity of the active layer formed on iron is of the same order of thickness, and depends on the water-content of the sulphuric acid in the same way as does that on aluminium. I. Lifschitz and M. Reggiani found the valve action is reduced by illumination.

F. Marx described an **iron accumulator** with two iron negative electrodes, and an intermediate porous carbon block as positive electrode; the electrolyte is a hydrochloric acid soln. of ferric chloride, which is reduced by the discharge and oxidized by the charge. The Akkumulatoren Werke tried the cell with an iron electrode, alkali-lye, or a soln. of sodium carbonate, potassium dichromate, or phosphoric acid, and an electrode of ferric oxide; and A. P. T. Tully, iron in a soln. of ammonium chloride, and carbon in nitric acid or bromine water. C. R. Hardy studied the screening effect of ferrous hydroxide on the iron anode.

Several measurements have been made of the **decomposition voltage** of ferrous salt soln. The current-potential curves of these soln. show a break corresponding with the decomposition voltage. The cathode potential does not show such a break, because hydrogen is evolved simultaneously with the iron. The minimum voltages required for the separation of iron from ferrous salt soln. were found by F. W. Küster to be:

$FeSO_4$ . . .	1·0N-	0·5N-	0·1N-	0·05N-
H_2SO_4 0·1N- . .	0·753	0·743	0·733	0·873 volt
H_2SO_4 0·01N- . .	0·693	0·663	0·736	0·733 ,,
H_2SO_4 0·001N- . .	0·673	0·653	0·678	0·663 ,,

and for 0·1N-$FeSO_4$ with 0·01N-H_2SO_4 the values for foil and wire cathodes are respectively 0·683 and 0·747 volt, and with no acid, 0·648 and 0·673 volt. Hence, iron is deposited on the foil before it is deposited on the wire. G. Coffetti and F. Förster tried the effect of gradually increasing the current density—ampères per sq. cm.—at the cathode in the electrolysis of N-$FeSO_4$, time constant. The voltage, E_H, at which iron and hydrogen are simultaneously formed, and the current yield are as follow:

Current density . .	0·00113	0·00227	0·00455	0·0091	0·0182
Acidity	0·0025N-	0·005N-	0·0075N-	0·01N-	0·02N-
E_H	0·70	0·71	0·73	0·75	0·79
Current yield . . .	20	31	38	—	56

F. Förster found the effect of temp. and current density, $D10^{-4}$ amp. per sq. cm., to be:

D . . .	182	91	45	22	11	5	
E_H 20° . .	−0·72	−0·70	−0·685	−0·67	—		volt
E_H 50° . .	0·62	0·61	−0·59	−0·58	−0·57	−0·56	,,
E_H 75° . .	0·57	0·55	−0·545	−0·54	—		,,
E_H 95° . .	—	−0·52	−0·51	−0·51	—		,,

S. Glasstone found that with a copper cathode and N-$FeSO_4$ the decomposition potential is:

	15°	36°	55°	70°	90°
E . .	−0·68	−0·55	−0·49	−0·46	−0·46 volt

and W. A. Noyes, with neutral N-$FeCl_2$:

	20°	50°	102°	122°	182°
E_H	−0·66	−0·45	−0·14	−0·18	−0·23 volt

Observations were also made by G. Coffetti and F. Förster, W. A. Noyes, C. Marie and N. Thon, F. Meunier, and A. Smits and A. H. W. Aten. E. Müller and J. Janitzki studied the effect of rubbing on the potential in soln. of acids, bases, and neutral salts; E. S. Hedges, the periodic electrodeposition of iron from soln. of potassium ferrous cyanide; V. Sihvonen and G. Kerkkänen, the effect of a magnetic field on the electrolytic potential; and U. Sborgi, on the anodic behaviour of iron.

A. F. W. von Escher found that in the electrolysis of a soln. of zinc and ferrous sulphates in equal proportions, the alloys deposited at 18°, and at 90° with small current densities consist principally of zinc; an excess of iron in the deposit under these conditions can be obtained only when the proportion of ferrous sulphate is preponderating. In Fig. 274 the results with a soln. containing $0{\cdot}01N\text{-}H_2SO_4$ and $Fe^{\cdot\cdot}:Zn=9:1{\cdot}5$, at 90°. The transition from high to low proportions of iron occurs at low current densities. The transition to deposits with a high proportion of zinc occurs at the higher current densities. The current efficiency is below 90 per cent. at low current densities, and above that value at high current densities. When the ratio of Fe : Zn is 9 : 0·63, the transition occurs at a current density of 0·035 or 0·040 amp. per sq. cm.; with the ratio 9 : 1, at 0·022 amp. per sq. cm.; and at 9 : 1·5, at about 0·020 amp. per sq. cm. S. Glasstone studied this subject; W. H. Creutzfeldt, the deposition of iron from soln. of copper and iron salts; and J. Prajzler, the simultaneous deposition of iron and other metals related to iron.

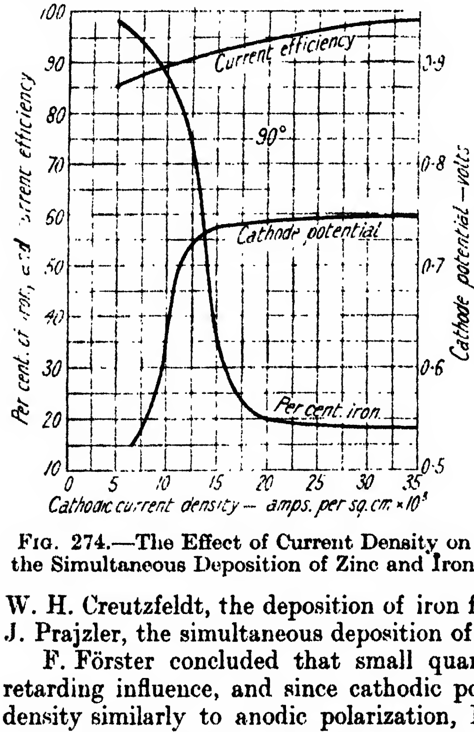


FIG. 274.—The Effect of Current Density on the Simultaneous Deposition of Zinc and Iron.

F. Förster concluded that small quantities of zinc, like hydrogen, exert a retarding influence, and since cathodic polarization varies here with the current density similarly to anodic polarization, F. Förster speaks of *cathodic polarization*—*vide infra*, passivity. The phenomenon was discussed by G. Grube, and A. Smits.

The **polarization** of iron electrodes was studied by M. le Blanc, F. Förster, E. Vogel, E. Liebreich, A. Smits and A. H. W. Aten, and C. M. Gordon and F. E. Clark. G. Grube observed that whilst anodes of nickel, cobalt, copper, gold, and platinum do not become polarized when ferrocyanide in alkaline soln. is electrolytically oxidized, anodes of iron, nickel copper, cobalt, lead, and silver become polarized in a neutral soln. of potassium ferrocyanide and ferricyanide, and anodes of iron, lead, silver, and zinc become polarized also in alkaline soln. of these substances. In all these cases there is evidence of the formation of a surface film of oxide, and it must be assumed that in these cases the oxidation of the ferrocyanide is effected by the intermediate formation of peroxides. Since at electrodes of gold and platinum in neutral and alkaline soln., at electrodes of nickel, cobalt, and copper only in alkaline soln., of potassium ferrocyanide and ferricyanide oxidation of the former salt takes place at the same potential and with the same velocity, it is improbable that the passivity of these metals is due to a layer of oxide; it is probably due to the effect of the oxygen charge of the electrode in retarding the liberation of cations from the metal. It is shown that an electrode immersed in alkaline ferrocyanide-ferricyanide soln. becomes more fully charged with oxygen than in neutral soln., and this explains the greater passivity in alkaline soln. In the case of iron, the oxygen charge does not completely hinder the liberations of $Fe^{\cdot\cdot}$-ions from the metal, and therefore there is the possibility of the formation of a surface film of oxide on the anode.

W. J. Müller observed that iron dissolves anodically at all current densities without measurable polarization; and that the current-voltage curves of iron anodes show that the passive state is preceded by the formation of a film of a basic salt or hydroxide of iron which causes a local increase of current density, and the high current density inaugurates the passive state. According to E. Liebreich, during cathodic polarization, the charged hydrogen first formed at the cathode is absorbed either by the metal or by the solution, leaving a film of solution containing an excess of hydroxyl ions which react with the metal to form basic salts or hydroxide; as the polarization increases, the increasing quantities of hydrogen produced reduce these salts again to metal, after which the hydrogen is evolved in bubbles.

F. Förster, and H. Lee found that the yield is increased by raising the temp. M. M. Tichwinsky, also, found that 0·3 volt more is required for the separation of iron from a soln. of ferrous sulphate in darkness than in light. C. Benedicks and R. Sundberg found that the potential of a carbon steel is affected by light provided that some ferric ions are present. A photo-cell was constructed by means of two strips of stainless steel, since, when immersed in a soln. of ferrous sulphate, light increases the value of the electrode potential, making the steel slightly more basic.

A. Finkelstein measured the current-voltage curves at the anode for soln. of ferrous salts, and the results are shown in Fig. 275; and for soln. of ferric chloride at the cathode, in Fig. 276. The breaks in the curves with 0·1*N*-, 0·01*N*-, and 0·001*N*-$FeCl_3$ occur respectively at E_H=0·82, 0·79, and 0·75 volt. The soln. were all 0·1*N*- with respect to hydrochloric acid. The current, *C*, is expressed in arbitrary units. A. Finkelstein said that the break occurs at the cathode when the iron itself separates in the ferric state; and this very quickly is reduced to ferrous iron, which then dissolves in the ferrous salt soln.—*vide infra*, passive iron. A. Finkelstein also determined the e.m.f. of iron electrodes against various soln., and observed that the addition of potassium cyanide to the soln. greatly lowers the e.m.f.; and in soln. of mixed ferrous and ferric salts, the e.m.f. decreases as the ferrous salt is replaced by ferric salt. C. Fredenhagen discussed whether at the electrode during the electrolysis of ferrous or ferric salt soln. (i) a direct change $Fe^{\cdot\cdot}+(\epsilon)\rightleftharpoons Fe^{\cdot\cdot\cdot}$ occurs, as supposed by A. Finkelstein, or (ii) whether the action involves the secondary changes $H^{\cdot}+(\epsilon)=H$, or $2OH'+2(\epsilon)=H_2O+O$, and subsequently $2H+2Fe^{\cdot\cdot\cdot}=2Fe^{\cdot\cdot}+2H^{\cdot}$, or $O+Fe^{\cdot\cdot}+H_2O=Fe^{\cdot\cdot}+2OH'$. According to R. Abegg and J. Neustadt, the potential of ferrous and ferric salts dissolved in

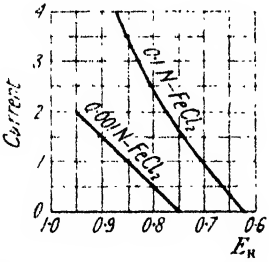


FIG. 275.—Current-Voltage Curves for Ferrous Chloride Solutions at the Anode.

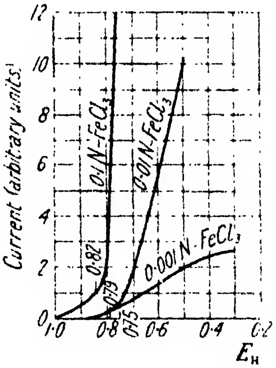


FIG. 276.—Current-Voltage Curves for Ferric Chloride Solutions at the Cathode.

pyridine is constant, showing that the change is direct $Fe^{\cdot\cdot}+(\epsilon)-Fe^{\cdot\cdot\cdot}$. In the first case, the speed of the electrical change depends on the diffusion of the iron salts to the electrodes, and in the second case, on the speed of the chemical reactions as well. The speed of the chemical reactions are very great, so that the speed of the electrical change depends only on the rate of diffusion. Z. Karaoglanoff observed that the rate of reduction of a ferric salt by electrolysis depends on the rate at which ferric ions can be changed into ferrous ions at the electrode, and on the rate at which ferric ions can diffuse into the layer of soln. in contact with the electrode. In a soln. which is not stirred, convection also occurs; owing to the changes of composition and density in the soln. near the electrode, convection currents are produced which tend to keep up the concentration of the ferric ions at the electrode. The same considerations hold good for the oxidation of a soln. of a ferrous salt. The time t during which a current C must flow in order to diminish the concentration of ferric or ferrous ions at the electrode to such a value that hydrogen (or oxygen) is evolved in a soln. of concentration c, is given by $C\sqrt{t}=kc$, where k is a constant which is proportional to the square root of the diffusion coefficient of the salt. This formula is shown to hold good for ferrous and ferric salts so long as the current is not too small. For very small currents, convection at the electrode suffices to maintain the concentration of the ferrous ions above the limit at which gas is evolved. The potential of the electrode during the period in which the concentration of the iron salt is diminishing is also measured, and the curves obtained are found to have the general form required by the assumptions that the loss of ferric ions at the electrode is being replaced by diffusion, and that the relation between the potential of the electrode and the concentration of the soln. is given by R. Peters' formula: $E_H=RT\log\{x/(1-x)\}+E_0$, where x denotes the fractional part of the iron which is present as ferrous salt. T. Graham's experiments show that ferrous and ferric ions diffuse at about the same speed.

In the electrolysis of iron salts, the acidification of the soln. lowers the yield, and unfavourably influences the nature of the deposit. Neutral soln. give the best results; but, as shown by G. Coffetti and F. Förster, and A. Ryss and A. Bogomolny, with the discharge of $H^{\cdot}$-ions at the cathode, there is a tendency to form some ferrous hydroxide which oxidizes easily, and is apt to spoil the deposit. It is therefore advisable to add to the electrolyte some substance which hinders the precipitation of the hydroxide, and forms complex iron-ions. A. Classen, B. Neumann, and E. F. Smith recommended forming complex citrates, tartrates, or oxalates for the electrodeposition of iron for analytical purposes, but ordinary chemical processes are usually more convenient for the determination of iron. F. Braun discussed the **electrostenolysis** of iron—*vide* cobalt.

According to A. Skrabal, two kinds of iron are produced by electrolysis. Type-*A* is white, compact, and very hard, and it is obtained by electrolyzing a soln. of a ferrous salt with an iron anode, and small current density; while type-*B* is greyer in colour, less compact, and softer than type-*A*; it is produced when a platinum anode with a large current density is employed, and a soln. of a complex ferrous salt. By varying the conditions between these two extremes, intermediate types may be formed. By electrolyzing a soln. of ferrous ammonium sulphate with a platinum cathode, an anode of electrolytic iron, and an e.m.f. of about 0·4 volt, the deposit is silvery white and sometimes crystalline. It dissolves slowly in warm, dil. sulphuric acid, and rusts in moist air. Sometimes specimens are obtained which are scarcely attacked by acids or halogens. Type-*A* is always hard, and it usually scratches glass; it is also brittle, but it loses these qualities when it is heated to redness. When the iron is exposed to air, it slowly loses occluded hydrogen, and more rapidly when it is immersed in hot water. This loss of hydrogen does not diminish its hardness and brittleness. A. Skrabal thinks that iron of type-*A* is γ-iron, and it is therefore unstable at ordinary temp. When heated, it changes into stable α-iron which is soft. It cannot be hardened by heating and sudden quenching, owing to the high temp. at which γ-iron changes into β-iron. The presence of large quantities of hydrogen is attributed to the greater solvent action of γ-iron, which is known to dissolve carbon much more readily than α-iron. H. Lee, F. Haber, and others have studied the hydrogen content of electrolytic iron—*vide infra*, action of hydrogen. W. J. Müller and K. Konopicky discussed the residual current; and A. M. Hasebrink, the electrolysis of a soln. of potassium nitrate with iron electrodes.

About 1820, T. J. Seebeck[4] first observed that heat could be transformed into electrical energy—the so-called **thermoelectric force**—without the intervention of a liquid, and he arranged a number of metals and alloys in the order of their thermoelectric effects; he also noted that changes in the order occurred as the temp. was gradually raised, but J. Cumming had also observed that when wires of copper, gold, etc., were gradually heated in contact with iron, the current generated rose to a maximum, fell off, and was reversed at a red-heat. F. T. Trouton observed that a thermoelectric current is produced in iron and steel by a *moving source* of heat, for if an iron or steel wire be heated to redness at any one point of its length, and the source of heat, such as a Bunsen flame, be moved along, an electric current is set up in the direction in which the flame travels. By means of clockwork the flame can be caused to move continuously, and a continuous circuit obtained. There are, however, no signs of e.m.f. in the circuit until the recalescent point is passed; then re-glow takes place behind the moving flame and the cooling effect in front. This thermal difference is thought to be an effect of the resultant e.m.f., for it ceases when the flame ceases to move, and is absent in those metals where recalescence does not occur. Hot iron is thermoelectrically negative to cold iron, but at the critical point a large increase in the e.m.f. is suddenly developed. H. Tomlinson has shown that iron at a bright red-heat in contact with iron at the temp. of the air develops an e.m.f. of about one-twentieth of a volt, or upwards of twice that between a bismuth and antimony couple with a temp. difference of 100° between their junctions. E. D. Campbell and B. A. Soule compared the thermoelectric force of the two ends of a cooling bar of iron. The thermoelectric force of metals was studied by J. Galibourg, S. W. T. Smith and co-workers, P. Nicolau, and R. Cazaud; G. Tammann, G. Tammann and G. Bandel, A. Egal, and E. D. Campbell and W. C. Dowd studied the effect of heat-treatment, etc., on the thermoelectric force of these metals against iron.

The thermoelectric force of a couple made of annealed and unannealed iron showed a sharp maximum at 490° and a minimum at 790°. The e.m.f. of iron against *platinum* at 100° when the cold joint is at 0°, was found by W. Jäger and H. Diesselhorst to be 1·45 millivolt, where the positive sign means that the current flows through the cold junction to the platinum; J. Dewar and J. A. Fleming gave 1·91 millivolt; G. K. Burgess and H. Scott, 1·88 millivolt; and E. Wagner, 1·77 millivolt. A. Goetz gave for $E\times10^{-6}$ volt per degree, with purified iron against platinum:

	650°	700°	750°	800°	850°	900°	910°
$E=$	12·0	14·5	17·0	18·5	19·0	19·5	10·5

	950°	1000°	1100°	1200°	1300°	1400°	1405°	1450°
$E=$	11·0	12·5	15	18	19·5	23	26	27

G. K. Burgess and H. Scott's results for the thermoelectric force of a platinum-iron couple with iron of 99·968 per cent. purity, are shown in Fig. 277. They say: the A_3-transformation in iron is indicated by a marked discontinuity, Ac_3 being always above Ar_3. The arrests are located at approximately the same temp. by the thermal, crystallographic, magnetic, electrical resistance, dilatational and thermoelectric methods, namely, Ar_3 just below 900°, and Ac_3 slightly above 910° C. These physical discontinuities are apparently all a measure of the same transformation. At the A_2-arrest, the thermoelectric force-temp. curve has a break, or change in direction; and the other physical properties, except the crystallographic change, which has not been detected at A_2, appear to undergo abrupt but slight modification—except for the magnetic change, which is relatively enormous here. It is considered that the A_2- and A_3-transformations are essentially different in kind, but nevertheless both have a distinct physical existence; or, in other words, A_2 and A_3 are critical points that may be said to delimit α-, β-, and γ-iron. There appears to be no break or discontinuity in the thermoelectric properties of iron between 0° and 768°; the actual shape of the curve for the thermoelectric force is, of course, contributed to by both the iron and the platinum. At about 880°, in the β-range, there appears to be a slight discontinuity in the thermoelectric properties of iron. The subject was also studied by J. F. T. Berliner, and J. Galibourg. J. Thiele studied the effect of ageing on the result. W. Broniewsky observed a critical point at 1020° with a thermocouple of platinum and electrolytic iron. G. Belloc obtained the results summarized in Fig. 278 for steels containing different proportions of carbon against platinum. The minimum at 380° has not been explained. He said that his observations show that β-iron forms solid soln. with α-iron between 730° and 750°, and with γ-iron between 950° and 1020°. Some other explanation than this is probably needed. M. von Laue and G. Siljeholm observed an abnormal effect near the A_3-arrest. Observations were also made by O. Chwolson, J. R. A. Mousson, H. G. Magnus, and W. Thomson (Lord Kelvin), who found that hard-tempered steel is the negative to soft steel. For couples of magnetized and non-magnetized iron, *vide infra*. The differentials of the platinum-platinum rhodium couple, and of the platinum-electrolytic iron couple with temp. were measured by W. Schneider, and the curve for the platinum-iron couple, plotted in Fig. 280, shows a change of direction at A_2, and sharp breaks at A_3 and A_4. Some hysteresis is shown at the A_3-arrest.

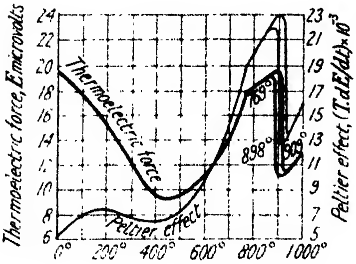


FIG. 277.—The Thermoelectric Force and Peltier Effect with the Platinum-Iron Couple.

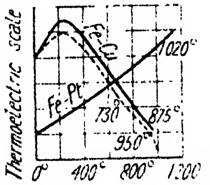


FIG. 278. — Thermoelectric Force of the Iron-Platinum and Iron-Copper Couples.

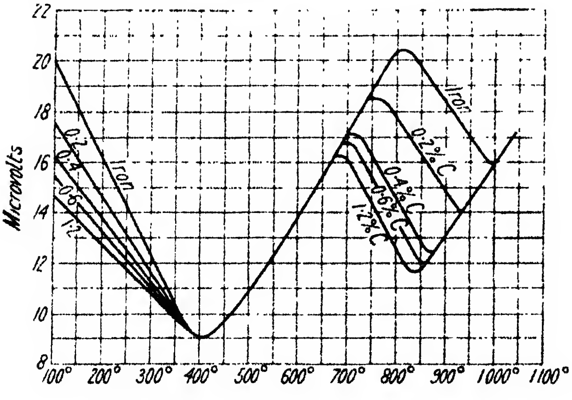


FIG. 279.—The Thermoelectric Force of Platinum against Iron-Carbon Alloys.

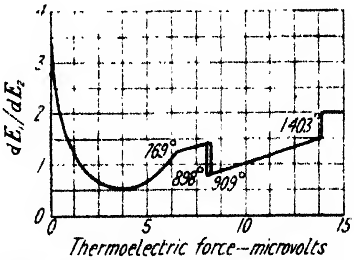


FIG. 280. — The Thermoelectric Force of the Iron-Platinum Couple against a Platinum-Platinum Rhodium Couple.

W. H. Keesom and co-workers measured the thermoelectric force of iron against a gold-silver alloy between −256° and 20°. C. Dannecker measured the e.m.f. of iron against *constantan* and found for the e.m.f. in millivolts:

	−185°	−80°	0°	100°	300°	500°	700°	900°
E.m.f. .	−7·0	−3·4.	0	+5·1	+15·1	+25·7	+36·2	+47·9

F. Hoffmann and A. Schulze obtained values between 0·1 and 1·0 millivolt larger. R. von Dallwitz-Wegner studied the subject. W. Rohn, E. P. Harrison, and L. Holborn and co-workers obtained for iron against *nickel*:

	−185°	0°	100°	300°	500°	700°	900°	1100°
E.m.f. .	−5·08	0	+3·13	+9·2	+11·8	+14·9	+19·5	+23·7

J. P. Joule found that ordinary cast iron is thermoelectrically negative towards *copper*. H. K. Onnes and G. Holst gave for iron against copper at −192°, −250°, −268·74°, and −269·80°, respectively −1·293, −1·319, −1·309, and −1·309 millivolts. E. L. Dupuy and A. M. Portevin found the thermal e.m.f. of various steels against copper, in millivolts, when the steel contained up to 0·05 per cent. of silicon; up to 0·09 Mn; up to 0·025 P; 0·022 S; and 0·011 As:

Carbon . .		0	0·07	0·24	0·44	0·79	1·12	1·58 per cent.
Annealed	−80°	12·20	18·71	10·90	9·50	7·90	5·90	6·61
	100° .	8·70	8·55	7·65	6·20	5·40	4·10	4·15
Hardened	−80°	—	12·35	9·81	5·10	0·92	−5·15	−6·40
	100° .	—	8·73	6·93	3·46	−1·32	−5·70	−15·80

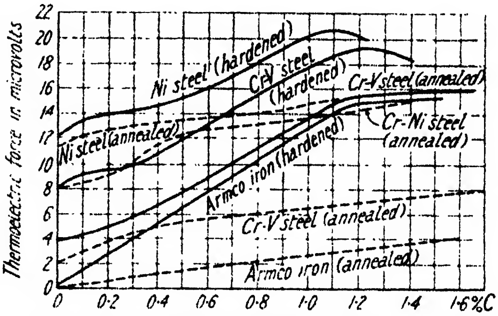


FIG. 281.—The Thermoelectric Force of Iron and Some Alloys.

For these percentages of carbon, *c*, for annealed steels, the e.m.f. in millivolts per degree between −78° and 0° is $E=5\cdot6c+12\cdot2$, and between 0° and 100°, $E=4\cdot6c+8\cdot7$; and for hardened steels between −78° and 0°, $E=-16\cdot7c+13\cdot5$, and between 0° and 100°, $E=-13\cdot9c+9\cdot9$. The decrease in the e.m.f. with increasing carbon is more rapid with hardened than with annealed steels, owing to the passage of carbon into solid soln. in the quenched steels. For the effect with alloy steels, *vide* the respective alloys. E. Dubois found that the thermoelectric effect against copper becomes electronegative after the metal has been heated and subsequently cooled. R. Nübel studied the effect with iron and hydrogenized iron. E. D. Campbell and B. A. Soule examined the thermoelectric force of electrolytic iron against quenched carbon, silicon, nickel and manganese steels at 950°. The effects of tempering alloy steels at about 110° were greater than with the carbon steels. E. D. Campbell and H. W. Mohr obtained the results summarized in Fig. 281, for the thermoelectric force in microvolts per degree, with alloys hardened by quenching at 950°, and then annealed at 800°. W. H. Ross, and C. W. Heaps discussed the thermoelectric force of transversely and longitudinally magnetized iron.

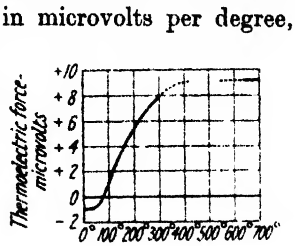


FIG. 282.—The Effect of the Annealing Temperature on the Thermoelectric Force of Steel against Silver.

W. Broniewsky observed a critical point at 730° with a thermocouple of copper and electrolytic iron—dotted line, Fig. 281. This temp. is probably a low reading for the 769° of W. Schneider. There was also a break at 950°. E. P. Harrison's results for the iron-copper couple, continuous line, Fig. 278, showed a break at 859°, which is near the A_3-arrest. Observations on the subject were made by F. E. Bash. V. Strouhal and C. Barus gave the results shown in Fig. 282 for the thermoelectric force of *silver* against hardened steel, and the same steel annealed at different temp. P. G. Tait found that the thermoelectric force of iron against *lead* is 16·2 microvolts at 20°, and 14·74 at 50°; the thermoelectric power, $dE/d\theta = 17 \cdot 15 - 0 \cdot 04828$, and the neutral point, is 356°. Observations were also made by A. Matthiessen, and E. Becquerel. P. G. Tait also noticed that the thermoelectric force of iron alters suddenly in a remarkable way at a red-heat. P. Nicolau examined the thermoelectric force of iron against mercury. G. Borelius observed a number of critical points in the thermoelectric force of the couple of iron and tungsten—*vide supra*, the allotropes of iron.

H. F. Newall, and F. T. Trouton observed that the change which occurs when iron or steel passes through a red-heat can be shown by the thermoelectric current generated when a short portion of wire is made red-hot by the flame of a lamp, if the flame is moved slowly, the direction of the current depends on the direction in which the flame travels. W. F. Barrett called the phenomenon *thermoelectric hysteresis*. H. le Chatelier, and O. Boudouard attempted to apply the phenomenon to the study of allotropic changes; C. Benedicks devised an apparatus for locally heating a wire by a small electric furnace through which the wire travels with a uniform speed. No discontinuity in the thermoelectric effect corresponding with the A_2-arrest was observed; but there is a marked discontinuity corresponding with the A_3-arrest. For magnetized and non-magnetized wires, *vide infra*. C. R. Darling and R. H. Rinaldi found with a couple of iron and an alloy of tin with 60 per cent. of bismuth shows a re-inversion, for with the cold junction at 0°, the e.m.f. is zero when the hot junction is at 0°, 100°, or 350°; during the first interval it is negative with a maximum of 0·5 mvolt, for the second interval, positive with a maximum at 0·13 mvolt; and it becomes increasingly negative above 350°.

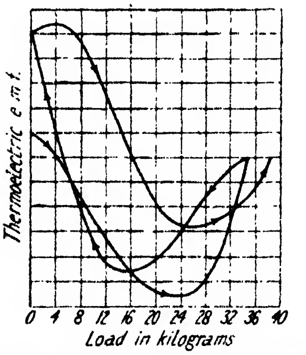


FIG. 283.—The Effect of Load on the Thermoelectric Properties of Iron.

According to A. Goetz, when a thermocouple of iron is so arranged that one of the wires is heated through the transition temp., there is a big decrease in the thermoelectric power as iron passes from the α- to the β-state, and a big increase as the iron passes from the γ- to the δ-state. Iron with the body-centred lattice structure is positive with respect to iron with the face-centred structure. E. Cohn, and J. A. Ewing found that there is much hysteresis of the thermoelectric properties of iron with respect to stress. The effect of a load on the thermoelectric properties of iron, and the hysteresis are illustrated by Fig. 283. The subject was also studied by W. Thomson (Lord Kelvin), C. A. P. Turner, H. G. Magnus, G. W. von Tunzelmann, and R. Overbeck. S. W. J. Smith and co-workers, and L. J. Neuman studied the thermoelectric force between annealed and strain-hardened specimens of iron; O. Tesche, between α- and γ-iron; H. Broili, and J. Kousmine, between magnetized and non-magnetized iron; and M. Maclean found for a thermocouple of drawn and undrawn wires of annealed steel an e.m.f. of 0·1028 microvolt per degree difference of temp. With iron wires one unstretched and the other stretched, the thermoelectric current passes from the unstretched to the stretched wire, and

Total load	250	500	750	1000	1250	1500	1750	2000 grams
Temporary elongation	-	-	0·023	0·03	0·06	0·19	0·39	--
Permanent elongation	-	-	-	0·02	0·027	0·08	0·23	3·41
Microvolt per degree	0·000912	0·006216	0·006216	0·07192	0·09485	0·09430	0·08696	0·07576

For O. L. Kowalke's observations on the thermoelectric force of the cobalt-iron thermocouple, *vide infra*, cobalt; and for couples of iron with aluminium-nickel, and copper-nickel alloys, *vide infra,* nickel alloys. A. Smits and J. Spuyman studied the iron and tin thermocouple. P. W. Bridgman found the thermoelectric effect, E volts, of iron against *lead* at atm. press. to be $E=(16{\cdot}18\theta-0{\cdot}0089\theta^2-0{\cdot}000086\theta^3)\times10^{-6}$ volts for annealed ingot iron; $E=(15{\cdot}92\theta-0{\cdot}0106\theta^2-0{\cdot}000056\theta^3)\times10^{-6}$ volts for hard-drawn ingot iron; and $E=(16{\cdot}56\theta-0{\cdot}0033\theta^2-0{\cdot}000122\theta^3)\times10^{-6}$ volts for annealed commercial iron. The thermoelectric force at different temp. and press., p kgrms. per sq. cm., of a junction of compressed and uncompressed metal was:

		Annealed ingot iron			Hard-drawn ingot iron			Commercial iron		
p . . .		2,000	6,000	12,000	2,000	6,000	12,000	2,000	6,000	12,000
E	10° .	−0·08	−0·27	−0·84	−0·01	−0·21	−0·57	−0·04	−0·22	−0·75
	20° .	−0·08	−0·28	−0·99	+0·02	−0·24	−0·74	−0·03	−0·29	−1·12
	30° .	+0·03	−0·10	−0·81	0·10	−0·11	−0·54	+0·04	−0·19	−1·10
	40° .	0·17	+0·22	−0·41	0·23	+0·21	+0·01	0·15	+0·07	−0·82
	60° .	0·66	1·27	+1·40	0·62	1·43	2·20	0·46	0·93	+0·44
	80° .	1·21	3·15	4·89	1·27	3·40	6·12	1·02	2·47	3·19
	100° .	1·67	4·60	7·68	2·30	6·69	12·80	2·34	5·68	9·56

E. Wagner found for a couple of simple iron wires, one element of which is at a press. of a kgrm. per sq. cm. higher than the other, $12{\cdot}5\times10^{-12}$ volt per degree between 0° and 100°, and that the current flows through the hot joint from the metal at the lower press. to that at the higher press. The subject was studied by A. E. Caswell. P. W. Bridgman found that the thermal e.m.f. from annealed ingot iron when one piece is subjected to a tension T up to 500 kgrms. per sq. cm., is $E=(0{\cdot}0120T-0{\cdot}0_5235T^2)\times10^{-6}$ volts at 52°, and $E=(0{\cdot}0223T-0{\cdot}0_242T^2)\times10^{-6}$ volts at 95°. The e.m.f. is from the unstretched to the stretched wire at the hot junction. H. Tomlinson observed that the thermoelectric force is increased by longitudinal traction, and also by a longitudinal magnetic force. K. Tsuruta discussed the effects of longitudinal stress on the thermoelectric properties of iron. S. L. Brown and L. O. Shuddemagen found for the thermoelectric force of iron against *cupric oxide,* and also against *ferrosic oxide,* when the cold junction is 20°, and the hot junction:

	CuO				Fe_3O_4			
	100°	322°	497°	642°	90°	265°	517°	693°
E.m.f. .	0·085	0·280	0·410	0·503	0·030	0·104	0·211	0·300 volt

G. Borelius and F. Gunneson quenched wires from a series of gradually rising temp., and made the wires into couples with untreated wires, and plotted the results against temp. The proportion of occluded gas modified the curves, but with gas-free metal, there were many breaks in the curves. R. Nübel studied the thermoelectric force of hydrogenized and ordinary iron, where the current flows from the uncharged to the charged metal. F. C. Thompson and E. Whitehead observed critical temp. in the thermoelectric force of iron against platinum. A. Goetz observed that with iron of a high degree of purity there is a great decrease in the thermoelectric force as the metal passes from the γ- to the α-state, and an increase on passing from the α- to the γ-state, so that the body centred lattice structure is thermoelectrically positive to the face centre. E. D. Campbell and H. W. Mohr investigated the thermoelectric potential of iron and iron-carbon alloys. W. Ogawa studied the activation of galena by iron salts for a **radiodetector**; I. Stransky, iron; and W. Jackson, steel-carborundum as a radiodetector.

G. K. Burgess and H. Scott's results for the **Peltier effect** are summarized in Fig. 277. A. Campbell found the neutral point in the Peltier effect with cadmium and iron is 144°; with zinc and iron, 196·7°; and he also observed the Peltier effect with iron and nickel-silver. The subject was discussed by E. H. Hall. U. P. Lely studied the effect with iron and copper. The Peltier effect, p volts, with iron against lead was found to be $P=(16{\cdot}18-0{\cdot}0178\theta-0{\cdot}000258\theta^2)(\theta+273)\times10^{-6}$ volts for annealed ingot iron;

$P=(15 \cdot 92-0 \cdot 0212\theta-0 \cdot 000168\theta^2)(\theta+273)\times10^{-6}$ volts for hard-drawn ingot iron; and $P=(16 \cdot 56-0 \cdot 0066\theta-0 \cdot 000366\theta^2)(\theta+273)\times10^{-6}$ volts for commercial iron. And the Peltier effect, P, in joules per coulomb, at different temp. and press., p kgrms. per sq. cm., for a junction of compressed and uncompressed annealed ingot iron, was:

		0°	20°	40°	60°	80°	100°
p	2,000	−3·3	+0·9	+5·6	+9·3	+8·8	+7·5
	6,000	−10·9	+2·6	+12·2	+24·7	+34·3	+14·9
	12,000	−38·3	+1·2	+15·7	+50·0	+62·2	+35·8

According to P. W. Bridgman, the **Thomson effect,** σ volts, with iron against lead was $\sigma=(-0 \cdot 0178-0 \cdot 000516\theta)(\theta+273)\times10^{-6}$ volts per degree for annealed ingot iron; $\sigma=(-0 \cdot 0212-0 \cdot 0003333\theta)(\theta+273)\times10^{-6}$ volts per degree for hard-drawn ingot iron; and $\sigma=(-0 \cdot 0066-0 \cdot 000732\theta)-(\theta+273)\times10^{-6}$ volts for annealed commercial iron. The thermoelectric effect, $\sigma\times10^{-8}$ joules per coulomb per degree, between the compressed and uncompressed annealed ingot iron, was:

		0°	20°	40°	60°	80°	100°
p	2,000	+17	+23	+25	+5	−10·6	−5·6
	6,000	+79	+56	+37	+79	−11	−121
	12,000	+347	+106	+63	+180	−56	−194

J. Young observed that with annealed wires between 40° and 300°, the Thomson effect increases with the carbon-content; it decreases regularly with a rise of temp. up to 200°, when it becomes irregular, and then passes through a minimum value. The curves for the thermoelectric force of iron or nickel against platinum show a break in the neighbourhood of the Curie point. This corresponds with a more or less rapid change in the Thomson effect, or the "specific heat of electricity." This subject was studied by J. Dorfman and co-workers; and the electronic theory of the phenomenon, by E. C. Stonier. H. E. Smith found that the Thomson effect with iron is $\sigma\times10^{-6}=-2 \cdot 125$ cals. per coulomb per degree; it decreases with tension by becoming less negative until the elastic limit is reached, when the effect increases with tension and follows a definite cycle on removing and restoring the strain. The Thomson effect in iron and steels was studied by J. Young, who found that the effect increases with the carbon-content and passes through a minimum value near 250°.

The so-called **Hall effect,** discovered by E. H. Hall[5] in 1879, refers to the phenomenon which occurs when an electrical current passing between two points in a thin metal plate is introduced into a magnetic field so that the plane is at right-angles to the magnetic field, whereupon the equipotential lines, located by the voltmeter, are distorted so that the electrical current no longer has the same potential as before. The e.m.f., E, set up is given by $E=-RHi/d$, where H denotes the magnetic field; i, the current; and d cm. the thickness of the plate—all other magnitudes are expressed in absolute units. If R denotes the Hall coeff., A. W. Smith found that $R\times10^6=10,300$ for iron with $H=17,000$ gauss at 18°; E. H. Hall and L. L. Campbell, $R\times10^6=7940$ for $H=5300$ at 13°; F. Unwin, $R=10^6=8700$ at 18°; H. Zahn, $R\times10^6=10,800$ for $H=6290$ at 18°; J. Königsberger and G. Gottstein, $R\times10^6=10,000$ at 18°, and H. B. Peacock gave $R\times10^6=16,000$ at 18° for films of iron $270\mu\mu$ thick. W. L. Webster studied the Hall effect with single crystals of iron; and A. Mazzari, the effect of very intense magnetic fields on the phenomenon. The Hall effect was also measured by E. Bossa, M. Cantone and E. Bossa, E. M. Pugh and T. W. Lippert, W. Y. Chang and W. Band, L. J. Neuman, H. B. Peacock, J. C. Steinberg, and P. I. Wold; and H. Atherthum obtained values between −253° and 18°, for values of H not stated; and W. Frey, values between 235° and 1100° for $H=4090$ to 5500, with a critical point between 620° and 920°:

	−283°	−190°	−79°	18°	235°	470°	620°	920°	1000°	1100°
$R\times10^6$	1140	1330	4090	11,230	4610	13,200	21,800	1620	735	459

O. M. Corbino observed that when a uniform radial current flows through a circular disc of metal, placed in a magnetic field normal to the plane of the disc, there is produced a circular current, the density of which is inversely proportional to the radius. The phenomenon is called the **Corbino effect.** If C denotes the circular current; I, the radical current; M, the mutual inductance between the current C and the coil placed near the disc; and m, the standard mutual inductance, then $MC=mI$. The value of m/H referred to that of copper, unity, is 16·4, and the corresponding value for the Hall effect, copper unity, is 21·9 in a field $H=3700$. Observations were made by E. P. Adams and A. K. Chapman. A. K. Chapman found that for iron, with a low field, the value of m/H is zero up to a field of about $H=760$ (Fig. 284), it then rises to a sharp maximum at 950°; falls to half the maximum value for $H=500$; and slowly increases up to $H=10{,}000$. Below $H=300$, the Corbino effect undergoes a reversal.

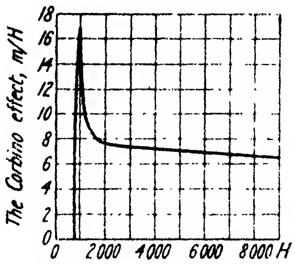


FIG. 284.—The Corbino Effect with Iron.

Ferromagnetic substances behave rather differently from diamagnetic and paramagnetic substances, for the transverse Hall effect in the latter cases are directly proportional to the magnetic field for all fields obtainable, whilst with ferromagnetic substances, direct proportionality holds only up to the region of maximum permeability, as indicated by E. M. Pugh; and above that point, A. W. Smith found that the rate of increase of the Hall effect with the field decreases. A. Kundt, and the early workers thought that the effect with ferromagnetic substances was proportional to the intensity of magnetization, I, rather than to the induction, B, the quantity always measured. At low fields, B and I could not be distinguished, but at higher fields, near the saturation point, the Hall effect was shown to be more nearly proportional to the magnetic intensity, I, than to either the magnetic induction, B, or the magnetic field, H. E. M. Pugh found the Hall effect with steel to be a single-valued, linear function of the intensity of magnetization, I, but neither a single-valued nor a straight-line function of either the magnetic induction, B, or the magnetic field, H. This applies to both the virgin curves and the broad hysteresis loops. A. W. Smith and R. W. Sears found that the Hall e.m.f., ϵ, for ferromagnetic substances can be written $\epsilon=R_0H+R_1I$, where R_0 is a constant nearly independent of the material, and R_1 is a constant which may have any value, positive or negative, depending on the material examined.

The so-called **Ettingshausen-Nernst effect,** discovered by A. von Ettingshausen and W. Nernst in 1886, refers to the phenomenon which occurs when a current of heat is flowing in the thin metal plate, and the plate is introduced into a magnetic field so that the plate is at right-angles to the field, whereupon difference of potential is developed under conditions where, without the magnetic field, no difference occurred. The e.m.f., E, set up is $E=QbH(dT/dl)$, where b cm. denotes the width of the plate; H, the magnetic field; and dT/dl the temp. gradient in the plate, of length, l cm., in degrees of temp. per cm.—all other magnitudes in absolute units. Let Q denote the Ettingshausen-Nernst coeff. F. Unwin found that $Q\times10^6=520$ for iron at 18°; H. Zahn, $Q\times10^6=1050$ for $H=6290$ gauss at 18°, and $Q\times10^6=-1660$ at 55°; E. H. Hall and L. L. Campbell, $Q\times10^6=+860$ for $H=5550$ at 31°; and at 60°, $Q\times10^6=-980$; and A. W. Smith gave $Q\times10^6=-810$ for $H=17{,}000$ to 18,000 at 60°. P. W. Bridgman discussed the relationship between the four phenomena.

The so-called **Ettingshausen effect,** discovered by A. von Ettingshausen in 1886, refers to the phenomenon which occurs when an electric current is passing between two points in a thin metal plate which is then placed in a transverse magnetic field, whereupon a difference of temp. is developed between the upper and lower faces where no difference exists in the absence of the magnetic field. Let dT denote the difference of temp. between two points ; H, the magnetic field ; l, the length of the plate ; and d, the thickness of the plate in cm., then, expressing magnitudes in absolute units, $dT=PH/d$. If P denotes the Ettingshausen coeff., E. H. Hall and L. L. Campbell found that $P\times10^9=-49{\cdot}3$ when $H=5300$ at 13° ; and $-61{\cdot}2$ at 84°. F. Unwin observed $P\times10^9=-43{\cdot}0$ at 18° ; H. Zahn, $P\times10^9=-57$ for $H=6290$ at 18°, and -67 at 20°.

The so-called **Leduc effect,** discovered by A. Leduc in 1886, refers to a phenomenon which occurs when heat is flowing between two points in a thin metal plate placed in a transverse magnetic field, whereupon a variation in the thermal conductivity occurs which does not take place when the plate is not in a magnetic field. If dT denotes the difference of temp. between two points ; H, the magnetic field ; b cm., the breadth of the plate ; and dT/dx the temp. gradient in degrees per cm.—and expressing magnitudes in absolute units, $dT=SHb(dT/dx)$. Let S denote the Leduc coeff. F. Unwin found that $S\times10^9=520$ at 18° ; H. Zahn, $S\times10^9=390$ for iron with $H=6290$ gauss at 18°, and 687 for steel at 55° ; for iron, E. H. Hall and L. L. Campbell gave $S\times10^9=560$ for $H=5000$ at 51° ; 429 for $H=6500$ at 44° ; 608 for $H=7300$ at 48°, and 632 for $H=17{,}000$ to 18,000 at 60° ; and A. W. Smith, $S\times10^9=392$ for $H=11{,}900$ at 56·9°. S. T'ao and W. Band studied the e.m.f. produced when a magnetic field is applied parallel to a temp. gradient.

According to F. Robin,[6] the spark from an electrostatic machine or induction coil produces on the polished surface of steel tiny craters which are formed by the flow of the metal under shock. These holes are visible under the microscope, but to the naked eye, the metal preserves its polished surface. Around this zone there is formed a yellowish aureole—possibly two—formed of oxide ; it is clearly marked in carbon steels with a low percentage of carbon, strongly marked in cast iron, and feebly marked in dead-soft steels. It is hardly visible with pure iron, chromium steel, and chromium-tungsten steel.

H. Schmick and R. Seeliger [7] studied the mechanism of the **arc discharge** with an iron cathode and found the loss of material is definitely not proportional to the current, and it varies primarily as the degree of cooling of the cathode. The loss is not confined to the local point, but is distributed over the whole neighbouring area. A. Günther-Schulze found the normal cathode potential fall of iron, V volts, to be, in :

	Argon	Neon	Nitrogen	Oxygen	Air
V	168	153	215	352	337 volts

The subject was studied by K. Rottgardt, A. Schaufelberger, R. Seeliger and M. Reger, G. Gehlhoff, G. Gehlhoff and K. Rottgardt, E. Warburg, H. E. Ives, E. Blechschmidt, V. L. Chrisler, W. G. Duffield and co-workers, W. Ramberg, W. Neuswanger, W. L. Cheney, E. Lau and O. Reichenheim, G. E. Doan, H. Schüler, R. Defregger, W. Heuse, F. H. Newman, E. H. Owen and P. Wright, H. Dziewulsky, and C. A. Skinner. M. Haitinger measured the intensity of the ultra-violet rays from the iron arc-light, and found it to be greater than in the case of all the other metals which were tried. The cathodic spluttering of iron was discussed by W. Crookes. H. Nagaoka and T. Futagami obtained cinematographic photographs of electrically exploding iron wires. R. Seeliger and H. Wulfhekel studied the loss of material from the cathode of the iron arc ; and H. P. Waran, K. Meyer and A. Günther-Schulze, and T. Baum, the cathodic spluttering of iron in the discharge tube. I. Klemencic studied the behaviour of iron towards electrical oscillations—*vide infra* for the influence of oscillations on magnetized iron. H. F. Richards [8] found that the **dielectric constant** of steel is not infinity, but 3·1.

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§ 22. Magnetic Properties of Iron and Iron-Carbon Alloys

The laws of **magnetism** were worked out largely by experiments on the magnetic properties of iron and steel, but it is comparatively rare, in past years, to find full information available as to the nature of the specimens employed. The experiments, however, served their purposes in developing certain principles, and descriptions will be found in the works of J. A. Ewing,[1] T. F. Wall, F. Auerbach, E. Schmidt, W. von Westphal, and many others. Indeed, all textbooks on magnetism are mainly concerned with this element, since iron is king of the magnetic metals. Metals strongly attracted by a magnet are said to be **ferromagnetic**—*e.g.*, iron, steel, nickel, cobalt, and some alloys. Substances which are feebly attracted by a magnet, and which when placed in a magnetic field have a tendency to set themselves with their axes parallel to the lines of force, or have a tendency to pass from the weakest to the strongest part of the field, were said by M. Faraday to be **paramagnetic**—*e.g.* oxygen, and platinum. Ferromagnetism is a special case of paramagnetism. Substances which are feebly repelled by a magnet, and, when placed in a magnetic field, have a tendency to set themselves with their axes at right-angles to the lines of force, or to pass from the strongest to the weakest part of the field, are said to be **diamagnetic**—*e.g.* bismuth is more diamagnetic than any other metal. More substances are known which exhibit diamagnetism than paramagnetism. According to T. Carnelley, on examining M. Faraday's list of paramagnetic and diamagnetic substances:

> The following rule *invariably* holds good without a single exception in the case of the 38 elements to which it can be applied. Those elements belonging to the even series of the periodic system are always paramagnetic, whereas those elements belonging to odd series are always diamagnetic.

And H. E. J. G. du Bois added that, notwithstanding gaps, uncertainties, and exceptions, in the periodic classification of the elements :

> We can detect in the magnetic, as in all the other physical and chemical properties, a periodic variation. The series of paramagnetic elements, which, on the whole, are also very refractory, are found on the descending branches, or in the minima of the atomic volume curve for the solid elements, whilst the more easily fusible, diamagnetic elements occupy the ascending portions and the maxima of the curve.

The paramagnetic and diamagnetic states of many alloys depend on the strength of the applied magnetic field, and K. Overbach applied the term **metamagnetic alloys** to such alloys. For instance, a copper-zinc alloy is paramagnetic in weak fields, but the susceptibility rises to a maximum as the strength of the field increases, and the alloy then becomes diamagnetic. Brass becomes metamagnetic if a few thousandths of iron be present, whilst zinc with up to 4·7 per cent. of iron is independent of the field.

The effect of one magnet on another is greater, the greater the distance between the poles of the magnet, so that both the strength, m, of the poles of a magnet, and the distance between the poles are required in order to determine the effect of one magnet on another. The product of the pole strength, and the distance between the poles is called the **moment of the magnet**, M. The force of a magnet on a distant magnetic needle is doubled by doubling the distance between its poles ; and a magnet with poles half as strong as another magnet, would have the same magnetic moment, provided the poles of the weaker magnet were twice as far apart as the poles of the stronger magnet. The poles of the longer magnet would have only half the volume of steel as those of the second, so that if the moment of each magnet be defined by its volume, v, the quotient, $I = Mv$, is called the **intensity of magnetization,** and indicates the magnitude of the moment per unit volume, or the pole strength per unit area. If the moment be divided by the mass of the magnet, the quotient is called the **specific intensity of magnetization,** and indicates the magnitude of the moment per unit of mass.

When a substance placed in a magnetic field becomes magnetized, there is a relation between the magnetism it acquires and the magnetic force which acts upon it. The force of a magnetic field is represented by H, so that the field is said to be of strength H gauss. The lines of force between the unlike poles of two bar magnets are conducted better by some substances than others. The lines of force between the two magnets in air, are represented diagrammatically by Fig. 285, and when a piece of iron is placed in the gap, by Fig. 286. The crowding of the lines into the iron make it appear as if the lines of force find it easier to go through iron than through air ; the iron appears to be a better conductor for the lines of force than is the case with air. This is expressed by saying that the **magnetic permeability** of iron is greater than is that of air ; or, conversely, the **magnetic reluctivity** of air is greater than that of iron. The permeability of a medium is hence defined as its conducting power for lines of magnetic force when compared with that of air. If H denotes the number of unit lines of force per sq. cm., in the magnetic field, H measures the strength of the magnetic force ; and if B denotes the number of lines of induction per sq. cm. in the material when placed in the field, B measures the **magnetic induction** or **flux density** of the material. The magnetic permeability

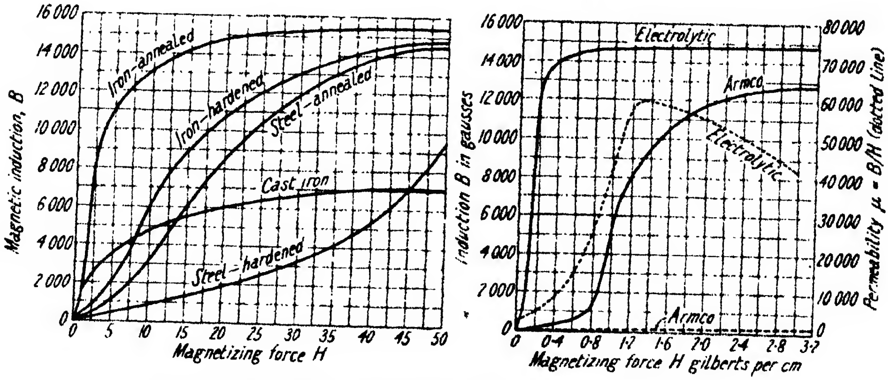
FIGS. 285 and 286.—Linear Force between two Unlike Magnetic Poles in Air, and with a piece of Iron in the Gap.

of the substance is measured by the ratio of B to H, and this ratio is symbolized by μ. Thus, the magnetic permeability $=\mu=B/H$.

Instead of representing the magnetizability of a substance in terms of the permeability, it can be expressed as a relation between the intensity of magnetization, I, and the strength of the magnetic force, H. The ratio of these two magnitudes is called the **magnetic susceptibility,** so that $\chi=I/H$. The magnetic induction, B, or the total number of lines of force per sq. cm. in a specimen, is equal to the sum of two lots—H lines due to the magnetic field, and $4\pi I$ lines per sq. cm. due to the effect of the field upon the specimen, or $B=H+{}^4I$. Since $I=\chi H$, and $B=\mu H$, it follows that $\chi=(\mu-1)I^4\pi$. If the permeability $\mu=1$, as is the case with air, the magnetic susceptibility $\chi=0$. In paramagnetic substances, where μ is greater than unity, the susceptibility is positive; and in diamagnetic substances, where the permeability μ is less than unity, the susceptibility is negative. Hence, when a paramagnetic substance acquires a magnetization I, which is in the same direction as the force, B is greater than H; and conversely for diamagnetic substances, B is less than H. The value $4\pi I$ is taken to represent the **saturation value** of the magnetism with the magnetic force, H.

When soft iron is magnetized, it loses its magnetization much more readily than hard steel. The power of retaining magnetization when the inducing influence is withdrawn is called the **retentivity,** or **remanence,** and the magnetism retained is called the **permanent or residual magnetism.** Soft iron may retain more residual magnetism than steel, but it is unstable and more readily lost than is the case with steel. Material which retains a good portion of its magnetization, despite disturbing influences, is said to have a large **coercivity.**

If a long, thin, unmagnetized iron rod be placed in the solenoid through which a current of any desired strength can be passed, and if the current be gradually increased while the values of the magnetizing force, H, then, the induction or flux density, B, and the intensity of magnetization, I, may be determined at different stages of the operation, so as to show the relation between the magnetism acquired by the iron rod, and the magnetic force acting upon it; the relations of the magnitudes can be represented by the permeability, μ, or BH-curve, since $\mu=B/H$; or by the susceptibility, χ, or IH-curve, since $\chi=I/H$. The values for B and H for some samples of iron and steel are shown in Fig. 287. With a magnetizing force of 2·5 gauss, annealed soft iron has $B=8000$; cast iron, 3000; hardened iron, 1000; and hardened steel, about 400. When $H=10$, the value for soft iron is becoming horizontal; but with hardened iron and annealed steel, until H is 40 to 45; and when $H=50$, the value of B for hardened steel is still rising, but the other metals are practically saturated. The curves show, in general, three stages of progress. At the beginning, when H is small, changes in the value of



FIGS. 287 and 288.—The BH- or Magnetic Induction Curves.

H produce only small changes in the value of *B*, where the permeability is small; in the next stage, where the curve rises rapidly, small changes in the value of *H* produce large changes in the value of *B*. The permeability thus rapidly increases to a maximum. In the third stage, the metal is saturated, and the curve is nearly horizontal, showing that changes in the value of *H* have very little influence on the value of *B*.

The measurements of E. Gerold on the effect of chemical composition on the magnetic induction are summarized in Fig. 289. The continuous curves are for carbon, the dotted curves are for silicon. The effect of additions of 1 per cent. of aluminium, silicon, copper, molybdenum, manganese, and chromium are indicated in Fig. 289.

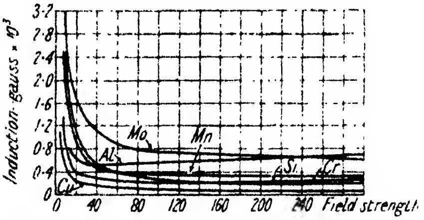


FIG. 289.—The Effect of Different Elements on the Magnetic Induction of Iron.

J. Coulson found that the magnetic moment of iron decreases on hydrogenization, attaining, in time, a value of 5 to 27 per cent. less than the original value. L. W. McKeehan found that the magnetic permeability of single crystals of iron, prepared by high-temp. treatment in hydrogen, are greater than that of crystals obtained by D. Foster, W. Gerlach, R. Chevallier, and K. Honda and S. Kaya by other methods. Observations showed that the high permeabilities were not due to the large size of the crystals, but rather to the treatment with hydrogen at a high temp. A comparison of the magnetization curves, Fig. 290, and the hysteresis loops, Fig. 291, of ordinary annealed iron, and of hydrogenized iron, due to P. P. Cioffi, shows that permeabilities of 130,000 can be obtained when the coercive force is 0·05 gauss, and the hysteresis loss—*vide infra*—for maximum induction B_m=14,000 is 300 ergs per c.c. per cycle. W. E. Ruder, E. Gumlich, and F. P. Wilson reported that the magnetic properties of iron are improved by heating the metal in hydrogen, although E. Gumlich, T. D. Yensen, and F. S. Tritton and D. Hanson did not get such good results by heating the metal in vacuo, in nitrogen, or slightly oxidized atmospheres. J. Würschmidt, L. W. McKeehan and co-workers, and T. W. and W. T. Richards studied the subject. N. A. Ziegler obtained high permeabilities with specimens containing several large crystals, and he considered that the results could be

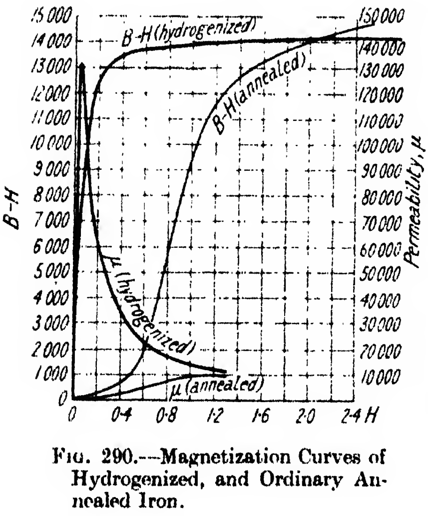


FIG. 290.—Magnetization Curves of Hydrogenized, and Ordinary Annealed Iron.

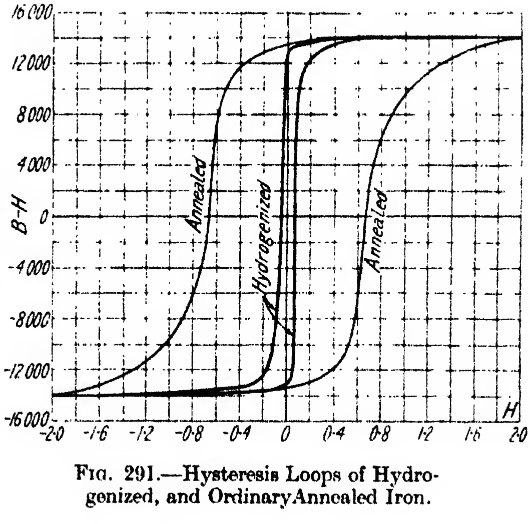


FIG. 291.—Hysteresis Loops of Hydrogenized, and Ordinary Annealed Iron.

obtained only with single crystals; A. Hayes reported higher permeabilities by melting iron in a low press. carburizing atm., and made no mention of the grain-size of the crystals. P. P. Cioffi considered that the high permeabilities obtained with hydrogenized iron are due to absorbed hydrogen, since if the high permeability iron be re-heated to a high temp. in a vacuum of 10^{-8} mm., it assumes the permeability of ordinary iron subjected to the vacuum treatment. The drop in permeability is attributed to the loss of absorbed hydrogen. R. Forrer and J. Schneider studied the effect of annealing iron in hydrogen; and H. Gries and H. Esser, the effects of occluded hydrogen, oxygen, and nitrogen.

W. Köster found that the effect of the precipitation of nitrogen at 100° on the coercive force diminishes linearly as the degree of cold-working is reduced, so that the coercive force of annealed steel increases as the cold-working is increased, on tempering at 100°, after a 5 per cent. reduction by cold-working, the coercive force attains a maximum and then falls off with further cold-working. When the nitrogen is again brought into soln., by tempering at 300°, the effect of cold-working on the coercive force is again restored, showing that the coercive force is compounded additively of an amount conditioned by the degree of cold-working, and an amount conditioned by the distribution of the structural constituents. The changes in the magnetic behaviour of cold-worked steel at temp. between 100° and 300° are to be attributed to the precipitation or soln. of nitrogen, and to no other cause.

The effect of heat-treatment on the magnetic properties of an eutectoid steel was examined by E. Maurer, C. W. Burrows and F. R. Fahy, and C. Nusbaum and co-workers. There is a rapid rise of the maximum and residual induction, and a more pronounced decrease in the coercive force with the cold-work which attends the drawing at temp. of 150° and 250°. The results for the induction, and the reluctivity of an eutectoid-carbon steel, quenched in water from 800°, by C. Nusbaum and co-workers are indicated by the curves, Fig. 292, representing three stages in the magnetization. In stage I, the magnetization curve showing the relation between the induction and magnetization force is nearly linear, and the molecular magnets have been displaced only slightly from their position of stable equilibrium; in stage II, the molecular magnets pass from a state of stability through an unstable state into a new position of stability—the curve in this region is very steep with magnetically soft substances, and more gradual with magnetically hard substances; whilst in stage III, the alignment of the molecular magnets approaches more and more to the direction of the magnetizing force as it increases in magnitude. The slope of the curve also decreases. The reluctivity curve also shows the three stages very well; but with magnetically soft substances, the first two stages almost vanish, and with magnetically hard substances, they become more pronounced. C. P. Steinmetz suggested that both of these are stages of instability, and that, if the specimen whose magnetic properties are being determined is simultaneously subjected to vibration or to an alternating magnetic field applied at right-angles to the unidirectional field, H, these two characteristic stages practically vanish; further, that it is probable that the stable relation between the field intensity, H, and the flux density, B, is expressed over the entire range from zero to infinity by the above linear relationship.

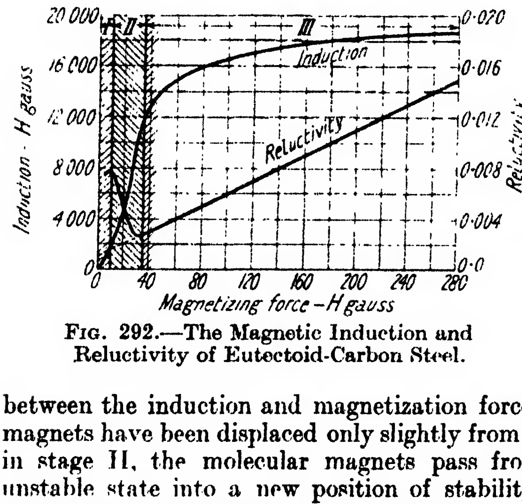


Fig. 292.—The Magnetic Induction and Reluctivity of Eutectoid-Carbon Steel.

C. Nusbaum and co-workers examined the effect of drawing at different temp. an eutectoid steel quenched from 800°. B. O. Peirce showed that for electrolytic iron and forms of iron approaching χ^{-1}, in degree of purity, the relation between the reciprocal of the susceptibility, and magnetizing force is linear—in one case, $\chi^{-1}=0{\cdot}0108+0{\cdot}000575H$. The regions I, II, and III are well-defined in the curves for eutectoid steel, but there is a slight deviation from the linear relation, as shown by the dotted lines. The temp. of drawing is indicated in the diagrams. According to G. Tammann, the intensity of magnetization of a solid soln. is less than that of the more magnetic of the two constituents and also less than would be calculated from a knowledge of the proportion of the constituents. K. Honda also showed that cementite is nearly one-tenth as magnetic as iron, and it becomes non-magnetic at 215°. As a quenched high-carbon steel is repeatedly drawn to increasingly high temp., the magnitude of the magnetic transformation of cementite increases and reaches its maximum in the neighbourhood of 300°. C. Nusbaum and co-workers take these facts to indicate that in the interval of temp. between 150° and 250°, the cementite is thrown out of solid soln., and thus that in martensite the cementite is in solid soln. It also indicates the completion of a previously suppressed transformation, which completion may be considered as the beginning of the metallographic constituent troostite.

In region I, the break in the reluctivity curve in the entire region is taken to show that two magnetically different constituents are present. The non-homogeneity may be due to one of two causes or both, viz. (1) the presence of another constituent, (2) the stresses set up in the material during the quenching operation. The effects of tension were discussed by E. Villari, and K. Honda and S. Shimizu—*vide infra*—and of compression by C. M. Smith and G. W. Sherman. The stresses undoubtedly play an important part, but are not necessarily the predominating factor.

In region II, the material behaves like a homogeneous substance. K. Honda has shown that in this region the carbon is in the form of cementite. There are thus present two magnetically different materials. This is taken to mean that the cementite is evidently distributed very uniformly in very finely divided particles (ultra-microscopic in size) throughout the entire mass of the ferrite, and there are no separate cementite and ferrite crystals. This colloidal soln. is generally considered to be troostite—*vide supra*. In region III, the colloidal soln. of cementite here begins to flocculate, forming aggregates of continually increasing size, which finally attain such dimensions as to produce a magnetically non-uniform or inhomogeneous material, as is indicated by a more or less marked break in the reluctivity line. The line of demarcation between regions II and III then marks the transition between the regions of magnetic homogeneity and non-homogeneity. Since this transition is so sharply defined, it may be chosen as the beginning of the metallographic constituent sorbite.

C. Nusbaum and W. L. Cheney examined the influence on the magnetic and other properties of an eutectoid carbon steel of different rates of cooling from 800°. Some of the results are summarized in Table XLI. The induction increases as the rate of cooling is varied from air-cooling to slow furnace-cooling. Microscopic observations of the different specimens show that the air-cooled material consists largely of sorbite with intervening patches of coarse pearlite containing free ferrite; with slower lime-cooling most of the sorbite passes into lamellar pearlite, whilst patches of coarse pearlite, and free ferrite are still present; in the specimens cooled more slowly in the furnace, there are patches of lamellar pearlite which decrease in size as the rate of cooling is diminished. The matrix of each consists largely of divorced pearlite—cementite particles in a matrix of ferrite. The grain-size of the cementite particles increases as the rate of cooling decreases. C. Nusbaum and W. L. Cheney conclude:

> With decrease in the cooling rate there is a marked increase in the value of the maximum induction for a given value of the magnetizing force, an increase in the magnitude of the maximum permeability, and a decrease in the magnitude of the coercive force. As the structure is changed from an essentially sorbitic one, through lamellar pearlite to divorced

pearlite, there is a gradual shifting of the break in the reluctivity line toward the origin. Also the difference between the magnitudes of the real and apparent values of the maximum intensity of magnetization is greatest when the structure is that of lamellar pearlite. There is a marked agreement between the values of the coercive force and the scleroscopic hardness, as influenced by the various cooling rates, except when the specimen is held at a temp. of 650° for a definite time.

TABLE XLI.—THE EFFECT OF RATES OF COOLING ON THE PROPERTIES OF EUTECTOID CARBON STEEL.

Time (min.) at 800°	Method of cooling	Time (min.) cooling from 800° to 650°	Maximum permeability.	Magnetic induction (H gauss)			Residual induction ($H_m = 150$)	Coercive force ($H_m = 150$)	Saturation intensity of magnetization (c.g.s. units)	Scleroscopic hardness.	Sp. resistance (microhms)
				15	150	100					
—	Air-cooled	·	385	5,150	16,100	20,050	10,050	13·4	1564–1520	43·3	0·2025
—	Lime-cooled	—	437	6,150	16,300	20,000	10,540	12·4	1550–1500	42·3	0·2006
12	Furnace-cooled	56	630	9,300	16,100	20,030	12,300	10·18	1580–1490	33·0	0·1941
13	Furnace-cooled	78	630	9,300	16,100	20,030	12,300	10·0	1600–1430	30·4	0·1950
20	Furnace-cooled	200	698	10,000	16,300	20,000	13,360	9·2	1612–1430	29·9	0·1931
13	Furnace-cooled	90	633	9,300	16,100	20,080	11,970	9·2	1540–1400	33·6	0·1963

According to C. W. Burrows, the permeability at room temp. increases with a rise of temp. for small inductions, and decreases for high ones; and the change in the induction per degree rise of temp. is greatest in the region of maximum permeability. R. L. Sanford's observations are summarized in Fig. 293. T. Spooner studied the phenomenon with silicon steels.

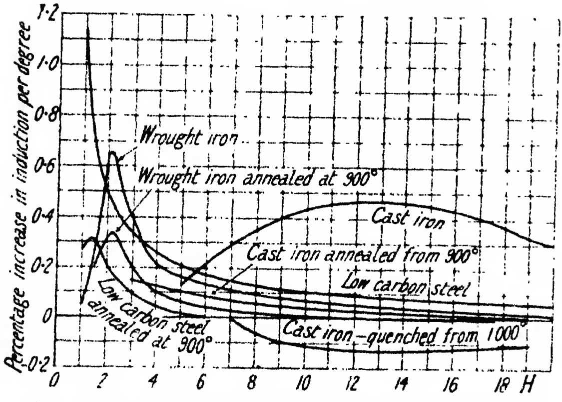


FIG. 293.—The Effect of Temperature on Magnetic Induction.

L. W. Wild measured the magnetic intensity and coercive force of some steels after being quenched from about 900°, and after 24 hrs'. re-heating at different temp. There is usually a large drop in the coercive force between 200° and 300°, and this is attributed to the cementite coming out of soln. and thereby becoming magnetic. The humps in the curves at about 500° are attributed to the cementite partially entering into soln., and not precipitating on cooling. The nickel steel behaves very much like the carbon steel; the chromium steel with 87 per cent. of iron has about 67 per cent. of the saturation intensity of iron and is scarcely affected by the tempering; the coercive force on tempering does not drop so steeply as with other steels. The rise at about 900° is more marked than it is with tungsten steels. There is a hump at 400° in the coercive force curve of chromium steel, at 600° with tungsten steel, and at 700° with nickel steel. H. Pécheux found the permeability decreases regularly with increasing carbon-content for annealed steels, but this relation does not hold good for the same samples after tempering. E. A. Watson considered that in a correctly hardened steel for magnets, the non-magnetic γ-iron should be completely transformed so that austenite is not present, nor should there be any segregation of the carbide and ferrite so that the change associated with Ar_3-arrest should be suppressed. The desirable constituent is the first transformation product from the γ-state. A. A. Dee could detect no difference in the magnetic properties of steels quenched from 300°, although, according to F. C. Thompson and E. Whitehead, the carbide change can be suppressed by suitably cooling from this temp.—*vide supra*. According to G. A. Ellinger, the first application of heat in the tempering of quenched, 0·75 per cent. carbon steel is attended by an increase in magnetization which is believed to represent stress release, caused by the precipitation of carbon from the supersaturated solid soln. of carbon in α-iron. The degree of tempering depends upon temp. and time, the first stage being completed at 200° in about 6½ hours. The precipitated carbon combines with iron in the range between 200° and 300° to form iron carbide. This combination is progressive with time, being completed at 300° in about 1 hr. From 300° to 700° no further magnetic changes occur upon holding the specimen at constant temp., consequently no further constitutional changes take place in this range, but the carbide coagulates to form larger and larger particles. An increase in the magnetization at about 235° indicates the decomposition of austenite, the decomposition being completed in about 45 mins. at that temp.

W. Köster observed that the coercive force of plain carbon steels increases linearly with the carbon-content irrespective of whether the cementite is globular or lamellar, but the rate of increase is smaller with the globular cementite. The coercive force of a steel with banded pearlite is two to three times as great as that of a similar steel in which the cementite is globular. J. R. Adams and F. E. Goeckler studied the influence of the history of the metal on the coercive force and residual reduction; and E. Maurer and F. Stäblein measured the coercive force of cementite. A. W. Smith and co-workers found that increasing the percentage of carbon in steels decreases the magnetic permeability by increasing the amount of carbides in soln., and owing to the asymmetry in the atomic structure making the alignment of the molecular magnets difficult. With annealed bars, the carbides separate from the solid soln., and the effect of carbon is much less. The maximum reluctivity is a linear function of the carbon-content of hardened steel up to 0·8 per cent. of carbon, for annealed chromium steel it is a maximum with about 0·5 per cent. of carbon, and a minimum with about 0·8 per cent. According to R. L. Dowdell, steels for magnets should be treated so that they have the greatest hardness possible without acquiring an undue tendency to cracking. T. D. Yensen and N. A. Ziegler observed that the elements, boron, carbon, zinc, nitrogen, oxygen, sulphur, cobalt, copper, manganese, and nickel, which lower the A_3-point and raise the A_4-point, have a bad effect on the magnetic properties of iron; those which raise the A_3-point and lower the A_4-point—*e.g.* aluminium, arsenic, silicon, tin, and vanadium, but not phosphorus and titanium—have a good effect on the magnetic properties; whilst the insoluble elements have very little effect on the magnetic properties.

As shown by W. Schmidt, and others, steel responds to weak magnetizing forces more quickly than iron; and the susceptibility of soft steel for small magnetizing forces is greater than that of iron. For fields below 0·06 c.g.s. unit, the susceptibility of soft steel to that of iron is as 4 : 3; for fields of about 1·0 c.g.s. unit, the susceptibilities are about the same; and for fields of greater strength, the susceptibility of iron exceeds that of steel. T. D. Yensen's values for vacuum-fused electrolytic iron, and armco iron are summarized in Fig. 288. The results show that whilst the induction curve for armco iron gives an initial bend characteristic of iron in general, the bend becomes very much less pronounced with iron of a high degree of purity, and T. D. Yensen said that "it is not inconceivable that it may disappear for the perfect iron crystal."

The permeability of iron at the beginning of magnetization is very small. C. Gutton and J. Mihul found the permeability of soft iron is constant for small field-strengths up to $H=1$ gauss, and it then increases with the field-strength. C. Baur, and J. A. Ewing found that for values up to $H=0{\cdot}384$, the magnetic susceptibility can be represented by $\chi=14{\cdot}5+110H$; the permeability by $\mu=183+1382H$; the intensity of magnetization by $I=14{\cdot}5H+110H^2$; and the magnetic induction by $B=183H+1382H^2$. Lord Rayleigh found that the proportionality holds good when the magnetic field is excessively reduced, and that the formulæ $\chi=6{\cdot}4+5{\cdot}1H$, and $\mu=81+64H$ hold good for values of H ranging up to 1·2 c.g.s. units. The viscosity or time-lag which occurs in the effect is most noticeable when the magnetizing force, H, is feeble.

C. Fromme observed that with moderately strong magnetizing forces the curves for the permeability and induction, and for the susceptibility and intensity of magnetization have points of inflexion; and this phenomenon was also observed by J. Haubner, W. R. Crane, L. W. Wild, A. Perrier, J. A. Ewing, R. H. M. Bosanquet, and S. Bidwell. J. A. Ewing and W. Low showed that with very strong fields, the induction, B, has no apparent limit, whilst there is a finite or saturation value for the intensity of magnetization, I. Thus, with Swedish wrought iron, in strong fields:

H .	6,690	8,900	95,100	10,000	10,360	10,810	10,880	11,200
B .	2,796	29,730	30,820	31,210	31,630	31,720	32,060	32,360
I .	1,700	1,660	1,700	1,690	1,700	1,670	1,690	1,690
μ .	4·18	3·34	3·24	3·12	3·09	3·05	2·94	2·90

whilst with cast iron:

H .	3,900	6,400	7,710	8,080	9,210	9,700	10,610
B .	19,660	21,932	22,830	23,530	25,580	24,900	25,600
I .	1,250	1,240	1,200	1,230	1,220	1,210	1,190
μ .	5·04	3·42	2·96	2·91	2·67	2·57	2·46

The intensity of magnetization reaches a saturation value beyond which no sensible increase occurs even though the strength of the field be doubled; but there is no sign of any limit to the value of B. K. K. Darrow gave 1706 gauss as the saturation capacity of iron at 20°, and 1742 gauss at −253°. He also gave 19,000 as the permeability of electrolytic iron. P. Weiss' value for the saturation capacity agrees with that given by K. K. Darrow. E. Dussler and W. Gerlach found that the saturation capacity of iron falls off with a rising temp. In a single crystal, in the tetragonal direction, at 20°, saturation was reached at about 150 gauss; at 629°, at 4·5 gauss; at 680°, at 3·5 gauss; and at 738°, at 2·5 gauss. H. E. J. G. du Bois also observed that iron at 0° in moderately strong fields, shows the following relations between the magnetizing force, H, and the intensity of magnetization, I:

H .	100	200	400	600	800	1000	1200
I .	1410	1520	1627	1677	1697	1705	1710

K. Honda and S. Shimizu gave for Swedish iron at different temp.:

−186°	H .	2·23	5·00	15·4	44·7	135·0	221·8	385	543
	I .	77	578	1085	1302	1464	1543	1636	1681
21·5°	H .	1·76	3·39	7·00	33·7	108·8	225·4	390	547
	I .	86	431	858	1264	1424	1536	1623	1660
714°	H .	0·13	0·26	0·50	1·39	2·48	22·46	258·6	377
	I .	49	115	338	533	597	744	829	834
1214°	H .	92	286	442	—	—	—	—	—
	I .	1·4	2·8	3·1	—	—	—	—	—

Observations were made by H. Esser. J. R. Ashworth discussed the relationship between the strength of the alternating current and the intensity of magnetization; E. H. Williams, and J. A. Ewing and W. Low, the effect of transverse joints on the magnetism of iron bars; and R. L. Edwards observed that the magnetic properties of iron films suffer an abrupt change when the thickness exceeds about $50 m\mu$, and an abrupt decrease in the coercive force. The subject was studied by W. Köster, C. Maurain, A. J. Sorensen, and J. H. Howey. H. E. Malmström observed no ageing effect. R. L. Sanford and co-workers found that as the diameter of steel wire decreases by wear, the magnetic permeability increases for low values of H, and increases for high ones. H. G. Byers and A. F. Morgan found that the magnetization of passive steel is more difficult than that of ordinary steel. H. Pender and R. L. Jones, and A. G. Hill studied the effect which a variable magnetic field during annealing has on the magnetic properties; and

TABLE XLII.—MAGNETIZATION CONSTANTS OF IRON.

Field-strength	Electrolytic iron (C = 0·024; S, 0·001; Si, 0·004; Mn, 0·008; P, 0·008)				Swedish charcoal iron (C = 0·027; S, 0·002; Si, 0·006; Mn, 0·030; P, 0·099)				Cast iron (C = 3·109; S, 0·061; Si, 3·279; Mn, 0·560; P, 1·050)			
	Un-annealed		Annealed		Un-annealed		Annealed		Un-annealed		Annealed	
H	B	μ	B	μ	B	μ	B	μ	B	μ	B	μ
0·25	—	—	2,200	3,800	300	1,200	310	1,240	—	—	—	—
1·00	600	600	10,240	10,240	5,000	5,000	6,350	6,350	—	—	—	—
5	8,920	1,780	14,470	2,890	1,290	2,580	12,940	2,590	570	114	2,950	590
10	12,750	1,280	15,500	1,550	14,600	1,460	14,630	1,460	1,960	196	5,150	515
100	18,380	185	18,050	180	16,900	340	17,120	340	9,320	93·2	9,950	99·5
1,000	22,520	22·5	22,570	22·6	22,120	22·1	22,040	22·0	15,900	15·9	16,200	16·2
4,500	26,110	5·8	26,150	5·8	25,690	5·7	25,680	5·7	20,870	4·65	21,200	4·72
R	11,440		10,850		11,405		9,850		5,100		5,300	
H_c	2·82		0·375		1·06		0·76		11·4		4·6	
μmax	1,850		14,600		5,400		6,400		240		620	
η	0·00308		0·00078		0·00131		0·00105		0·0114		0·00437	
I_∞	1720·5		1721·5		1,687		1685·5		1306·5		1,333	
$4\pi I_\infty$	21,620		21,632		21,200		21,180		16,417		16,750	

TABLE XLIII.—MAGNETIZATION CONSTANTS OF STEELS.

H	(C = 0·044; Si, 0·004; Mn, 0·400; P, 0·044; S, 0·027)				(C = 0·56; Si, 0·18; Mn, 0·29; P, 0·076; S, 0·035)				(C = 0·99; Si, 0·10; Mn, 0·40; P, 0·04; S, 0·07)			
	Un-annealed		Annealed		Not hardened		Hardened		Not hardened		Hardened	
	B	μ	B	μ	B	μ	B	μ	B	μ	B	μ
0·25	240	960	3,100	12,400	—	—	—	—	—	—	—	—
1·0	2,300	2,300	10,200	10,200	200	200	57	57	89	89	42	42
5	12,150	2,430	15,000	3,000	2,400	480	290	58	500	100	240	48
10	14,100	1,410	15,680	1,570	7,250	730	620	62	1,650	165	500	50
100	17,890	180	18,280	183	16,420	164	13,780	138	15,800	158	9,820	98
1,000	22,350	22·4	22,320	22·3	21,000	21·0	20,530	20·5	20,040	20·0	17,410	17·4
4,500	25,920	5·75	25,930	5·75	25,030	5·55	24,650	5·48	24,260	5·40	22,260	4·95
R	10,600		11,050		10,650		10,630		13,000		7,460	
H_c	1·46		0·37		7·1		44·3		16·7		52·4	
μmax	4,200		14,800		710		170		375		110	
η	0·00157		0·00054		0·00695		0·0271		0·0150		0·0337	
I_∞	1704·5		1704·5		1639·5		1,606		1577·5		1416·5	
$4\pi I_\infty$	21,419		21,419		20,602		20,180		19,823		17,800	

K. Honda and Y. Shimizu, and G. Tammann and co-workers, the effect of cold-work.

A selection from the data of E. Gumlich and co-workers is given in Tables XLII and XLIII. Here H denotes the strength of the magnetic field; B, the induction; μ, the permeability; R, the reluctivity; H_c, the coercive force; η, the factor in C. P. Steinmetz's equation;, and I_∞, the saturation value. Observations were also made by S. Curie, T. Matsushita, E. M. Pugh, L. Holborn, S. Guggenheim, and R. A. Hadfield and B. Hopkinson. P. Weiss gave for the saturation value of purified iron, $I_\infty=1706$, and $4\pi I_\infty=21440$; B. O. Peirce, $I_\infty=1733$, and $4\pi I_\infty=21780$; A. Campbell, $I_\infty=1717$, and $4\pi I_\infty=21580$; and E. Gümlich, $I_\infty=1720{\cdot}5$, and $4\pi I_\infty=21620$. For iron alloys with p per cent. of carbon, E. Gumlich gave $4\pi I_\infty=21620-1580p$, when p is less than 1 per cent., and the alloy is slowly cooled, while for higher values of p, he gave $4\pi I_\infty=20100-930(p-1)$; for alloys quenched from 850°, when p is less than 1·2 per cent., $4\pi I_\infty=21620-3200p$; and when quenched from 1100°, when p is less than 1·1 per cent., $4\pi I_\infty=21620-2060p$. P. Weiss and R. Forrer calculated by extrapolation that the saturation intensity of a gram of iron is 12,393. C. F. Burgess and A. H. Taylor studied the permeability of purified electrolytic iron; and H. Sachse, of iron dispersed in alumina, silica, or strontium sulphate. N. A. Ziegler found that the magnetic permeability of unicrystalline iron is many times as great as that of polycrystalline iron. C. Nusbaum and co-workers observed a marked increase in the maximum induction of steels as the rate of cooling decreased; the maximum permeability also increased; but the coercive force diminished.

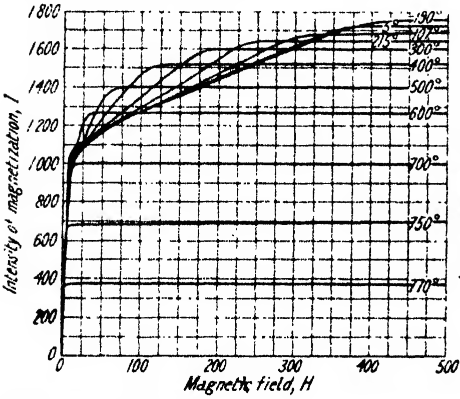


FIG. 294.—The Intensity of Magnetization of Polycrystals of Iron.

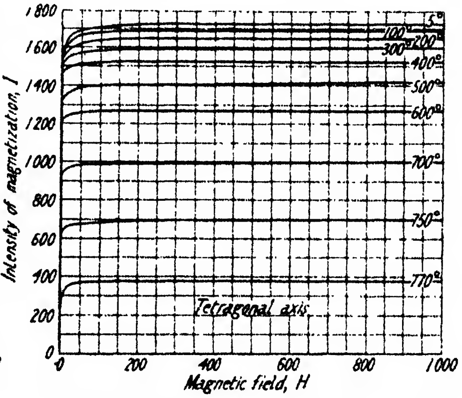


FIG. 295.—The Intensity of Magnetization of a Single Crystal of Iron (Tetragonal Axis).

W. Gerlach, and K. Honda and S. Kaya observed that the characteristic features of the magnetization curve of an iron rod of single crystals of iron are: (i) The curve is almost straight up to an intensity of magnetization of 1000 c.g.s. units; (ii) then the curve shows two sharp breaks or bendings; (iii) the saturation of magnetization is much more easily attained than in the case of polycrystals, its value being 1707 (20° C.) (this saturation value almost coincides with the value 1706 (19° C.) determined in a very strong field produced by an electromagnet); and (iv) the residual magnetism of single crystals is very small. The hysteresis-loss of the rods of single crystals and of those consisting of a gradual increasing number of polycrystals of iron were also measured. The results of K. Honda, H. Masumoto and S. Kaya are summarized in Figs. 294 to 297. K. Honda and S. Kaya studied the magnetization curves of single crystals and found that in the (111)-plane, the curves in the direction of the tetragonal, trigonal, and digonal axes, are almost straight up to intensities of magnetization of 1,400, 900, and 1,000.

The curves then show sharp breaks or bendings twice, sometimes one more break is observable, but is not so conspicuous as the other two. The saturation of magnetization is much more easily attained with single crystals than with polycrystals, and its value amounts to 1717. The saturation in the direction of the tetragonal axis is reached at 70 gauss, and in the digonal and trigonal axes at 650 and 450 gauss, respectively. In the (100)-plane, the direction of the tetragonal axis is more easily magnetizable than that of the digonal. In the (110)-plane, the directions of the tetragonal, digonal, and trigonal axes are in a decreasing order of magnetizability. In the (111)-plane, the space-lattice consists of a series of equilateral triangles. Below a field of 300 gauss, the direction of the sides of the triangle (the *b*-axis) is more magnetizable than the bisector of the triangles (the *a*-axis); but above that field, the contrary is the case. The characteristic features of the curves for magnetization in different directions are as follows: In the (100)-plane, both parallel and perpendicular components of magnetization vary with a period of 90°. For the parallel component, the direction of the tetragonal axis has the maximum magnetization, and that of the digonal, the minimum magnetization; but for the perpendicular component, the magnetization vanishes in the direction both of the tetragonal and digonal axes and attains a maximum or minimum between them. Below a field of 3 and above 500 gauss, the parallel component of magnetization in the (100)-plane is almost independent of the direction of the field. As the field increases beyond 3 gauss, the amplitude of the periodic change becomes greater, attains a maximum and afterwards gradually decreases. In the (100)-plane, these two components of magnetization vary with a period of 180°. For the parallel component, the principal and secondary maxima takes place respectively in the directions of the tetragonal and digonal axes, and the minimum in the directions of 55° and 125° from the tetragonal axis. For the perpendicular component, the magnetization vanishes in the directions of the tetragonal, trigonal, and digonal axes, and attains a maximum or a minimum between them. The amplitude of this periodic change varies in a similar way to the case of the (100)-plane. In the (111)-plane, the two components of magnetization vary with a period of 60°. In weak fields, the parallel component of magnetization in the direction of the sides of the equilateral triangles forming the space-lattice is a maximum and that in the direction of the bisectors of the vertical angle of the triangle is a minimum; but in a stronger field above 300, the opposite is the case. The perpendicular component of magnetization vanishes in these two directions and attains a maximum and a minimum between them. The magnetization of strips of iron depends on the orientation of the crystals with respect to the applied magnetic field. W. E. Ruder observed that the permeability of crystals having their cube edges perpendicular

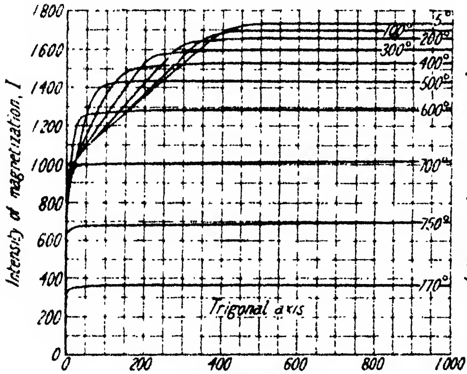


FIG. 296.—The Intensity of Magnetization of a Single Crystal of Iron (Trigonal Axis).

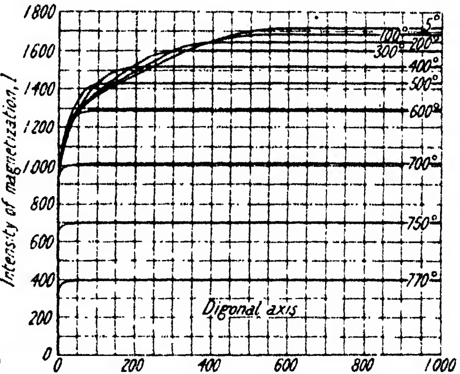


FIG. 297.—The Intensity of Magnetization of a Single Crystal of Iron (Digonal Axis).

and parallel to the direction of the applied flux is 10 to 25 times that which obtains when the crystals have their cube edges at an angle. The lowest magnetic permeability occurs when all the edges are 45° with the direction of the flux. The subject was also investigated by W. L. Webster, F. C. Powell, N. Akuloff, W. Gerlach, K. Beck, H. Gries and H. Esser, G. J. Sizoo, and N. A. Ziegler. W. Gerlach found that remanent magnetism is absent in ferromagnetic single crystals of iron of ordinary size; and J. Frenkel and J. Dorfman consider that the phenomena of retentivity and hysteresis, observed in ordinary ferromagnetic bodies, are connected with the inner stresses characteristic of their structure.

According to N. Akuloff, if a single crystal of iron or nickel be magnetized to a certain intensity, first in the direction of the principal axis, and then to the same intensity in any other direction, the difference in the resulting changes in length of the crystal parallel to the direction of magnetization, and the difference between the relative changes in electrical resistance and the area between the magnetization curves or the alteration in the internal energy, are all proportional to each other. N. Akuloff showed that for a single crystal of iron magnetized to its saturation value, the longitudinal and transverse changes of length accompanying changes in the direction of magnetization relative to the crystal structure can be explained by means of forces arising from the magnetic dipoles; and there is a direct proportionality between the energies involved in such changes in length and the energies required to produce the corresponding change of direction of magnetization. Both phenomena are due to the deviation of the same carrier of magnetic moment from its normal position of minimum energy in the crystal. According to P. Weiss and R. Forrer, the phenomenon of spontaneous magnetization shows that an unmagnetized body at ordinary temp. consists of small volumes magnetized in different directions so that the resultant effect is to give zero magnetic moment to the whole. Under the influence of a magnetic field, some of these elements change their directions or produce their resultant moment. According to K. Honda and coworkers, and W. Gerlach, the coercive force and hysteresis loss which occur in single crystals correspond to the energy loss in breaking up the circuits of flux in the iron, and the more nearly perfect the crystal, the smaller the hysteresis loss. The magnetization thus occurs in two ways: (i) by a change from one cubic axis to another and it occurs in weak fields of a few gauss; (ii) by a break from the cubic direction and it occurs only in strong fields. According to W. L. Webster, the value of the intensity of magnetization at which the break occurs will depend on the direction of the magnetic field relative to the crystal axes. When all the small elements in the crystal of iron have had their direction of magnetization changed to coincide as far as possible with the cubic directions nearest to the applied field, consistently with the condition that there should be no transverse magnetization, then any further increase of bulk magnetization must be produced by forced deviations from these cubic axes towards the direction of the applied field, and the knee will appear. The curves, Fig. 298, are based on those of K. Honda and S. Kaya. With an applied field along a cubic axis, the second process will not appear at all and the initial rapid rise should continue right up to complete saturation. For the (110) and (111) directions the transition should take place at intensities $\sqrt{\frac{1}{2}}$ and $\sqrt{\frac{1}{3}}$ of the saturation values. G. J. Sizoo found that with single crystals in which all mechanical strains had been eliminated by prolonged heating, hysteresis was present only in the region of low field-strength. There are discontinuities in the magnetization curve, and in the region above the

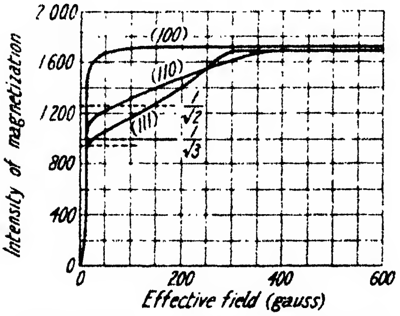


FIG. 298.—Magnetization Curves of Single Crystals of Iron.

last discontinuity, the specimen is completely magnetized; at this point, the hysteresis branch forms a continuation of the reversible part of the magnetizing curve. The retentivity has the same general value as for ordinary polycrystalline iron.

H. F. Parshall observed that the permeability of cast iron is diminished if cooled too rapidly, since combined carbon reduces the permeability. According to J. H. Partridge, the highest values for the induction and permeability are obtained with annealed cast iron. For high permeability, the graphite should be in the form of temper carbon; the combined carbon, low; and cementite absent. Cementite, added H. Nathusius, is a sure indication of poor magnetic properties. W. Köster and H. Tiemann studied the effect of annealing. H. F. Parshall said that between 2 and 3 per cent. of graphite has no perceptible effect on the permeability. An excess of sulphur favours combined carbon and reduces the magnetic quality. F. Goltze also found sulphur to be prejudicial to the magnetic properties of cast iron. H. F. Parshall concluded that silicon annuls the effect of sulphur, and no inferiority was observed until the proportion exceeded 2 per cent. P. Reusch said that silicon precipitates graphite, and precipitated graphite lowers the magnetic induction. H. Nathusius said that silicon improves the magnetic properties of cast iron. F. Goltze, and J. H. Partridge observed that silicon decreases the magnetic induction, and the coercive force and the hysteresis loss are reduced with silicon in cast and annealed iron. An excess of phosphorus over 0·7 per cent. reduces the magnetic quality; F. Goltze said that phosphorus reduces the permeability: and J. H. Partridge, that phosphorus has but little effect on the magnetic properties. H. F. Parshall showed that manganese has little effect when present in its usual amounts, and this agrees with P. Reusch's observations. F. Goltze, and J. H. Partridge found that manganese reduces the induction of cast and annealed iron, but with annealed iron, the coercive force and hysteresis loss are increased, and the remanent magnetism decreased. A. Schweitzer observed that up to 3 per cent. of aluminium reduced the magnetic properties of iron. J. H. Partridge observed that aluminium decreases the magnetic induction, permeability, and remanent magnetism, and raises the coercive force and hysteresis loss; whilst with the annealed iron, up to 1 per cent. decreases the induction and maximum permeability, but increases the coercive force and hysteresis loss. Amounts between 1 and 3 per cent. increase very much the induction and permeability, and decrease enormously the coercive force and hysteresis loss. J. H. Partridge said that chromium acts like manganese and is prejudicial to magnetic induction both in the cast and annealed alloy, and that nickel behaves similarly. The presence of sufficient nickel, or nickel and manganese makes *non-magnetic cast iron*. The iron should be entirely austenitic. The presence of cobalt increases the magnetic induction and remanent magnetism, and increases the maximum permeability of cast iron. The subject was discussed by H. O'Neil, P. Nicolau, and R. L. Sanford. W. F. Barrett found that the order of magnetic permeability of the alloys of iron is different from what is the case with the order of electrical conductivity. The most permeable alloys observed were those with silicon and aluminium; the magnetic permeability of an alloy with 2·5 per cent. of silicon (*q.v.*) exceeds that of annealed iron of a high degree of purity up to a field of 10 c.g.s. units; and with aluminium alloys, the magnetic permeability up to a field of 60 c.g.s. units exceeds that of the iron. The increased magnetic susceptibility of these alloys may be due to their action in removing traces of iron oxide from the metal.

R. Gans, and W. Steinhaus and E. Gumlich showed that the ideal, reversible permeability curve of mild steels is infinite in weak fields. C. Biéler-Butticez studied the effect of cold-work on the magnetic properties of iron. A. Kussmann and B. Scharnoff observed no relationship between the magnetic hardness or coercive force and the mechanical hardness with alloys of iron and nickel with copper, aluminium, and chromium; but C. Nusbaum observed that the coercive force of an eutectoid carbon steel is in a good agreement with the scleroscopic hardness when the steel has been cooled at different rates. W. M. Hicks found that aluminium, phosphorus, and arsenic decreased the coercive force and hysteresis loss of iron, and aluminium largely increased the permeability. G. Malmberg, and H. E. Diller discussed the effects of small proportions of different elements on the magnetic permeability of iron— *vide infra,* the alloys of iron.

The permeability was measured by A. M. Armour, M. Ascoli and F. Lori, J. M. Baldwin, R. Beattie and H. Gerrard, R. Becker, G. Belloc, R. Bown, A. Campbell, H. le Chatelier, W. L. Cheney, C. Chistoni and G. G. de Vecchi, S. S. Clark, R. E. B. Crompton, G. Delbart, H. E. Diller, C. V. Drysdale, E. Dumont, A. Durward, F. Erhardt, J. W. Esterline and R. B. Treat, J. A. Ewing, H. Frank, O. Frölich, R. Gans, F. Goltze, A. Gray, R. C. Gray, E. Gumlich and co-workers, E. P. Harrison, E. Haupt, C. Heinke, P. Holitscher, R. Hugues, A. Iliovici, H. Kamps, Y. Kato, A. E. Kennelly, W. N. Kernot, I. Klemencic, J. Königsberger, A. Koepsel, W. Köster, H. Lange, G. C. Marris, J. A. Mathews, D. Mazzotto, J. T. Morris and T. H. Langford, E. Müllendorff, W. H. F. Murdoch, B. Neumann, P. Nicolau, J. H. Partridge, B. O. Peirce, A. Perrier, Lord Rayleigh, P. Reusch, E. Rhoads, J. Sahulka, G. F. C. Searle, E. Schmidt, W. Schmidt, E. K. Scott, R. Shida, B. S. Summers, T. Swinden, R. van Tongel, M. E. Thompson, S. P. Thompson, A. M. Thiessen, J. Trowbridge and E. P. Adams, A. Turner, G. R. Wait, H. S. Webb, M. Wien, R. L. Willis, E. Wilson, and J. Würschmidt ; and H. Kamps studied the effect of a layer of oxide on the magnetic properties of iron.

A. W. Rücker measured the step-by-step magnetization of iron. S. Procopiu, and T. Spooner studied the effect of a superposed alternating field on the magnetic permeability of iron. E. W. Marchant found that the permeability of iron subjected to an oscillatory discharge of 10,000 to 100,000 cycles per second is not sensibly different from the result obtained by ballistic tests. The damping of the oscillations was more rapid with thicker iron wires ; and with cores of solid iron, the discharge was reduced to one-half oscillation. J. R. Martin, E. Krauter, W. Kartshagin, and W. Arkadieff measured the magnetic properties of iron for alternating fields from zero to very high frequencies ; R. Gans, and G. Vallauri for slowly rotating fields ; whilst M. J. O. Strutt, and L. Tonks measured the effects of a high-frequency rotating field—from 52,000 to 170,000 cycles per second. W. K. Mitiaeff reported an anomalous change in the permeability of iron at radio-frequencies, but it could not be verified by G. R. Wait and co-workers. R. Urbschat, E. M. Guyer, G. Laville, B. Wedensky and K. Theodortschik, O. M. Corbino, W. H. Eccles, W. K. Mitiaeff, J. B. Hoag and H. Jones, and C. Gutton and I. Mihul studied the permeability of iron at high frequencies ; and S. K. Mitra, the demagnetization of iron by electromagnetic oscillations of frequency up to 500,000 per sec. L. Tonks, and J. Grant also studied the behaviour of iron in electromagnetic fields of high frequency. M. Tschetverikova observed the demagnetization of iron in damped, magnetic, alternating fields, and with short Hertzian waves $\lambda=28$ to 1700 cm. Slow alternatic fields demagnetize iron only when the field-strength is below 2·3 gauss. No demagnetization was observed with undamped waves, and B. Wedensky and K. Theodortschik observed that there is an anomaly. Demagnetization phenomena were studied by R. Forrer and J. Martak in the permeability of iron in oscillating magnetic fields, but R. Bown, and G. R. Wait and co-workers observed no change in the permeability of iron exposed to radio-frequency vibrations.

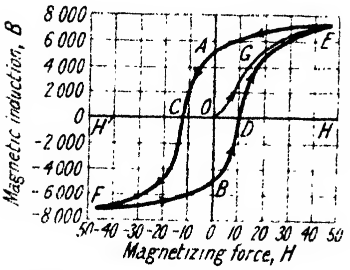


FIG. 299.—Cyclic Magnetization-Hysteresis Loop.

If a long, thin, unmagnetized rod be placed in the solenoid, and the current be gradually increased from zero to a maximum value, *OH*, Fig. 299, the resulting *BH*-curve will be represented by, say, *OGE*, where *HE* represents the maximum flux density or induction. Let the current be now reduced to zero, when the curve *EA* is obtained : here *OA* represents the flux density or residual magnetism or remanence. Let the current now be reversed in direction, thus tending to magnetize in the opposite direction, and gradually increased to a maximum *OH′*. The curve *ACF* is now obtained. Here *OC* represents the value of the reversed magnetizing force necessary to reduce the flux density to zero, or to wipe out the residual magnetism, or remanence. Here *OC* is the so-called **coercive force,** or a kind of *magnetic hardness*. On again decreasing the magnetizing current to zero, and reversing so as to increase the induction to its maximum value, the curve *FBDE* is traced. If the cycle be repeated, the curve will be retraced, but the initial path, *OGE*, is not followed unless the specimen is first completely demagnetized. The magnetic effects are liable to persist, or lag behind the applied force. Thus, the value of *B* when *H* is decreasing is always greater than when *H* is increasing. When *H* is zero, *B* still has a definite value, and a reversal of the magnetizing force is necessary to bring *B* to zero.

The time-lag of the intensity of magnetization, *I*, on the change of magnetizing force, *H*, is called the **magnetic viscosity.** When annealed wrought iron is subjected to a magnetizing force, and the force is changed, the magnetic viscosity shows itself as a lapse of time before the corresponding change in magnetic intensity is complete. The effect is most pronounced with small magnetic forces or with very small changes of the magnetizing force. C. Lapp found that electrolytic iron exhibits magnetic viscosity and that the viscosity is diminished by prolonged ageing at 130° to 190°, but at the expense of the magnetic properties of the metal. Annealing the electrolytic iron at 300° to 500° has the reverse effect. The reciprocal of the permeability of iron is termed the **reluctivity,** and T. F. Wall gives the values shown in Fig. 300 for the reluctivities of some ferromagnetic metals—annealed iron, annealed steels, cobalt, nickel and Heusler's alloy. C. Nusbaum and co-workers studied the relation between the reluctivity and the structure of eutectoid carbon steel—*vide supra*, Fig. 300.

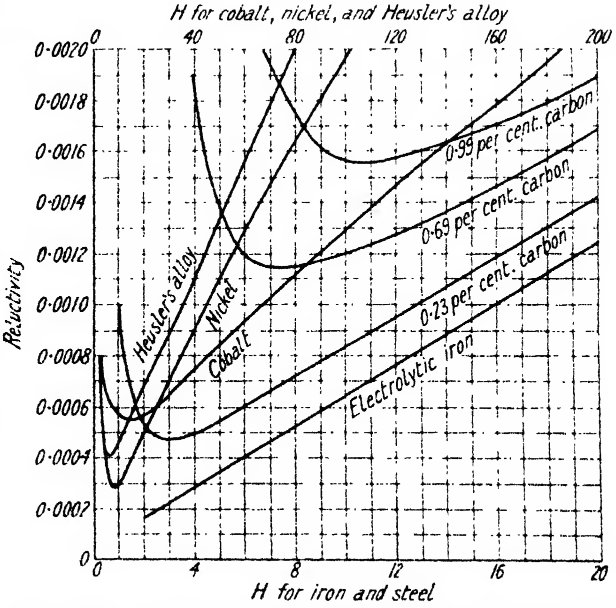


FIG. 300.—The Reluctivities of some Ferromagnetic Metals.

J. A. Ewing applied the term **hysteresis** to the lagging of the magnetic induction, or flux density, behind the magnetic force which produces it. E. Warburg showed that the area of the hysteresis loop is proportional to the energy lost in the specimen owing to the change in its magnetic condition. The energy, *W*, dissipated owing to the so-called **hysteresis loss,** represented by the area of the loop *FCAEDB*, Fig. 299, can be expressed in ergs per c.c. per cycle. This was verified by J. A. Ewing, J. Hopkinson, and Lord Rayleigh. The dissipation of energy produces a thermal effect which is observed during cyclic reversals of the magnetization.

The phenomenon was studied by J. A. Ewing, G. Kapp, A. Tanakadate, L. T. Robinson, J. P. Joule, W. R. Grove, J. G. S. van Breda, J. Jamin and G. Roger, F. W. Constant, M. Fukuda, L. Pilleux, A. Cazin, E. Edlund, Lord Kelvin, R. Gans, K. Uller, H. A. Dickie, W. M. Mordey and A. G. Hansard, C. E. Guye and A. Schidlof, H. Nathusius, A. Gradenwitz,

F. Niethammer, K. Seyama, M. E. Ricea and B. McCollum, E. E. F. Creighton, M. G. Lloyd and J. V. S. Fisher, R. Beattie and P. M. Elton, A. Ebeling and E. Schmidt, F. F. Martens, A. D. Adams, F. C. Langenberg and R. G. Webber, M. Brylinsky, R. G. Loyarte, N. Danielsen, C. E. Webb and L. H. Ford, E. Spuhrmann, S. W. Richardson and L. Lownds, L. M. Potts, A. Dina, R. Hiecke, G. F. C. Searle and T. G. Bedford, T. Gray, F. G. Bailey, G. G. Gerosa and co-workers, H. Nagaoka, W. Kunz, C. G. Knott, A. Abt, J. Swinburne and W. F. Bourne, W. H. Preece, J. Schneider, N. Nikitin, J. Trowbridge, J. Trowbridge and W. N. Hill, H. Herwig, J. Borgmann, E. Müllendorff, E. A. Watson, A. Kühns, P. Duhem, F. A. Weihe, E. Höller, H. F. Parshall, C. Maurain, E. Wilson, E. Schmidt, G. Hannack, A. Wassmuth, M. G. Lloyd, R. Richter, J. Herrmann, P. Weiss and V. Planer, G. Vallauri, J. H. Andrew and co-workers, P. H. Dudley, B. G. Churcher, C. W. Burrows and F. P. Fahy, N. J. Gebert, S. R. Williams, R. L. Sanford and co-workers, C. Nusbaum, H. Alfven, R. H. de Waard, W. Neumann, D. Foster, and E. Warburg and L. Hönig.

E. Warburg observed that 68 per cent. of the energy represented by the area of the hysteresis loop is dissipated as heat; A. Tanakadate observed 80 per cent.; I. Klemencic, 100 per cent.; and F. A. Weihe, 80 per cent. for iron, and 73 per cent. for steel. The subject was studied by W. B. Ellwood. According to W. B. Ellwood, on traversing the hysteresis loop from 290 to 20 gauss, heat is evolved by the iron; on passing from 20 to −6 gauss, the iron cools suddenly; from −6 to −90 gauss, the iron rapidly becomes warm; and as the field passes from −90 to −290 gauss, the iron is cooled. C. H. Willis emphasized the value of a high proportion of silicon in steel when it is desired to prevent losses by hysteresis and eddy currents. J. R. Ashworth studied the changes in the energy of iron cooling through the critical temp.; and N. W. McLachlan, the heat produced when iron is magnetized by high-frequency alternating currents. E. Condon discussed a possible directional hysteresis in iron.

A. J. Sorensen, R. L. Edwards, J. D. Hanawalt and L. R. Ingersoll, E. P. T. Tyndall, and L. C. Jackson discussed the magnetic properties of thin films of iron. C. Maurain found the thinnest film of iron showing magnetic properties was a millionth of a millimetre in thickness. E. F. Burton and B. Phillips observed that the magnetic susceptibility of a colloidal soln. of iron in methyl alcohol is stronger than it would have been if the iron were present as a ferric salt, and yet weaker than iron alone. It is concluded that each particle of iron is surrounded by a compound of iron—say, the hydroxide. The subject was studied by H. Isnardi, C. G. Montgomery, and R. Gans; whilst B. Speed and G. W. Elmen investigated the magnetic properties of compressed powdered iron.

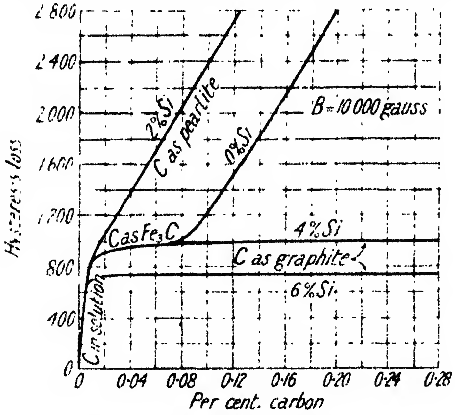


FIG. 301.—The Effect of Carbon on the Hysteresis Loss of Iron-Silicon Alloys.

T. D. Yensen summarized his observations on the effect of carbon and silicon on the hysteresis losses, in ergs per cm. cube per cycle for $B=10{,}000$, in Fig. 301. Every 0·001 per cent. of carbon raises the hysteresis loss about 10 per cent. provided less than 0·008 per cent. of the carbon is present in solid soln. so as to form part of the iron lattice. Nitrogen and oxygen are thought to behave similarly. With electrolytic iron containing 0·005 per cent. of carbon, the maximum permeability increased with addition of carbon from 25,000 to 61,000 with 0·06 per cent. of carbon, and 0·4 per cent. of oxygen. It is assumed that here the added carbon deoxidized the iron and left in the metal no oxygen and only about 0·005 per cent. of carbon. For hydrogenized iron, *vide supra*. S. Saito studied the saturation value of cementite and of the complex carbides with tungsten and with chromium.

T. D. Yensen showed that the hysteresis losses of iron are influenced by the grain-size. J. R. Ashworth studied the anhysteresis of iron, and the hysteresis of iron cooling through the critical temp.

The time lag in the magnetization of iron was attributed by C. Lapp to magnetic viscosity, and not to induced currents as supposed by R. M. Bozorth. J. Hopkinson and E. Wilson, E. Donati, and T. R. Lyle and J. M. Baldwin studied the rate of propagation of magnetism along iron rods. O. Grotrian showed that with a cylinder of iron magnetized in the direction of its axis, with low saturation, the magnetization of the periphery is greater than that of the axial portions. M. Ascoli and F. Lori discussed the distribution of induced magnetism in iron. I. Klemencic observed that the magnetic permeability of iron is different in circular and axial directions, and the phenomenon may be called magnetic double refraction. The permeability with soft iron is smaller around the axis than in the direction of the axis; and in the process of drawing hard iron or steel, the metal obtains a stronger permeability axially than in the circular direction. W. Penkert showed that when a long, straight bar is excited by a magnetizing coil saturated at the centre, the lines of force which pass through the coil do not keep in the iron up to the end, but emerge into the air at all points along the length of the bar. This explains why the induction of the bar falls off continuously as the distance from the central source of magnetization is increased.

According to W. M. Mordey, the slow change which occurs in the permeability of iron is not due to progressive magnetic fatigue caused directly by repeated reversals. Neither magnetic nor electric action is necessary for its production. It is a physical change resulting from a prolonged heating at a very moderate temp. The change is greater if pressure be applied during the heating, and it is not produced when iron is not allowed to rise in temp. more than a few degrees above atm. temp. A similar effect is produced by hammering, rolling, or heating to redness and cooling quickly, and the iron returns to its original state when re-annealed. The iron does not return to its original conditions if kept unused, and at ordinary temp., for long or short periods. D. Mazzotto found that the effect of ageing is a maximum at 131°. The subject was discussed by R. L. Dowdell, H. Kühlewein, and T. E. Green.

T. Sone examined the magnetic properties of electrolytic iron deposited in a magnetic field, and he found that the curve of initial magnetization lies considerably higher that it does with specimens obtained in a zero field; the loop of the hysteresis curve is also wider than it is with ordinary iron, but the magnetic field applied during electrolysis does not sensibly affect the hysteresis curve. The hysteresis curve of electrolytic iron deposited in a magnetic field becomes flatter with the lapse of time as the molecules settle down slowly to a state of equilibrium. Annealing hastens this change. H. Hanemann and P. D. Merica observed a close and nearly linear relation between the elastic limit of soft iron, and the values of the stress at which permeability maxima occur as the metal is elongated.

H. Barkhausen observed some discontinuities in the magnetization of certain ferromagnetic materials, which have been called the **Barkhausen effect.** The Barkhausen effect, dB/dH, represents the change of induction dB with change of magnetic field dH; the rate of change of induction being represented by dB/dt, and the rate of change of the magnetic field by dH/dt. H. Barkhausen, and B. van der Pol attributed the effect to the sudden re-orientation of groups or changes of molecular magnets, possibly all the magnets in a single crystal turning simultaneously. There is a larger effect in hard-worked than in annealed materials. The change occurs on the deeper parts of the hysteresis loops of hard-worked iron and permalloy. E. P. T. Tyndall found that the size of the discontinuities does not depend on the grain-size of silicon steel; and G. J. Sizoo made a similar observation with regard to electrolytic iron. R. M. Bozorth observed that the larger discontinuities on the steeper parts of the hysteresis loop correspond with the complete reversals of magnetization of about 10^{17} atoms, or a vol. of 10^{-6} c.c.

The effect has been studied by W. Gerlach, W. Gerlach and P. Lertes, J. D. Ball and W. E. Ruder, E. C. Stoner, B. del Nunzio, I. Langmuir and K. J. Sixtus, A. von Hippel and co-workers, W. Brandt, D. G. C. Luck, F. J. Beck and L. W. McKeehan, P. Weiss and G. Ribaud, K. Zschiesche, S. R. Williams, R. M. Bozorth and co-workers, F. Preisach, J. Frenkel and J. Dorfman, O. Tesche, A. Cisman, E. P. T. Tyndall and J. M. B. Kellogg, S. Procopiu, S. Procopiu and T. Farcas, K. J. Sixtus, K. J. Sixtus and L. Tonks, H. Biron, K. Steimel, and J. Pfaffenberger. C. W. Heaps and J. Taylor found that with high speeds of magnetization there are more and smaller discontinuities as the speed is slightly reduced; and with large reductions of speed, there are fewer discontinuities in ordinary specimens than for high steels. The mechanical Barkhausen effect obtained by twisting or stretching occurs with iron and annealed nickel, and it almost disappears when the magnetization approaches saturation. A hard steel ball of fine homogeneous structure showed no discontinuities. D. Foster observed no breaks in the knee of the magnetization curve of single crystals of iron. R. Forrer also observed that the Barkhausen effect is strongly influenced by internal strains. E. P. T. Tyndall did not accept the hypothesis of W. Gerlach and P. Lertes, and K. Zschiesche said that the effect depends on magnetostriction, but it is in agreement with the work of L. W. McKeehan, and C. W. Heaps and J. Taylor. The strains set up by magnetostriction—*vide infra*—when relieved discontinuously produce the jumps of induction. H. Rindfleisch studied the effect of helium and neon on the Barkhausen oscillations.

The magnetization curves and hysteresis loops of single crystals of iron made by W. Gerlach show breaks or abrupt changes of slope; and this was also confirmed by E. Dussler and W. Gerlach, H. Gries and H. Esser, and G. J. Sizoo. On the other hand, D. Foster, E. Wollman, and D. Foster and R. M. Bozorth observed no breaks in the curve. The discrepancy is due to the need, in the former case, for applying corrections for the field intensity which usually goes through a rather sharp maximum in the same range of magnetization as is occupied by the knee of the curve. R. Goldschmidt discussed the relation between permeability and hysteresis.

C. P. Steinmetz obtained an empirical relation between the work, W, lost by hysteresis effects, $W=\eta B^{1\cdot6}$, when η is constant for any one specimen, and it is called the *coefficient of hysteresis*. J. A. Ewing said that 1·59 is more in accord with the published data than 1·6 for the general constant. The formula is applicable for the range of magnetization used in electrical engineering, but is not applicable for very weak or very strong magnetic fields. The subject was investigated by J. A. Ewing and H. G. Klaassen, W. Elenbaas, A. E. Kennelly, J. A. Fleming and co-workers, M. Nakamura, H. F. Parshall, etc. The values of η for soft iron ranges from 0·001 to 0·003; for annealed high carbon steel, 0·008; and for hardened steel, 0·025. Some values for steels with different heat-treatments are indicated in Table XLIII. C. P. Steinmetz observed that for many kinds of iron, the ratio η/H_c, is a constant—here H_c denotes the coercive force. For H with a maximum of 500, S. Curie obtained linear relation between the coercive force and the hysteresis coefficient. The following values were given by C. P. Steinmetz, W. F. Barrett and co-workers, A. Ebeling and E. Schmidt, E. Gumlich and E. Schmidt, S. Curie, and C. Benedicks:

$H_{\text{max.}}$.	40	45	90	100	150	205	500	505
η/H_c .	0·00131	0·00105	0·00103	0·00110	0·00105	0·00092	0·00072	0·00062

$H_{\text{max.}}$ . . .	4·9	10·1	14·4	18·9	23·5	30	82
η/H_c . . .	0·0066	0·0026	0·0023	0·00155	0·00128	0·00114	0·00098

C. Benedicks studied the relation $\eta/H_c=0\cdot00067+0\cdot0257/H_{\text{max.}}$; E. Gumlich and E. Schmidt, and C. Benedicks, the relation $\mu=aR/H_{c\text{max.}}$, where R denotes the remanence, and a is a linear function of the coercive force, $a=\alpha+\beta H_c$, where α and β are constants; and C. Benedicks, the relation $R=I_\infty H_c/a$. D. Foster found that with single crystals of iron, the hysteresis loop is characterized by extremely steep sides with sharp corners and high remanence. The coercive force for $H_{\max.}=30$ gauss is 0·4 gauss, and in respect to the effect of orientation there is a qualitative agreement with earlier work. The initial permeability is about 175. The maximum permeability occurs at a field intensity of about 0·8 gauss. N. Akuloff observed that the remanence and hysteresis loss with single crystals can be expressed as a function of the magnetization, and are not affected by mechanical stresses, but L. W. McKeehan and co-workers do not agree with this statement.

According to T. D. Yensen, the values given by different investigators for the magnetic permeability of the purest available forms of "iron" have risen in a remarkable way, from H. A. Rowland's 2,500 obtained in 1873, to his own value of 61,000 obtained in 1928. His summary of the results is given in Table XLIV.

TABLE XLIV.—THE MAGNETIC PERMEABILITY OF "IRON."

Material	Max. permeability	Permeability H (gilberts per cm.)			B=10,000		Coercive (gilberts per cm.)	Hysteresis loss (ergs per c.c. per cycle)	Authority
		0	0·01	1·0	0·5	1·0			
Wrought iron	2,500	-		-	-		-	-	H. A. Rowland (1873)
,,	2,600	-			-	-	-	3,000	J. A. Ewing (1885)
Swedish iron	2,600	-	-	-	1,000	2,000	0·92	2,700	W. F. Barrett (1900)
Wrought iron	8,350	-				-	0·50	c. 1,500	E. Gumlich, E. Schmidt, (1901)
Elect. iron—annealed	11,000	- -			-		- -	-	E. M. Terry (1910)
Iron (0·4 per cent. Si)	11,600	-	—	—	—	-	c. 0·45	c. 1,400	E. Gumlich, P. Goerens (1912)
Elect. iron—annealed	11,500	—		-	11,200	9,600	- -	1,400	M. Breslauer (1913)
Elect. iron—vac. fused	19,000	—	-	- - -	18,800	12,500	c. 0·22	810	T. D. Yensen (1914)
,,	25,800	-	-	- -	23,600	14,000	0·20	660	T. D. Yensen (1915)
Elect. iron—vac. fused (0·15 per cent. Si)	50,000	- -	-	- -	27,000	14,500	0·09	290	T. D. Yensen (1915)
,,	41,500	-	-	1,700	27,000	14,600	0·17	500	T. D. Yensen (1920)
,,	61,000	1,150	2,600	46,600	28,600	15,500	0·09	300	T. D. Yensen (1928)
Armco iron	7,000	250	260	320	1,000	4,300	0·72	2,100	H. D. Arnold, G. W. Elmen (1920)

Values greater than $\mu=40{,}000$ were obtained by using electrolytic iron previously fused in vacuo, and by the addition of 0·15 per cent. of silicon, values exceeding $\mu=50{,}000$ were obtained. The effect of the silicon was attributed to its cleansing action in removing oxides. By extrapolating values for iron with traces of impurities, indications were obtained that iron will be obtained with an enormous permeability, and a zero hysteresis. Annealed, electrolytic iron with only 0·06 per cent. of carbon has been obtained with a permeability of 61,000, and a hysteresis loss of 300 ergs per c.c. per cycle. E. Wilson studied high permeability iron. R. L. Sanford and W. L. Cheney found the maximum induction and coercive force for Norwegian iron to be 15,900, and 5·0 respectively; for Bessemer steel, 15,900, and 9·0; for 0·85 per cent. carbon steel—annealed, 14,310, and 13·0; oil-quenched, 9380, and 53·0; and water-quenched, 9800, and 56·5.

C. Maurain examined the magnetic properties of iron deposited in a magnetic field; B. Speed and G. W. Elmen, the magnetic properties of powdered, electrolytic iron compressed into rods. R. Börnstein was unable to determine the relation between the density of iron and magnetization, but W. Trenkle observed that with compressed rods of iron powder and clay, with equal magnetizing forces, the magnetization and susceptibility of iron powder alone is always greater than that of a mixture of iron powder with a substance which cannot be magnetized. The magnetic saturation of iron powder is greater than that of the diluted powder. If the massive rod is distinguished from a rod composed of powder only by its density, the magnetization of iron falls with its density, and the magnetic saturation is less as the density is smaller. Hence, the magnetic force required to attain an eq. value of saturation is greater for iron alone than for diluted iron. Variations in density do not produce so great an effect on the course of magnetization, as variations of the dimensions of the elliptical or cylindrical form of the rods. W. Köster discussed the influence of inclusions in iron and steel on the coercive force.

H. Trosien, and T. Spooner investigated the effect of a superposed alternating field on the hysteresis loss. M. von Moos and co-workers, and O. von Auwers did not find that the hysteresis losses in watts increased proportionally with grain-size; and if N denotes the number of grains per sq. mm., the loss in watts $=\frac{1}{3}aN+b$, where a and b are constants.

Vibration increases the magnetic susceptibility of iron, and reduces the retentiveness and hysteresis. Three centuries ago W. Gilbert showed that a bar of iron can be magnetized by hammering it while it is situated in the earth's magnetic force. According to J. A. Ewing, a bar of iron held vertically and subjected to no mechanical disturbance, acquires only a very feeble trace of magnetism owing to the weakness of the vertical component of the earth's magnetism, but if sharply tapped, it becomes a fairly strong magnet, which persists after the bar has been withdrawn from the field, until it is expelled by further tapping or by the application of a moderately strong magnetic force of opposite sign. The magnetism acquired by an iron ship in building, and that acquired by the shock of rupture when iron or steel is broken in the testing machine are also examples of the phenomenon. Soft, annealed iron is most susceptible to the vibration, so that a gentle rubbing will impart magnetism to soft iron in the earth's magnetic field, or remove much of the residual magnetism left when a strong magnetizing force has ceased to act. The magnetic effects of hysteresis almost entirely disappear from soft iron if the piece be gently tapped during the application and removal of the magnetizing force. This subject was further investigated by W. Scoresby, E. Warburg, E. Wiedemann, G. Wiedemann, M. L. Frankenheim, L. Külp, M. Otto, R. Jouaust, G. Mars, C. Fromme, F. G. A. Berson, W. Brown, H. and F. Streintz, E. Villari, E. Fossati, J. A. Ewing, J. A. Ewing and H. G. Klaassen, J. Hopkinson and E. Wilson, G. Henrard, and E. D. Campbell and G. W. Whitney. H. Gewecke studied the effect of temp. on the retentiveness.

H. Tomlinson examined the effect of temp. and other conditions on the constants a and b in the relation $B=aH+bH^2$, where a denotes the initial permeability. The dissipation of energy depends on the value of b; and he found that the internal friction in any complete cycle may be decreased by repeating the cycle so that the molecules appear as if they are *accommodated* to the process. The accommodation of freshly annealed iron can be largely aided by repeatedly raising the temp. of the metal to 100°, and then allowing it to cool. The accommodation is disturbed by slight mechanical shocks, small changes of temp., or by magnetization beyond certain limits. Under these influences, the internal friction or viscosity may for a time, or even permanently, be considerably increased. The values of a and b are temporarily increased when the temp. is raised from 0° to 100°.

L. Tonks found that the susceptibility decreases with increasing frequency; the hysteresis angle tends to increase with frequency, and for a given frequency reaches a maximum for I at about 500; whilst the hysteresis energy loss per cycle, E, increases with frequency for constant magnetic intensity, and decreases for constant field. The exponent, a, in the equation $E=AH^a$ increases from 2·9 to 3·37 as the frequency is increased from 52,000 to 172,000 cycles per second. The subject was studied by W. E. Sumpner, M. MacLaren, N. H. Williams, S. W. J. Smith and J. Guild, B. Wedensky, B. Wedensky and K. Theodortschik, G. R. Wait, E. F. W. Alexanderson, J. Zenneck, and K. Kreielsheimer.

W. Gilbert observed that when an iron needle is red-hot, it is not attracted by the loadstone, but it is again attracted when the needle has cooled—*vide supra*, allotropes of iron. The phenomenon was also observed by J. Canton, R. Boyle, P. Erman, G. G. Hallström, H. B. de Saussure, P. Barlow and C. Bonnycastle, M. Mauritius, W. Ritchie, T. J. Seebeck, M. Faraday, E. Becquerel, T. Cavallo, A. Brugmans, and C. Matteucci. C. A. Coulomb studied the period of vibration of a heated magnetic needle in a field of known intensity. S. H. Christie noticed that when a magnet is heated, a sensible loss of magnetism occurs at about 38°; that the diminution of magnetic moment is not a linear function of the temp. because the rate of change increases with the temp., and that the moment of the magnet is increased, cooled by a freezing mixture, but returns to its original value when the original temp. is restored. H. A. Rowland found that the magnetic susceptibility of iron for small fields is greater at high temp. than at low ones, while for large fields, the reverse is true. C. Baur found that the rate of increase of permeability is greater for high than for low temp., while as a critical temp. is approached, the permeability decreases rapidly for strong and weak magnetic fields and finally approaches unity. R. Pictet found that with a compound horseshoe magnet, the strength of the magnetic attraction was 57·31 grms. at 30°; 61·04 grms. at 0°; 68·15 grms. at −50°; and 75·80 grms. at −100°. J. R. Ashworth found that when a magnet is heated to $\theta°$, and cooled, the relation of the intensity of magnetization, I, to temp. is represented by $I=I_0(1+a\theta)$, where the coeff. a is negative; but with drawn wire, a may be positive so that the magnet increases in magnetization as the temp. rises. The coeff. is positive only when the wire is in the commercial drawn state, for it becomes negative when the wire is annealed, or glass-hard. H. M. Loomis, and C. C. Trowbridge discussed the magnetic permeability at low temp.

The permeability was further investigated by W. Arkadieff, J. R. Ashworth, T. Berglund and A. Johansson, F. G. A. Berson, H. E. J. G. du Bois, R. Cazaud, H. le Chatelier, O. Claus, E. H. Crapper, E. Czerlinsky, L. Dufour, L. Dumas, E. Dumont, T. A. Edison, S. Evershed, F. P. Fahy, M. Faraday, L. Fraichet, C. Fromme, R. Gans, J. M. Gaugain, J. E. F. Gordon and W. Newall, J. Greger, K. W. Grigoroff, C. E. Guillaume, E. Gumlich, C. Hansteen, J. von Harlem, E. P. Harrison, S. Hilpert, K. A. Holmgren, K. Honda, K. Honda and S. Shimizu, K. Honda and Y. Ogura, J. Hopkinson, P. Joubin, G. Kapp, W. Kreielsheimer, A. T. Kupffer, J. Lamont, P. H. Ledeboer, F. Lydall and A. N. S. Pockington, N. N. Malov, H. Nathusius, R. A. Newall, F. Ollendorff, H. K. Onnes and A. Perrier, F. Osmond, A. Perkins, H. F. Parshall, E. Piola, D. Radovanovitch, P. Riess and L. Moser, A. W. Rücker, R. L. Sanford, W. Schneider, E. H. Schulz and W. Jonge, T. Schwedoff, W. Scoresby, J. B. Seth and co-workers, C. Shenfer, S. W. J. Smith and co-workers, F. Stäblein, A. F. Stogoff and E. I. Peltz, E. Take, H. Tomlinson, J. Trowbridge, C. R. Underhill, K. Volkova, A. Wassmuth, P. Weiss and J. Kunz, P. Weiss and H. K. Onnes, F. Wever and P. Giani, G. Wiedemann, M. Wien, L. R. Wilberforce, S. R. Williams, R. L. Wills, H. Wilde, W. Wolman and H. Kaden, and W. R. Wright, etc.

J. Hopkinson found that for small fields—say, 3 dynes—with wrought iron, a rapid rise of permeability begins at about 600°, reaches a maximum at 775°, and falls abruptly to unity at 785°; while for large fields, the permeability remained practically constant up to 600°, and then fell rapidly to unity. Mild steel behaved in a similar manner except that the permeability had a smaller maximum, and became unity at 735°; whilst for hard steel, the lowering of the maximum was more pronounced, and disappeared at 690°. During the cooling, the magnetism of wrought iron reappeared at practically the same temp. as that at which it disappeared, but with steels there was a marked lag which increased with the carbon-content. D. K. Morris observed that annealed Swedish iron gave temperature-permeability curves with a distinct minimum near 550°, and that this result was not obtained with charcoal iron. R. L. Wills observed that the maximum permeability occurs with weaker fields as the temp. is raised, and that the relation is nearly linear. With alloys, as the proportion of iron decreases, the difference of temp. between the disappearance and reappearance of magnetism is increased. W. del Regno, A. Regner, J. G. Gray and H. Higgins, F. Osmond, C. E. Guillaume, and E. Dumont also studied the subject with alloy steels. According to J. A. Fleming and J. Dewar, the permeability of annealed Swedish iron for all fields is less at low temp., while for un-annealed and hardened iron, it increases as the temp. is lowered. T. Claud observed that a reduction of the temp. lowered the hysteresis and permeability. K. Honda and S. Shimizu observed that the permeability and hysteresis loss in liquid air decreased for small fields, but increased for large ones. C. W. Waggoner obtained similar results for low-carbon iron. J. A. Fleming observed that annealed, low-carbon iron has an increased permeability for all fields at low temp., while in liquid air, annealed high-carbon steel has a smaller permeability. In a broad way, it appears as if a low temp. decreases the permeability of iron with a large proportion of carbon, and an opposite effect is produced with iron having a small percentage of carbon. J. Stauber found a lowering of the temp. diminished the hysteresis loss of these steels, but with higher magnetizing fields 30 gauss—both permeability and hysteresis-loss increased with a decrease of temp. C. Barus and V. Strouhal observed that the prolonged action of steam on magnets reduces their magnetic power very considerably; but if re-magnetized, they are less sensitive to deterioration from heat and vibrations. R. Forrer and J. Schneider found that the magnetization of iron annealed at 200° to 400° and at 450° to 900° is different, and, in consequence, they supposed that there are two allotropes, both of which are stable at ordinary temp.

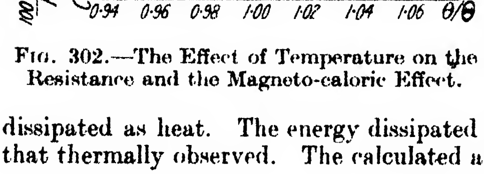


FIG. 302.—The Effect of Temperature on the Resistance and the Magneto-caloric Effect.

W. B. Ellwood studied the change of temp. which occurs during magnetization. F. Bitter also studied the magneto-caloric effect. K. Honda and co-workers found for the heat evolved during magnetization, the net energy of magnetization is less than 50 per cent. of the total energy, and the greater part of the applied energy is dissipated as heat. The energy dissipated on magnetization nearly coincides with that thermally observed. The calculated and observed data are:

	Calculated total energy of magnetization (ergs)	Calculated loss of energy on magnetization (ergs)	Observed evolution of heat (ergs)	Calculated energy stored by magnetization (ergs)
Carbon steel . . .	$4·6 \times 10^4$	$2·38 \times 10^4$	$2·2 \times 10^4$	$2·23 \times 10^4$
Tungsten steel . .	$8·73 \times 10^4$	$5·31 \times 10^4$	$4·1 \times 10^4$	$3·43 \times 10^4$
Magnet steel . . .	$20·7 \times 10^4$	$13·2 \times 10^4$	$15·0 \times 10^4$	$7·50 \times 10^4$

H. H. Potter measured the magneto-caloric effect as a function of temp. The quantity is represented as a product of the sp. ht., *c*, and the rise of temp. The results for fields of 7000 gauss are indicated in Fig. 302, along with the effect of temp. on the change in the resistance produced by a magnetic field of 7000 gauss. Θ denotes the Curie temp., 1050° K. The changes in resistance are proportional to changes in magnetic energy.

M. B. Moir found that the magnetic quality of steel and cast iron improves as the temp. rises from 150° to 190°. The subject was studied by F. Robin,

S. W. J. Smith and F. Guild, and L. Néel. P. Curie studied the variation in the magnetic properties of diamagnetic, paramagnetic, and ferromagnetic substances for temp. ranging up to 1370°. Diamagnetic water, quartz, and potassium nitrate kept the same magnetic susceptibility over a wide range of temp., whilst the susceptibility of bismuth steadily falls as the temp. rises to the m.p.; it drops abruptly at the m.p., but the susceptibility of the molten metal remains independent of a subsequent rise of temp. The susceptibility of paramagnetic substances like oxygen falls as the temp. rises, so that the susceptibility between 20° and 450° varies inversely as the absolute temp. According to **Curie's law,** the product of the magnetic susceptibility and the absolute temp. over this range is nearly constant, and this value is called **Curie's constant.** With ferromagnetic substances like iron, the case is not the same. The results with different field-strengths, H, are summarized in Fig. 303. The curve for the intensity of magnetization for $H=25$ is nearly parallel with the temp. axis up to about 550°, but when $H=100$, the intensity of magnetization falls steadily as the temp. rises, and both begin to drop very rapidly as the temp. reaches 750°, the so-called *Curie point*—*i.e.* the temp. at which the metal passes from the ferromagnetic to the paramagnetic state—and at 800° the magnetic intensity is very small. It is therefore necessary to magnify the ordinate scale about a thousand times in order to show the results graphically. This has been done in Fig. 303. At A, 930°, the slope of the curve decreases, and is very slight up to B, 1280°, where all at once the intensity of magnetization becomes 50 per cent. greater. After this the curve has a downward slope to C. At about 750°, ferromagnetic iron changes continuously into a paramagnetic substance; the corresponding change with magnetite is 530°, and with nickel 340°. The facts can be interpreted a different way by plotting the specific susceptibility against temp., as has been done in Fig. 304. The breaks in the curves correspond with the change from α-iron to β-iron at 678°, when the iron ceases to be strongly magnetic; as the temp. rises farther, the susceptibility increases, then falls rapidly to 920° when there is a change from β-iron to γ-iron; the decrease in the susceptibility with rise of temp. is very small up to about 1400°, when there is an abrupt rise as γ-iron changes into δ-iron; thereafter there is a gentle decline in the susceptibility. P. Dejean, R. B. Fehr, and N. Crane studied the transformations of iron at the Curie point. R. Forrer said that the two Curie points observed with ferromagnetic metals represent two different properties. One can be attributed to spontaneous orientation of the elementary magnets, and the other to hysteresis. Three temperature regions can be distinguished for ferromagnetic metals. In the first, at low temp., spontaneous orientation and hysteresis occur together. In the second, between the two Curie points, only one of these conditions is met with. In the normal case it is hysteresis (*e.g.* nickel, iron, cobalt, etc.), otherwise it is spontaneous orientation (*e.g.* the ferro-cobalts). In the third region neither of these properties is found. For ferromagnetic magnetization the

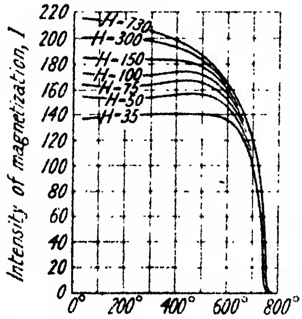


FIG. 303.—The Effect of Temperature on the Magnetization of Iron.

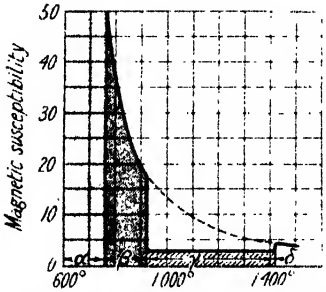


FIG. 304.—The Effect of Temperature on the Magnetic Susceptibility of Iron.

two properties are necessary. M. Faraday suggested that all metals might be ferromagnetic at low enough temp., and that it happens with iron and nickel that the transformation temp. is higher than the ordinary temp. of the atmosphere.

By plotting the relation between the intensity of magnetization and field-strength at different temp., P. Curie showed that as near the Curie point as 740·5°, there is a considerable rise in the intensity of magnetization as the field-strength increases; and a few degrees rise of temp., say, to 744·2°, reduces the intensity of magnetization to about half its value at 740·5° for, say, $H=320$; while the intensity at 820° is too small to be represented on the diagram. The line is curved at 740·5°, and is linear at 749·9° and upwards. P. Curie emphasized the analogy in the form of the curves connecting, on the one hand, the density and temp. of a gas near its critical state, and on the other, the intensity of magnetization and temp. of iron near the critical temp. Compare Figs. 303 and 304. R. Ruer, and R. Ruer and K. Bode gave 769° for the temp. of magnetic transformation. K. Honda found that the critical point of carbon steels is not affected by the intensity of the magnetic field; and L. H. Adams and J. W. Green, that it is not affected by pressure. P. Dejean compared the results obtained with a cylindrical bar with those of a similar bar composed of 120 small cylinders. S. Hilpert considered that it is not necessary to assume the formation of β-iron between 700° and 760° to account for the magnetic and sp. ht. anomalies at this temp. The change may be the result of an absorption of energy which attends the breaking up of the polar arrangement of the magnetic molecules by their more energetic vibration at high temp. E. Dussler measured the dependence of the magnetization of crystals of iron on temp. along both the diagonal and tetragonal axes between the temp. of liquid air and the Curie point. At all temp. the B-H curve is initially linear and inflects suddenly, slowly attaining saturation. The linear portion of this curve is independent of temp., but the higher the temperature the smaller is the field at which saturation is attained and the lower is the saturation magnetization. The variation with temp. of the magnetization at the point of inflexion and the saturation value both follow an exponential law.

J. R. Ashworth, following up a suggestion of P. Curie, developed a relation between magnetism and temp. analogous to J. D. van der Waals' relation between the press. and temp. of gaseous and liquid fluids—**1**. 13, 4. If H denotes the magnetic field-strength; I, the intensity of magnetization; I_0, the maximum intensity of magnetization; $a'I_0^2$, the maximum intrinsic field; R, the reciprocal of Curie's constant in vol. units; and T, the absolute temp., then J. R. Ashworth's equation for ferromagnetic substances has the form $(H+a'I^2)\left(\frac{1}{I}-\frac{1}{I_0}\right)=R'T$, which is based on $(p+aD^2)\left(\frac{1}{D}-\frac{1}{D_0}\right)=RT$, where p, D, and T respectively denote the press., density, and absolute temp. of the fluid, and a, D_0 and R are constants. For iron, the constants are $(H+7{\cdot}6I^2)(I^{-1}-0{\cdot}0_35935)=3{\cdot}56T$. As with the equation of J. D. van der Waals, constants may be calculated for the critical state when $T_c=785°+273°$. The subject was further discussed by W. Peddie. K. Honda and S. Kusakabe studied the effect on the magnetization of temp. near the critical point; and observations were made by L. F. Bates, T. Spooner, and S. Wologdine. R. H. Fowler and P. Kapitza studied the relation between magneto-striction and the Curie point. H. G. Movius and H. Scott noted the similarity of the magnetic transformations of ferrite and cementite.

Observations on electrolytic iron were made by A. L. Holz, J. Stauber, M. Otto, W. Leick, and K. Schild. W. Leick found the results with iron deposited from soln. of different salts to be about the same, but E. M. Terry observed that differences exist for small fields and vanish for fields over 100 dynes. After annealing at 1000°, the samples become practically the same for all fields. Discontinuities in the magnetic properties were found by D. K. Morris to occur at 150°; by C. Maurain, at 180° and 300°; by W. H. Dearden and C. Benedicks, at 120°;

J. H. Andrew and co-workers, between 50° and 150°; F. C. Thompson and E. Whitehead, 160° to 200°; and by S. R. Roget, at 135°. K. Honda, and S. W. J. Smith found a change on heating with cast iron and high-carbon steel at about 160°, and it was completed at 215°; and on cooling, the change starts at 215°, and finishes about 160°. The magnitude of this change is roughly proportional to the amount of free cementite present. K. Honda also observed a thermal change between 130° and 215°. The actual temp. varied with the strength of the magnetizing field.

E. M. Terry's magnetization curves, obtained with different field-strengths, between —190° and about 780°, for un-annealed electrolytic iron, and for the iron annealed at 780°, are shown in Fig. 305. E. M. Terry's values for the permeabilities are shown in Fig. 306. There is a sudden rise in the permeability for low fields just before the α-iron is transformed into β-iron. The highest value for the permeability was 11,000 with a field of $H=0{\cdot}5$ dyne. H. Wilde said that the magnetism of magnetic substances decreases with a rise of temp., and that the apparent increase which may occur is due to a surface resistance which may disappear by raising the temp., by increasing the magnetizing force, or by decreasing the mass of the substance. D. K. Morris obtained a maximum of 14,600 for $H=0{\cdot}2$ dyne with Swedish iron; R. L. Wills, 17,200 for $H=0{\cdot}172$ dyne with wrought iron. The effect of annealing was studied by H. Kamps, and G. Dillner and A. F. Enström.

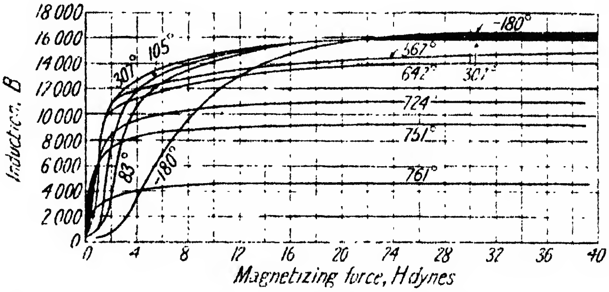


FIG. 305.—Magnetization Curves for Annealed Electrolytic Iron at Different Temperatures.

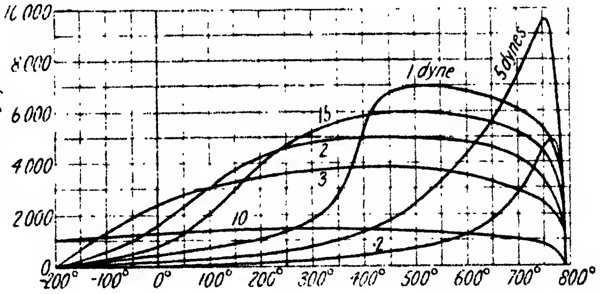


FIG. 306.—The Effect of Temperature on the Permeability of Annealed Electrolytic Iron.

D. K. Morris observed three maxima before the critical point is reached, and these correspond approximately with the breaks in the cooling curve observed by W. C. Roberts-Austen at 250°, 533°, and 766°. No sign of a depression in the temperature-permeability curves such as was obtained by D. K. Morris for wrought iron, at 550°, with all except the strongest fields, was observed. F. Osmond attributed this to a lowering of the temp. of transformation from α- to β-iron. Since E. M. Terry did not observe the effect with electrolytic iron, the phenomenon is not a characteristic of iron, but rather of iron associated with impurities. The effect of annealing is to increase the maximum permeability about 50 per cent., whilst for small fields, the increase is many-fold, Fig. 306. For example:

	23°	780°	1000°	1100°	1200°	1300°
Maximum permeability .	1,040	3,070	9,080	11,000	8,750	7,120

C. C. Duell tried to explain the drop in magnetization of cementite steels in the range from 150° to 220°, by assuming that carbon is soluble in α-iron but that the carbide is not, and that the drop in magnetism is due to certain atoms of free carbon going into soln. as carbide. The cementite line *ES* can be extended until it intersects the zero carbon line at *X*, Fig. 307, which is near 220°. This is taken to be the limiting point of the solubility of carbon in iron, so that near this temp. carbon can go into soln., but carbide cannot. The second, singular point on the magnetic curve at 300° marks the formation of the carbide. The carbon in martensite exists as carbon and not carbide ; and the formation of iron carbide, which begins at about 300°, corresponds with the formation of troostite from martensite. The presence of alloying elements causes the A_3-line to occur at progressively higher or lower temp., so that in the absence of carbide, the continued addition of carbon causes the A_3-line to change with progressively lower temp. along the line *GSY*, Fig. 307. G. Hannack found that with tungsten steels the remanence, and maximum induction decrease as the percentage of carbon increases, whilst the coercive force increases. S. W. J. Smith and co-workers found that the residual moment of a magnetized rod of annealed steel is reversed when the temp. is raised to 180°. The effect occurs only with iron containing the laminated ferrite–cementite eutectoid. R. L. Sanford observed that the reluctivity of homogeneous iron is a linear function of the magnetizing force, but the linear relationship does not apply when a tension or stress is applied to the wire. H. Kühlewein studied the magnetic after-effect.

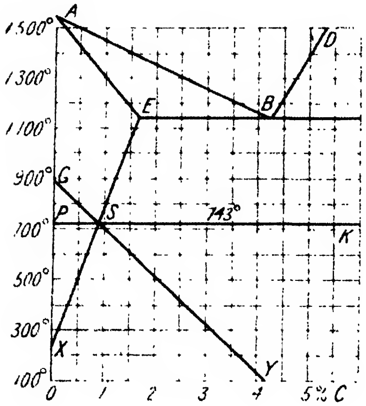


Fig. 307.—Hypothetical Course of the Carbon and Cementite Solubility Curves.

G. J. Sizoo found that increasing the grain-size of electrolytic iron decreases the coercive force and the work of hysteresis, but increases the maximum permeability, whilst the remanence remains constant. Some results are indicated in Table XLV. O. von Auwers found that the grain-size affects the coercive force, remanence, and permeability, but not the saturation value and sp. resistance. The effect of grain-size is less marked after heating in hydrogen, and still less by heating in vacuo. The influence of grain-size on the magnetic properties is secondary in nature, being dependent on surface contamination by oxides and carbides. W. Köster found that the size and arrangement of finely-divided particles in ferromagnetic alloys have a considerable influence on the magnetic properties.

Table XLV.—The Effect of Grain-size on the Magnetic Properties of Electrolytic Iron.

Mean diam. of crystals in mm.	Coercive force in gauss	Remanence in gauss	Maximum permeability	Hysteresis work $B_{\max.}$ = 10,000 ergs. per c.cm.
11	0·388	9460	8050	1485
7	0·400	9360	7680	1542
6·3	0·376	9460	8200	1480
2·7	0·407	9430	8050	1475
1·2	0·428	9450	7300	1710
0·7	0·462	9460	7550	1750
0·6	0·465	9360	6970	1740
0·3	0·515	9300	6850	1780
0·1	0·794	8050	4090	5200

G. Wiedemann showed that the first effect of a change of temp. on the magnetism of iron and steel is not reversible. With residual magnetism, a cyclic process of heating and cooling, or of cooling and heating, reduces the magnetism. Observations in this direction were made by H. I. Wild, M. Mauritius, O. Claus, O. Unverdorben, G. Claude, A. T. Kupffer, G. Poloni, J. M. Gaugain, F. G. A. Berson, C. Baur, and L. Favé. According to J. A. Ewing, if the magnetizing force of iron is maintained during a cyclic process of heating and cooling, or of cooling and heating, there is an increase of magnetism. In both cases, in general, after many repetitions of the changes of temp., the change of magnetism becomes cyclic. In the earliest stages there appears to be, as J. A. Ewing expresses it, a progressive shaking in of magnetism if that is induced, and a progressive shaking out of magnetism if that is residual. The phenomenon is often conspicuous in the first cycle, and it can often be traced in the second or even later cycles. By repeating the cycle of temp. changes often enough, these progressive changes disappear, and the effects of heating and cooling—magnetizing force constant—are reversible. J. A. Ewing found that no hysteresis occurred in the changes which were observed with moderate variations of temp., but when the range of temp. includes the critical region where magnetization disappears on heating and reappears on cooling, a marked hysteresis occurs. The disappearance and reappearance of magnetization connected with $\alpha\beta$-change do not occur at the same temp. This is particularly the case with the alloy steels (*q.v.*) observed by J. Hopkinson, and others. D. K. Morris found that the hysteresis of the *BH*-curve becomes enormously reduced as the temp. approaches the chief critical point, and the hysteresis tends to disappear. Thus, with a sample of iron annealed at 1150°, with cycles of magnetization between the limits $B=4550$, the hysteresis losses, in ergs per cm. cube per cycle, were:

	18°	137·5°	249°	352°	457°	634°	695°	764·5°
Hysteresis loss .	613	555	508	475	379	264	178	81

In addition to the changes just indicated, heating produces a slow deterioration in the magnetic properties, reducing the permeability, and raising the hysteresis. The action is very slow at comparatively low temp. The heat generated in a transformer by currents in the coils, and by hysteresis in the core makes the temp. in the transformer higher than that of its surroundings, and thus reduces the efficiency of transformers. G. W. Partridge studied the effects; and J. A. Ewing found that the results are not due to the repeated reversals of magnetism; nor are they due to a kind of fatigue produced by repeated reversals of mechanical strain. W. M. Mordey observed that the increased hysteresis is solely due to the prolonged heating; and S. R. Roget confirmed this by observations on the effect of prolonged exposure at temp. between 50° and 700°. A few weeks' exposure at 50° produces an appreciable effect in raising the hysteresis, and lowering the permeability. K. Daeves found the losses in dynamo and transformer sheets increase regularly by 0·1 watt-kgrm. for every 0·04 per cent. of carbon for steels with 0·04 to 0·11 per cent. of carbon. As silicon rises from 3·7 to 4·2 per cent., the loss diminishes by 0·05 watt-kgrm. for every 0·04 per cent. of silicon, but increases slightly with higher proportions of silicon. Phosphorus up to 0·02 per cent. slightly increases the loss, but beyond that point there is an improvement. Manganese between 0·05 and 0·3 per cent. has no perceptible influence.

According to E. M. Terry, the temp. of transformation from the ferromagnetic to the paramagnetic state is near 785°, which is in agreement with the data for the transition temp. of α- to β-iron (*q.v.*). J. Hopkinson gave 786° for soft iron with 0·01 per cent. of carbon; 734° for mild steel with 0·126 per cent. of carbon; and 695° for hard steel with 0·962 per cent. of carbon. D. K. Morris gave 780° for a sample with 0·08 per cent. of carbon; R. Ruer and F. Goerens gave 769°; E. Gumlich, 765°; T. Ishiwara, 780°; P. Weiss and G. Föex, 775°; while for cementite, K. Honda and H. Takagi gave 215° for temp. of magnetic transformation. The magnetic transformation of the iron-carbon alloys were studied by G. Rümelin and R. Maire.

Reverting to P. Curie's law that the magnetic susceptibility varies inversely as the absolute temp., χI=constant, P. Weiss obtained a relation between the intensity of magnetization, and inferred that in the temp. immediately above that of the magnetic transformation, Curie's point, the susceptibility should be inversely proportional to the excess of temp. above the transformation point. P. Weiss and H. K. Onnes calculated values for the magnetic moment per gram-atom, which P. Weiss called the *gram-magneton*; and this magnitude, when divided by Avogadro's number, gives the moment of what he regarded as the ultimate magnetic corpuscle which he called the *magneton*. The magneton is supposed to play a *rôle* in magnetism, like that played by the electron for electricity. The number of magnetons per molecule is related to Curie's constant in a simple manner. From the results of P. Pascal, P. Weiss and G. Föex, O. Liebknecht and A. P. Wills, and E. Feytis, it was found that the calculated number of magnetons per molecule rarely depart by more than 1 or 2 per cent. from the integral values required by the theory. The subject was studied by J. Kunz, B. Cabrera, W. W. Stifler, etc. K. Honda and co-workers, however, found that Curie's law is not general, and consequently P. Weiss' magnetism is open to question. H. K. Onnes and co-workers found that the relation χT=constant is in some cases valid down to the temp. of liquid nitrogen, and below this temp., the constant continually decreases in value. In some cases, the constant decreases continuously from room temp. downwards, so that the relation $\chi(T+\delta)$=constant holds down to the temp. of liquid nitrogen, but not at lower temp. Again, the susceptibility may change little with temp., and between the temp. of liquid nitrogen and liquid hydrogen, is almost independent of temp.

E. M. Terry found that the magnetic susceptibility of electrolytic β-iron, between 780° and 920°, follows Curie's law only approximately, because the curve showing the relation between the reciprocal of the susceptibility and temp. is not a straight line, but concave upwards. Curie's law is not even approximately obeyed in the γ-region, for there is an interval of nearly 500° throughout which the susceptibility remains almost constant. At 1407°, there is an abrupt increase as γ-iron passes into the δ-form. Throughout the δ-region, up to the m.p., 1530°, the susceptibility decreases almost linearly with temp.; the susceptibility shows a marked decrease on melting, so that the molten iron has values approximately corresponding to an extension of the curve for γ-iron. The susceptibility curve for iron passing through the A_3-arrest shows a marked hysteresis with the A_3-arrest. The steepest part of the curve occurs at 918° on a rising and at 903° on a falling temp. No real hysteresis was observed with the latter, but the return to γ-iron on the cooling curve is gradual, not abrupt. Observations on the Curie point were also made by T. Ishiwara, P. Weiss and G. Föex, K. Renger, D. Radovanovitch, K. E. Guthe, P. Curie, R. H. Fowler and P. Kapitza, R. Forrer, and W. Schmidt. As indicated above, the Curie point of cementite corresponds with the A_0-arrest, at about 220°. K. Honda and H. Endo found the magnetic susceptibility, χ, of cementite to be:

	800°	900°	1000°	1100°
χ . . .	$24{\cdot}3\times10^{-5}$	$24{\cdot}0\times10^{-6}$	$23{\cdot}7\times10^{-6}$	$23{\cdot}5\times10^{-6}$

According to K. Renger, the effect of field-strength, H gauss, on the transformation point, θ, is represented by $\theta=757+0{\cdot}14\sqrt{H}$,

H . . .	0	1,438	2,903	5,095	8,144	10,430	11,930
θ . . .	757°	762·0°	764·5°	767·0°	770·0°	771·5°	772·6°

C. Benedicks gave the results indicated in Table XLVI for the effect of chemical composition and heat-treatment on the magnetic properties of steels. C. Benedicks represented the effect of carbon on the intensity of magnetization, I, when ΣC denotes the carbon value as in the case of the electrical resistance (*q.v.*), by

$$I_{\max.}=1000\sqrt{5{\cdot}23-(\Sigma C+0{\cdot}59)^2}-710$$

E. Gumlich's results for the effect of carbon on the coercive force, in c.g.s. units,

TABLE XLVI.—THE EFFECT OF THE COMPOSITION OF STEEL ON ITS MAGNETIC PROPERTIES.

	Carbon (per cent.)	Intensity of magnetization		Coercive force, H_c	Remanence, R	Hysteresis loss, W	Hysteresis Coeff., η
		I mean for $H = 206{\cdot}2$					
Forged	0·08	1222	1455	1·8	26·2	13,400	0·0027
	0·45	1156	1376	10·9	140	52,200	0·0012
	0·55	1147	1366	12·9	161	54,000	0·0119
	0·90	1125	1339	17·5	216	73,000	0·0166
	1·20	1074	1278	17·5	215	71,400	0·0175
	1·35	1058	1260	18·7	231	73,000	0·0183
	1·50	1029	1225	17·6	213	65,400	0·0172
	1·70	954	1136	13·4	161	52,200	0·0155
Tempered	0·08	1239	1475	1·0	13·6	11,600	0·0023
	0·45	1074	1279	26·0	280	86,800	0·0210
	0·55	1048	1248	34·9	421	115,000	0·0293
	0·90	864	1029	45·4	380	115,200	0·0399
	1·07	716	852	48·3	321	100,200	0·0470
	1·14	640	762	50·2	289	93,900	0·0526
Annealed	0·08	1238	1473	1·1	14·4	8,300	0·0019
	0·45	1168	1390	5·5	76	34,500	0·0074
	0·55	1168	1390	6·9	95·5	37,800	0·0081
	0·90	1134	1349	9·9	136	47,500	0·0107
	1·20	1083	1289	11·7	160	56,800	0·0137
	1·35	1063	1265	12·5	171	57,900	0·0144
	1·50	1033	1230	10·9	145	50,900	0·0133
	1·70	962	1145	8·8	213	40,600	0·0119

are summarized in Fig. 308, and S. Curie's curve for the effect of carbon on the remanence or retentivity of steel is shown on the same diagram. A. W. Smith and co-workers found the minimum reluctance, the reciprocal of the maximum permeability is a linear function of the carbon-content to 0·8 per cent. for hardened steels, and for annealed steels it is somewhat greater. E. Maurer and K. Schroeter proposed estimating the austenitic content of hardened steel from the magnetic saturation capacity. The observations of the effect of the tempering temp. by J. H. Andrew and co-workers are summarized in Table XLVI. A. W. Smith and co-workers observed that the minimum reluctivity, *i.e.* the reciprocal of the maximum permeability, is a linear function of the carbon-content up to 0·8 per cent. for hardened steels, and for annealed steels the rate of increase is rather greater; and for annealed chromium steels, the value is a maximum at about 0·5 and a minimum at about 0·8 per cent. carbon. According to W. L. Cheney, the tempering of hardened iron-carbon alloys between 200° and 250° causes a rapid rise in the induction, which becomes less marked with increasing temp., eventually reaching a maximum and then decreasing. At the same time marked changes take place in the coercive force, especially for tempering temp. between 200° and 300°, when the greatest decrease occurs, and at 470°, where there is a sharp increase. In some cases two values are obtained for the saturation intensity of magnetization; this is shown by microscopical examination to be due to the presence of two constituents in the material. The maximum permeability of certain alloys shows great differences as compared with small differences in other properties, due to changes in the second stage of the process of magnetization. In the annealed alloys the steepness of

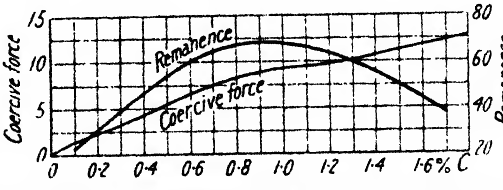


FIG. 308.—The Effect of Carbon on the Coercive Force of Steel.

the magnetization curves and the maximum permeability vary with the carbon-content. The intensity of magnetization has a double value for all carbon percentages below 1·5 per cent. and a triple value for the 1·55 per cent. carbon alloy, and decreases with the carbon-content. As a result of the investigation it is shown that any slight changes of structure produced by heat-treatment cause marked changes in the magnetic properties of iron-carbon alloys. P. Weiss and R. Forrer discussed the magnetic properties of cementite. M. Nakamura studied the effect of carbon and silicon on the magnetic properties of electric steel, and found that the permeability is increased as the proportion of carbon decreases. If the decrease is too great, the deoxidation of the steel is incomplete, and the permeability is decreased. With less than 0·12 per cent. carbon, the permeability is usually low. Silicon increases the permeability up to a certain limit dependent on the proportions of carbon and manganese, and it acts in virtue of its deoxidizing qualities. The permeability increases as the proportion of manganese decreases up to a certain limit, beyond which it becomes smaller.

O. von Auwers, T. D. Yensen, and G. J. Sizoo observed that with increasing grain-size, the coercive force, and hysteresis decrease, and the maximum permeability increases. The effect is also marked with the remanence. The relations between the magnetic properties and hardness have been the subject of investigations by J. Lamont, C. Ruths, J. M. Gaugain, C. Fromme, C. Baur, A. von Waltenhofen, T. Gray, A. Righi, W. Metcalf, R. Pictet, etc.; and the specific effects of the carburization of iron, by C. A. Coulomb, P. Barlow, J. Müller, H. Meyer, J. Jamin, A. von Walthofen, A. R. S. Trève, A. R. S. Trève and L. Durassier, C. R. Underhill, L. Holborn, W. Negbaur, J. Hopkinson, K. Zickler, J. A. Ewing and W. Low, J. C. Poggendorff, R. Pictet, G. B. Airy, L. M. Cheesman, W. Beetz, A. L. Holz, G. Ascoli, J. Trowbridge, G. Poloni, W. Metcalf, A. Righi, and C. Barus and V. Strouhal. T. Matsushita and K. Nagasawa found a maximum at about 400°. T. Matsushita measured the magnetic hardness or coercive force of quenched steels.

V. S. Messkin discussed the effect of cold-work on the magnetic properties of steel; and E. Gumlich and E. Volhardt, the influence of rolling on the magnetic properties. According to V. S. Messkin, the remanence of a plain carbon steel with 0·78 per cent. of carbon decreases considerably with light rolling, but increases again with heavier rolling; the maximum permeability changes similarly, but with a greater reduction than 30 per cent. it decreases again. The coercive force increases steadily during rolling, and attains about double its original value when the thickness has been reduced about 80·8 per cent.; with subsequent annealing, the coercive force decreases rapidly with rise of temp. up to 450°, and thereafter more slowly. The maximum remanence is obtained after annealing at 600°, and it is greater than before rolling. The cold deformation of steel produces on the magnetic qualities an effect similar to that obtained by quenching. P. Goerens studied the effect of heat-treatment on the remanence and permeability; and on the coercive force and hysteresis loss in ergs per cm. cube; and also on the effect of cold-work on the maximum permeability and coercive force of steels. According to E. Maurer, there is no perceptible difference in the magnetic properties of steels worked cold and at a blue-heat.

C. S. Yeh found that in the range of press. up to 12,000 kgrms. per sq. cm., the change of magnetization with a constant field, H, is linear. With a field range of 0 to 100 gauss, the press. coeff. of magnetization per unit vol. is negative for iron. The perceptible change of magnetization has a maximum of $-5·5$ per cent. per 1000 kgrms. per sq. cm. for $H=1·2$. The percentage change decreases rapidly on both sides of the maximum, and approaches the axis asymptotically for large values of H.

The observed press. coeff. for slightly carbonized iron are:

H . .	0·26	0·52	0·78	0·93	1·30	1·82	4·69	52·0
B . .	244	1048	1915	2800	5480	7050	11,200	18,760
dB/B_0 .	−1·30	−1·88	−2·66	−2·38	−1·89	−1·46	−0·73	−0·01

For purified iron, the temp. and press. coeff. are :

H		0·43	0·86	1·30	1·73	2·16	4·32
Temp. coeff.	$p=0$	+0·147	+0·232	+0·263	+0·126	+0·072	—
	$p=7050$	+0·177	+0·247	+0·264	+0·135	+0·79	—
Press. coeff.	25°	−3·25	−4·80	−5·51	−4·36	−3·14	−1·20
	100°	−0·99	−3·69	−5·39	−3·70	−2·61	−1·23

The results for iron with 0·10 per cent. of carbon are :

H	0·57	1·70	2·83	4·53	11·32	22·64	33·96
B	300	1920	4870	7640	12,210	15,000	16,170
dB/B_0	0·57	−1·59	−1·52	−1·06	−0·58	−0·25	−0·10

The results for iron with 0·30 per cent. of carbon are :

H	0·69	1·24	14·8	1·98	2·96	3·96	4·94
B	263	614	851	1588	3610	5510	7090
dB/B_0	−1·66	−1·80	−1·88	−2·05	−2·36	−2·02	−1·70

The percentage change of magnetization is thus very sensitive to the proportion of carbon present. The absolute value of the press. coeff. of magnetization per unit vol. is less at a higher temp. The retentivity of iron decreases under press. Observations were also made by H. Nagaoka and K. Honda, and F. C. Frisbie.

About 1847, C. Matteucci noticed an increase in the magnetism of an iron bar when it is pulled lengthwise ; G. Wertheim confirmed this ; and E. Villari observed that the character of this effect is reversed if the magnetization is strong enough. As a result, the effect of pull is to increase the magnetism of a weakly magnetized bar, and to reduce the magnetism of a strongly magnetized bar. The phenomenon is now called the **Villari reversal**, and it was rediscovered by Lord Kelvin about 1878. If the relation between the intensity of magnetization and the magnetizing force when no pull is applied, and again when the rod is under tension be plotted, Fig. 309, there will be a point where the two curves intersect. This point is called *Villari's critical point.* It corresponds with the field-strength at which the pull does not affect the intensity of magnetization. The subject was investigated by J. A. Ewing, who found that the effects of stress are, in general, much greater with metal hardened by mechanical work than with soft, annealed iron. Each curve, Fig. 309, for annealed iron lies at first higher and then lower than the curve for any greater load, corresponding with the fact that the presence of a load is favourable to magnetization when the intensity of magnetization is small, but unfavourable when it is great. A pulling load is unfavourable to residual magnetism left after a strong field has been applied, though it is favourable to the residual magnetism left after magnetization by a weak field. The influence of pull on residual magnetism is of the same kind as its influence on induced magnetism, showing the large effect which a moderate pull has in augmenting the susceptibility with respect to feeble magnetizing forces, and when the state approaches saturation, the presence of load is unfavourable to magnetization. Even with the weakest fields, the susceptibility is increased only when the load is moderate. Too great a load is prejudicial whether the magnetization be weak or strong. The upper lines of abscissæ, Fig. 309, refer to the upper three curves, and the lower abscissæ to the

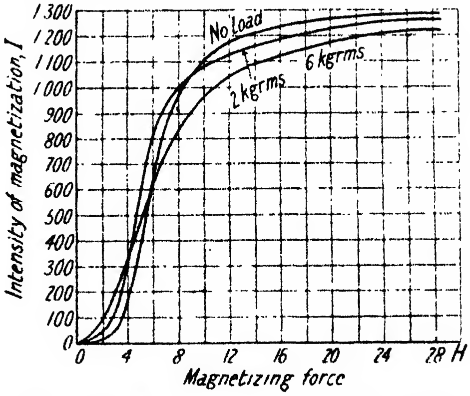


FIG. 309.—Magnetization of Annealed Iron while subjected to Longitudinal Pull.

lower three curves. J. B. Seth and co-workers followed the change in the intensity magnetization produced by stretching an iron wire in a weak magnetic field. The subject was studied by H. Tomlinson.

When the magnetizing force is kept constant, and the longitudinal pull is varied, the changes which occur in the intensity of magnetization are, in general, similar to those indicated in Fig. 309, but they are complicated by hysteresis effects. The initial effects of applying stress resemble those produced by vibration even though no vibration occurs during the loading, and they do not disappear when the stress is removed. Starting from *a*, Fig. 310, J. A. Ewing showed that a wire hardened by stretching, demagnetized, and exposed to a magnetizing force of 0·34 c.g.s. units has very little magnetization. The effects of applying and removing the load are illustrated by the dotted curve *abc*, but when the load is applied and removed a second time, the magnetic changes become nearly cyclic, as shown by the continuous lines in the same diagram. This shows that in the first loading, there is a progressive increase of magnetization superposed on a cyclic effect. If a stronger field is applied, the effects of the first loading are increased enormously, and after that, the magnetic changes are nearly cyclic. The effect of loading and unloading progressively decreases the residual magnetization and the cyclic changes are of the same general type as those which occur when the magnetization is excited by an external field. The subject was discussed by A. Heydweiller, L. Fraichet, K. Honda and S. Shimizu, H. Nagaoka and K. Honda, and C. Chree.

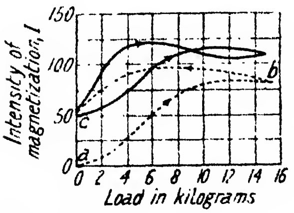


FIG. 310.—The Effect of Applying a Load to Magnetized Iron.

The hysteresis effects of magnetism with changes of load do not depend on the rate at which the load is applied, nor on the interval of time which elapses before the observations are made. After the condition obtained by the application of a load is reached, the magnetization does not appreciably alter. The effects of hysteresis disappear almost entirely when the test-piece is exposed to mechanical vibration or tapping during or after the changes of load. The repetition of loading with annealed iron produces a cyclic state in which there is less total magnetism than is the case with the hardened metal; a light loading will produce an increase, and unloading a decrease, of magnetism; with moderately heavy loads, these effects are reversed.

The stress-strain diagrams, previously considered, show the existence of reversible and irreversible molecular changes during the loading and unloading of an iron wire; the thermoelectric properties of iron under the influence of variations of pull, also show the existence of analogous molecular changes; while the loading and unloading of iron, within the elastic limit, before beginning magnetization, also affects the magnetic susceptibility, owing to the irreversible changes in the orientation of the molecules. These residual effects of past loads on the magnetic susceptibility exhibit hysteresis with regard to the loads which cause them; and the residual effects may be annulled by subjecting the piece to magnetization by reversals, and by tapping the piece smartly so as to cause vibration. For instance, J. A. Ewing found that if a magnetization curve be taken with iron wire subjected to a pull of 3 kgrms., and if, after complete demagnetization, the load be raised to 4 kgrms., and 1 kilogram be removed, and a second magnetization curve be taken, the two curves will be different in spite of the fact that the wire may have been previously subjected to many times that amount of load, so that it appeared to be mechanically in a stable state.

C. Matteucci showed that when a rod of soft iron, exposed to a longitudinal magnetizing force, is twisted, its magnetism is reduced by torsion in either direction. The subject was examined by M. Choron, G. Wertheim, E. Becquerel, C. A. Coulomb, H. Gerdien, H. Tomlinson, A. Banti, F. Braun, L. Zehnder, A. Campetti, C. Barus,

K. Schreber, F. J. Smith, H. Nagaoka, H. Nagaoka and K. Honda, H. Bouasse and A. Berthier, W. Brown, J. E. Pellet, E. Warburg, S. Meyer, G. Wiedemann, and Lord Kelvin. As with the effects of all stresses, there is an initial, irreversible effect which is revealed when the cycle of strain is repeated. This initial effect depends on the past history of the metal, but in soft iron the cyclic effect is such that twisting to either side reduces the induced magnetization, and untwisting increases it. Lord Kelvin found that the changes of magnetization under these conditions exhibit hysteresis. The changes in the magnetism induced in an iron wire by a constant magnetic field, as one end of the wire is twisted to and fro, while the other end is held fixed, ultimately assume the general form of Fig. 311. If the effects of hysteresis were eliminated by vibration, a single parabolic curve would appear with its vertex at the top of the diagram. Accordingly, in the absence of hysteresis, the influence of torsion in reducing the induced magnetism is indefinitely small for small angles of twist, and at first increases in proportion to the square of the twist.

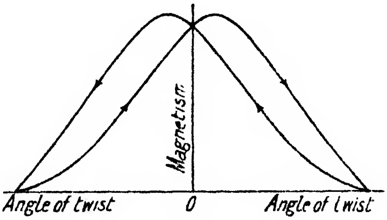


FIG. 311. -The Effect of Twist on the Magnetism of Iron.

Lord Kelvin showed that what he called an aelotropic quality is developed in the magnetic susceptibility of iron, for if the metal is subjected to longitudinal or transverse pull or push, the susceptibility will be greater along than it is across the lines of pull, or the susceptibility will be less along than it is across the lines of push, provided the magnetization is not strong enough to pass Villari's critical point. In a torsional strain, each portion of the twisted rod suffers a simple shearing stress which is made up of a pulling stress in a direction inclined at 45° to the direction of length, and an equal pushing stress inclined at 45° and at right-angles to the pulling stress. This produces a kind of helical magnetization in which there is a circular component superposed on the original longitudinal magnetization. The lines of magnetization no longer coincide in direction with the lines of magnetic force. The effect of a small angle of torsion on the longitudinal component of magnetization is small, but as the angle of torsion increases, the growth of the circular component reduces the longitudinal magnetization, for magnetization in one direction lessens the magnetization in other directions. The influence of magnetic aelotropy is always present with torsional stresses, although the effects may be masked by other influences *e.g.* hysteresis.

As shown by G. Wiedemann, and Lord Kelvin, longitudinal magnetization may be produced by twisting a circularly magnetized wire; and G. Wiedemann, and C. G. Knott observed that if an iron wire be circularly and longitudinally magnetized, it becomes torsionally strained or twisted although no external mechanical force has been employed. J. A. Ewing, D. E. Hughes, L. Zehnder, and H. Nagaoka found that there is a sudden development of circular magnetization when a longitudinally magnetized rod is suddenly twisted, or when a longitudinal magnetizing force is suddenly applied to a rod held in a state of torsion. The joint effects of pull and torsion were studied by H. Nagaoka, L. Zehnder, C. G. Knott, etc. The effect of magnetization on the bending of iron and steel was discussed by G. Wertheim, and C. M. Guillemin.

J. P. Joule said that the total volume of an iron rod is not altered by magnetization, and the subject was studied by G. Wertheim, H. Buff, H. Nagaoka, H. Nagaoka and E. T. Jones, E. T. Jones, H. Nagaoka and K. Honda, K. Honda and K. Kido, K. Honda and S. Shimizu, S. Shimizu and T. Tanakadate, I. Kruckenberg, P. McCorkle, L. W. McKeehan and co-workers, J. Orland, J. Orland and P. del Pulgar, P E. Shaw and S. C. Laws, C. Benedicks, F. C. Powell, J. H. Handley, J. R. Hobbie, S. R. Williams, S. R. Williams and O. Koppius, A. Schulze, A. Esau, G. Dietsch and W. Fricke, W. N. Bond, T. Hayasi, M. Kersten, P. Kapitza, P. Asteroth,

L. W. Austin, L. W. Austin and K. Guthe, W. L. Webster, W. Brown, R. A. Houstoun, M. Cantone, C. W. Burrows, G. Kirchhoff, H. von Helmholtz, S. Sano, I. Kolacek, S. J. Lochner, A. Heydweiller, R. Gans, H. Rensing, L. W. McKeehan, C. W. Heaps, C. G. Knott, A. de la Rive, W. Beetz, A. M. Mayer, W. F. Barrett, A. Righi, C. Chree, B. Rosing, A. Berget, A. Bock, P. I. Bachmetjeff, L. T. More, A. Schulze, B. B. Brackett, J. S. Stevens, E. Rhoads, G. A. Shakespear, C. Barus, E. van Aubel, D. O. S. Davies, L. Tieri, and J. C. McLennan.

It will be observed that in the **Joule effect,** when a magnetic (or ferromagnetic) field is produced along a ferromagnetic bar, the bar is lengthened or shortened in the direction of the field, according to the nature of the metal and the intensity of the induction; and conversely, a lengthening or shortening of the bar produces a variation in the intensity of the longitudinal magnetization. In **Wiedemann's effect,** a longitudinally magnetized, ferromagnetic bar is twisted when an electric current, which creates a transverse magnetic field, is passed along it; and conversely, in the **Matteucci effect,** when a longitudinally magnetized bar is twisted, an e.m.f. is produced along the bar.

C. G. Knott, and S. Bidwell found that the transverse contraction exceeds the longitudinal expansion, so that the total volume is reduced, δv—**magnetostriction**—thus, for tubes with H=50,125, and 250 c.g.s. units, the respective values of $\delta v \times 10^7$ were −5·9, −12·3, and −13·0. If the total volume is reduced by magnetization, the *specific gravity* will be increased. K. Honda and K. Kido found an expansion for the magnetostricton of iron with H over 370, and a contraction for smaller values of H, thus:

H	23·0	77·2	125·1	193·9	273·8	371·9	571·6
$\delta l/l \times 10^6$	1·70	3·03	2·54	1·77	0·68	−0·42	−1·68

The phenomenon was also studied by C. G. Knott and A. Shand, W. F. Barrett, A. M. Mayer, E. Piazzoli, A. Schulze, A. S. Kimball, A. Wassmuth, W. Fricke, R. Gans and J. von Harlem, and G. Hoffmann. K. Honda and S. Shimizu's observations for the change in length $\delta l/l \times 10^{-6}$ with variations of temp. are illustrated by Fig. 312. A. Schulze's results on the change in length of different kinds of iron and different heat-treatments are summarized in Fig. 313.

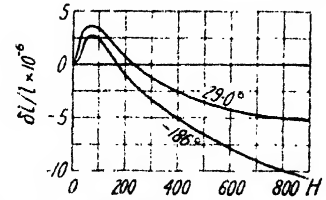


FIG. 312.—The Effect of Temperature on the Magnetostriction of Iron.

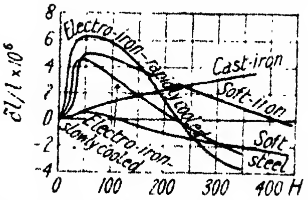


FIG. 313.—The Effect of Purity and Heat-treatment on the Magnetostriction of Iron.

K. Honda and T. Terada found the magnetostriction, or change of length with magnetization, $\delta l/l \times 10^{-6}$, with a tension of 1627 grms. per sq. mm., increases from −0·22 to 1·80 as H increases from 3·8 to 35·3, and it then decreases to −4·34 as H rises to 384; and with a tension of 5538 grms. per sq. mm., the change in length $\delta l/l \times 10^6$ decreases from −0·06 with H=3·2 to −6·58 with H=380. The change of elasticity, $\delta E/E \times 10^2$, is small, and with a load of 1627 grms. per sq. mm., it gradually increases with the field from 0·9 to 1·7 as H changes from 10 to 100, and it then falls to 1·4 as H changes to 350; while with a load of 4754 grms. per sq. mm., it changes from 0·4 to 0·8 as H changes from 10 to 350. The change in the coeff. of rigidity $\delta K/K \times 10^2$ with a load of 3113 grms. per sq. mm. is represented by −0·03 for H=24·5, 0·40 for H=146·2; and 0·25 for H=385. The change in Poisson's ratio, $\delta\sigma/\sigma \times 10^2$, is such that it passes from −2·2 for H=10 to −10·2 for H=350, when the load is 3270 grms. per sq. mm. The change of magnetization δl_i with longitudinal loading and δl_c with cyclic loading for loads in tension T grms. per sq. mm., is:

T	1562	3086	4648	6211	7777 grms. per sq. mm.
$H=1\cdot25$ δl_i	6·8	23·2	56·8	100·9	146·3
$H=1\cdot25$ δl_c	0·9	1·9	3·2	4·5	6·9
$H=366\cdot6$ δl_i	−2·7	−5·1	−8·0	−10·6	13·3

K. Honda and T. Terada also found that with a constant tension the magnetization increases rapidly in low fields and gradually approaches saturation. They also examined the effect with a constant twist, and with a combined twist and tension on the magnetization. In all cases the reciprocal nature of the changes of strains by magnetization and of the changes of magnetization by strain were established. For instance, magnetic elongation under constant tension and of magnetization under constant tension; of elongation by tension under a constant field, and the change of magnetization by tension under a constant field; of magnetic twisting under a constant couple, and magnetization under a constant twist; and of the change of rigidity under a constant field; and the change of magnetization by twist under a constant field. J. B. Seth and co-workers studied the effect of stretching on the intensity of magnetization of single crystals of iron. J. S. Rankin found that high-carbon steels show a smaller magnetostriction than soft carbon steels, but that the effect of hardening a steel by tensile overstrain increases the magnetostriction, though this change in extension does not depend simply on the amount of tensile extension. It is assumed, in agreement with W. L. Webster, that when a rod is overstrained, the axes of a large proportion of the constituent crystals veer into the direction of the longitudinal axes of the rod, and it is necessary only that a majority of the grains be so arranged to account for the increased magnetostriction. For N. Akuloff's observations with single crystals, *vide supra*.

G. W. Pierce studied the effects which occur when a magnetized rod has superposed on it an alternating axial magnetic field of a frequency in the neighbourhood of the natural mechanical frequency of the rod. The rod when under the influence of magnetostriction can be made to act like quartz crystals under the influence of piezoelectricity. If a ferromagnetic rod or tube is clamped so that it lies along the axis of a coil, the combination becomes an electrical vibrational instrument. This phase of the subject was studied by K. C. Black.

The magnetostriction of single crystals of iron was observed by W. Gerlach, E. Dussler and W. Gerlach, H. Kornfeld, G. S. Mahajani, and N. Akuloff. K. Honda and Y. Mashiyama found that in the (100)-plane, taken in the direction of the tetragonal axes (100), the longitudinal effect of the magnetic expansion is positive for all magnetizing fields; it increases at first rapidly, and afterwards slowly. The transverse effect is just the reverse of the longitudinal one. As the inclination of the direction of the tetragonal axis to the direction of the field increases, the longitudinal expansion in strong fields becomes less, and at an inclination of 15°, the expansion-field curve already shows an inconspicuous maximum at 200 gauss. At an inclination of 30°, the maximum is already attained at 80 gauss, and the decrease of expansion in stronger fields is considerable, the expansion changing into contraction at above 400 gauss. At an inclination of 45° (100), that is, in the direction of the digonal axis, only a small expansion is observable below 120 gauss, above which a marked contraction is noticed. The transverse effects are just the reverse of those of the longitudinal, except in the direction of 45°, in which a small initial contraction is not observable. The longitudinal effect of the magnetic expansion is maximum in the direction of the tetragonal axes and minimum between them; the expansion-orientation curves are sinusoidal, having a period of 90°. The amplitude of the curves increases with the field. The transverse effect is just the reverse of the longitudinal, so that no further remarks are necessary.

In the (110)-plane, in the direction of the tetragonal axes, the longitudinal expansion is a maximum; in the direction of the digonal axes, a small maximum is found; and in the direction of the trigonal axis, a minimum is observable. Thus the expansion-orientation curves have a period of 180°, instead of 90° as in (100)-plane. The transverse effect in the same plane is just the reverse of the longitudinal with respect to the orientation. In the (111)-plane, for three orientations, 0°, 15°, 30°, of the crystal with respect to the magnetic field, the longitudinal effects are all similar; that is, as the field is increased, the magnetic expansion increases slowly at first and then rapidly, and after reaching a maximum, it steadily decreases, till it changes into a contraction. As the inclination increases from 0° to 30°, the expansion gradually increases, and, on the other hand, the contraction decreases. The transverse effect is the reverse of the longitudinal above described.

According to N. Akuloff and co-workers, if a single crystal of iron be magnetized up to an intensity I, first in the direction of the principal axis, and next, to the same intensity, in any other direction, then the differences between the changes in length, dl/l, of the crystal parallel to the directions of magnetization, are proportional to the differences between the corresponding changes of resistance, dR/R, and to the energy changes, $\sigma_s-\sigma_0$, between corresponding magnetization curves in the HI-diagram, or $a(dl/l)_s-(dl/l)_0=b(dR/R)_s-(dR/R)_0=c(\sigma_s-\sigma_0)$. The crystal lattice is supposed to be distorted by the rotation accompanying the change in the direction of magnetization away from the direction of easiest magnetization. There is therefore a difference in length of unit rods parallel to the different crystal directions when complete magnetization occurs. When a cube of iron, on an atomic scale, is completely devoid of magnetization, it becomes slightly distorted when it acquires its normal spontaneous magnetization. It becomes longer along the cubic axis of magnetization than it does along the axes at right-angles. Hence, continued W. L. Webster, demagnetized iron is considered as a mosaic made up of asymmetrical small volumes with their direction of distortion distributed equally along the three cubic axes. The resultant dimensions of a cube of demagnetized iron will be symmetrical, but will be a complicated average between the two dimensions of the distorted magnetized cube. When magnetization takes place along a cubic axis there must be a longitudinal expansion, with a lateral contraction gradually increasing as the various volume curves become parallel. For the (110)-direction, as magnetization proceeds there is at first a concentration of the axes of distortion of the many small volumes along the two cubic axes nearest the direction of magnetization. There must therefore be an initial expansion continuing till the third axis has been completely abandoned. Further increase of magnetic intensity can only be produced by deviation from the cubic axes, and the corresponding contraction is sufficiently large to overwhelm the expansion due to increasing uniformity.

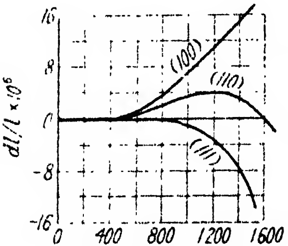


FIG. 314.- The Magnetostriction of Single Crystals of Iron.

With the (111)-axis, the three cubic directions are symmetrically disposed and there is no real increase in uniformity before the deviational distortion appears; consequently no initial expansion is observed. It may be pointed out that the contraction should set in for all directions at a point corresponding to the bend in the I/H curve, a result with which the experiments are in reasonable agreement.

H. G. Dorsey measured the magnetostriction of different carbon steels, and some of his results for the magnetostriction as a function of the field-strength, H, are summarized in Fig. 316, and as a function of the intensity of magnetization, I, in Figs. 315 and 316. He showed that the maximum elongation decreases with the carbon-content up to 0·9 per cent. carbon, and then increases; it may be represented by $(\delta l/l\times10^8+C-4\cdot2)(\delta l/l\times10^8-3\cdot1C+2\cdot13)=0$, where C denotes the percentage of carbon; and if K denotes the magnetic susceptibility $(K+185C-194)(K-40C+4)=0$. Similarly, but not so definitely, the value of H at which the iron rods retract to their original length drops to a minimum value at about 0·9 per cent. carbon. $\delta l/l$ is practically the same $-1\cdot4\times10^{-6}$ when $H=300$. The rods were still contracting when the field-strength attained 1600; but for $H=1500$, the greater the carbon-content, the less the contraction. The modulus of elasticity decreases with the proportion of carbon, or the amount of shortening in strong fields varies directly as the modulus. Slowly cooled steels have greater elongations and susceptibilities than when quenched. There are accidental exceptions for soft iron. Magnetostriction depends on the previous history of the specimen. The percentage elongation in the middle of a 40-cm. rod of soft iron is nearly three times as great as for the entire rod. The values also depend on the lengths of the rods used for observations. R. H. Fowler and P. Kapitza studied the relation between magnetostriction and the Curie point; and S. R. Williams, and S. L. Quimby, the theories of magnetostriction.

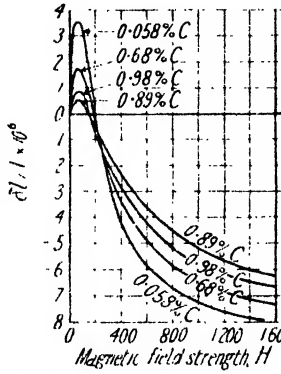


FIG. 315.—Magnetostriction as a Function of the Field-strength.

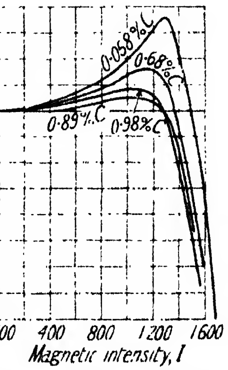


FIG. 316.—Magnetostriction as a Function of the Magnetic Intensity.

J. Coulson examined the effect of occluded *hydrogen* on the magnetization of iron, and found a drop of 5 to 19 per cent.; and A. Kussmann and H. J. Seemann, the effect of cold-rolling. The *elasticity* of iron and steel exercises but a feeble influence on the magnetization. G. Wertheim showed that if iron be exposed for a long time to a magnetizing force, the coeff. of elasticity is reduced a little, and the reduction persists after the magnetizing force is withdrawn. K. Honda and T. Tanaka found that the moduli of elasticity, E, and rigidity, K, of carbon steels are increased by magnetization. Thus, for iron alone:

H . .	9·5	27·2	90·4	213	332	405
$\delta E/E \times 10^2$.	0·143	0·384	0·553	0·665	0·700	0·700
H . .	13·2	33·8	76·1	134	202	465
$\delta K/K \times 10^2$.	0·40	1·03	1·62	2·02	2·20	2·45

The rate of increase in weak fields is greater than in strong fields. H. Tomlinson studied the influence of magnetism on the internal friction and torsional elasticity of metals, and found: (i) When the deformations produced by the oscillations are small, the internal friction of a torsionally vibrating wire of iron or steel is not affected by sustained longitudinal magnetization of moderate amount. The internal friction is also not affected by the sustained magnetization even when the latter is carried to the point of saturation, provided the magnetizing current, previously to experimenting, be reversed a great number of times. When no previous reversals have been made the internal friction is slightly increased by intense magnetism. (ii) When the deformations produced by the oscillations are large the internal friction is very sensibly increased by sustained longitudinal magnetization of large amount. (iii) The torsional elasticity is entirely independent of any sustained longitudinally magnetizing stress which may be acting upon an iron or steel wire, provided the deformations produced by the torsional oscillations be small. When the deformations are large, the number of oscillations executed in a given time is very slightly lessened by sustained longitudinal magnetization of large amount. (iv) When the magnetizing current is interrupted and, to a greater extent, when it is reversed repeatedly whilst the wire is oscillating, the internal friction is increased, provided the magnetizing stress be of moderate amount. The increase of internal friction may become very considerable when the magnetizing stress is great. When the number of interruptions or reversals in a given time of the magnetizing current exceeds a certain limit the effect on the internal friction begins to decline. (v) When the deformations produced by the oscillations are small, the torsional elasticity is not affected by either repeatedly interrupted or reversed longitudinal magnetization even when the magnetizing stress is large. (vi) There exists a limit of magnetic stress within which no permanent rotation whatever of the molecules is produced. This limit may be widened by previous repeated reversals of a large magnetizing stress. (vii) The passage of a moderate electric current, whether sustained or interrupted, through a torsionally vibrating wire of iron, steel, or nickel does not affect, except by heating, either the internal friction or the torsional elasticity, provided the deformations produced by the oscillations be small. (viii) The effect of longitudinal magnetization, even when carried to the point of saturation, on the longitudinal oscillation of an iron or steel wire, is *nil*. (ix) The passage of an electric current, whether sustained or interrupted, through a longitudinally oscillating wire of iron or steel does not, except by heating, affect the number of oscillations executed in a given time. (x) When the deformations produced by the oscillations do not exceed a certain limit, the internal friction cannot apparently depend upon the *permanent* rotation of the molecules about their axes. When, however, the deformations exceed this limit, the internal friction becomes very sensibly larger, and does partly, if not mainly, depend upon the permanent rotation to-and-fro of the molecules about their axes. The limit can be widened by allowing the wire to rest after suspension with oscillations at intervals, by annealing, and by repeated heating and cooling. According to A. Esau and H. Kortum, when ferromagnetic substances are vibrating under torsion, and simultaneously subjected to an alternating, longitudinal magnetic field, a maximum vibration occurs when the period of the field is less than the natural period of the system. Y. Kidani and R. Sasaki found a minimum in the temp. curve showing the tensile strength of magnetized steel, and there is also a change of temp. in the resistance to compression test as the metal passes from the elastic to the plastic state. The lines of magnetic induction of the metal in the elastic state are increased during the tensile test, and decreased in the compression test; the magnetic induction lines of the metal in the plastic state are decreased during both tests. There is no appreciable change of magnetic induction during the compression of a test-piece having no initial permanent magnetization. M. F. Fischer observed that the similarity of the magnetic changes accompanying repeated stresses and those produced by the removal of externally-applied static stresses indicates that the observed changes may be due to the partial relief or redistribution of initially existing internal stresses. C. W. Burrows, H. Styri, C. R. Jones and C. W. Waggoner, and C. W. Waggoner studied the relation of the tensile stress to the magnetic properties of carbon-iron alloys. K. Tangle, J. S. Stevens and H. G. Dorsey, G. Moreau, A. Gray and A. Wood, N. J. Gebert, R. L. Sanford, G. Guzzoni and D. Faggiani, L. von Hamos and P. A. Thiessen, H. Styri, E. Giebe and E. Blechschmidt, F. Bitter, L. Fraichet, C. Chree, P. Mishin and V. Bazilevich discussed the relation between the mechanical and magnetic properties of steel; and A. Kussmann and H. J. Wiester, the effect of a magnetic field on the ageing of hard steel

B. Wedensky and K. Theodortschik found that the magnetic permeability of iron in weak fields of wave-length 54 to 705 metres is not constant. There is a sharp maximum for $\lambda=100$ lying between two minima. Observations were also made by W. Arkadieff. R. G. Loyarte gave for the relation between the frequency, n, of the Hertzian oscillations and the magnetic permeability:

$n \times 10^6$ . .	0	3·75	5·4	6·33	7·48	300	495
μ . . .	158	114	114	122	122	58·4	42·2

A. Kussmann and B. Scharnoff found that in solid soln., in which the mechanical hardness, electrical resistance, etc., are higher than with pure metals, the coercive force, or magnetic hardness is only slightly changed. No direct connection between mechanical and magnetic hardness was observed. In heterogeneous mixtures, the coercive force is much higher, independently of the mechanical hardness. This is attributed to the tension set up by the contraction of the ferromagnetic material in the mixture. E. G. Herbert, and H. Esser and H. Cornelius found that work-hardened metals are still further hardened by magnetic treatment; and the subject was studied by A. Kussmann and H. J. Wiester, and Y. Matuyama. K. S. Seljesater and B. A. Rogers, W. Jellinghaus, L. W. Wild, and K. Heindlhofer studied the magnetic testing of hardness. The application of magnetic analysis to detect flaws, and the correct heat-treatment was discussed by R. L. Sanford and co-workers, P. H. Dudley, J. A. Mathews, E. G. Herbert, C. W. Burrows and F. P. Fahy, S. R. Williams, N. J. Gebert, C. Nusbaum, R. L. Sanford, A. V. de Forest, J. Würschmidt, W. B. Kouwenhoven, E. Maurer and K. Schroeter, and J. S. Hoffhine.

E. Wartmann observed that magnetization had no influence on the sound figures produced by iron or steel plates. C. G. Page observed that a sound may be produced in the magnetization of iron or steel rods. The phenomenon was studied by M. Delezenne, J. P. Marrian, C. Matteucci, G. Wertheim, H. Buff, P. I. Bachmetjeff, R. M. Ferguson, P. Reiss, W. Beatson, A. de la Rive, and M. Ader. According to N. Ruhmkorff, the hardness of the filings of magnetized iron is greater than is the case with non-magnetized iron; but W. Rollmann could detect no difference. M. Trève stated that iron cast from the molten state in a magnetic field is finer grained than if cast in the ordinary way. W. F. Barrett said that iron which has solidified in the molten state in a magnetic field is harder and tougher than if cast in the ordinary way; but these statements have not been confirmed. W. Brown measured the subsidence of the torsional oscillations of iron wires when subjected to the influence of direct and alternating magnetic fields up to 800 c.g.s. units. He also measured the fatigue of iron wires when subjected to the influence of longitudinal and transverse alternating magnetic fields. E. Bauer discussed the relation between the magnetization and the dilation and compressibility. K. Honda and T. Tanaka found that the elastic constants of steel are increased by magnetization.

C. Barus could not obtain satisfactory evidence of the various effects of magnetic force by means of a static method of measurement, and he thus failed to verify H. Tomlinson's results obtained by a vibration method. He showed that during the first phase of annealing, the effect of magnetization on the rigidity of steel is almost *nil*, but the effect becomes marked in the second phase of annealing. If the wire be supposed to pass continuously from the hard to the soft state, the increase of the magnetic coeff. of rigidity, μ, is particularly pronounced after the variations of the thermoelectric, the galvanic, and the viscous properties have practically subsided. C. Barus found for magnetized steel:

			Viscosity $\phi \times 10^6$	Rigidity $\mu \times 10^3$
Steel	Glass-hard		3	0·06
	Annealed at	100°	4	0·08
		190°	4	0·08
		360°	22	0·42
		450°	25	0·48
	Soft		41	0·78
Soft iron			95	3·63

R. Seidek and A. Pompe observed that the resistance of an iron wire to tensile stress is increased by the magnetization of the metal in a definite proportion to the increasing strain on the metal, and similarly reduced in an almost equal proportion as the strain is diminished. Repeated strainings of one and the same wire tend to produce in it a constant magnetic condition. R. Cazaud studied the self-magnetization of steels during torsion. Torsion produces a negative variation on the magnetic flux in mild steels containing less than 0·5 per cent. of carbon, and a positive variation with steels in which the carbon-content exceeds 0·5 per cent. With extra hard steels, cast steels, and some alloy steels of martensitic structure, the variation of flux with torsion is continuous. Repeated torsions cause the steels to approach a state of magnetic saturation; and cold-working tends to increase the variations produced in the magnetic flux of torsion. S. R. Williams found that the permeability of cast-iron rods is changed by tension, and concluded that J. T. Rood's observation to the opposite effect is wrong.

P. G. Maggi reported that the *thermal conductivity* of iron is altered by magnetization. According to H. Tomlinson, the thermal conductivity of a bar of soft iron is diminished by temporary longitudinal magnetization, and increased by transverse magnetization, whilst in the case of steel of different degree of hardness, magnetization produces the same kind of effect. The change with soft iron is at least 10 per cent.—possibly more; whilst the change for thermal and electrical conductivities is not very different. A. Naccari and M. Bellati could detect no influence of magnetization on the thermal conductivity of iron, but A. Battelli, A. Lafay, and E. Fossati observed the alteration in this property with magnetization. Indeed, D. Korda said that thermal conductivity decreases along the lines of magnetic force and is unaffected across them *vide supra*, thermal conductivity. H. M. Brown found that with a longitudinal magnetic field of 10,000 gauss, the ratio of the thermal conductivity 0·179 cal. per sq. cm. per degree with no field, to the conductivity in the magnetic field is 0·9886; and with transverse fields of 8000 and 4000 gauss, the ratios are, respectively, 1·000, and 0·996. P. S. Epstein studied the *specific heat* of ferromagnetic materials; J. A. Becker, the effect of magnetization on the absorption of X-rays; J. H. J. Poole, the effect on the photo-electric properties; and E. Reeger, the magneto photo-phoresis of aerosols. J. R. Ashworth discussed the relations between the magnetic and thermal constants. B. V. Hill found that the sp. ht. decreases with an increase in magnetic permeability.

N. W. Fischer thought magnetized iron to be a worse and J. H. Abraham a better *electrical conductor* than non-magnetized iron. Both observations were considered by K. W. Knochenhauer to be doubtful. E. Edlund observed that the *electrical resistance* of iron by temporary magnetization is increased in the direction of its magnetic axis by about 1 in 3000. W. Beetz also found an increase in the resistance in the direction of the magnetic axis, but not with transverse magnetization. W. G. Adams observed a decrease in the resistance of hard steel, and an increase with soft steel on magnetization. Observations were made by Lord Kelvin, G. de Lucchi, A. Gray and E. T. Jones, G. Barlow, J. A. Mathews, F. Auerbach, E. D. Campbell, W. Guertler, E. Gumlich, N. H. Frank, A. Garbasso, H. Tomlinson, M. Cantone, P. Kapitza, W. Meissner and H. Scheffers, O. Stern, O. Stierstadt, D. A. Goldhammer, and H. Herwig—*vide supra*, electrical resistance. The relation between the electrical conductivity and ferromagnetism was discussed by J. Dorfman and R. Jaanus, and E. D. Campbell. J. R. Ashworth discussed the relation between the thermal and magnetic properties of iron; and for the effects of polarized light on magnetized films of iron—*vide supra*, optical properties. M. de Broglie, T. D. Yensen, K. T. Compton and E. A. Trousdale, and A. H. Compton and O. Rognley studied the action of X-rays on the supposed ultimate magnetic particle of iron, and concluded that the most minute crystal aggregations in solid iron are not oriented by a magnetic field; that the ultimate magnet cannot be a group of atoms like the chemical molecule; and that the atom as a unit cannot account for ferromagnetism. J. C. Stearns tried unsuccessfully to detect a change in the intensity of the X-ray beam reflected from a crystal of silicon steel under the influence of a magnetic field; and he concluded that electrons revolving in orbits within the atom cannot account for ferromagnetism. C. W. Heaps studied the effect of a transverse magnetic field on the electrical resistance of iron. The changes of resistance with longitudinal and transverse magnetic fields was studied by C. G. Knott. L. Grunmach observed an increase of resistance in fields up to 8000 gauss, beyond which a decrease occurred. C. G. Knott observed no initial increase. He found that under the influence of longitudinal magnetization the electrical resistance of iron and steel is increased, but this increase is notably diminished when the longitudinal magnetizing force is superposed cyclically upon a steadily sustained transverse magnetization. In the highest transverse fields used, the change of resistance due to the superposed longitudinal field was in most cases very small. Under the influence of a transverse magnetization the electrical resistance of iron and steel is diminished, and this diminution becomes markedly greater when the transverse field is superposed cyclically upon a steadily maintained longitudinal field. In certain cases the change of resistance due to the transverse magnetizing force was more than doubled when this field was superposed upon the steadily maintained longitudinal field.

The effects of magnetization on the resistance of single crystals of iron, observed by W. L. Webster, are indicated in Fig. 317. In spite of the enormous change of length for the (100)-direction, there is practically no change of resistance. There is also a parallelism. Consequently the change of resistance is caused by the distortion of some sort of electron lattice by the pulling away of the magnetic axes of the electrons from their normal cubic direction; and a cube of iron magnetized along a cubic axis remains electrically isotropic in spite of its magnetostrictive distortion. These conclusions are borne out by the transverse magneto-resistance effect. In this case there is a small change of resistance roughly proportional to the applied field, which appears in all cases and is probably of the same nature as the change occurring in all metals, ferromagnetic or not. There is, in addition, a change depending for sign and magnitude on the directions of the current and magnetic field. This is the definitely crystalline effect, and it has the important property of vanishing whenever the magnetic field is parallel to a cubic axis—that is, whenever the magnetic condition of the iron is normal.

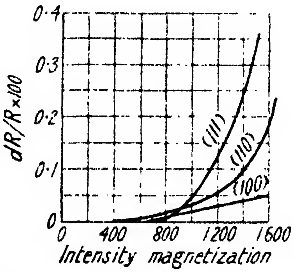


Fig. 317.—The Effect of Magnetization on the Resistance of Single Crystals of Iron.

For N. Akuloff's observations with single crystals, *vide supra*. For the effect of a magnetic field on the *electrode potential* of iron, *vide supra*. E. M. Pugh found that a break in the linear relations of the Hall effect coincides with the maximum permeability. According to J. Trowbridge, the magnetic permeability of iron wires exercises an important influence upon the decay of electrical oscillations of high frequency. The influence is so great that the oscillations may be reduced to half an oscillation on a circuit of suitable self-induction and capacity for producing them. It is probable that the time of oscillation on iron wires may be changed. Consequently, currents of high frequency, such as are produced in Leyden jar discharges, magnetize iron.

C. Barus and V. Strouhal observed that the *thermoelectric force*, *E*, of the copper-iron couple is very slightly greater with magnetized iron; for non-magnetized iron, $E=0{\cdot}0_31305(\theta-\theta_1)-0{\cdot}0_6262(\theta^2-\theta^2{}_1)$; and for magnetized iron $E=0{\cdot}0_31308(\theta-\theta_1)-0{\cdot}0_6261(\theta^2-\theta^2{}_1)$. The couple with magnetized and non-magnetized wire has a thermoelectric force of $E=0{\cdot}0_637(\theta-\theta_1)+0{\cdot}0_815(\theta^2-\theta^2{}_1)$. H. Tomlinson, W. H. Ross, C. W. Heaps, R. Schaffert, S. Seass, A. Battelli, M. Chassagny, and P. I. Bachmetjeff also made observations on this subject. In 1856, Lord Kelvin (W. Thomson) showed that a thermo-couple consisting of magnetized and unmagnetized iron of the same hardness and form, furnishes an electric current in one case from unmagnetized to longitudinally magnetized iron through the hot junction, and in another from transversely magnetized to unmagnetized iron through the hot junction; consequently, also from transversely to longitudinally magnetized iron through the hot junction. A. Battelli observed an increased

Peltier effect with magnetized iron, but magnetization has no perceptible influence on the *Thomson effect*. W. K. Mitiaeff found that the magnetic permeability of iron in a constant field of 600 gauss is reduced by *electromagnetic waves* of length 55 to 114 metres—*vide supra*. G. A. Carse and D. Jack observed no difference in the electron emission from magnetized and unmagnetized iron.

According to H. A. Rowland and L. Bell, they embedded two iron rods in insulating material, so that the point of one and the side of the other were laid bare by removing the insulation, and placed the rods in a beaker between the poles of an electromagnet, and connected them with a galvanometer. Then, when they are acted on by chemical reagents, no current is produced when perpendicular to the lines of force; and when parallel, a current is produced, the sharp-pointed rod forming the negative element; soon afterwards reversal takes place. The direction of the current is independent of that in the magnet. Similar, but much weaker, effects are produced with nickel and cobalt. The action is greatest with substances which, like nitric acid, attack the iron without the evolution of hydrogen. The reversal can be annulled by preventing motion in the liquid by means of gelatin or sand. The e.m.f. varies from 0·0001 to 0·02 volt. The evolved hydrogen probably acts mechanically in reducing the current. The protection of the pointed end from the reagents is due to the increased energy required to remove the iron. No differential action was observed with plane surfaces, but where a point occurs, some protection ensues, so that elevation increases in size.

P. Weiss, and P. Weiss and R. Forrer gave 11 and 15 for the magnetic moment of α-iron; and 14 for γ-iron. The subject was studied by N. Akuloff, C. J. Gorter, P. Weiss and G. Föex, R. W. Roberts, E. C. Stoner, S. J. and L. J. H. Barnett, R. H. Fowler and F. C. Powell, W. J. de Haas, O. Laporte and A. Sommerfeld, C. Sadron, A. Sommerfeld, P. Weiss and co-workers, and A. Wolf. Basing an argument on the supposed constitution of magnetic oxide of iron, F. Gross assumed that iron has the constitution

$$\begin{array}{l}\mathrm{Fe}\\ \ddot{\mathrm{F}}\mathrm{e}\end{array}\!>\mathrm{Fe}$$

P. Weiss, and L. A. Welo and O. Baudisch measured the magnetic moments of iron salts; and S. S. Bhatnagar and co-workers found that there is a slight increase in the paramagnetism when iron salts are adsorbed on charcoal, and when adsorbed on charcoal the salts are diamagnetic. This is thought to favour the view that the adsorption is a process of chemical combination. J. H. van Vleck studied the susceptibility of the iron salts. P. Collet and F. Birch discussed the paramagnetism of the iron in potassium ferricyanide; L. A. Welo, in $Fe_3(CH_3COO)_6(OH)_2Cl$. R. H. Weber found the atomic magnetism of iron in $\frac{1}{2}Fe_2(SO_4)_3$ and $FeSO_4$ to be respectively 0·01521 and 0·01276. The magnetic properties of various iron compounds were studied by L. Cambi and co-workers, G. Föex, L. C. Jackson, and W. Klemm and co-workers; the photo-magnetic effect of salts in soln., by D. M. Bose and P. K. Raha; and the magnetic properties in relation to the periodic law, by P. Weiss.

W. Sucksmith and L. F. Bates, and F. Coeterier and P. Scherrer studied the gyromagnetic effect. O. W. Richardson showed that if the magnetic properties of ferromagnetic substances are due to the rotation of electron orbits in the atom, a change in the magnetic moment, M, should be accompanied by a change in the angular momentum, U, such that $U/M=2m/e$, where m and e are the mass and charge of an electron respectively. If K denotes the ratio $U/M : 2m/e$, then K for iron is about half the theoretical value, for $K=0{\cdot}503$. Observations were made by O. Dahl and J. Pfaffenberger, A. P. Chattock and L. F. Bates, S. J. and L. J. H. Barnett, A. Serres, W. Sucksmith, and J. W. Fisher. F. Ehrenhaft studied the magnetophoresis and the electrophoresis of iron.

T. D. Yensen observed that there is no evidence of any change in the crystal units of iron when subjected to a strong magnetic field, and hence it is probable that the magneton is an atomic property. The theory of ferromagnetism was discussed by N. Akuloff, H. S. Allen, J. R. Ashworth, O. von Auwers and co-workers, S. J. Barnett, W. F. Barrett and W. Brown, E. Bauer, R. Becker and co-workers, F. Bitter, F. Bloch, D. M. Bose, L. Brillouin, L. Bruninghaus, B. Cabrera, F. W. Constant, C. G. Darwin, J. Dorfman and co-workers, J. A. Eldridge, W. B. Ellwood, E. Englert, P. S. Epstein, H. Fahlenbrach, G. F. Fitzgerald, A. V. de Forest, R. Forrer, R. H. Fowler and F. C. Powell, J. Frenkel, J. Frenkel and J. Dorfman, O. E. Frivold, R. Gans, W. Gerlach, O. Halpern, W. Heisenberg, T. Hirone and T. Hikosaka, K. Honda, E. Howells, D. R. Inglis, J. C. Jackson, W. Jäger and W. Meissner, P. Jordan and V. Fock, J. Kelen, K. Kreielsheimer, J. Kunz, O. Laporte, G. N. Lewis, G. H. Livens, F. H. Loring, R. G. Loyarte, H. Ludloff and C. Reymann, L. W. McKeehan and co-workers, G. S. Mahajani, E. Merritt, A. E. Oxley, L. Pincherle, F. C. Powell, S. L. Quimby, F. Regler, J. C. Slater, J. H. Smith, J. C. Stearns, E. C. Stoner, W. Sucksmith, R. Swinne, E. Teller, E. M. Terry, N. Tunazima, F. Tyler, E. Vogt, W. L. Webster, P. Weiss, P. Weiss and R. Forrer, L. A. Welo, E. H. Williams, R. L. Wills, J. F. T. Young, and F. Zwicky.

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§ 23. The Chemical Properties of Iron

According to G. Tammann,[1] the effect of cold-work on iron is to make the metal less noble, or more basic. The lower limit of the temp. of reactions between solids was found by G. Tammann to correspond with the temp. at which the space-lattice of a solid begins to change. Fairly good agreement was observed for the beginning of the reaction between tungsten, molybdenum, copper, titanium, beryllium, phosphorus, manganese, aluminium, or silicon and iron, and iron-nickel or iron-cobalt alloys. The subject was studied by E. Scheil.

F. Duran and C. H. Teckentrup found that the absorption of **argon** by electrolytic iron is purely adsorption. F. Fischer and F. Schröter observed no evidence of combination when iron is sparked beneath liquid argon. V. Kohlschütter and R. Müller investigated the spluttering of iron electrodes in gaseous argon; and V. Kohlschütter and co-workers, F. Fischer and co-workers, B. Walter, and J. Stark discussed whether or not the phenomenon is due to the formation of an unstable endothermal compound. Similarly also with **helium.** W. A. Tilden found that helium is less readily absorbed by iron than is the case with hydrogen. A. Sieverts and E. Bergner found that argon and helium do not show a measurable solubility in solid iron at 1200° and 1400°, or in molten electrolytic iron at 1500°, whilst W. Ramsay and M. W. Travers detected no diffusion of argon or helium through iron. The subject was studied by E. Martin, and W. Frankenburger and co-workers. The gases occluded by meteoric irons are mainly the carbon oxides, nitrogen, methane, and hydrogen; though W. Ramsay, and H. D. Campbell and J. L. Howe reported the presence of occluded argon and helium in meteoric iron. F. Paneth and W. D. Urry found that iron meteorites contain up to $36{\cdot}15\times10^{-6}$ c.c. of helium per gram; and terrestrial iron, $1{\cdot}05\times10^{-6}$ c.c. per gram.

M. Poljakoff[2] observed that when **hydrogen** at 3 to 5 mm. press. is passed over iron at 400° to 800°, no luminescence occurs, but if a small stream of oxygen or air is added to a point remote from the metal, a violet, green, or yellow luminescence occurs. The luminescence is not produced by a mixture of hydrogen and oxygen.

Iron readily absorbs or occludes gases, and it may take up ten to twenty times its own vol. of gas when it is heated in a furnace, and the gas consists mainly of carbon monoxide and dioxide, nitrogen, and hydrogen. The gases are given off when the metal is heated in vacuo. A number of observations by (1) G. Allemann and J. Darlington, (2) G. W. Austin, (3) T. Baker, (4) E. Becker, (5) G. Belloc, (6) O. Boudouard, (7) L. Cailletet, (8) G. Charpy and S. Bonnerot, (9) J. W. Donaldson, (10) P. Goerens, (11) P. Goerens and J. Paquet, (12) E. Goutal, (13) T. Graham, (14) L. Guillet, and R. A. Hadfield, (15) H. M. Howe, (16) R. Hugues, (17) L. Jordan and J. R. Eckman, (18) P. A. Klinger, (19) E. Maurer, (20) P. Oberhoffer and E. Piwowarsky, (21) P. Oberhoffer, E. Piwowarsky, and

O. von Keil, (22) J. Parry, (23) H. M. Ryder, (24) L. Troost and P. Hautefeuille, (25) A. Vita, and (26) T. Zyromsky are summarized in Table XLVII.

Other observations were made by E. Améen and H. Willners, J. O. Arnold, G. W. Austin, L. Baraduc-Muller, P. Bardenheuer and W. Bottenberg, O. Bauer, H. Bessemer, H. Braune, H. le Chatelier and B. Bogitch, J. E. Fletcher, R. K. Gratigny, G. Guillemin and B. Delachanal, L. L. Hasse and H. Shenck, P. L. T. Hèroult, O. Herting, W. Hessenbruch, B. Hird, H. M. Howe, G. d'Huart, D. E. Hughes, R. Hugues, J. E. Hurst, J. E. Johnsen, W. H. Johnson, S. Kern, P. A. Klinger, F. Körber and H. Ploum, J. W. Langley, A. Ledebur, G. Lewkonja and W. Baukloh, A. G. Lobley and C. L. Betts, A. McCance, A. Magnus and B. Klar, E. von Maltitz, E. Maurer, V. S. Meskin and Y. M. Margolin, A. S. de Osa, N. Parravano and A. Scortecci, N. Parravano and C. R. del Turco, E. Piwowarsky, E. Piwowarsky and H. Esser, H. Ploum, F. Rapatz, W. Rohn, T. E. Rooney and G. Barr, E. H. Schulz, C. J. Smithells, T. C. Sutton and H. R. Ambler, W. A. Wesley and co-workers, N. A. Ziegler, etc., are summarized in Table XLVII. The effervescence and spitting of molten steels was discussed by H. D. Hibbard. Observations on the absorption of hydrogen by iron and steel were made near the middle of last century by H. St. C. Deville, E. Frémy, L. Troost and P. Hautefeuille, H. St. C. Deville and L. Troost, L. Cailletet, and T. Graham. Later observations were made by A. J. Allmand, G. P. Baxter, M. le Blanc, C. F. Burgess, J. Cournot, J. Grant, W. Hessenbruch, E. Heyn, G. d'Huart, A. Ledebur, H. Lee, D. J. McNaughton, E. Martin, J. H. Meidinger, E. Muller and K. Schwabe, B. Neumann, J. Parry and A. E. Tucker, N. B. Pilling, F. Rapatz, T. W. Richards and G. E. Behr, W. C. Roberts-Austen, F. Schmitz, E. H. Schulz, A. Sieverts, H. S. Taylor and R. M. Burns, M. Thoma, A. Villachon and G. Chaudron, H. Wedding and T. Fischer, and J. H. Whiteley.

J. Parry noticed that the solubility of hydrogen in iron increases with a rise of temp. As a rule, the solubility of gases in water decreases with a rise of temp., whereas in the case of molten metals, the solubility increases. In non-aqueous solvents, there are often minima in the solubility curves, and even in the case of water there are indications that it behaves more like non-aqueous solvents when its temp. is raised, and the complexity of its molecules—**1.** 9, 7 is simplified. If the effect of temp. on the solubility of gases in molten metals is in accord with the principle of accommodation—**2.** 18, 4—the solubility will increase with a rise of temp. when the process of dissolution is endothermal, and it will decrease with a rise of temp. if the process is exothermal. These deductions are quite independent of the mechanism of the process of dissolution.

According to T. Graham, iron at a red-heat is capable of taking up and holding when cold 0·46 vol. of hydrogen; and he added that it is difficult to impregnate malleable iron with more than one vol. of hydrogen under atm. press., but meteoric iron from Lenarto contains three times that amount. Hence he inferred that "the meteorite has been extruded from a dense atmosphere of hydrogen gas, for which we must look beyond the light, cometary matter floating about within the limits of the solar system." B. Neumann and F. Streintz observed that iron can occlude 9·3 to 19·17 times its vol. of hydrogen; and L. Troost and P. Hautefeuille found that charcoal iron heated for 48 hrs. in hydrogen at 800° absorbed 0·7 vol. of gas, whilst wrought iron absorbed 0·16 vol., and cast steel, 0·10 vol. G. P. Baxter observed no occlusion of hydrogen by iron obtained from the oxide by reducing it in hydrogen; and E. Heyn found that iron heated in hydrogen at 1000° absorbed 0·16 vol. of gas. H. Wedding and T. Fischer found that a gram of grey pig-iron at 800° absorbed 0·0079 mgrm. of hydrogen; iron from the converter, 0·0027 mgrm.; basic ingot iron, 0·0014 mgrm.; open-hearth ingots, 0·033 to 0·043 mgrm.; ingot when dulled, 0·12 to 0·17 mgrm.; wrought iron, 0·0018 to 0·017 mgrm.; and electrodeposited iron, 2·8 mgrm.—*vide* Table XLVII. T. C. Sutton and H. R. Ambler said that steel abruptly exposed to a high pressure and temp.—*e.g.* when cordite is exploded in a steel vessel—absorbs as much as 30 c.c. of gas per gram of metal, an amount which is larger than has been observed under other conditions. The gases are retained firmly below 600°, and are not all eliminated at 1000° under reduced press. The heat of absorption of the gas is estimated to be 0·75 cal. per c.c. of mixed gas. W. Frankenburger and co-workers studied

TABLE XLVII.—OCCLUDED GASES IN IRON AND STEEL.

Author	Iron or steel	C per cent.	Gas—c.c. per 100 grms. metal	Percentage composition of gas by volume					
				CO	H_2	N_2	CO_2	CH_4	O_2
1	Horse-shoe iron .	—	31	54·1	28·0	14·0	3·9	—	—
2	Iron . . .	—	—	8·4 12·2	33·7 -38·6	49·2-57·9	—	—	—
3	Steel . .	-	0·41 1·56	11·5-63·6	22·7- 82·1	6·4 12·5	2·3	—	—
3	Wrought iron .	—	2·68 3·7	14·3 58·4	1·4- 72·0	0·8-13 7	11·9	—	—
4	Steel . .	—	—	24·3	52·6	6·5	16·6	—	—
5	Siemens-Martin .	0·05	—	5·6-13·5	52·5- 60·9	33·2 36·4	-	—	—
5	Puddled iron .	0·03	-	40·3 45·5	15·6--30·8	23·8 39·0		—	—
6	Siemens-Martin .	0·12	50·86	23·0--71·0	25·0-72·0	3·0– 4·0	2·0	—	—
7	Iron filings and wire .	—	—	28·3 -60·6	30·6- 43·1	4·4 15·7	4·4 12·9	—	—
8	Steel . .	0·9		48·1	49·6	1·4	0·5	0·4	—
9	Steel . .	—	18·0- 19·5	27·7--47·0	—	—	53·0 72 3	—	—
10	Thomas-Gilchrist	0·07	15·5	75·9	11·1	12·7	0·3	—	—
10	Siemens-Martin .	0·10	11·6	81·7	10·2	3·9	4·2	—	—
10	Electro-steel .	0·15	25·0	78·3	11·7	5·3	4·7	—	—
10	Crucible steel .	0·40	11·9	81·6 .	6 1	11 5	0·8	—	—
11	Thomas-Gilchrist	0·04	106			.	—	—	—
11	Siemens-Martin .	0·07	70			-	—	—	—
11	Electro-steel .	0·10	31	—	—		—	—	—
12	Liquid steel .	0·13	80 6	45·6	52 1	0·4	1·2	0·7	—
12	Crucible steel .	0·90	134·0	14·9	52·5	0·1	1 9	0·6	—
13	Siemens-Martin .	0·49	135	45·1	54·3	0·6		—	—
13	Crucible steel .	1·10	173	44·2	55·4	0·4	—	—	—
13	Cast iron . .	3 50	24	23·0	73·9	3·1	—	—	—
14	Siemens-Martin .	0·14	45·0	60 8	11·1	23·0	2·9	—	2·2
14	5 mins. after Mn addition . .	0 22	34·5	52 5	11·0	31·6	2·0	—	2 9
	15 mins. after Mn addition .	0·18	29 0	50 6	5·5	37·4	1 0	—	5·5
	After Si and Al addition .	0 23	14 3	16 0	27·5	51·0			5·5
15	Thomas-Gilchrist	0·05- 0·08	22·0 40 0	70·0 72·1	15·1 16 7	5·0 10 6	3 1- 8·3	—	—
15	Siemens-Martin .	0·08 0·15	38 0 46·0	70·2	13·1 21·0	3·7 -11·4	5·1 - 5·3	—	—
15	Electro-steel .	0·08 0·45	13·0 94·0	7·7 -47·4	42·7- 59·0	0·7 - 9·4	0·7 -33·3	—	—
15	Crucible steel .	0·27 0·47	51·0 152·0	39·2 65·8	26·7 32·6	4·2 - 9·1	3·3-19·1		—
16	Bessemer steel .	0·10	2800	8·4-56·1	1·1- 21·2	25·1- 84 2	0·6 1·0	—	2·4–6·3
17	Silicon steel .		-	46·8	12·3	37·3	3·6		—
18	Thomas-Gilchrist	0 05 0·06	35 ·78	69·3 70·8	8·0–12·8	9·7- 12 0	8·2 -10·0	—	—
18	Siemens-Martin .	0·09 -0·20	63 -92	47 1-74·0	9·2–37·8	3·7 16·8	1 1	—	—
19	Thomas-Gilchrist	31·0	-	—	—	100	—	—	—
19	Siemens-Martin .	23 9 -78·5	-	.	31·3	68·7 100	.	.	—
19	Ferromanganese .	702 8	-	2·2	41·0	43·2	13 6	—	—
20	Thomas-Gilchrist	—	96·3	13·4	27·7	13·5	15·5	-	—
20	Siemens-Martin .	1 68	19·6	4·0	—	—	96·0	—	—
21	Thomas-Gilchrist	—	40·99	60·5	21·8	5·6	12·1	—	—
21	After deoxidation	—	102·96	62·7	22·1	6·2	9·0	-	—
21	Siemens-Martin .	0·5	31·7	14·3	71·3	—	11·4	—	—
21	After deoxidation	—	114·8	77·8	20·2	—	2·0	—	—
22	Nickel steel .	—	.	46·30	52·41	0·24	0·74	0·31	—
22	Silicon steel .	-	-	37·59	60·90	0·19	1·05	0·27	—
22	Chromium steel .		—	44·85	52·41	0·54	1·92	0·28	—
22	Manganese steel .	—	—	37·10	60·28	0·33	1·91	0·35	—
23	Open-hearth steel	-	—	—	*nil*–0·0011	—	-	..	0·028–0·083

		C per cent.	Gas—c.c. per 100 grms. metal	Per cent. by weight			
				CO	H_2	N_2	CO_2
24	Siemens-Martin (basic) .	1·20	66·117	0·0067–0·1277	0·0001–0·0014	0·0018–0·0412	0·0010 -0·0510
24	Siemens-Martin (acidic) .	0·45	15·0- 77·5	0·0012–0·0863	0·0002–0·0008	0·0031–0·0693	0·0049–0·0374
24	Thomas-Gilchrist	0·07 0·37	3·75- 174	0·0006-0·1538	0·0006-0·0035	0·0021–0·0738	0·0015 -0·0187
24	Bessemer .	0·25 -0·71	12·0–102·0	0·0000–0·1750	0·0001–0·0062	0·0031-0·0543	0·0010–0·0275
24	Crucible . .	0·37	5·5-79·0	0·0019–0·0831	0·0001–0·0008	0·0033–0·0650	0·0020–0·0374
24	Open-hearth iron . .	—	—	—	*nil*–0·0011	—	—

		Vol. of gas per vol. of iron c.c.	Composition of gas by volume					
			CO	H_2	N_2	CO_2	O_2	CH_4
25	Electrolytic iron .	28·6	25·7	65·3	7·6	0·7	0	—
26	Electrolytic iron .	30·0	34	49–51	7·0	6·0	—	2–4

the absorption of hydrogen by highly dispersed iron; and L. Baraduc-Muller, the absorption of gases by liquid steel.

A. Sieverts found that raising the *temperature* favours the absorption of hydrogen. Iron wire absorbs increasing amounts of hydrogen when it is heated in an atm. of that gas from 400°, upwards; but on cooling, the absorbed gas is evolved. Representing the amounts of hydrogen in mgrms. of gas per 100 grms. of iron, or in vols. of hydrogen per unit vol. of iron:

	400°	775°	827°	852°	930°	1136°	1450°	m.p.	m.p.	1650°
Mgrm. .	0·035	0·201	0·242	0·264	0·431	0·632	1·079	1·20	2·40	2·79
Vol. . .	0·031	0·176	0·211	0·231	0·377	0·552	0·943	1·05	2·10	2·44
	Solid.								Liquid.	

The results are plotted in Fig. 318. There is a break in the curve corresponding with the $\alpha \rightleftharpoons \gamma$-transformation; and there is a marked increase in the solubility of the gas as the metal passes from the solid to the liquid state of aggregation between 850° and 900°; but no singularity was observed about the A_2-critical point. A. Skrabal also noted that hydrogen dissolves more readily in γ-iron than it does in α-iron. G. Tammann and J. Schneider observed that after α-iron has undergone the γ-transformation, it no longer absorbs hydrogen at 300°. K. Iwase observed that reduced iron absorbs hydrogen at different temp. in accord with the solubility curves shown in Fig. 319, and that the solubility, S c.c. of gas at n.p. θ per 100 grms. of metal, can be represented by the linear equations $S=1{\cdot}685+0{\cdot}016(\theta-200)$ for α-iron; and $S=13{\cdot}445+0{\cdot}1293(\theta-910)$ for γ-iron. G. Borelius, represented the solubility, S, of hydrogen in α-iron by $S=ae^{1720/T}$, and in γ-iron, by $S=ae^{1920/T}$, where a denotes a constant which varies with the temp., but has nearly the same value for all metals at high temp. H. S. Taylor and R. M. Burns, found that at 25°, one vol. of metal absorbs 0·05 vol. of hydrogen, and $<0{\cdot}05$ vol. at 110° and 218°; W. A. Dew and H. S. Taylor, that one gram of iron at 0°, 110°, 218°, and 305° absorbs respectively 0·0074, 0·0028, 0·0195, and 0·0116 c.c. of hydrogen. Observations were made by E. Martin, N. I. Nikitin, and A. Sieverts and E. Jurich. K. Iwase found that the solubility of hydrogen in cast iron is smaller, the higher is the proportion of *contained carbon*. The results with cast iron containing 3·5, 4·0, and 4·3 per cent. of carbon are shown in Fig. 320. Steel also dissolves more hydrogen than does cast iron. E. Martin's results agree better with those of A. Sieverts than with those of K. Iwase. C. J. Alexander examined the effect of liquid air temp.

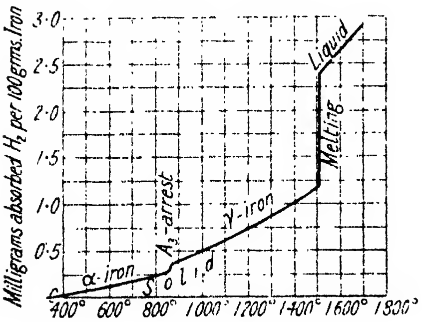


FIG. 318.—The Solubility of Hydrogen in Iron at Different Temperatures.

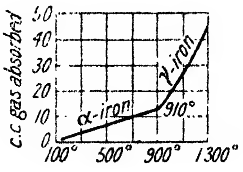


FIG. 319.—The Solubility of Hydrogen in Iron.

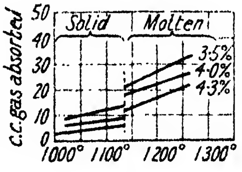


FIG. 320.—The Solubility of Hydrogen in Cast Iron.

G. Tammann and J. Schneider's observations show that the metal *hardened by* *cold-rolling* absorbs hydrogen at 300° more rapidly and to a greater extent than does the soft metal, but the reverse obtains with electrolytic hydrogen. The metal softened at 1100° absorbs electrolytic hydrogen much more rapidly than the hard metal. The octahedral planes of the crystals of the metal absorb hydrogen the fastest.

W. Heald, and W. Frankenburger and K. Mayrhofer studied the absorption of hydrogen by *thin films of iron.* L. Troost and P. Hautefeuille showed that *pyrophoric iron* reduced from the oxide by hydrogen at a low temp., decomposed water slowly at ordinary temp., and rapidly at 100°; the decomposition is more rapid the finer is the state of subdivision of the metal. The adsorbed hydrogen can be removed in vacuo without interfering with the pyrophoric character. According to T. W. Richards and G. E. Behr, finely-divided iron, obtained by reducing the oxide at a relatively low temp., 570°, has the power of absorbing hydrogen, but the potential of the metal is not appreciably affected thereby, unless the surface is fully charged with hydrogen when the potential is somewhat lowered. When iron which has been heated in an atm. of hydrogen or nitrogen is suddenly cooled by plunging it in water, it absorbs hydrogen from the water in a specially active form in virtue of which the potential is raised by about 0·15 volt. This hydrogen is not readily removed when the iron is kept in water or in a soln. of potassium sulphate, but it is rapidly expelled when the iron is placed in a soln. of ferrous sulphate, and the potential returns to its normal value.

According to N. I. Nikitin, the gas dissolved by pyrophoric iron at −185° represents a true surface adsorption, because it can be completely pumped off at ordinary temp., and it is in accord with the adsorption equation $a=kp^{1/n}$. He found pyrophoric iron is inert between −80° and 16°; and at higher temp. it absorbs the gas in increasing quantities. Pyrophoric iron reduced from the oxide at 515° to 525° absorbs v c.c. of hydrogen, reduced to n.p. θ per 5 grms. of metal when the press. is p mm.:

	−185°				380°				510°
p . . .	92·4	229·7	521·0	627·0	70·4	274·6	449·0	694·5	734·2 mm.
v . . .	3·2	5·3	7·7	8·3	3·5	4·4	4·9	5·2	6·10 c.c.

G. Tammann and J. Schneider found that the *rate of absorption* of hydrogen at different temp. can be represented by the slopes of the curves in Fig. 321, where the vol. of the gas is expressed in c.c. at n.p. θ per 100 grms. of metal. K. Iwase's results for solid and liquid cast iron are summarized in Fig. 322. G. Tammann and J. Schneider found that the velocity of absorption of hydrogen is greater, the larger is the number of icositetrahedral planes in the surface layer. The number of such planes decreases after heating the metal to a higher temp., and the rate of absorption shows a corresponding diminution. Observations on the rate of absorption were also made by G. Tammann and F. Laass.

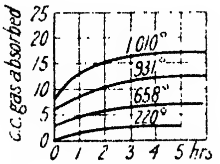


FIG. 321.—The Rate of Absorption of Hydrogen by Iron.

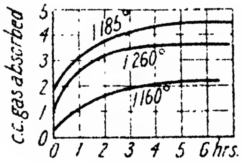


FIG. 322.—The Rate of Absorption of Hydrogen by Cast Iron.

A. Sieverts found that at a constant temp., the solubility, S, of hydrogen in iron is directly proportional to the *pressure*, p, of the gas, so that $S=kp^{\frac{1}{2}}$. G. Borelius and F. Gunneson added that this rule applies to iron, but, according to G. Borelius, not to steel. A. Sieverts found that with press. below 100 mm., the solubility of hydrogen in iron decreases more rapidly with falling pressures than corresponds with this relation. G. Tammann studied the effect of cold-work on the absorption of hydrogen; and H. Jellinek, the effect of the press. of the gas on the electrical resistance of the metal.

According to W. H. Johnson, and O. Reynolds, when pieces of iron or steel are immersed in sulphuric or hydrochloric acid, washed, and dried, there is an increase in weight of 0·0005 to 0·06 per cent. owing to the saturation of the metal with nascent hydrogen. On prolonged exposure to air, or more rapidly on heating, the hydrogen is evolved, and the metal regains its original physical properties. A. Ledebur found that the iron may absorb twenty times its vol. of hydrogen when placed in dil. sulphuric acid; and that cast iron behaves in a similar way. According to J. H. Andrew, the intercrystalline, amorphous cement between the ferrite crystals plays a part in conveying the gas into the interior of the solid metal. Thus, when a piece of wrought iron is immersed for some time in a sat. soln. of sodium hydroxide at 100°, the mass becomes brittle because the gas is absorbed more rapidly in the amorphous intercrystalline layers than by the crystals themselves, and the expansion of these layers forces the crystals apart and weakens their cohesion. After remaining longer in the soln. of sodium hydroxide, the iron loses its brittleness, because the hydrogen gradually diffuses into the crystals from the intercrystalline cement. Electrolytic iron, being already sat. with hydrogen, is unaffected by sodium hydroxide. M. Thoma said that iron is readily supersaturated with hydrogen when it comes in contact with nascent hydrogen either in the voltameter or that which is being generated on its own surface by the action of an acid. From the surface of the supersaturated iron, hydrogen is again spontaneously liberated, and the amount obtained is proportional to the extent of surface. J. H. Meidinger, and R. Lenz noticed that electrolytic iron may be contaminated with occluded hydrogen, and that at 100°, about a tenth of the total amount of occluded hydrogen is expelled, about two-thirds is given off at a dull red-heat, and only at 1000° is the metal freed from the gas. F. Haber discussed this question. R. Lenz found that when electrolytic iron is heated in a porcelain tube, the total amount of gas evolved varies from 20 to 96 vol. per cent. of gas per vol. of iron. The gas given off at 600° contained 58·5 vol. per cent. of hydrogen; 18·8, N; 11·3, CO; 10·1, CO_2; and 1·3, H_2O; whilst that evolved at a bright red-heat contained 43·2, H; 8·9, N; 22·7, CO; 17·8, CO_2; and 7·4, H_2O. It was thought that the steam and carbon monoxide were formed by the reaction between iron, carbon dioxide, and hydrogen. Observations were also made by L. Guillet, R. Hugues, H. O. von Samson-Himmelstjerna, A. Thiel and W. Hammerschmidt, M. Thoma, and R. A. Hadfield—*vide* Table XLVIII. F. Winteler gave, for deposits of electrolytic iron 0·08 mm. and 0·14 mm. in thickness, per 1 vol. of iron:

	H_2	N_2	CO	CO_2	H_2O-vapour	Total gas
0·08 mm. .	53·4	15·5	15·1	12·7	3·3	97·7 vol. per cent.
0·14 mm. .	60·3	5·6	26·7	4·3	3·0	21·2 ,, ,,

The presence of hydrogen in electrodeposited iron, in amounts varying from 0·0076 to 0·0262 per cent., was observed by S. Maximowitsch, C. F. Burgess and C. Hambuechen, W. M. Hicks and L. T. O'Shea, and A. Skrabal. The relations between the current density, concentration, acidity, and temp. of the soln. of ferrous sulphate on the proportion of occluded hydrogen, were studied by F. Förster, G. Coffetti and F. Förster, and W. A. MacFadyen. According to H. Lee, the hydrogen-content decreases with the duration of the electrolysis, with decreasing current density, with increasing acidity of bath, and with decreasing conc. of iron in the soln. The results of H. Lee are summarized in Fig. 324 for layers of iron of different thickness. According to R. Kremann and H. Breymesser, the hydrogen and iron are simultaneously liberated at the cathode, and the liberation of hydrogen can be prevented if the electrolysis be carried out under a high press. of hydrogen. Iron deposited under 20 atm. press. of hydrogen were composed of larger crystals than when deposited under 1 atm. press. of hydrogen. The metal obtained at the higher press. contained less occluded hydrogen, and it was also softer, and less brittle.

G. Borelius found that for iron, but not steel, the conc. of the occluded hydrogen is proportional to the sq. root of the current density. The press. eq. of the current density for a 2 per cent. soln. of sodium hydroxide at an ampère per sq. cm. is 17,000 atm.

T. W. and W. T. Richards observed that a magnetic field has no perceptible influence on the electrode potential of iron, but with iron having occluded hydrogen, the potential is definitely lowered; the change is roughly proportional to the strength of the magnetic field. With a given magnetic field, the decrease in the overvoltage is approximately proportional to the overvoltage itself, amounting, with a strong magnetic field, to about 5 per cent. of the value of the overvoltage. It is assumed that the magnetic field affects the potential not because of any change in the affinity between hydrogen and iron, but because of some change in the texture of the occluding metal due to magneto-striction. For the effect of the adsorbed hydrogen on the magnetic properties of iron, *vide supra*, the magnetic properties of iron. J. A. Kendall discussed the formation of a cell with one plate of iron through which hydrogen is passing.

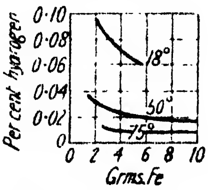


Fig. 323.—The Effect of Temperature on Occluded Hydrogen.

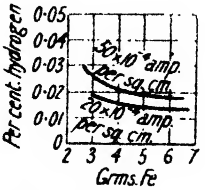


Fig. 324.—The Effect of Current Density on Occluded Hydrogen.

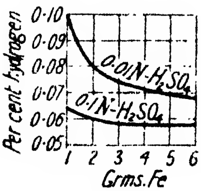


Fig. 325.—The Effect of Acidity on Occluded Hydrogen.

T. Graham discussed the **nature of the occluded hydrogen** in palladium, and he regarded it as a special form of hydrogen which he called *hydrogenium*—**1**. 7, 6. The occluded hydrogen is specially active chemically, and W. Ramsay attributed this activity to the presence of hydrogen in the monatomic condition. This inference is in harmony with the observations of T. W. Richards and G. E. Behr, T. W. and W. T. Richards, E. G. Mahin, S. Satoh, A. F. Penton and T. A. White, T. Franzini, T. S. Fuller, M. Thoma, G. Charpy and S. Bonnerot, W. H. Johnson, O. Reynolds, A. Coehn, and A. Winkelmann—*vide supra*. O. Faust's experiments on the chemistry of the iron electrode support this view; like T. W. Richards and G. E. Behr—*vide supra*—it was found that the electrode potential of spongy iron with occluded hydrogen is 0·39 volt, and without the hydrogen, 0·44 volt. A. Sieverts observed that for the occluded gas, $vp_{\frac{1}{2}}$ is constant; and for gaseous phase, vp is a constant. From the partition law, it follows that the hydrogen is occluded in the form of monatomic molecules. At very low temp., N. I. Nikitin's observations agree with the assumption that the adsorbed hydrogen is in the molecular state. A. Villachon and G. Chaudron believed that in liquid iron some hydrogen is present as a hydride; and W. Frankenburger and K. Mayrhofer found that when iron vapour condenses in an atm. of hydrogen, the film has Fe : H approximately as 1 : 2—*vide infra* for the hydrides. F. Duran and C. H. Teckentrup considered the absorption of hydrogen is a case of pure adsorption; L. Guillet and co-workers thought that a hydride is formed at the higher temp., and it dissociates below 250°.

The *permeability* of iron to hydrogen was observed by H. St. C. Deville and L. Troost, who found that the metal is permeable to ordinary hydrogen when it is heated to redness; and this fact was confirmed by T. Graham. L. Cailletet found that nascent hydrogen could pass through an iron vessel immersed in sulphuric acid at ordinary temp. H. M. Ryder's observations on the effect of temp. on the permeability of soft steel, and those of V. Lombard on electrolytic iron, are summarized in Fig. 326, and V. Lombard's observations on the effect of press. on the permeability of electrolytic iron are summarized in Fig. 327. M. Bodenstein, and M. Knobel and R. B. Norton expressed the rate of penetration of iron by hydrogen, D, as a function of the overvoltage, E. The subject was discussed by T. S. Fuller. E. Piwowarsky and H. Esser attributed the permeability of cast iron for gases to the presence of macroscopic flaws. B. Beer studied the subject. A. Winkelmann used an iron tube, closed below, as cathode in the electrolysis of a soln. of sodium hydroxide. The *rate of diffusion* of hydrogen formed on the exterior of the tube, into the interior, was found to be independent of the press. between 0 and 890 mm. of mercury. The rate of diffusion is not affected by reducing the external press. from 1 to 1·5 atm. It was accordingly inferred that the actual press. of the hydrogen on the outside of the iron tube is not of the same order as the internal press. and is not less than 58 atm. The independence of the internal press. agrees with the assumption that it is ionic or atomic, and not ordinary molecular hydrogen that is concerned in the process of diffusion. At a constant temp., the rate of diffusion increases more slowly than the current strength, and it is approximately proportional to the potential difference. The increase in the rate of diffusion, δ, with temp., $\theta°$, was rapid, and approximated to $\delta=\delta_0(1+0{\cdot}04550\theta)$ for a constant current, or to $\delta=\delta_0(1+0{\cdot}05610\theta)$ for a constant potential difference. G. Charpy and S. Bonnerot noted that the hydrogen as it diffuses through iron or steel at ordinary temp. acquires a special chemical activity. They showed that no diffusion occurs in steel tubes at ordinary atm. press. below 325°; the osmosis is perceptible at 350°; and it increases about 40-fold when the temp. is raised to 850°. The diffusion of gases in metals was studied by D. Alexejeff and L. Savinina, M. Bodenstein, A. H. W. Aten and P. C. Blokker, O. W. Richardson and co-workers, G. C. Schmidt and T. Lücke, C. A. Edwards, and by G. Borelius and F. Gunneson. W. E. Deming represented the rate of diffusion of hydrogen through iron by $d(p^{1/n})/dt=k/c\triangle^2p^{1/n}$, where p denotes the press. of the gas, and c the amount absorbed per unit vol. under unit press. For the steady state, the amount, dm, of hydrogen diffusing through an area, a, of thickness, dx, with press., p, and $p+dp$, in the time, dt, is: $dm=ka\triangle p^{1/n}dt$. A. Jaquerod and S. Gagnebin observed that the rate of diffusion of hydrogen in iron increases suddenly at about 200°, and other discontinuities occur at the Curie point, and at about 900°, when β-iron changes into γ-iron. A. H. W. Aten and M. Zieren, and T. S. Fuller discussed the penetration of iron by cathodic, nascent, or atomic hydrogen, and emphasized the difference between the behaviour of this form of hydrogen and ordinary gaseous hydrogen. A. Coehn considered that the experiments on the rate of diffusion of hydrogen in iron support the view that the absorbed hydrogen is in the form of electrons and protons. E. G. Mahin inferred that the hydrogen occluded by iron which has been pickled in acid diffuses in the metal in the atomic condition, and is liberated at the surface as molecular hydrogen.

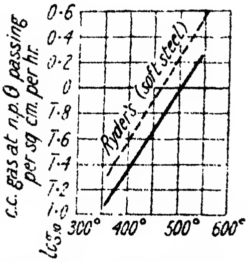


FIG. 326.—The Effect of Temperature on the Hydrogen Permeability of Iron.

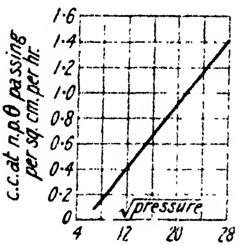


FIG. 327.—The Effect of Pressure on the Hydrogen Permeability of Iron.

N. B. Pilling observed that the *evolution of occluded hydrogen* from electrolytic hydrogen begins at about 100°, and attains a maximum at about 200°; H. Esser, J. Cournot, and C. F. Burgess and O. P. Watts, that the complete expulsion of the gas occurs above the a_3-point, —950° to 1050°; and O. W. Storey, that after heating to 910° to 1000°, electrolytic iron has the structure of ordinary iron; at 500° to 600° hydrogen is given off, but no change in structure is perceptible. B. Cazaud and

R. Hugues noted that there are discontinuities in the rate of evolution of the hydrogen attended by changes in the mechanical and magnetic properties of the metal; G. Borelius and F. Gunneson, that the variation in the rate of removal of occluded hydrogen and nitrogen from iron at different temp. shows a number of irregularities; and G. Tammann, and R. Hugues attributed some of the irregularities to the possible presence of hydrides. According to G. Belloc, the evolution of the occluded gas, when the metal is heated, is connected with the critical points of iron, and it may be divided into three stages: (i) the evolution begins at a variable, ill-defined temp. between 150° and 400°; the velocity, or dv/dt-curve (where v denotes volume), has a small minimum at 200°, and a small maximum at 300°, but the evolution of gas in the region of α-iron is very small, and tends to increase with temp. (ii) Between 500° and 600°, the dv/dt-curve exhibits a large maximum at the transition point of α- into β-iron, and then falls off to a minimum approaching zero at the end of the conversion. The transformation of cementation-carbon into temper-carbon has no marked influence on the result. (iii) The evolution of gas begins again with the transformation of β- into γ-iron, and after passing through a maximum, increases with temp. The gas first given off is nearly all carbon dioxide, and at about 550°, it disappears, and nitrogen makes its appearance and persists at all higher temp.; but the amount is small, not rising above the mean value of 10 per cent. Above 400°, carbon monoxide and hydrogen are alone evolved in proportions which may alter suddenly with temp. According to O. Boudouard, the results of heating iron in its various forms in vacuo at 1100°, with fifteen days' exposure to air between consecutive treatments, show that it is very difficult to extract the gases contained in iron and steel. Even after the third ignition at 1100°, the amount of gas retained by filings was 0·5 of the total vol., and 20 per cent. with sheet-iron and bar-iron. According to F. C. G. Müller, the gases sometimes regarded as occluded by iron are really mechanically held in the pores, for they are liberated on boring, and only a little additional gas is obtained when the borings are heated to redness in vacuo. The subject was also discussed by A. Pourcel, J. Parry and H. A. Brustlein, as well as by G. Alleman and C. J. Darlington, A. H. Allen, E. Améen and H. Willners, G. W. Austin, T. Baker, L. Baraduc-Muller, M. Barré, H. Bessemer, P. H. Brace and N. A. Ziegler, H. Braune, L. Cailletet, J. R. Cain, J. R. Cain and E. Pettijohn, H. Cassel and T. Erdey-Gruz, G. Charpy and S. Bonnerot, J. W. Donaldson, A. Friedmann, P. Goerens, P. Goerens and J. Paquet, E. Goutal, G. Hailstone, W. Herwig, W. Hessenbruch, W. Hessenbruch and P. Oberhoffer, P. Hird, L. Jordan and J. R. Eckman, E. Kahrs, O. von Keil, S. Kern, P. A. Klinger, W. Kusl, J. W. Langley, A. Ledebur, E. Liebreich, E. von Maltitz, E. Maurer, E. Münker, P. Oberhoffer and co-workers, A. S. de Osa, J. Paquet, N. Parravano and A. Scortecci, E. Piwowarsky, T. C. Poulter and L. Uffelman, F. Rapatz, P. Regnard, A. Ruhfuss, H. M. Ryder, O. Seth, J. E. Stead, J. E. Stead and S. Pattinson, G. Tammann, L. Troost and P. Hautefeuille, A. E. Tucker, U. le Verrier, A. Villachon and G. Chaudron, A. Vita, W. H. Walker and W. A. Patrick, H. Wedding, and A. Wüster and E. Piwowarsky. According to E. Améen and H. Willners, the gases: CO, CO_2, H_2, N_2, CH_4, and H_2O are dissolved by liquid steel, and when the steel hardens, these gases can react. The relation $CO_2 : CO$ is taken as a measure of the oxidation of the steel at a given temp. The CH_4 and H_2O content is a measure of the dissolved quantities of CO, CO_2, and H_2. Nitrogen is found chiefly in steels from the converter.

R. Hugues studied the rates of removal of hydrogen from about 20 c.c. of electrolytic iron, and L. Guillet and A. Roux, the vol. of gas removed from electrolytic iron at different temp. G. Hägg discussed the mol. vol. E. Heyn observed that the adsorption of hydrogen produces no perceptible effect on the microstructure, although it embrittles the metal. When cast iron is heated at 730° to 1000° in contact with hydrogen and then chilled, it becomes considerably more brittle than when similarly heated in air and chilled. If, however, the metal is allowed to cool slowly in hydrogen, it remains tough, and at temp. below 730° its properties are not affected by hydrogen. A cast iron containing 0·37 per cent. of carbon was found to behave in the same way as one containing only 0·05 of carbon and 0·01 of silicon. By heating the metal in nitrogen at a red-heat, the effect of the treatment with hydrogen is destroyed. In the case of iron containing very little carbon, the brittleness is partly removed by heating in boiling water, or even by long exposure to the air at the ordinary temp., and is completely destroyed by heating at 200° to 250°. Iron containing more carbon retains its properties much more obstinately. A superficial layer after treatment with hydrogen was found to show a greater flexibility, hence the hydrogen must penetrate below the surface. The density of the metal is not affected by the treatment with hydrogen. D. Alexejeff and M. Polukaroff studied the effect of hydrogen on the tensile properties of electrolytic iron. The results of A. Ledebur exposing wires of the metal to the action of acids are indicated in Table XLVIII. According to L. B. Pfeil, occluded hydrogen has a remarkable weakening effect on the intercrystalline boundary of iron—*vide supra*, hydrogenized iron. This applies not only to the boundaries between very large crystals, but also to the boundaries between the very minute crystals of which ordinary iron consists. The strength of the boundary between two single crystals has been shown to be about 8½ tons per sq. in., and of the boundary between very small crystals about 17 tons per sq. in. It is probable that this marked difference is due, not to any real variation in the strength per unit area, but to the difference in the ratio between the actual area of fracture and the cross-sectional area of the test-piece in the two cases. This ratio is much greater in the case of the aggregate than it is in the case of the two large crystals. In addition to its effect on the boundaries, hydrogen decreases the cohesion across the cubic cleavage planes, a pull of 5 tons per sq. in. applied at right-angles to the cleavage plane being sufficient to cause separation. Occluded hydrogen does not prevent deformation by slipping on the icositetrahedral planes of the iron crystal. Judging from the behaviour of the single crystals during these tests, it

TABLE XLVIII.—THE EFFECT OF OCCLUDED HYDROGEN ON THE MECHANICAL PROPERTIES OF IRON.

Metal	Tenacity (tons per sq. in.)		Elongation (per cent.)		Number of times metal could be bent	
	Normal	Hydrogenized	Normal	Hydrogenized	Normal	Hydrogenized
1. Uncleaned wires in 1 per cent. H_2SO_4, for 24 hrs. examined after 3 days .	54·54	54·66	3·5	2·8	10·2	8·0
2. Cleaned wires immersed 23 hrs. in 2·5 per cent. H_2SO_4, and examined immediately . .	54·09	56·00	3·4	2·7	7·4	3·0
3. Wires connected with a block of zinc and immersed 3 hrs. in 2·5 per cent. H_2SO_4, and examined immediately .	52·76	52·19	2·0	2·2	10·0	3·9
4. Wires treated as in 3, but examined 4 days later .	51·11	51·17	3·0	2·2	10·1	7·2
5. Wires treated as in 3, but heated to cherry redness for 15 mins. in an inert atm.	27·24	28·51	17·9	16·9	16·2	14·6

seems improbable that the hydrogen has even any important effect on the resistance to movement along the slip planes. The effect of hydrogen on the finely crystalline iron is very much less marked at temperatures a little above room temperature. Under these conditions the crystal boundaries are not so greatly weakened. Fracture takes place mainly *through* the crystals after they have been drawn down by slipping, but the point at which fracture occurs is determined by cracks which form as a result of a limited cleavage and intercrystalline failure. The cracks probably originate in those crystals so set at the surface of the test-piece as to present a cleavage plane at right-angles to the stress, these being particularly liable to fracture at low stresses. The minute notches so produced lead to large cracks which, decreasing the effective cross-section of the test-piece, cause a low value to be recorded for tensile strength. F. C. Lea observed that nascent hydrogen liberated at a cathode penetrates the crystal boundaries of mild steel, nickel, and stainless steel with 15 per cent. Cr, and 10 per cent. Ni. The penetration does not affect the tensile strength of these materials, but it lowers considerably the elongation of specimens of mild steel. The transverse cracks which develop indicate that the tearing of crystals apart at their boundaries occurs at fractures. The hydrogen interferes with the slip that takes place on certain crystal planes and which, under ordinary conditions, continues apparently across the crystal boundaries. Hydrogen escapes quickly after the current ceases, even at ordinary temperatures, and after heating at 100° the properties of the material are restored. Hydrogen in the cathode does not diminish the resistance to impact of mild steel and its effect on repeated stress seems of itself unimportant. The fractures under repeated stresses, however, show that the penetration of hydrogen has an important bearing upon the nature and form of fracture of a plastic material, which under repeated torsional stress, fails in a manner similar to quenched and tempered materials. Consequently the presence of the hydrogen at the crystal boundaries does not increase the concentration of stress in the repeated stress experiments, nor in the impact tests, but affects the continuity of slip and causes a crack to occur as in the quenched and tempered materials, and suggests that in all such materials the failure is at the boundaries, while the failure of plastic materials occurs by cracking within the crystal. Observations on the subject were made by J. H. Andrew, H. C. H. Carpenter and C. F. Elam, J. Coulson, C. A. Edwards and co-workers, C. F. Elam, T. S. Fuller, L. Jacque, S. C. Langdon and M. A. Grossman, P. Longmuir, F. Osmond and G. Cartaud, S. W. Parr, W. Rosenhain and D. Ewen, O. P. Watts and C. T. Fleckenstein, M. Majima, V. S. Meskin and Y. M. Margolin, M. Okochi, R. Hugues, L. Guillet and J. Cournot, B. Bogitch, and M. Guichard and co-workers.

According to W. C. Roberts-Austen, the heating curve of iron charged with occluded hydrogen shows breaks at 261° and 487°, and these breaks do not appear if the metal has been previously heated in vacuo. G. Borelius and F. Gunneson observed a number of irregularities in the thermoelectric force at approximately −5°, 150°, 220°, 300°, 460°, 530°, and 600°. There is also a marked increase in the absorption of hydrogen at the Curie point, 760°. It is thought that the phenomena may be due either to unknown modifications of iron, or to the existence of solid hydrides. G. Sirovich stated that there is an abrupt change in the rate of expansion of iron, and low-carbon steels at 370°; and he inferred that this represents a transformation point in addition to the usually-recognized critical points. H. S. Rawdon and co-workers also observed this irregularity, but said that it is not due to a polymorphic transformation, because the break in the curve is too irregular with different samples. The phenomenon is attributed to "some condition resulting from the presence of iron oxide in the iron"; and it may be due to the recrystallization of very fine grained metal resulting from the reduction of iron oxide by hydrogen at this low temp. N. B. Pilling noted the effect of hydrogen on the hardness of iron; R. S. Williams and V. O. Homerberg, on the ductility; and E. A. Harding and D. P. Smith, on the changes in length and the electrical resistance. R. Nübel discussed the thermal energy of hydrogenized iron. E. Rupp studied the optical properties of iron with a film of adsorbed hydrogen. A. Sieverts observed that the dissolution of hydrogen between 20° and 920° had no perceptible influence on the electrical resistance; but H. Kleine found that the resistance increased when the metal contained occluded gas. H. Gries and H. Esser examined the effect of occluded hydrogen on the magnetic properties of the metal.

G. Charpy and S. Bonnerot found that when iron at 600° to 900° is exposed for a long time to a current of hydrogen, no gas is absorbed but the physical properties of the metal are modified, it being softened by prolonged diffusion of the gas, which exercises a reducing action, removing such constituents as sulphur, phosphorus, and carbon in the form of their hydrides, the desulphurization being particularly rapid. The iron thus undergoes a process of purification by the passage of the hydrogen, and this may possibly explain certain of the anomalies in the metallurgy of iron and steel, when hydrogen is formed by the contact of water vapour with the hot metal. Observations on this subject were made by A. Johansson and R. von Seth, L. Jordan and F. E. Swindells, G. W. Austin, A. Bérard, F. Schmitz, F. Wüst and C. Geiger, F. Wüst and E. Sudhoff, G. Charpy, J. V. Emmons, H. S. Rawdon and co-workers, H. le Chatelier, J. H. Whiteley, E. D. Campbell and co-workers, O. E. Harder and co-workers, F. C. Langenberg and H. M. Boylston, V. Lombard, R. Schenck, and L. Forquignon. P. D. Merica noted the injurious effect of absorbed gases on the magnetic properties of iron (*q.v.*).

R. Schenck, and A. Johansson and R. von Seth represented the *decarburization of iron* by hydrogen by the reaction $Fe_3C+2H_2 \rightleftharpoons 3Fe+CH_4$ at 750°. The assumption is made that the carburization is effected by methane, but possibly other hydrocarbons are also concerned in the reactions. Fig. 328 represents qualitatively the equilibrium curves between carburized iron and hydrogen, when the dotted line represents the equilibrium conditions for the reaction $C+2H_2 \rightleftharpoons CH_4$. The ferrite-austenite line ends at a fixed point corresponding with 0 per cent. methane, and at the temp. of the A_3-arrest for iron alone. The intersection points of the curves are dependent only on the carbon press. of the different solid phases discussed in connection with the decarburization of cast iron. Small methane percentages at 900° to 1000° prevent the decarburization of hydrogen. R. Schenck found the intersection point between the carbon, hydrogen, and methane equilibrium curve and the ferrite-austenite line to be 720°. The relation between the percentage of carbon and the time of heating in the decarburization of steel by hydrogen at 1050° is shown in Fig. 329. G. W. Austin found that decarburization by dry hydrogen is much slower than by moist hydrogen. The subject was studied by J. Ciochina—*vide supra*, O. Schmidt, A. Korczynsky, R. Hocart, A. E. Mitchell and A. L. Marshall, and F. H. Constable. A. S. Ginsberg and A. P. Ivanoff, and O. Schmidt studied iron as a catalyst in the hydrogenation of various compounds; H. Remy and H. Gönningen, the $2H_2+O_2$ reaction; A. Quartaroli, the reducing action of the iron-copper couple; K. F. Bonhoeffer showed a correspondence between the adsorption of hydrogen and catalytic activity; and G. B. Kistiakowsky, the ionization potential of hydrogen adsorbed on iron. According to E. D. Campbell, the best temp. for the elimination of impurities by exposure to hydrogen is 950° to 1000°; a gas containing a small proportion of water-vapour is most efficient. The decarburization occupies on average four or five days. For example:

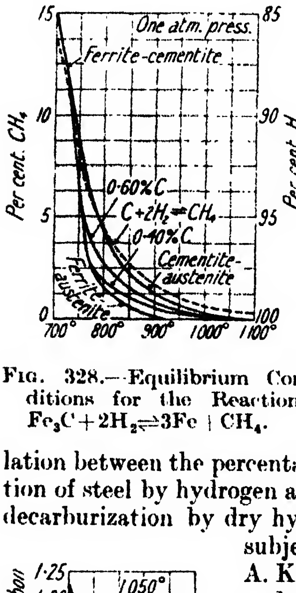


FIG. 328.—Equilibrium Conditions for the Reaction: $Fe_3C+2H_2 \rightleftharpoons 3Fe+CH_4$.

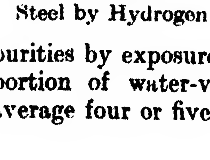


FIG. 329.—The Decarburization of Steel by Hydrogen.

Treatment	Per cent. carbon		Per cent. sulphur	
	Before	After	Before	After
4 days	0·094	0·076	0·025	0·017
5 days	0·354	0·017	0·026	0·014
8 days	1·184	0·005	0·018	0·006
12 days	1·150	0·133	0·023	0·026

T. Thomson[3] suggested that an **iron hydride,** or rather a *ferruretted hydrogen gas*, mixed with much hydrogen, is formed when iron is dissolved in dil. sulphuric acid. It was supposed that the ferruretted hydrogen was not removed from the gas by passing through four wash-bottles containing potash-lye, and a tube filled with asbestos. A. Dupasquier gave a long description of the supposed gas, but C. R. Fresenius and J. Schlossberger showed that the alleged properties of ferruretted hydrogen corresponded with those of hydrogen contaminated with hydrogen phosphide and sulphide, when no iron is present. Hence, the existence of ferruretted hydrogen is not established. H. Reinsch believed in the existence of such a gas; but E. Erlenmeyer, and C. A. Cameron could find no evidence to support the hypothesis. J. A. Wanklyn and L. Carius suggested that when ferrous iodide is treated with zinc ethyl, a **ferrous dihydride,** FeH_2, is formed: $FeI_2+Zn(C_2H_5)_2=ZnI_2+FeH_2+2C_2H_4$, but the evidence is not at all satisfactory. The alleged hydride may be iron with occluded hydrogen; A. Villachon and G. Chaudron were of the opinion that a hydride is possibly formed in liquid iron; W. Frankenburger and K. Mayrhofer, when iron vapour is condensed in an atm. of hydrogen; and G. Borelius and F. Gunneson, when hydrogen is occluded by iron. T. Weichselfelder and B. Thiede observed that when ferrous chloride is treated with an ethereal soln. of magnesium phenyl bromide, a black powder of iron dihydride, FeH_2, is formed; and if ferric chloride be employed, **iron hexahydride,** FeH_6, appears as a black, viscid oil. E. Piwowarsky observed no evidence of the existence of hydrides in hydrogenized iron; L. Guillet and co-workers thought that one is formed stable above 250°.

The effect of **air** and **oxygen** on iron is discussed elsewhere in connection with the corrosion and tarnishing of iron; with the reduction and formation of the various oxides of iron: and with the production of iron. In 1782, S. Rinman[4] reported that dry air does not corrode iron, but moist air does; and a few years later, W. Higgins stated that iron does not rust in dry oxygen, and explained the phenomenon by assuming that

> It is the oxygen of the water which unites to the iron, while the oxygen of the gas is condensed by the liberated hydrogen in the nascent state, so as to reproduce water. This is effected by a double influence which is so obvious as not to require an explanation.

P. A. von Bonsdorff made a similar observation—*vide infra*; S. U. Evans also noted that air dried by sulphuric acid did not corrode iron in a month under conditions where moist air corroded the metal; and E. Schröder and G. Tammann, and W. R. Dunstan and co-workers observed that iron showed no signs of change when kept for 3 months in dry oxygen at 34°; R. Ruer and J. Kuschmann observed that finely-divided iron, reduced by hydrogen from the oxide at 750°, does not absorb air, but there is a slight oxidation on exposure to dry air, for 100 grms. of iron increased 30 mgrms. in weight. Iron filings also oxidized slightly in dry air. G. Tammann estimated that at 15°, dry oxygen would produce a visible film on iron in 25×10^{17} years.

W. Hardy and M. Nottage found that a polished steel cylinder placed on a steel plate remained at a distance of 4μ above the plate in clean dry air. Pressure applied to the top cylinder made the two surfaces approach more closely, but on removing the pressure, the air film returned to 4μ. This thickness remained constant for glass to glass and steel to steel. The subject was studied by S. H. Bastow and F. P. Bowden, and H. E. Watson and A. S. Menon.

P. Gladky found from 0·021 to 0·974 per cent. of oxygen equivalent to 0·23 to 0·33 per cent. of ferrous oxide in various samples of iron and steel—*vide infra*.

ferrosic oxide, the corrosion of iron, and ferrous oxide. J. A. Pickard, A. Ledebur, A. H. Allen, A. K. Silin, J. E. Stead, L. Romanoff, M. A. Grossmann, J. Cournot and L. Halm, and S. Kern discussed the oxygen-content of iron and steel; and H. W. Gillet, the action of oxygen on the iron-carbon system. The oxygen-content of iron and steel is indicated in Table XLVII; the binary system iron-oxygen has been discussed by F. Schönert, F. Czopiwsky and S. Orzechowsky, and others in connection with ferrous oxide; and the ternary system Fe–O–H, and Fe–O–C, by H. Nishimara—*vide supra*, the blast-furnace reaction. W. R. Shimer and F. O. Kichline found a maximum of 0·074 per cent. oxygen in Bessemer steel when cooled quickly after a long after-blow. Oxygen leaves a bath of molten steel in a few minutes, so that few steels have much more than 0·03 per cent. oxygen. W. Austin found that the product obtained by melting a mixture of iron and iron oxide had 0·288 per cent. oxygen. F. Schmitz found 0·113 per cent. oxygen in Thomas-Gilchrist steel. E. A. Harding and D. P. Smith noted the occlusion of oxygen by iron electrodes.

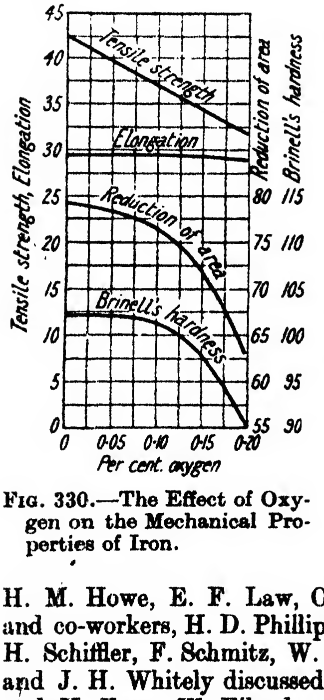


FIG. 330.—The Effect of Oxygen on the Mechanical Properties of Iron.

F. Durau and C. H. Teckentrup showed that the absorption of oxygen by electrolytic iron is a chemical process. A. Ledebur said that 0·1 per cent. of oxygen makes iron no longer forgeable, for it is then red-short; and the subject was discussed by F. Hatlanek. E. F. Law said that iron and manganese oxides can be detected as black spots under a magnification of 1000. F. R. Eichoff considers it to be doubtful if oxygen makes iron red-short, because of the high proportion in welded iron. It is assumed that the affinity of iron for oxygen, and of carbon for iron, increases with a rise of temp., while the affinity of carbon for oxygen increases relatively little under these conditions. Hence, carbon monoxide is formed at a certain temp. during the cooling of the iron, while above this temp. the oxygen and carbon are dissolved in the iron without acting on one another. F. Roll found that the presence of oxygen partly favours and partly hinders the decomposition of the carbide in cast iron. J. R. Cain, G. F. Comstock, H. Diergarten, J. R. Eckman and co-workers, W. Eilender and W. Oertel, E. W. Fell, W. Galbraith, J. D. Gat, P. Gladky, M. A. Grossmann, E. Gumlich and P. Goerens, F. Hatlanek, C. H. Herty and J. M. Gaines, H. D. Hibbard, H. Hochstein, A. Holtz, H. M. Howe, E. F. Law, O. Meyer, R. Moldenke, A. Niedenthal, P. Oberhoffer and co-workers, H. D. Phillips, F. Rapatz, J. Reschka and co-workers, H. Schenck, H. Schiffler, F. Schmitz, W. L. Stork, L. Treinen, A. E. White and J. S. Vanick, and J. H. Whitely discussed the presence of unreduced oxides in iron; H. Gries and H. Esser, W. Eilender and R. Wasmuth, and J. A. Lanigan, the effect of oxygen on the hardness—with 0·030 per cent. of oxygen, Brinell's hardness was 70·2, and with 0·141 per cent., 79·6; F. C. Thompson and R. Willows, the production of a banded structure in hot-worked, hypo-eutectoid steel; and E. W. Fell, J. R. Cain, and A. Niedenthal, the red-shortness produced by oxygen in iron. A. Wimmer's observations on the influence of oxygen on the mechanical properties of iron are summarized in Fig. 330, where the tensile strength is expressed in kilograms per sq. mm.; and the elongation and reduction of area in percentages. W. McA. Johnson made observations on the subject. H. Gries and H. Esser examined the effect of oxygen on the magnetic properties of iron. F. W. Lürmann, J. V. McCrae and R. L. Dowdell, F. Giolitti, F. C. Moorwood, C. H. Herty and co-workers, A. McCance, C. H. Desch, G. F. Comstock, P. Bardenheuer and K. L. Zeyen, L. Persoz, H. M. Boylston, and J. R. Cain investigated various deoxidizing agents for steel—*vide* aluminium, manganese, silicon, titanium, etc.; and E. R. Thews arranged possible deoxidizing agents in the order of their affinity for oxygen: Mg, Al, Si, Mn, Zn, P, Sn, and Cd; and in the order of their capacity for oxygen: Si, Al, P, Mg, Mn, Zn, Cd, and Sn. C. H. Herty and co-workers studied the deoxidation of steel by aluminium, and found that it proceeds more quickly than is the case with silicon—*vide* aluminium-iron alloys. A. K. Silin studied ferromanganese as a deoxidizer; P. Blum, and C. H. Herty and co-workers, silicon; E. Diepschlag and H. Schürmann, phosphorus; W. Zieler, zirconium; P. Blum, and E. Lemaire, calcium; E. Lemaire, magnesium; P. Blum, boron; J. R. Cain, manganese, silicon, titanium, and aluminium; C. H. Herty and G. R. Fitterer, manganosilicon; J. H. Whitely, hydrogen at 950°; and A. Glazunoff, and A. Hiorth, sodium. *Vide supra*, the growth of iron.

In the sixteenth century, Paracelsus said that "when iron is fused in the furnace, it sends forth limpid, clear sparks which rise to a height, and that as soon as these appear, unless the iron be at once removed from the fire, it will be burnt up like straw." G. C. Lichtenberg, and J. Ingenhousz found that when iron is heated to whiteness in air or oxygen, it burns with vivid sparking, forming ferrosic oxide. In air, the combustion soon ceases, but in oxygen, combustion continues if the piece of iron be thin, and the high temp. produced may volatilize some of the iron which is then oxidized to ferric oxide. According to L. F. Bley, and G. Magnus, finely-divided iron suspended from a magnet burns when placed in a flame, and when the flame is removed, the ferrosic oxide which remains is also ferromagnetic. The early experiments on the combustion of iron were discussed by E. von Lippmann, and E. Cohen. S. S. Sakowsky and E. W. Butzker showed that with oxygen under a high pressure, iron and steel burn readily and completely, and if once ignited propagate a flame with explosive velocity. According to R. Phillips, R. Adams, S. Stratingh, and F. d'Arcet, if a bar of iron be heated until it emits sparks—welding-point—it will burn even in the air if the blast of the bellows be strongly directed upon it, or if it be swung rapidly round—by tying a rod to a piece of cord at one end, and heating the other end white-hot; when the cord is swung rapidly round, a brilliant circle of sparks, resembling fireworks, is produced by the combustion of the metal. J. Percy mentions that the old nailmakers availed themselves of the combustibility of iron at a high temp. to keep their nails hot during the process of forging. "There is a little blowpipe connected by a tube with a small pair of bellows and a jet of air is thrown on the iron when it is becoming too cold, and immediately the temp. is much raised." When a piece of flint is struck by a piece of steel, fine particles of the metal are detached by the stone, and brought to such a temp. that they fire in air, and ignite tinder. Hence, as found by H. Davy, a flint and steel in vacuo gives but very feeble sparks. W. G. Hildorf and C. H. McCollain, C. M. Bigger, P. K. von Engelmeyer, G. M. Enos, A. K. West, M. Bermann, E. Pitois, and L. Demozay studied the nature of the sparks removed by the attrition of different kinds of steel against a grindstone, and proposed that the results be used as a test of the nature and quality of steel. According to A. Pourcel, the method was suggested in 1804 by J. C. de Manson. M. Fink and U. Hofmann observed the oxidation produced by rolling friction in dry air. H. P. Walmsley studied the nature of the smoke of aerosol obtained by burning iron between electrodes.

According to H. Moissan and C. Moureu, iron powder, prepared by the reduction of ferrous or ferric salts, is chemically more reactive than compact iron; and the powder obtained by reducing the oxide, carbonate, or oxalate in hydrogen at 440° is pyrophoric, for it becomes incandescent when exposed to moist air. If the pyrophoric iron be kept at 310° to 320° for about 48 hrs., A. Smits and co-workers observed that it is no longer pyrophoric, and the change is accompanied by an increase in vol. It is said that pyrophoric iron consists of a mixture of different kinds of iron molecules which are not in a state of equilibrium. C. G. Fink and C. L. Mantell discussed the pyrophoric qualities of commercial ferrum reductum, of freshly reduced iron. C. Johns said that in growing molten steel, the surface remains optically clean for a short time, and the period is longer the higher is the temp. The surface is protected from oxidation by a barrage of metal vapour. As the temp. falls, the vap. press. is reduced until finally the oxygen penetrates to the metal and oxidation begins.

The attack of iron by oxygen or air was studied by J. Keir, C. Becker, J. B. Trommsdorff, C. F. Bucholz, J. L. Gay Lussac, J. H. Hassenfratz, N. J. Conté, J. B. Guyton de Morveau, N. J. B. Guibourt, M. M. Hall, J. R. Bréant, K. Inamura, J. Zumstein, S. Clegg and J. Farey, L. J. Thénard, J. L. Proust, M. Darso, M. Delaville, J. Cuthbertson, E. Jordis and W. Rosenhaupt, K. Hoffmann, G. Tammann and co-workers, S. Tour, and N. B. Pilling and R. E. Bedworth—*vide infra*, the tarnishing, and scaling of iron. J. V. Emmons, H. Scott, E. H. Schulz and P. Niemeyer, and A. Johannson and R. von Seth, the surface decarburization of iron when it is heated in air or oxygen; and H. C. Greenwood, by heating it in a bath of lead dioxide.

C. Dufraisse and R. Horclois said that the wide distribution of iron in nature and in the respiratory pigments of the higher animals makes a study of its catalytic activity of importance. Iron is usually but not exclusively a positive catalyst for autoxidation. It can act both as an anti-oxygenic and as a pro-oxygenic catalyst. Ferrous oxide is anti-oxygenic towards furfural; ferric hydroxide, towards alkaline soln. of sodium sulphite; ferric chloride, for benzaldehyde, and for furfural; ferrous iodide, for benzaldehyde and acrolein; ferric acetylacetonate, for sodium sulphite in feebly acidic soln., and for furfural; oxyhæmoglobin carboxylhæmoglobin, and methæmoglobin, for furfural; acrolein, and sodium sulphite; α-chlorohæmin, for furfural; β-chlorohæmin, hæmatin, dimethylester of α-chlorohæmin, and β-bromohæmin, for furfural, acrolein, sodium sulphite and benzaldehyde.

W. Manchot found that iron reacts with oxygen at a temp. only slightly higher than that at which it reacts with **ozone.** Iron rendered passive by immersion in nitric acid, or by being used as anode in dil. sulphuric acid, reacts almost instantly in the cold with 3 per cent. ozone, whereas active iron shows no such sensitiveness towards ozone.

The rusting of iron in moist air at ordinary temp. has been discussed elsewhere. C. Girtanner, in 1788, communicated a paper: *Ueber die Auflösbarkeit des Eisens in reinem Wasser.* According to M. M. Hall, N. J. B. Guibourt, E. Ramann, S. Birnie, A. Job and R. Reich, and J. A. N. Friend, pyrophoric iron decomposes **water** at ordinary temp., and, according to S. Birnie, some hydrogen is evolved. W. van Rijn said that mercury accelerates the reaction with pyrophoric iron. J. A. Wanklyn and L. Carius found that iron does not decompose water at 50° but does so at 100°, giving off hydrogen; E. Ramann also found that iron decomposes boiling water; J. R. Baylis obtained a little hydrogen even at ordinary temp.; and L. T. Alexander and H. G. Byers found that hydrogen is developed from the action of water on iron at ordinary temp. when felspar is ground in a steel ball mill. S. Micewicz found that at 100°, the rate of evolution of hydrogen from water on contact with powdered iron is diminished in the presence of sodium and potassium chlorides, it is slightly increased by calcium chloride, and very much increased by magnesium chloride. E. Berl and co-workers found that the attack of iron by distilled water increases with the temp. and with the pressure; thus, with 10 grms. of powdered iron, during 16 hrs., and at 100 and 200 atm. press., the vols. of hydrogen developed were respectively 160 c.c. and 480 c.c.; and the percentages of iron in the product were 98·21 and 94·45, and of ferrous oxide, 0·87 and 5·51, respectively. L. Troost and P. Hautefeuille observed that aluminium, if present, accelerates the reaction. Boiling soln. of alkali hydroxides behaved similarly. H. V. Regnault observed that iron is decomposed by steam, and the action of steam on iron has been discussed in connection with the iron oxides, and the reactions in the blast-furnace—*vide infra,* ferrosic oxide. P. P. Fedotéeff and T. N. Petrenko represented the reaction with steam at 1000° to 1100°, $Fe \rightarrow FeO \rightarrow Fe_3O_4$, and with mixtures of steam and air, $Fe \rightarrow FeO \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$. The action of steam on iron was also studied by J. A. N. Friend and co-workers, A. G. Christie, A. Fry, F. Körber and A. Pomp, F. G. Straub, E. Piwowarsky, G. Dessus and co-workers, W. H. Hatfield, J. K. Rummel, W. L. Denman and E. Bartow, and R. Kattwinkel. W. Kraus studied the kinetics of the reaction; and J. Chipman, the state of equilibrium in the oxidation of liquid iron by steam over the range from 1550° to 1770°. Ferrous oxide is said to be formed, and the free energy of the reaction $Fe+\frac{1}{2}O_2=FeO$ is $-31200-1{\cdot}0T$. K. Murata found that the partial press. of hydrogen corresponding with the reaction: $3Fe+8H_2O \rightleftharpoons Fe^{\cdot\cdot}+2Fe^{\cdot\cdot\cdot}+8OH'+4H_2$ is 566 atm.

The wearing away of metal plates by the action of steam was examined by J. Walter; A. A. Cary, and F. Westhoff studied the corrosion of wrought and cast iron by dry steam; W. Campbell and J. Glassford, the corrosion of cast iron by superheated steam; T. S. Fuller, the effect of steam on the endurance tests; and C. B. Marson and J. W. Cobb, and H. T. Angus and J. W. Cobb, the scaling of steel in atmospheres of steam. J. K. Rummel found that the corrosion of steel by superheated steam at press. up to 3450 lbs. per sq. in., is negligible up to about 430°; and in some cases up to 650°. The presence of oxygen in the steam favours the attack. The subject was studied by W. H. Hatfield, G. Dessus and co-workers, I. N. Hollis, A. A. Cary, A. S. Mann, E. F. Miller, R. G. C. Batson, J. A. N. Friend and co-workers, W. Campbell and J. Glassford, F. N. Bushnell, W. Krauss, P. Askenasy, R. G. Edwards, B. Houghton and D. C. Weeks, and A. B. Williams and C. W. Welsh. The action of water on iron has been studied by G. Schikorr—*vide infra*, the corrosion of iron. The decomposition of steam by iron powder at about 250° is a convenient and rapid method of preparing hydrogen of a high degree of purity. S. S. Bhatnagar and S. L. Bhatia studied the rate of evaporation of adsorbed water from iron. J. V. Emmons found that steel heated in steam was decarburized more than when heated in hydrogen, carbon dioxide, or in air. H. Remy discussed the catalytic activity of iron on detonating gas; I. Moscicki and J. Broder, the spheroidal state of water on iron; and A. Sellerio, the force necessary to remove brass frozen on to iron and other metals by an intermediate film of water.

L. J. Thénard, and G. T. Moody found that dil. soln. of **hydrogen dioxide** has no visible action on iron, though it is catalytically decomposed by the metal; the converse result, by W. R. Dunstan and co-workers, is attributed to the use of impure hydrogen dioxide. Cast iron is rapidly attacked by hydrogen dioxide, and it is assumed that the sulphur, and phosphorus which it contains as impurities are oxidized by the hydrogen dioxide to form acids. Hydrogen dioxide in alkaline soln., say, $0{\cdot}2N$-NaOH or NH_4OH, does not attack iron of a high degree of purity, although oxygen is set free from the dioxide. Under similar conditions, cast iron acquires a thin film of a bronze-coloured oxide. W. R. E. Hodgkinson and A. H. Coote, H. Tatu, N. Floresco, R. Kuhn and A. Wassermann, and H. Wieland and W. Franke studied the action of hydrogen dioxide on iron, and the last-named found that with conc. soln., 0·5 to $5{\cdot}0N$-H_2O_2, there is no perceptible action, but with dil. soln. the iron rusts. E. Pietsch and co-workers also observed that if the surface of the metal is homogeneous there is no action, but if, by incomplete polishing, etc., the surface is heterogeneous, rusting occurs. A. von Kiss and E. Lederer studied the catalytic decomposition of hydrogen dioxide in the presence of iron-ions. As indicated below, the rate of dissolution of iron in acids is hastened if hydrogen dioxide be present. W. L. Dudley observed that when iron is treated with fused **sodium dioxide,** red crystals of $Fe_2O_3.H_2O$ are formed; and T. Wallace and A. Fleck observed the attack with a fused mixture of sodium hydroxide and dioxide. W. Guertler and T. Liepus observed that iron is attacked in less than 8 days by chlorine water, sea-water, sea-water and air, rain-water and air, and a soln. of magnesium chloride; it is attacked in less than 8 hrs. by 10 and 50 per cent. soln. of sodium hydroxide; and it is stable for 48 hrs. in an alkaline soln. of hydrogen dioxide. Observations on the action of sodium dioxide on iron were made by W. G. Mixter, W. H. Hatfield, C. Zenghelis and St. Horsch, and E. Leidié and L. Quennessen. J. L. Gay Lussac, and L. J. Thénard found that when iron powder is heated with **potassium peroxide,** K_2O_4, potassium is formed; and St. Meunier found that when iron is fused with the peroxide, a ferrate is formed.

According to H. Moissan,[5] **fluorine** slowly attacks compact iron at ordinary temp.; but when the metal is warmed, it burns with sparks; and at a red-heat, the absorption of fluorine is rapid, and much heat is evolved. Powdered iron reacts with fluorine below redness with incandescence; and iron reduced by hydrogen combines with great energy in the cold. H. Moissan and J. Dewar observed that the reaction proceeds quietly at −185°; and C. A. Crommelin, likewise, at −253°. T. Andrews noted that dry **chlorine** does not attack iron, although the moist gas quickly corrodes the metal. A. Lange observed that liquid chlorine when dry does not attack compact iron at ordinary temp., and this enables liquid chlorine to be preserved in iron reservoirs. Analogous observations were made by A. Fürth, and W. A. Masel, whilst H. Gautier and G. Charpy noted that at ordinary temp. liquid chlorine attacks iron very slowly. Iron is readily corroded by moist chlorine at ordinary temp.; P. A. von Bonsdorff noticed that air containing traces of chlorine quickly corrodes the metal. G. Tammann and W. Köster studied the rate of attack of iron by chlorine. The corrosion of iron by chlorinated water was examined by G. L. Clark and R. B. Iseley, M. L. Hamlin and F. M. Turner, C. G. Gillespie, and N. V. Lothian and A. R. Ward. When iron is heated in the dry gas it volatilizes and condenses in what H. Davy called " beautiful minute crystals of extraordinary splendour "; which J. Davy showed were ferric chloride. According to O. Ohmann, if a small ball of steel-wool be sprinkled with antimony, or, according to R. Böttger, with Dutch metal, and then plunged into chlorine, it is ignited at ordinary temp. Observations were also made by M. Rosenfeld. G. Tammann and co-workers examined the rate of attack of iron by the halogens. W. Guertler and T. Liepus found that iron is attacked in less than eight days by chlorine water. H. E. Fierz-David discussed iron and iodine as chlorine carriers in the chlorination of benzene derivatives. T. Andrews observed that dry **bromine,** like dry chlorine, does not attack iron. J. B. Berthemot found that, as in the case of chlorine, bromine does not act on iron in the cold, but when the vapour of bromine is passed over heated iron wire or turnings, J. B. Berthemot, A. Scheufelen, and J. von Liebig observed that combination, accompanied by a vivid glow, occurs. The reaction was studied by H. Gautier and G. Charpy, P. Höfer, L. Mathesius, L. Schneider, F. Wüst and N. Kirpach, and A. Fürth, G. Tammann and W. Köster studied the rate of attack. J. Nicklès observed that iron is attacked by an ethereal soln. of bromine; J. B. Berthemot also observed that iron dissolves in bromine-water; and P. Berthier found that a mass of graphite, iron carbides, etc., remains when cast iron or steel is digested with bromine-water. According to L. Carius and J. A. Wanklyn, S. de Luca, F. Fischer, L. B. Parsons, I. L. Bell, G. Tammann, C. L. Jackson and I. H. Derby, when iron is heated with an excess of **iodine,** ferrous iodide, not ferric iodide, is formed. N. Floresco, B. L. Meredith and W. G. Christiansen, and G. Tammann and W. Köster studied the rate of attack of iron by iodine. G. C. Fleury found that iron and iodine, in the presence of water, interact to form ferrous iodide. The reaction is supposed to occur in stages first forming ferric iodide which decomposes into ferric oxide and hydrogen iodide, and the latter, acting on free iron, forms ferrous iodide; and J. J. Berzelius, and P. Berthier noted that a mass of graphite, iron carbides, etc., remains when cast iron or steel is digested with iodine-water. V. A. Kistyakovsky and I. V. Krotoff studied the corrosion of iron by iodine vapours. L. B. Parsons observed no reaction with iron and iodine in the presence of carbon tetrachloride, carbon disulphide, chloroform, quinoline, pyridine, heptane, ethyl benzene, and benzene in which ferrous iodide is insoluble, but a slow reaction occurs in alcohol, ether, and acetone in which the ferrous iodide is slightly soluble. H. E. Fierz-David observed that iron associated with iodine is a powerful catalyst in the chlorination of benzene derivatives. A. Schükareff, and R. G. van Name and co-workers studied the rate of dissolution of iron in an aq. soln. of iodine and potassium iodide. J. T. Dunn showed that glycerol retards the reaction. W. Engelhardt studied the action of an aq. soln. of iodine on the hydrosol of iron. L. B. Parsons found that whilst an alcoholic, ethereal, or acetone soln. of iodine reacts with iron, the metal is not perceptibly attacked by soln. of iodine in carbon tetrachloride chloroform, carbon disulphide, quinoline, or pyridine.

O. Ruff and H. Krug observed that **chlorine trifluoride** reacts with iron with incandescence. G. Gore observed that reduced iron develops no hydrogen in dry liquid **hydrogen fluoride** at −7° to −18°. According to C. Poulenc, hydrogen fluoride slowly attacks reduced iron at a red-heat, forming ferrous fluoride ; a soln. of the same salt was obtained by C. W. Scheele, J. J. Berzelius, and O. Ruff and E. Ascher by dissolving iron in a soln. of **hydrofluoric acid**—hydrogen is at the same time evolved. G. Gore found that dry, liquid **hydrogen chloride** does not attack iron. F. Durau and C. H. Teckentrup showed that the absorption of hydrogen chloride is a chemical process. According to F. Wöhler and J. von Liebig, and P. Junius, ferrous chloride is formed when hydrogen chloride is passed over red-hot iron filings. R. E. Wilson and W. H. Balke, K. A. Hofmann and F. Hartmann, and C. Matignon examined the action of hydrogen chloride and oxygen on the metals. P. A. von Bonsdorff noticed that air containing traces of hydrogen chloride quickly corrodes iron. C. H. Desch, and A. de Waele discussed the action of hydrogen chloride in flue gases derived from the combination of coal containing chlorides. U. R. Evans observed that in air containing traces of carbon dioxide and hydrogen sulphide, the metal remained " dry " in the ordinary sense of the term ; in hydrogen chloride, the specimens lost their lustre, and acquired a whitish-grey, frosted appearance, and they remained " dry," but on exposure to damp air, water was absorbed and the surface became covered with a damp, brown rust. Hence, so long as hydrogen chloride is in excess, ferrous chloride is formed, but on exposure to air, this is oxidized to hydrated ferric oxide, and ferric chloride which attracts moisture making the surface appear " damp."

When iron is dissolved in **hydrochloric acid,** a soln. of ferrous chloride is formed and hydrogen is evolved : $Fe+2HCl=FeCl_2+H_2$—a reaction studied by F. Isambert, etc. Measurements of the speed of the reaction were made by C. M. Guldberg and P. Waage in 1867. H. Kreusler observed that iron reduced from the oxalate and then melted in vacuo is not perceptibly attacked by boiling hydrochloric acid ; but B. Lambert and J. C. Thomson found that the hydrogen is liberated briskly even when electrolytic iron of a high degree of purity is employed ; T. Ericson-Auren and W. Palmaer, and M. Centnerszwer and co-workers stated that pure metals do not dissolve in acids, and H. Moissan found that finely-divided pure iron dissolves in acids without residue. A. Thiel and J. Eckell showed that with non-homogeneous metal, the parts where the homogeneity is interrupted are the centres of attack. W. Palmaer found that electrolytic iron dissolves more slowly at 25° than does grey cast iron ; the respective velocities are 0·0145 and 1·5 ; P. Nicolardot, that a soln. of hydrogen chloride in absolute alcohol dissolves iron without the evolution of hydrogen. A. de Hemptinne observed that the heat of dissolution is modified a little in the presence of a magnetic field. G. Tammann and K. Bochoff found that when dil. sulphuric acid or hydrochloric acid acts on iron, in a closed vessel, the reaction comes to an end before all the metal is dissolved. The potential of the metal becomes electronegative owing to the dissolution of hydrogen by the metal ; the hydrogen also becomes more electronegative. The embrittling of iron by the absorption of some of the hydrogen during the action was indicated above. The action of **hydrobromic acid** was studied by A. J. Balard, and it resembles that of hydrochloric acid ; and likewise also with **hydriodic acid.** W. Palmaer found that there is a well-defined period of induction which, at 25°, varies with the conc. of the acid, thus :

	N-	0·5N-	0·4N-	0·2N-	0·1N-HCl
Period of induction . .	100	150	230	260	330 minutes

F. J. R. Carulla, and E. Prost showed that hydrochloric acid is particularly active in its attack on cast iron. J. M. Weeren made similar observations with respect to the action of acids on iron as were made with respect to zinc. T. Turner observed that cast irons containing large flakes of graphite are more susceptible to attack by acids than is the case with close-grained, white cast iron. Hence, white cast iron is better for use in acid-resisting plant. Cast irons low in phosphorus, and close-grained, withstand acids very well. It is assumed that ferrite is more readily attacked by acids than are the carbides, so that the resistance of white cast irons is attributed to the carbides. Grey cast irons are more porous, and O. Kröhnke observed that when white cast iron is immersed in acids, the ferrite is dissolved, whilst the graphite, cementite, and phosphide remain *in statu* without disturbing the original, outward shape of the mass. The carbides are more readily attacked by alkalies than is ferrite. The subject was studied by M. Ballay, and W. Palmaer. H. Endo observed that 5 hrs'. exposure of iron, at 25°, to the action of hydrochloric acid of different conc. resulted in the following losses—Fig. 331—expressed in grams per sq. cm. :

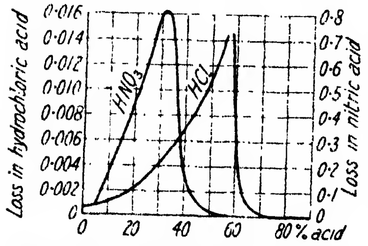


FIG. 331.—The Action of Hydrochloric and Nitric Acids on Iron.

HCl.	5	20	40	50	55	65	75	90 per cent.
Loss	0·000950	0·002313	0·007156	0·010348	0·014150	0·000825	0·000377	*nil*

Y. Utida and M. Saito, W. Guertler and B. Blumenthal, Y. Yamamoto, H. Edwards, and H. Endo and K. Nakawaga also studied this subject. W. H. Hatfield measured the solubilities of different forms of iron, and of iron alloys in conc. hydrochloric acid of sp. gr. 1·18. Cylinders of the metal approximately 0·5 in. diam., and weighing 50 grms., were immersed in about 85 c.c. of acid, at 15°. The losses stated in grms. per sq. cm. in 24 hrs., were :

		N-HCl	5 per cent.	25 per cent.	50 per cent.	Conc. HCl
Electrolytic iron . .		0·0085	—	- -	—	0·0860
Armco iron . . .		0·0116	- -	—	- -	0·1385
English wrought iron .		0·1416	...	—	—	0·2217
Steel, 0·29 per cent. C	15°		0·0490	0·1367	0·1842	—
	40°		0·0866	0·4088	0·6107	...
	60°		0·0879	0·4042	0·8341	-
	80°		0·0928	0·4112	0·7356	—

G. Tammann and F. Neubert's results with steel containing different proportions of carbon are summarized in Fig. 332. 3·6N-HCl was employed. The results are taken to support the theory of local elements.

W. Palmaer studied the action of hydrochloric acid on grey pig-iron, and obtained the results indicated in Fig. 333, at 25°. The velocities are expressed in terms of the changes in the e.m.f. of the metal. There is a well-marked period of induction; and it was found that the presence of potassium, ammonium, or magnesium chloride had very little influence on the results. With zinc, the addition of zinc salts depresses the speed of the reaction in a marked way, but with grey pig-iron, the effect of ferrous salts is insignificant. W. Bauhuis found that both polished and rough electrolytic iron are active in hydrochloric acid, and that the metal dissolves at characteristic rates in acids of different concentrations, and there is a well-defined period of induction. The addition of halides retard the rate of dissolution, and this the more, the higher the at. wt. of the halogen; oxidizing agents accelerate the speed of dissolution in the acid. H. O. Forrest and co-workers studied the initial rate of corrosion. H. Endo observed that the presence of oxygen dissolved in 0·05 per cent. hydrochloric acid raises the rate of dissolution of iron over seventy times what it is in the absence of oxygen, and with 5·0 per cent. acid, over fifteen times. The subject is further discussed in connection with the corrosion of iron. J. A. N. Friend reported that specimens of cast iron and mild steel, measuring 4·5×0·8×0·65 cm., and weighing about 22 grms., were immersed in 500 c.c. of hydrochloric acid for 8 hrs. at 17°, under comparable conditions, and that the losses were:

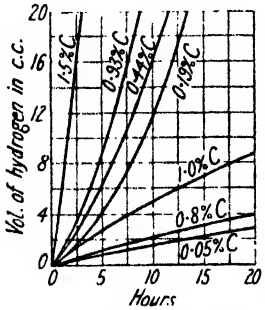


FIG. 332.—The Effect of Carbon on the Solubility of Iron in Hydrochloric Acid.

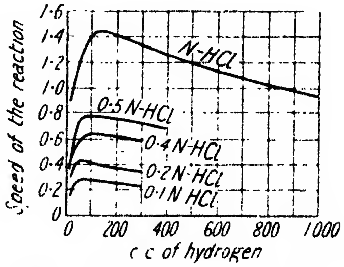


FIG. 333.—The Action of Hydrochloric Acid on Grey Pig-Iron.

HCl	0	N-	$2N$-	$4N$-	$6N$-	$7N$-	$8N$-	$9N$-	$10N$-
Cast iron	0·009	10·67	14·61	19·45	19·36	17·22	15·78	14·29	9·03
Mild steel	0·0053	0·612	0·786	0·968	1·957	3·31	5·38	9·94	13·27

As in the case of sulphuric acid (*q.v.*), the rate of dissolution of cast iron rises to a maximum and increasing concentrations of acid, and then falls. With mild steel, the rate of dissolution rises steadily as the concentration of the acid increases. F. Schmitz found that with pieces of steel containing 0·06, 0·42, and 0·92 per cent. of carbon and 20×20×10 mm. with a 4 mm. hole, lost respectively, 1·130, 1·140, and 0·511 per cent. in 180 hrs. in dil. hydrochloric acid (1 : 10), and in conc. acid, respectively, 23·070, 19·750, and 14·340 per cent.

J. T. Conroy measured the effect of varying the *concentration* of hydrochloric acid, and found that with soln. containing [HCl] grms. per litre, the rates of evolution of hydrogen in c.c. per hour were:

[HCl]	25	50	150	200	250	300	350 grms. per litre
H_2	5	8·5	15	30	85	250	470 c.c. per hour

As the conc. of the acid increases in arithmetical progression, the rate of action over a considerable range increases in a geometrical progression, so that the rate of dissolution is doubled for each increase of 30 grms. of HCl per litre in the acidity of the soln. Observations on the action of acids on iron were made by C. F. Burgess and S. G. Engle, K. Daeves and co-workers, V. Duffek, M. Faraday, J. A. N. Friend, R. Gans and co-workers, A. Geissel, L. F. Girardet and T. R. Kou, H. G. Haase, W. H. Hatfield, E. Heyn and O. Bauer, W. H. Johnson, G. B. Jones, J. Keir, P. Kötzschke and E. Piwowarsky, J. Priestley, F. W. Richardson, W. D. Richardson, J. Sauvageot and L. Lauprète, J. W. Shipley and co-workers, J. B. Trommsdorff, G. Walpert, H. W. Webb, W. G. Whitman and R. P. Russell, and R. E. Wilson. R. Girard found that with soln. of sulphuric, hydrochloric, carbonic, and carbolic acids with a concentration less than 0·1N, polished steel and cast-iron plates are similarly attacked. W. G. Whitman and co-workers observed that with carbonic and hydrochloric acids, the results were somewhat similar, as illustrated by Fig. 334, for with a H'-ion conc. less than 0·000001, or $p_H=6$, the curves of attack coincide. G. Tammann noted that cold-work increased the speed of dissolution of iron in dil. acids. L. McCulloch found that if a rubber band be wrapped tightly round a piece of soft iron, and the whole left in dil. hydrochloric acid for a few weeks, the pitting is greatest beneath the rubber, showing that the acid attacks the metal in the capillary spaces between the metal and rubber more vigorously than it does on the exposed surfaces—*vide infra*, the corrosion of iron. U. R. Evans and J. Stockdale showed that if a small cathodic current be applied to iron whilst the metal is immersed in a pickling acid, the attack is reduced.

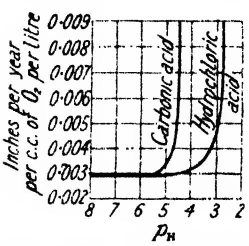


FIG. 334.—The Attack of Iron by Acids.

The effect of *temperature* is such that the rate of dissolution is nearly doubled for each 10° rise of temp. with acids having between 25 and 216 grms. HCl per litre. A. Sieverts and P. Lueg found that the dissolution of iron in hydrochloric acid at 78° is approximately proportional to the cube of the conc. of the acid. The temp. coeff. of the rate of dissolution is 2·0 to 2·3 per 10° between 50° and 78°. W. S. Calcott and J. C. Whetzel, and J. T. Conroy found that the logarithm of the rate of dissolution of iron in acids is a linear function of the temp. Observations were also made by J. R. Baylis. W. Palmaer found that there is a maximum in the effect of temp. of the speed of dissolution of grey cast iron in hydrochloric acid of various concentrations. There is no complication by the formation of a passive film. The high temp. coeff. of the reaction is due to the change in the viscosity of the soln. which permits the rapid removal of ferrous chloride soln. from the surface of the metal. The temp. coeff. increases with increasing conc. of acid; and the addition of ferrous chloride scarcely affects the velocity of the reaction. According to A. Thiel and W. Ernst, the difference observed between the quantity of gas evolved during the spontaneous dissolution of a metal in acids, and the quantity evolved when the metal is in combination with another metal serving as cathode, depends entirely upon the resistance of the liquid medium.

According to O. P. Watts and N. D. Whipple, a reduction of *pressure* favours the dissolution of iron and zinc in acids, and E. W. Greene and O. P. Watts found that a reduction of press. lowered the rate of corrosion in amalgamated zinc by removing depolarizing oxygen, and with unamalgamated zinc in the absence of oxygen, or amalgamated zinc, a reduction of press. accelerated the action by facilitating the escape of hydrogen gas. W. Rohn found that in 10 per cent., cold hydrochloric acid, purified, unannealed iron lost 0·12 grm. per sq. dm. in 1 hr. and 0·5 grm. in 24 hrs.; and 33·8 grms. per sq. dm. in 1 hr. in the hot acid. The action was less vigorous with annealed iron. Observations were made by W. Guertler and T. Liepus, and B. Kindt. C. Barus showed that the rate of dissolution of steel wire hardened by drawing is greater than is the case with soft metal. M. A. Rozenberg and V. A. Yuza, and L. V. Pisarzhevsky found that a *magnetic field* retards the action of the acid on iron.

O. P. Watts and N. D. Whipple found that the addition of hydrogen dioxide quickens the attack of hydrochloric acid. J. T. Conroy observed that the presence of arsenic in the acid retards its activity, and if the quantity is large enough to cover all the iron with a film of arsenic, the reaction, at ordinary temp., may be stopped. According to O. P. Watts and co-workers, the protective effect of arsenic is due to polarization by hydrogen, and this is in accord with the observation that the corrosion of the protected iron is stimulated by oxidizing agents—*e.g.* hydrogen dioxide observed by E. Salkowsky, A. Quartaroli, and O. P. Watts and N. D. Whipple; and that the arsenic does not protect the iron from corrosive agents—*e.g.* ferrous salt soln.—which do not evolve hydrogen by their action. A. S. Dwight mentions a case of acid corrosion by water containing sulphuric acid derived from the oxidation of smelter fumes, which was stopped by the addition of arsenic to the water. E. Heyn and O. Bauer, and C. F. Burgess and S. G. Engle showed that although arsenic in the acid retards the attack by sulphuric and hydrochloric acids, arsenic in the iron favours the attack. According to H. H. Gray and M. B. Thompson, the nitrogenization of iron increases its resistance to attack by hydrochloric acid, and this the more with low-carbon than with high-carbon steels. G. Batta, and R. C. Griffin observed that the rate of attack of hydrochloric acid on wrought iron, cast iron, and steel is greatly retarded if 1 per cent. of formaldehyde be present. H. J. Prins found that the presence of a reducible substance like nitrobenzene or benzaldehyde accelerates the rate of dissolution of iron in acids; and M. B. Rane and M. Prasad found that alkaloids—narcotine, nicotine, and brucine—retard the action of hydrochloric acid. A. Sieverts and co-workers found that in the action of sulphuric and hydrochloric acids on iron, ferrous sulphate, methyl sulphate, ammonium chloride, tetramethylammonium chloride, choline hydrochloride, and taurine have no inhibiting effect. Potassium cyanide, caffeine, theobromine, coniine, pyramidone, pyridine, atropine, quinoline, *iso*quinoline, and codeine had a slight inhibiting effect. Nicotine, veratrine, cocaine, and cinchonine were more effective, whilst α- and β-naphthaquinolines, strychnine, brucine, narcotine, and quinine were very effective. The most effective inhibitant was an "extract" consisting of the ether-soluble basic constituents of crude anthracene. It was found that the amount of inhibition was much the same in both acids, but with theobromine, nicotine, cinchonine, narcotine, and quinine, the inhibiting effect was more marked in hydrochloric acid. The authors conclude that all compounds containing pyridine nitrogen are more or less effective inhibitants. For slight amounts of poisoning, an increase of temp. reduces the inhibition: for larger amounts, it has no effect. O. Vogel said that nitrogen ring compounds generally retarded the reaction. A. Sieverts and P. Lueg proposed the empirical formula: $(K_0-K_c)/K=ac^b$, where K_0 is the rate of soln. with no poisoning; K_c is the rate of soln. at poison conc. c, and a and b are constants depending on the nature of the poison. The formula breaks down if more than about 75 per cent. of the inhibiting agents is present—*vide infra*, sulphuric acid. G. Walpert attributed the inhibition to adsorption by the metal.

In agreement with A. Sieverts and P. Lueg, A. Krieger found that the rate of dissolution of iron in $6N$-HCl at 78° is proportional to the surface of the metal. If the metal has been annealed at a red-heat, the rate of dissolution is depressed. If l denotes the length of the wire; k_2, the velocity constant; and N, the normality of the acid:

HCl . . .	$3N$-	$4N$-	$5N$-	$5{\cdot}25N$-	$5{\cdot}50N$-	$5{\cdot}75N$-	$6N$-
$k_2\times 100$ . .	13·1	17·7	28·3	36·7	47·7	58·7	67·5
$k_2\times 100/\sqrt{l}$ . .	3·99	5·39	8·61	11·2	14·5	17·9	20·5
$k_2\times 100/N^5\sqrt{l}$.	1·18	0·46	2·68	2·74	2·60	2·58	2·47

The rate of dissolution of the iron in acid increases approximately with the fifth power, N^5, of the concentration. The retardation in the rate of dissolution by α-naphthaquinoline and α-chrysidine is in agreement with A. Sieverts and P. Lueg's formula. The retardation is dependent on the mol. wt. and on the constitution of the "poison." Amongst substances of the same mol. wt. but of different constitution, some—*e.g.* α-naphthaquinoline—are very poisonous; whilst other isomeric forms—*e.g.* acridine—are non-poisonous even with conc. of 2 millimols per litre. Increasing the size of the molecule with substances of like chemical constitution greatly reduces the toxicity—*e.g.* chrysidine is less poisonous than naphthaquinoline. Very small additions of α-naphthaquinoline and of α- and β-chrysidine accelerate the dissolution of iron in $6N$-HCl—*e.g.* with up to a millimol of chrysidine per litre; consequently, the concentration-velocity curves show a maximum for small concentrations. On increasing the "toxic dose," the curves show a decline and afterwards a remarkable rise for a short stretch. Thus, with α-chrysidine and 6N-HCl at 78·2°:

α-Chrysidine .	0	0·125	0·25	0·50	1·0	2·0 millimol per litre.
$100k_1$ . .	61·9	63·5	62·6	62·5	63·3	58·4

There is a very marked induction period with chrysidine. According to J. A. Aupperle, the presence of antimony chloride inhibits the action of hydrochloric acid on iron; and, according to C. F. Burgess, arsenic acts similarly; whilst W. D. Richardson observed no accelerating influence was produced in the action of hydrochloric acid, though O. P. Watts and H. C. Knapp observed that corrosion is stimulated by the presence of these salts. C. Moureau and C. Dufraisse showed that the tendency of various easily oxidized substances to combine with oxygen may be reduced or multiplied by the addition of a third substance in very small proportion. W. Palmaer, and J. G. A. Rhodin discussed the application of the facts to the corrosion of iron and steel.

H. H. Gray and M. B. Thompson found that the greater the carbon-content of steel, the less is its resistance towards hydrochloric acid—*vide infra*, nitrogen. The subject was studied by K. K. Jarvinen, F. Schmitz, and L. Aitchison. T. Turner observed that when cast iron is attacked by dil. acids, the iron is first dissolved, the carbides and phosphides being more resistant; with alkaline corrosion, however, the impurities are first dissolved, and iron is dissolved last. A. J. Hale and H. S. Foster found that at temp. between 17° and 20°, plates of cast iron and wrought iron having 1 sq. dm. of area exposed, lost respectively 3·0 and 0·17 grm. with a litre of 0·2N-HCl for 4 hrs.; respectively 18·2 and 19·0 grms. with half a litre of the same acid per day for 7 days; and respectively 2·9 and 3·3 grms. during 28 days' exposure in half a litre of acid. U. R. Evans observed that iron in contact with 1·3N-HCl slowly gave off hydrogen, but if a piece of nickel was in contact with the iron, the gas came off more quickly, but copper and tin did not have any appreciable effect. W. D. Richardson found that grey cast iron containing graphite is attacked by N-HCl much more quickly than open-hearth iron of a higher degree of purity, but the corrosive action of the acid on the latter is greatly increased if a trace of a platinum salt be added so as to produce metallic platinum in contact with the iron. This treatment had no accelerating influence on the corrosion of cast iron. Thus, with plates 15 sq. cm., open-hearth iron and cast iron lost respectively 0·12 and 8·7 grms. per hr. in N-HCl, and respectively 10·5 and 8·8 grms. per hr. in N-HCl along with a trace of platinum salt. C. F. Burgess and S. G. Engle found that the loss in grams per sq. inch per hour, at 22°, on a 17-hr. run, with N-HCl, was 0·2146 grm. with electrolytic iron; 0·0083 grm. with electrolytic iron heated to 1000° and slowly cooled; 0·0095 with soft sheet iron, low in carbon, used for transformer plates; 0·0026 grm. for tempered steel used in the manufacture of knife-blades; and 0·1058 grm. for ordinary cast iron. E. L. Nichols, and H. A. Rowland and L. Bell investigated the action of a magnetic field on the dissolution of iron in acids. G. Berndt, and S. S. Bhatnagar and co-workers found that the dissolution of iron in hydrochloric acid is reduced by a magnetic field, and F. K. Bell and W. A. Patrick found that copper in contact with iron decreases the speed of soln. in acids, but not so with platinum or silver.

The early observations on the peculiar nature of the gases evolved when cast iron, or steel is treated with hydrochloric acid or sulphuric acid, have been indicated in connection with iron carbide—**5**. 39, 20. The hydrogen which is evolved is accompanied by the vapour of a malodorous oil or oils, as by arseniuretted, phosphuretted, and sulphuretted hydrogen, and possibly also methane. F. A. Abel and W. A. Deering showed that the combined carbon of steel furnished hydrocarbon gases when dissolved in hydrochloric acid, and the reaction was studied by S. Cloëz, H. Moissan, F. Mylius and co-workers, H. Hahn, E. Heyn and co-workers, etc. R. Schenck and co-workers found that with

	Cast iron (2·5 per cent. C.)	Steel	
	Cementite, Pearlite	Hardened at 1150°. Cementite, Austenite, Martensite	Hardened at 780°. Cementite, Martensite
Methane	1·02	3·53	3·19
Ethane	0·10	0·50	0·45
Ethylene	0·27	0·50	0·47
Propylene	7·08	24·37	25·21
Butylene	4·00	10·25	9·08
Amylene	1·25	3·36	4·20
Hexene	1·15	4·37	5·21
Octene	0·80	3·02	3·36
Carbon	78·04	38·82	42·10
Loss	6·29	11·28	6·37

L. G. Knowlton said that the presence of depolarizers—potassium permanganate, nitric acid, chlorine, etc., prevent this reaction. F. Osmond and J. Werth found that in the anodic dissolution of annealed steel in dil. hydrochloric acid, a skeleton of graphite is formed. According to V. Tantin, the phosphorus in iron slowly forms phosphine during the action of the dil. acid; and, according to G. Craig, and H. Rocholl, part of the sulphur forms hydrogen sulphide. J. L. Proust passed the gases through alcohol, and separated the oil which was arrested by diluting the alcohol with water; A. Schrötter collected the oil by passing the gas through dil. sulphuric acid. The solid residue which remained undissolved consisted of a mixture of graphite, iron carbides, amorphous carbon, and also silicon, etc. This residue has been examined by A. E. Jordan and T. Turner, W. A. Tilden, B. Sandrock, C. J. B. Karsten, J. Hull, J. Percy, E. Prost, J. J. Berzelius, B. Kosmann, C. E. Schafhäutl, J. F. Daniell, and F. Kohn, and it appears to be related with the product which is obtained when cast iron has been exposed for many years to the action of sea-water—*vide infra.*

A. D. White found that aq. **hypochlorous acid** slowly attacks iron with the evolution of both hydrogen and chlorine; whilst a soln. of **bleaching powder** attacks iron with the evolution of oxygen; and G. N. Quam, H. P. Pearson, O. F. Hunziker and co-workers, and H. W. Young and A. W. Peake examined the corrosive action of soln. of bleaching powder. H. P. Pearson found that iron is energetically attacked by a soln. of **sodium hypochlorite.** W. S. Hendrixson observed that dil. and conc. soln. of **chloric acid** attack iron—the metal is dissolved without the evolution of hydrogen, and the chloric acid is reduced. W. S. Hendrixson found that **perchloric acid** is not reduced by iron. G. Lunge and A. Deggeler examined the corrosion of iron by aq. soln. of **potassium chlorate.** R. Böttger observed that finely-divided iron burns vigorously in heated potassium chlorate; and M. Hönig, that it likewise burns in heated **potassium perchlorate**—the violence of the reaction can be reduced by diluting the chlorate with sodium carbonate. The reaction was studied by E. Berger. According to A. Connell, iron dissolves in a boiling soln. of **iodic acid,** forming a ferrous iodate.

Iron has a strong affinity for **sulphur,** and the two elements readily combine with incandescence when heated to redness—*vide infra,* iron sulphides. The affinity of the two elements was studied by E. Schürmann,[6] O. Schumann, E. F. Anthon, R. Winderlich, K. Jellinek and J. Zakowsky, J. Zakowsky, E. V. Britzke and A. F. Kapustinsky, and W. Guertler. Manganese had the greatest affinity for sulphur, then followed Cu, Ni, Co, Pb, Ag, and Sb. Iron comes between copper and lead. C. Frick compared the heats of formation of the metal sulphides, and found that aluminium and magnesium come before iron. According to J. G. Gahn, J. L. Proust, J. J. Berzelius, and A. Evain, when sulphur is in contact with a red-hot bar of iron, the elements unite to form a fusible iron sulphide. R. Hare found that if sulphur be heated to redness in the gun-barrel of a muzzle-loader, closed at one end, the vapour of sulphur escapes at the nipple, and a piece of iron wire held in the vapour burns with a bright light to form the sulphide; according to G. C. Winkelblech, if a small piece of potassium or sodium be placed at the end of a piece of iron wire, ignited, and plunged into the vapour of sulphur, the metal burns, forming iron sulphide. N. Lemery observed that if a paste be made with water and a mixture of equal parts of iron filings and sulphur, the mixture becomes so hot that it can be scarcely held in the hand. If several pounds of the mixture be buried in the ground, the earth is raised and burst asunder—*Lemery's volcano*—as the iron is sulphurized. N. Lemery based a theory of volcanoes on this reaction. O. Ohmann observed that iron powder reduced at a low temp. ignited spontaneously in sulphur vapour. G. Tammann and K. Schaarwächter found that the attack of iron by sulphur begins at about 210°, and increases rapidly up to 500°. W. P. Jorissen and C. Groeneveld discussed the velocity of propagation of the reaction in mixtures of iron and sulphur; and W. P. Jorissen and B. L. Ongkiehong added that the upper limit of the reaction with mixtures of iron, aluminium, and sulphur is approximately 43 per cent. of iron and 57 per cent. of a mixture of 62·5 per cent. aluminium, and 39·5 per cent. of sulphur. The action of sulphur on metals was also examined by E. Priwoznik, A. Colson, and O. Bauer and H. Arndt. H. Schmidt, and A. E. Wood and co-workers studied the corrosion effects of sulphuric acid sulphur compounds—mercaptans, alkyl sulphides and sulphites, sulphonic acids, sulphoxides, sulphones, and thiophene —dissolved in naphtha.

The binary system: Fe–S, and the ternary system: Fe–S–C, have been studied by H. Hanemann and A. Schildkötter, G. Ritzau, R. Vogel and G. Ritzau, and others—*vide infra*, iron sulphides. There is a ternary eutectic in the system: Fe–FeS–Fe_3C at 975°. There are three kinds of crystals—binary solid soln. of iron with carbon, cementite, and iron sulphide. W. F. Holbrook and co-workers studied the diffusion of sulphur in molten iron.

According to C. J. B. Karsten, the action of sulphur on iron is very detrimental, so that proportions which can scarcely be determined by analysis make the metal red-short. The presence of 0·03375 per cent., for example, made the metal red-short, and prevented its being welded. C. J. B. Karsten also said that sulphur expels carbon from iron at a high temp., so that spiegeleisen, sat. with carbon, and melted with sulphur in a crucible, caused a separation of carbon as a sooty deposit on the under-surface of the resulting ferrous sulphide. Sulphur also turns grey cast iron white. This phenomenon interested J. Percy, who concluded that when the sulphur in cast iron exceeds 2·5 per cent., the co-existence of graphite is impossible, and the metal is necessarily white. W. J. Keep questioned if the evil effects attributed to sulphur are all deserved, but T. D. West, and J. Roberts did not agree. The former found that 0·2 per cent. of sulphur is enough to ruin any casting; and the latter stated that in some cases 0·214 per cent. greatly affected the strength. If manganese is absent, the sulphur helps to keep the carbon as carbide producing hard iron, while if a high proportion of manganese be present, manganese sulphide will be formed, and the hardening effect will be neutralized. F. Wüst, and W. J. Keep showed that the presence of other elements may affect the action of sulphur; thus, silicon may correct to some extent the deleterious action of sulphur. H. I. Coe showed that silicon neutralizes the action of the sulphur by forming a silicon sulphide. The subject was discussed by A. Hayes and H. E. Flanders, J. Mehrtens, H. S. Rawdon, and J. O. Arnold and G. R. Bolsover. F. Wüst and J. Miny observed that the formation of graphite is affected by sulphur according to the proportion of manganese present; with sufficient manganese, the effect of the sulphur is neutralized—thus, the presence of 0·30 per cent. of manganese will prevent the hardening effect of 0·20 per cent. of sulphur. M. Hamasumi noted that with a low proportion of manganese, Brinell's hardness steadily rose as the proportion of sulphur increased from 0·019 to 0·196 per cent. E. Piwowarsky found that with a low proportion of manganese, the sulphur should not exceed 0·08 to 0·10 per cent; and M. Hamasumi said that up to 0·1 per cent. did no harm.

The subject was studied by E. Adamson, S. G. Afanaseff, A. Allison, J. O. Arnold and G. B. Waterhouse, F. E. Bachman, A. A. Blair and P. W. Shimer, G. K. Burgess, J. B. Cabot,

J. R. Cain, A. Carnot and E. Goutal, F. J. R. Carulla, J. Ciochina, H. I. Coe, C. Diegel, G. Dillner, E. W. Fell, H. E. Field, G. A. Forsberg, N. J. Gebert, R. C. Good, W. Guertler, G. Hailstone, F. W. Harbord and A. E. Tucker, K. Hasegawa, C. R. Hayward, J. Henderson, C. H. Herty and co-workers, H. D. Hibbard, K. Hilgenstock, W. N. Hindley, A. H. Hiorns, T. E. Holgate, A. L. Holley, H. M. Howe, J. E. Hurst, M. Janoyer, G. R. Johnson, J. E. Johnson, W. J. Keep, K. Köhler, B. Kosmann, A. Lissner, A. Lodin, P. Longmuir, J. Massenez, T. Mauland, E. Maurer and W. Haufe, A. Messerschmidt, R. Moldenke, A. Niedenthal, P. Oberhoffer, R. H. Palmer, L. Piedbœuf and J. R. Marechal, W. J. Priestley, E. W. Rettew and L. A. Lanning, J. Roberts, H. Schenck, J. Shaw, O. Simmersbach, A. E. M. Smith, E. K. Smith and F. B. Riggan, R. H. Smith, G. J. Snelus, J. E. Stead, F. Stille, B. Stoughton, E. R. Taylor, B. Thomas, F. E. Thomson, E. E. Thum, T. Turner, O. Wedemeyer, F. Wüst, and F. Wüst and F. Schüller.

A. Fry discussed the diffusion of sulphur in iron. The system: iron-sulphur has been discussed elsewhere; it was studied by W. Treitschke and G. Tammann, K. Friedrich, F. Sauerwald and W. Hummitzsch, and E. Becker. E. Becker observed that virtually no solid soln. are formed with α-, β-, or γ-iron. The transformation points of iron are not changed, so that the γ-iron passes to β-iron at 898°, and β-iron passes to α-iron at 768°; but W. Treitschke and G. Tammann observed that the first of these points is lowered more than the second by the presence of ferrous sulphide, and with less than 92 per cent. of iron, there is only one break in the cooling curve at 800°, and this is probably connected with the soln. of ferrous sulphide in γ-iron. The deleterious effects produced by, say, 0·02 per cent. of sulphur are attributed to the brittle character of the solid soln. rich in iron; and when over 2 per cent. of sulphur is present, to the presence of a readily fusible layer of sulphide between the particles of iron. This explanation was also given by J. E. Stead. The effect of sulphur on the carbon-iron system was investigated by D. M. Levy, J. E. Stead, and T. Liesching, but the data are not sufficient to form the ternary diagram. T. Liesching prepared alloys with over 2 per cent. of sulphur, and found that when the proportion of carbon was high the material separated into two layers—one containing 26 to 28 per cent. of sulphur and 0·22 to 0·32 per cent. of carbon; and the other 2·05 to 2·25 per cent. of sulphur and 3·04 to 3·43 per cent. of carbon. D. M. Levy, and T. Liesching observed that sulphur lowers the m.p. of the iron-carbon alloy from 50° to 75° for 1 per cent. of sulphur. Even with a high proportion of sulphur, the pearlitic transformation remains unchanged at 695° to 706°. D. M. Levy showed that with up to 1·0 per cent. of sulphur, the surface of sections of the metal is bright and even, but marked all over by the pattern of the pearlite; and with over 1 per cent. of sulphur, the sections were pitted all over by the excess of sulphide in the alloy. The saturation point for sulphur in iron-carbon alloys with 2·73 per cent. of carbon is rather less than 0·9 per cent. In this case the sulphur remains uniformly diffused throughout the mass, but with higher proportions, more sulphide occurs in the upper than in the lower part. The following arrests were observed in the cooling curve of iron with 2·7 per cent. carbon and

Sulphur .	0·005	0·081	0·23	0·43	0·85	1·14	1·31	1·25	34·8 per cent.
Arrests .	.	.	.	. .	---	. .	1204°	1204°	1206°
	1279°	1277°	1239°	1247°	1236°	1189°	1189°	1190°	—
	1138°	1133°	1132°	1128°	1128°	1122°	1133°	1127°	—
	887°	887°	856°	863°	865°	870°	872°	866°	–
	—	—	—	—	—	972°	892°	980°	977°
	695°	696°	695°	696°	698°	692°	697°	695°	—

The arrest at 1279° is due to the solidification of iron holding carbon to the extent of 1·5 per cent.—that is, austenite; and as the temp. falls below 1000°, the carbide falls out of solid soln. W. H. Hatfield suggested that the action is continuous, not abrupt. D. M. Levy said that the arrest at 1138° is due to the splitting up of the eutectic with 4·3 per cent. of carbon into cementite and austenite. The arrest at 887° is attributed to the separation of cementite from austenite, but this was questioned by W. H. Hatfield on the ground that the separation of cementite is continuous, not abrupt. The arrest at about 950° occurs with samples containing free sulphide. The pearlite arrest is at 695°. J. E. Stead investigated the cooling curve of iron with 2·98 per cent. combined carbon, no graphite, 0·29 per cent. of manganese, 1·89 per cent. silicon, 0·27 per cent. sulphur, and 1·62 per cent. phosphorus. The arrest at 1149° is the primary f.p. where the separation of austenite begins; that at 1074° is due to the breaking up of the iron-carbon eutectic into cementite and austenite; that at 945° is due to the freezing of the ternary eutectic of Fe–P–C; and that at 773° is due to the formation of pearlite. G. Tammann and W. Salge studied the residues left after treating the metal with an acidified soln. of ammonium persulphate. H. Sawamura, and F. Roll observed that sulphur partly favours and partly hinders the separation of graphite in cast iron.

With less than 0·8 per cent. of sulphur, D. M. Levy found no sulphide in the pearlite areas representing primary austenite, but it is found in the eutectic separating between 1120° and 1130°, and J. E. Stead also observed the $Fe(Fe_3C)$–$Fe(FeS)$ eutectic. D. M. Levy thought the films of sulphide help to preserve the carbide from dissociation. J. E. Stead showed that in the absence of manganese some sulphur crystallizes with the carbide, and that it is that portion of sulphur which crystallizes with the carbide which is mainly responsible in preventing the separation of graphite and in making the carbide stable. The nature of the sulphide constituents of iron were discussed by E. Heyn, R. Baumann, G. J. Ward and A. H. Longden, H. Schottky, E. Blanchi, P. Oberhoffer, and P. Oberhoffer and A. Knipping. J. H. Andrew and D. Binnie found that sulphur may be retained in soln. by iron when a molten iron-sulphur alloy is rapidly chilled, and the deposition of iron sulphide occurs on re-heating the alloy above 900°. If manganese sulphide is soluble in iron, the solubility is very small. In the case of oxygen associated with sulphur, J. J. Porter, E. D. Campbell, and H. le Chatelier and M. Ziegler attributed the red-shortness to the presence of an iron oxysulphide. F. Osmond, A. Carnot and E. Goutal, J. O. Arnold and G. B. Waterhouse, J. O. Arnold and G. R. Bolsover, W. Heicke, and G. Röhl studied the system: FeS–MnS, and observed the formation of a manganese iron sulphide $Fe_3Mn_2S_5$. J. E. Stead, D. M. Levy, J. E. Hurst, W. H. Hatfield, and H. I. Coe showed that if manganese is present it combines with the sulphur to form manganese sulphide, and thus neutralizes its effects. W. H. Hatfield concluded that sulphur increases the stability of iron carbide at high temp., and thus hinders the breaking down of the carbides during the cooling of the metal. It is probable that the small percentage of sulphide associated with the carbide crystals accomplishes this action. H. I. Coe's inference that the sulphur separates as sulphide at the f.p. is not strictly correct, since a certain proportion is retained by the cementite carbide. The action is chemical, not mechanical, as suggested by D. M. Levy. E. D. Campbell, J. O. Arnold, and H. le Chatelier and A. Ziegler made observations on the diffusion of sulphur in solid iron. J. O. Arnold demonstrated the presence of ferrous sulphide in a mild steel free from manganese; and he also demonstrated the presence of manganous sulphide in manganiferous steels. The pale brown ferrous sulphide exists mainly in the form of sectional meshes, but sometimes occurs in the globular form. Manganous sulphide has a dove-grey colour, and exists almost exclusively as globules. J. O. Arnold and G. B. Waterhouse found that manganous sulphide is plastic at a yellow-heat. J. E. Stead doubted if the alleged manganous sulphide is really such; and J. O. Arnold and G. R. Bolsover indicated the probable existence in liquid commercial steels of an eutectic of ferrite and manganous sulphide which has a high f.p. J. O. Arnold found that the sp. gr. of steel is reduced from 7·8478 to 7·6903 as the proportion of sulphur increases from 0·03 to 0·97 per cent.

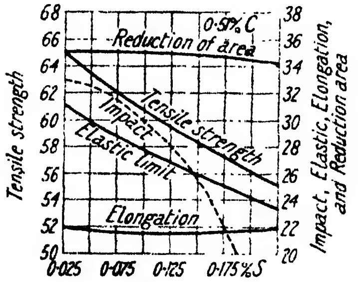


Fig. 335.—The Effect of Sulphur on the Mechanical Properties of Iron.

E. Piwowarsky showed that sulphur definitely tends to harden iron, and the effect increases with the rapidity with which the iron is cooled. J. S. Unger measured the mechanical properties of iron with 0·09, 0·32, and 0·51 per cent. sulphur, and the results for 0·51 per cent. of carbon are summarized in Fig. 335. The tensile strength and elastic limit are expressed in kilograms per sq. mm.; the elongation and reduction in area in percentages; and the impact test by the number of impacts required for fracture by a weight of 990 kgrms. falling 4·8 metres. A. Wimmer, and K. Taniguchi also made observations on this subject.

A. Holtz found that sulphur has very little influence on the magnetic properties of iron; but F. Goltze, and H. F. Parshall said that it reduces the magnetic properties of cast iron. According to H. von Jüptner, the sulphur in iron and steel may occur in different forms: (i) A compound which is decomposed by dil. acids, liberating hydrogen sulphide—J. O. Arnold and H. J. Hardy, F. H. Williams, L. Schneider, G. Hattensauer, etc., add that if proper precautions are taken, all the sulphur may be converted into hydrogen sulphide even when copper is present. (ii) A compound which on treatment with dil. acids liberates volatile methyl sulphide, $(CH_3)_2S$—F. C. Phillips, E. Prost, E. Franke, W. Schulte and L. Campredon, A. Barraud, D. M. Levy, O. Herting, T. Naske, F. Bischoff, G. T. Dougherty, etc. (iii) In a form which under certain conditions remains behind in the undissolved residue as an organic compound. The two latter forms may represent decomposition products of ore. The sulphurous residue was examined by L. L. de Koninck, C. R. Fresenius, E. Prost, H. Rocholl, etc. Its presence has been attributed to three causes: (*a*) the presence of cuprous sulphide insoluble in hydrochloric acid—F. Bischoff; (*b*) a graphitic residue—T. Turner; and (*c*) an organic compound which volatilizes with difficulty, and which may be distilled off by prolonged boiling with hydrochloric acid—F. C. Phillips. G. N. Huntley discussed sulphur as a cause of the corrosion of steel.

K. Oma observed that sulphur in electrolytic iron may be derived from the electrolyte or anode—*vide supra*. J. H. Nead, and C. H. Herty noted that molten iron absorbs sulphur from furnace gases containing sulphur dioxide. H. Caron observed that when manganese is added to cast iron containing sulphur, some sulphur is eliminated, and J. Massenez based a process for the desulphurization of iron by this reaction. The iron sulphide forms manganese sulphide which rises through the metal and joins the slag. E. H. Saniter showed that iron is desulphurized by adding calcium chloride or fluoride; E. Wilke-Dörfurt and H. Buchholz, by fluorides;. W. Zieler, by zirconium; and B. Bogitsch, and J. E. Stead demonstrated that sulphur is removed during the puddling process by the highly basic iron-slag. P. P. Berg and M. S. Pshonik, G. Tammann and H. O. von Samson-Himmelstjerna studied the desulphurization of steel with the alkaline earth oxides, and with the oxides of lead, zinc, manganese and iron. In molten cast iron, part of the sulphide may float on the surface as scum. H. H. Beeny, C. Bettendorf and N. J. Wark, E. Blanchi, J. Ciochina, E. W. Colbeck and N. L. Evans, W. Denecke and T. Meierling, E. Wilke-Dörfurt and co-workers, G. A. Drysdale, H. H. Ebert, L. F. Girardet and co-workers, K. Hilgenstock, E. J. Lowry, J. Mehrtens, R. T. Rolfe, L. Scharlibbe, and A. de Vathaire studied the desulphurization of iron by fluorspar, calcium chloride, soda-ash, lime, and rock salt; and A. Possenti, by acidic and basic slags. According to T. Turner, the small percentage of sulphur, rarely over 0·08, in foundry iron, is due to the conditions governing the blast-furnace operations. These conditions—temp., composition of burden and slags—are conducive to the retention of silicon, but not to the absorption of sulphur by the iron. Only a very small proportion of the sulphur in the charge is found in the molten iron. J. E. Stead confirmed T. Turner's observations on this subject. J. Ciochina discussed the effect of hydrogen in the process of desulphurization.

J. E. Stead pressed smooth bromide paper soaked with 3 per cent. sulphuric acid over the polished metal, washed the print to remove acid, then immersed it in a soln. of sodium thiosulphate to remove the excess of silver; and then washed and dried the paper. Brown stains showed the presence of manganese sulphide. This *auto-sulphur printing*, as it is called, was devised by R. Baumann for determining the distribution of the sulphide constituents. L. E. Benson, J. Durand, E. Heyn, D. M. Levy, S. Maeda, M. Niessner, P. Oberhoffer and A. Knipping, H. Patsch, F. Rogers, H. J. van Royen and E. Ammermann, and H. Schottky studied the process. The presence of sulphur in iron and steel is generally regarded as favourable to corrosion, as in S. Weinwurm's experiments with steel plates containing 1·08 per cent. of sulphur and 0·2 per cent. of manganese. According to A. L. Baikoff, the sulphur in good steel is present as manganese sulphide, and in S. Weinwurm's specimen there was not sufficient manganese to unite with all the sulphur.

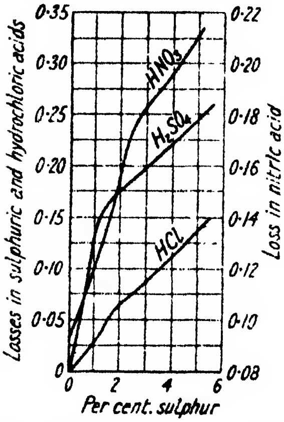


FIG. 336.—The Corrosion of Iron-Sulphur Alloys by Acids.

If the steel contains sulphides which have segregated, the heterogeneous metal may favour the development of local galvanic currents which stimulate corrosion, a subject studied by J. W. Cobb, G. Gallo, K. P. Grigorowitch, H. G. Haase, G. N. Huntley, V. V. Kendall and E. S. Taylerson, R. Stumper, and S. Weinwurm. Sulphur may be oxidized to sulphuric acid, and this favours corrosion. G. N. Huntley mentioned a case of the abnormal corrosion of boiler-plates through the oxidation of manganese sulphide in the steel; R. Stumper also found that the rate of corrosion of iron is accelerated by contact with iron sulphide; and G. R. Woodvine and A. L. Roberts noted that steel with segregated sulphur is more quickly corroded than steel free from these aggregates. H. Endo, Fig. 336, found the losses in grams per sq. cm., during 5 hrs'. attack at ordinary temp., with iron containing 0·34 to 0·42 per cent. of carbon, and

	Sulphur .	0·106	0·313	0·544	0·730	1·001	1·60	3·28	5·38 per cent.
Loss	H_2SO_4	0·01306	0·01755	0·02929	0·03454	0·09146	0·15872	0·19447	0·25976
	HCl .	0·01107	0·01252	0·01668	0·02080	0·03061	0·06559	0·09149	0·13657
	HNO_3	0·03491	0·04949	0·06108	0·07792	0·08025	0·13332	0·18383	0·20657

A. E. Wood and co-workers, L Tronstad and J. Sejersted, and H. Schmidt studied the corrosion of steel by soln. of sulphur, and of sulphur compounds in naphtha. W. Guertler and T. Liepus observed that iron is attacked by soln. of **sodium sulphide** in less than 24 hrs. C. van Brunt found that **sodium xanthate** forms a protective film of ferrous sulphide.

According to L. N. Vauquelin, iron in an aq. soln. of **hydrogen sulphide** in contact with air liberates hydrogen and turns black. Iron decomposes dry hydrogen sulphide. J. B. Fournier and F. Lang observed that liquid hydrogen sulphide had no perceptible action on iron at ordinary temp. for 11 years, or in 15 days at temp. up to 60°. J. B. Peel and P. L. Robinson found that hydrogen sulphide reacts with iron above 350°, forming ferrous sulphide. S. C. Britton and co-workers, J. M. Devine and co-workers, E. Dittrich, U. R. Evans, H. J. French, H. Gruber, W. P. Jorissen and B. L. Ongkiehong, F. J. Kayser, H. Schmidt,. A. Schulze, R. Stumper, G. Tammann and W. Köster, A. White and L. F. Marek, and R. E. Wilson and W. H. Balke studied the rate of attack of iron by hydrogen sulphide. P. A. von Bonsdorff, F. Hanaman, and U. R. Evans found that air containing traces of hydrogen sulphide rapidly corrodes iron. L. Biener, and F. Eisenstecken and L. Biener studied the mechanism of the sulphurization of iron by hydrogen sulphide. L. W. Vollmer and B. B. Westcott attributed the embrittlement of steel wire-rope, by hydrogen sulphide, to the absorption of hydrogen developed by the reaction $H_2S+Fe=FeS+2H_{nascent}$—*vide infra.* C. Menzel noted that a pump dealing with natural brine was much corroded by the hydrogen sulphide in soln.; and C. van Brunt found a pump dealing with a sulphide soln. was protected from corrosion by the formation of a film of sulphide—*vide infra*, and also the action of coal-gas on iron. J. Jahn observed that with iron in contact with hydrogen sulphide, at

	100°	154°	203°	259°	313°	414°	
Iron	588·5	582·4	591·2	580·7	591·2	735·8	mgrms.
Gain in weight . .	0·3	0·4	0·9	1·7	4·8	13·8	,,

and H. Gruber observed with pieces of iron 60×12×13 mm.,

	700°	800°	900°	1000°
Gain in weight . .	0·76	5·5	10·0	destroyed

A. E. Wood and co-workers studied the action of soln. of hydrogen sulphide in naphtha; and E. Rupp, the optical properties of films formed by hydrogen sulphide on iron. E. Beutel and A. Kutzelnigg studied the surface films produced by heating the metal in contact with the sulphides of copper, silver, mercury, and lead.

According to A. Lange, and A. Harpf, **sulphur dioxide** when dry has no action on iron, even at 100°, but in the presence of moisture the metal is slightly attacked. The action of sulphurous acid was examined by F. Schmitz, and B. Neumann and E. Goebel. F. Durau and C. H. Teckentrup found that the absorption of sulphur dioxide by electrolytic iron is a chemical process. According to U. R. Evans, when iron and steel are exposed over water sat. with sulphur dioxide, the metals become dark, and in 24 hrs., black. The filter-paper on which the samples rested acquired a rust-brown stain. The metal is soon covered with a yellowish-brown hydrated ferric oxide. H. Schiff, T. N. Morris, M. T. Burton, W. H. Hatfield, and F. Hanaman also studied the action of sulphur dioxide. L. Losana and G. Reggiani found that a mixture of $10CO_2+4CO_2+2O_2+48N_2+$traces of SO_2 +traces of hydrocarbons, saturated with water vapour at 16° to 20°, is more corrosive than air. J. Jahn observed that iron in contact with sulphur dioxide, at

	100°	150°	200°	250°	300°	400°	
Iron . . .	748·5	745·5	744·6	749·2	750·1	742·4	mgrms.
Gain in weight .	0·1	2·5	2·5	2·3	2·5	7·9	,,
Iron . . .	754·0	758·5	758·4	757·9	756·9	728·0	,,
Gain in weight .	0·1	0·1	0·1	0·3	0·4	10·7	,,

P. Chirvinsky said that the reaction $3Fe+SO_2=FeS+2FeO$ is exothermal and proceeds from left to right at fairly low temp. A. C. Halferdahl calculated the free energy of the reaction $3Fe+2SO_2=Fe_3O_4+S_2$ to be −61,000 cals. at 600°, and −26,700 cals. at 1400°; and for $4Fe+3SO_2=2Fe_2O_3+1\frac{1}{2}S_2$, −76,200 cals. at 600° and −18,100 cals. at 1400°. F. Schmitz found that the losses with **sulphurous acid** by 0·06, 0·42, and 0·92 per cent. carbon steel, 20×20×10 mm. with a 4 mm. hole, were respectively 20·630, 2·580, and 1·940 per cent. during 180 hrs'. attack. J. Rothe and F. W. Hinrichsen studied the action of sulphurous acid on iron. A. Lange found that liquid sulphur dioxide has little action on iron at ordinary temp., but under compression, or in the presence of moisture, the corrosion is appreciable. The corrosive action of town air, the air of railway tunnels, and smoke, all contaminated with sulphur dioxide, was discussed by R. C. Brenner, A. W. Carpenter, A. S. Cushman, S. L. Foster, L. de Gaetani, S. W. Griffin and W. W. Skinner, O. Haehnel, P. Longmuir, D. Meneghini, E. A. and L. T. Richardson, S. Rideal, J. Rothe and F. W. Hinrichsen, P. Siedler, and W. H. J. Vernon. The corrosive action of sulphurous acid on metals was studied by J. Uhl, and P. Schweitzer. P. Nicolardot studied the action of the acid on iron. H. J. Braun observed that wrought iron is sufficiently resistant to the action of **fluosulphonic acid** at 0°, 130°, and 150° that it can be employed for the retorts in manufacturing the acid. H. Moissan and P. Lebeau found that **sulphuryl fluoride** has no action on iron even at a red-heat. F. Wöhler said that liquid **sulphur monochloride** acts slowly on iron, but H. E. Patten observed no reaction; the subject was discussed by R. Dittmar, P. Nicolardot, B. W. Dunn, and

E. H. Harvey. E. Baudrimont found that boiling sulphur monochloride slowly attacks iron reduced by hydrogen, forming ferric chloride. P. Nicolardot said that the presence of nickel, silicon, chromium, or tungsten makes the iron more resistant to the attack. N. Domanicky found that the presence of ether accelerates the attack of iron by sulphur monochloride. H. B. North found that **sulphuryl chloride** acts on iron at an elevated temp., forming crystals of ferric chloride; and E. Fromm observed that a soln. of sulphuryl chloride in absolute ether does not act on iron. H. E. Patten observed that with **thionyl chloride**, iron is coated black. H. B. North and A. M. Hageman found that in sealed tubes at 150° to 200°, with thionyl chloride in excess, the reaction can be symbolized: $2Fe+4SOCl_2=2FeCl_3+2SO_2+S_2Cl_2$: and if the metal is in excess: $3Fe+2SOCl_2=2FeCl_2+FeS+SO_2$. K. Oma gave $2Fe+2SOCl_2=2FeCl_2+S+SO_2$.

The action of **sulphuric acid** on iron resembles in many respects the action of hydrochloric acid—*vide supra*, hydrochloric acid. It was discussed by J. W. Priestley at the beginning of the nineteenth century, and later by C. J. B. Karsten, and others—*vide* **5**. 39, 20. Sulphuric acid in all stages of dilution attacks iron; and in the case of the dil. acid, hot or cold, hydrogen is evolved; but, according to M. Berthelot, the conc. acid furnishes hydrogen in the cold, and at temp. exceeding 160° sulphur dioxide is the main product. R. H. Adie said that sulphur dioxide appears at 220°, and that no hydrogen sulphide is formed. P. Hart found that the finely-divided metal at 200° yields sulphur dioxide with sulphuric acid of sp. gr. 1·75. A. Ditte studied the products of the reaction with the conc. acid. C. W. R. Powell observed that the slow action of the conc. acid on iron at 25° to 30° furnishes ferrous sulphate—mostly anhydrous—sulphur dioxide, hydrogen, and water; and C. E. Fawsitt and C. W. R. Powell found that at 180° the sulphur dioxide which is evolved contains a small proportion of hydrogen sulphide, but no hydrogen. In general, cold or hot 61 per cent. acid furnishes hydrogen; but at higher concentrations sulphur dioxide, hydrogen sulphide and sulphur are formed. The 92 per cent. acid has very little action on iron: the action increases with increasing dilution; at 130° to 150° the 92 per cent. acid furnishes hydrogen and sulphur dioxide: the proportion of hydrogen decreases as the temp. rises to 250°. Sulphur begins to separate at about 210°. H. Endo found that the effect of oxygen dissolved in the acid is practically negligible with 95 per cent. sulphuric acid, but with decreasing concentration of the acid the effect increases until, with a 5 per cent. acid, the rate of corrosion is over fourteen times as fast as it is with a soln. free from dissolved oxygen. Observations were made by M. Ballay, S. C. Bate, C. F. Burgess and S. G. Engle, W. H. Creutzfeldt, G. Delbart, A. Ditte, V. Duffek, J. A. N. Friend and J. H. Dennett, R. Girard, L. F. Girardet and T. R. Kou, M. Centnerszwer and M. Straumanis, J. J. Healy, Y. N. Kojhevnikoff, J. Zamaron, W. Guertler and T. Liepus, W. H. Hatfield, G. W. Heise and A. Clemente, A. d'Heureuse, A. Larsson, B. Sandrock, J. Sauvageot and L. Lauprète, F. E. Thomson, W. M. Thornton and J. A. Harle, Y. Utida and M. Saito, G. W. Whitman and co-workers, M. Schunkert, and Y. Yamamoto. The speed of the dissolution of iron in dil. sulphuric acid was studied by C. M. Guldberg and P. Waage, G. Tammann and F. Neubert, and A. de Hemptinne. H. Bablik compared the speeds of attack by sulphuric and hydrochloric acids. C. Bizio discussed the action of fuming sulphuric acid on iron. H. Endo found the loss in grams per sq. cm. during 5 hrs'. action, at 25°, to be:

H_2SO_4 .	5	10	15	20	25	30 per cent.
Loss .	0·000699	0·000807	0·001250	0·008857	0·016840	0·036048

C. G. Fink and C. M. Decroly found that the loss of electrolytic iron in milligrams per sq. dm. per 24 hrs., with sulphuric acid of the percentage concentration:

H_2SO_4 .	5	10	25	50	75	90 per cent.
Loss .	3300	4020	15,200	2300	350	1120

J. I. Crabtree and G. E. Matthews observed a loss of 11·4 grms. per 100 sq. in. per day in 5 per cent. sulphuric acid. W. Bauhuis observed that electrolytic iron dissolves in sulphuric acid of different concentrations with characteristic velocities; there is a well-defined period of induction, which is more marked than is the case with hydrochloric acid. Both the smooth and rough metal dissolve actively; cathodic polarization makes no appreciable difference to the rate of dissolution, but anodic polarization passivates the metal. The addition of hydrochloric acid to sulphuric acid lowers the speed of the reaction, and the addition of halides to the sulphuric acid lowers the speed of dissolution of the metal, as is also the case with hydrochloric acid. The addition of oxidizing agents accelerates the speed of dissolution of the metal. W. Palmaer found that the period of induction is longer the slower the speed of dissolution of the metal. The subject is further discussed in connection with the corrosion of iron. G. Tammann and co-workers observed the effect of the hydrogen press. on the rate of dissolution of iron in sulphuric acid.

F. Schmitz found that the losses with 0·06, 0·42, and 0·92 per cent. carbon steel, 20×20×10 mm. with a 4 mm. hole, in sulphuric acid (1 : 10), were, respectively, 1·560, 2·740, and 54·920 per cent. during 180 hrs., and with conc. acid, respectively, 0·130, 0·145, and 0·110 per cent. B. Garre studied the effect of cold-work—torsion or tension—on the solubility of iron in dil. sulphuric acid, and some of his results are summarized in Fig. 337. W. Köster represented the influence of quenching and annealing on the solubility of iron with 0·1 per cent. of carbon in dil. sulphuric acid by Fig. 338. According to A. J. Hale and H. S. Foster, with a sq. dm. of cast iron and wrought iron, at 17° to 20°, and 0·2N-H_2SO_4, the losses were respectively 2·8 and 0·35 grms. with a litre of acid in 4 hrs.; respectively 16·0 and 17·0 grms. with half a litre of acid per day for 7 days; and 3·2 and 3·3 grms. with half a litre of acid in 28 days.

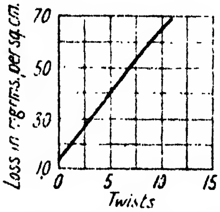


FIG. 337.—The Effect of Torsion on the Solubility of Iron in Dilute Sulphuric Acid.

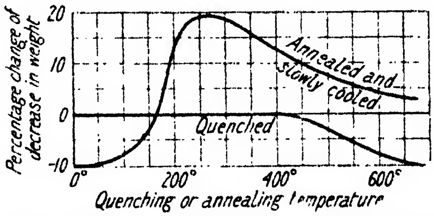


FIG. 338.—The Effect of Heat-treatment on the Solubility of Iron in Dilute Sulphuric Acid.

B. Lambert and J. C. Thomson found that the purified metal is very little affected by cold, dil. sulphuric acid, but dissolution readily occurs when the acid is warm. Conc. sulphuric acid has very little action on cast iron, hot or cold, provided access of air is excluded, for the moisture absorbed would dilute the acid and make it act more strongly. G. Lunge investigated the subject, and found with various samples of cast iron at 20°, 100°, and 295°, the average losses, grams per sq. cm. per hour, were respectively 0·021, 0·095, and 0·113 with an acid of sp. gr. 1·840; at 20°, 100°, and 200°, with an acid of sp. gr. 1·710, 0·018, 0·149, and 2·096 grms.; and at 20°, 100°, and 147°, with an acid of sp. gr. 1·530, 0·026, 0·300, and 1·564 grms. The general results showed that all acids down to sp. gr. 1·530 have very little action on cast iron at ordinary temp.; the action is stronger at 100°, and still more pronounced at the b.p. of the acid. With monohydrated sulphuric acid the losses in grams per sq. cm. with cast iron and wrought iron were 0·062 and 0·056 respectively in 6 days at 20°, and respectively 0·015 and 0·095 in 2 hrs. at 100°. Wrought iron is more susceptible to attack than cast iron, but at ordinary temp. it resists conc. sulphuric acid down to a little below a sp. gr. of 1·7000. If moisture be absorbed from the air the acid may become more dilute, and a strong corrosive action may occur. R. Knietsch obtained the following losses, in grms. per sq. metre per hour, during 72 hrs'. action at 18° to 20°, with the exclusion of air:

Per cent. H_2SO_4	Cast iron	Mild steel	Puddled iron
48·8	0·2177	—	—
61·2	0·1510	—	0·3032
67·7	0·0847	—	0·0789
73·4	0·0662	—	0·0623
79·7	0·1560	—	0·1159
83·7	0·1388	—	0·1052
85·1	0·1306		0·1034
88·2	0·1636	—	0·1417
90·6	0·1760	—	0·1339
92·0	0·0983	—	0·1040
93·0	0·0736	0·0987	0·0856
94·3	0·0723	0·0987	0·0708
95·4	0·1274	0·0933	0·1209
96·8	0·1013	0·0815	0·0988
98·4	0·0681	0·0533	0·0655
98·7	0·0589	0·0509	0·0570
99·2	0·0568	0·0418	0·0504
99·30	0·057	0·042	0·050
99·50	0·060	0·038	0·049
99·77	0·066	0·042	0·049
100·00	0·087	0·088	0·076

This shows that whilst dil. sulphuric acid readily attacks cast iron, the conc. acid does not attack it to any great extent until the acid exceeds the conc. represented by H_2SO_4. Thus, R. O. Davis found that the acid of sp. gr. 1·45 is very corrosive; the metal is but little attacked by an acid of sp. gr. 1·49, and the action is inappreciable with an acid of sp. gr. 1·50 to 1·55. With wrought iron, however, all concentrations are active until the conc. exceeds that required by the formula H_2SO_4 by some 27 per cent. Hence, added R. Knietsch, whilst cast-iron vessels are suitable for the preparation of hydrated sulphuric acid, it is dangerous to employ them for the fuming acid. W. H. Hatfield treated cylinders of iron, approximately 0·5 in. diam. and weighing about 50 grms., with about 85 c.c. of acid at 15°, and expressed the losses in grms. per sq. cm. per 24 hrs.; he found:

		N-H_2SO_4	5	10	25	50 per cent. H_2SO_4
Electrolytic iron		0·0057	—	0·0068	—	—
Armco iron		0·0099	—	0·0152	—	—
English wrought iron		0·1452	—	0·3610	—	—
Steel, 0·29 per cent. C	15°		0·1353	—	0·2027	0·0020
	40°		0·4004	—	0·8226	0·0060
	60°		0·4495	—	1·2552	0·0105
	80°		0·4958	—	1·2741	0·0112

Many other observations have been made on the relative resistance of cast iron, wrought iron, and steel to sulphuric acid—*e.g.* by J. Aston and C. F. Burgess, G. Delbart, H. Edwards, U. R. Evans, J. A. N. Friend, J. A. N. Friend and C. W. Marshall, L. Gruner, E. Heyn and O. Bauer, and J. Sauvageot and L. Lauprète—*vide infra*, corrosion. L. Aitchison, T. Andrews, P. Bardenheuer and K. L. Zeyen, O. Bauer, R. A. Hadfield and J. A. N. Friend, P. Kötzschke and E. Piwowarsky, E. Piwowarsky, W. Schreck, and T. Turner studied the influence of carbon. H. Endo showed that with steel having from 0·1 to 1·3 per cent. of carbon, the rate of action increases almost linearly with increasing proportions of carbon. F. Robin found that the solubility of steel in dil. sulphuric acid increases with the temp. of forging. For high-carbon steels, the maximum is at 300°; and with soft steels, 100° to 200°. The solubility diminishes rapidly with steels forged between 400° to 600°, and attains a minimum at 700° with soft steels, and at 800° with hard steels. For the effect of cold-work—twisting or bending—on the rate of dissolution of the metal, *vide infra.*

F. J. Daniell, and W. H. Johnson found that both iron and steel frequently become brittle after exposure for a short time to acid attack, and D. Sevoz, and

O. Reynolds attributed this to the presence of occluded hydrogen; and J. H. Andrew added that the hydrogen is absorbed by the intercrystalline cement and the resulting expansion forces the crystals apart and reduces their cohesion—*vide infra.* A. Ledebur observed that cast iron is not so sensitive as wrought iron, possibly owing to the altered solubility of hydrogen; when the container is in contact with fuming sulphuric acid, it is liable to burst or disintegrate, often with a loud noise. It is assumed that the acid penetrates the pores of the metal, liberating sulphur dioxide, hydrogen sulphide, and even carbon dioxide, which remain in the metal under high press., ultimately leading to rupture. The sulphur dioxide and hydrogen sulphide can be detected in the fractured metal by their odour. A. C. Cumming also noted a similar disruption with cast-iron vessels containing a mixture of sulphuric and nitric acids. It was concluded that crystals of salts forming in the interior of the iron were responsible for the disruption. T. F. Banigan found that cast-iron pipes and malleable castings frequently crack, without corrosion, after long exposure to sulphur trioxide fumes. Amorphous silicon alloyed with iron is rapidly oxidized by 15 per cent. oleum, but not by 96 per cent. sulphuric acid. Silicon carbide is not affected. The cracking is attributed to the effect of internal strains due to the increase in vol. of the particles of silicon when oxidized to silica.

J. A. N. Friend gave the following results for the effect of increasing concentrations of sulphuric acid on mild steel and grey cast iron under comparable conditions. The specimens measured 4·5×0·8×0·65 cms., they weighed 22 grms., and were in contact with 500 c.c. of acid for 8 hrs. at 15°, when the losses were

H_2SO_4 . .	0	0·5*N*-	*N*-	2*N*-	3*N*-	4*N*-	5*N*-
Cast iron .	0·0245	7·597	9·463	10·77	10·47	9·90	9·5
Mild steel .	0·0083	0·334	0·524	0·765	0·994	1·241	1·566

The attack on cast iron rises to a maximum and then falls; the conc. of the acid producing the maximum effect varies with different varieties of cast iron. The rate of dissolution of steel rises steadily with the conc. of the acid, and shows no maximum in the range examined. J. E. Stead attributed the fall in the rate of dissolution of the cast iron to the formation of a protective layer of sulphate which is not dissolved by the conc. acid. This agrees with the results of A. Larsson, but it does not explain why the same phenomenon does not occur with steel. M. P. Applebey and S. H. Wilkes, and L. McCulloch also attributed the passivity of iron in sulphuric acid to a film of sparingly-soluble sulphate. M. Mugdan said that the resistance of iron to conc. sulphuric acid is due to its assuming the passive state (*q.v.*). G. W. Heise and A. Clemente observed that iron becomes passive in sulphuric acid when 10 grms. potassium dichromate per litre are present in 0·5*N*-H_2SO_4; 50 grms. per litre in *N*-H_2SO_4; and in 2*N*-H_2SO_4 a passive state was not attained.

L. Aitchison found that the effect of carbon in steel exposed to 1 per cent. sulphuric acid is such that the losses in grams per 100 sq. cm. in 77 days in the dark are as follow, and similarly with 10 per cent. sulphuric acid during 45 days' action in the dark:

Carbon . . .	0·07	0·19	0·50	0·68	0·89	1·25	1·46 per cent.
H_2SO_4 1 per cent. .	2·88	3·48	3·34	4·15	4·25	4·38	6·65
H_2SO_4 10 per cent. .	7·02	7·15	4·57	6·90	10·82	3·57	4·90

A. Sieverts and P. Lueg observed that the inhibitory agents discussed above in connection with hydrochloric acid act similarly with sulphuric acid. Recommendations have been made at various times to retard the evolution of hydrogen—acid mist—in the pickling of iron by an acid, and prevent the embrittlement of the metal by hydrogen. Thus, S. E. Grove recommended nitre-cake, sumac, and water; S. W. Griffin, 1 per cent. of formaldehyde and hydrochloric acid; T. L. Bailey, glue, dextrin, glucose, and jelly; O. Vogel, 1 to 2 per cent. of anthracene residues, waste sulphite lye, crude anthracene, products obtained in the dry distillation of coal, and quinolinic derivatives; H. N. Holmes, 0·2 per cent. of formaldehyde, benzaldehyde, furfural, and acetaldehyde; and J. G. Schmidt and H. R. Lee, thiourea and substituted ureas. O. P. Watts found that with 19 per cent. sulphuric acid, at 30°, HCl, HBr, HF, Na_3AsO_4, $As_2(SO_4)_3$, KF, KBr, KI, NH_4Cl, NaCl, $HgCl_2$, $HgSO_4$, $SnCl_2$, Na_2SnO_3, $Cr_2(SO_4)_3$, $MnCl_2$, hydroquinone, and resorcin acted as retarding agents; KNO_3, $KClO_3$, $CuSO_4$, $AgNO_3$, Ag_2SO_4, $HgNO_3$, CrO_3, $CrCl_3$, K_2CrO_4, $K_2Cr_2O_7$, $Bi_2(SO_4)_3$, $KMnO_4$, and $PtCl_4$ acted as accelerating agents; whilst K_2SO_4, $(NH_4)_2SO_4$, H_3BO_3, $Sb_2(SO_4)_3$, and citric acid had no perceptible effect. W. H. Creutzfeldt noted the retarding action of various organic substances, tar, oil, etc.; and W. S. Calcott and I. E. Lee, of thiophenol, thio-β-naphthol, benzylmercaptan, isoamylmercaptan, or isopropylmercaptan in proportions of the order of 0·03 per cent. The subject was discussed by I. Apati, H. Bablik, G. Batta and E. Leclerc, E. L. Chappell and P. C. Ely, G. W. Emlen, J. E. Hansen and G. S. Lindsay, M. Omerz, H. Pirak and W. Wenzel, F. H. Rhodes and W. E. Kuhn, A. Sieverts and P. Lueg, F. N. Speller and E. L. Chappell, H. Staley, H. Sutton, K. Taussig, A. D. Turnbull, and J. C. Warner. According to A. D. Turnbull, carbohydrates like sugar or starch have a good influence on retarding the action of dil. sulphuric acid on iron. With cellulose, there is a reaction between water: $C_6H_{10}O_5+H_2O=C_6H_{12}O_6$; and the cellulose acts as an inhibitor. J. G. Schmidt and H. R. Lee observed that thiourea acts as an inhibitor of the action of sulphuric acid on iron. The Newport Co. found that 1 per cent. or less of thiourea or its substitution derivatives prevents or retards the action. J. C. Warner found that the rate of dissolution of iron in an aq. soln. may be diminished not only by substances which produce passivity at anodic areas, but also by substances which increase the hydrogen overvoltage at cathodic areas. This inference is supported by observations on the effect of gelatin, petroleum bases, and coal-tar bases on the rate of dissolution of a low-carbon iron in dil. sulphuric acid and on the hydrogen overvoltage at the metal surface in this soln.; but aniline and quinoline, which definitely retard dissolution, actually lower the hydrogen overvoltage measured at 10 milliamps. per sq. cm. Overvoltage measurements at lower current densities might remove this anomaly. O. Vogel found many nitrogen ring compounds act as retarders. F. H. Rhodes and W. E. Kuhn examined the inhibitory action of some heterocyclic compounds of nitrogen on the attack of iron by sulphuric acid:

Toluidine, triethanolamine, aniline, pyridine, picoline, piperidine, lutidine, collidine, 8-hydroxyquinoline, quinoline, phenylquinoline, 2-methylquinoline (quinaldine), crude quinaldine, 6-methylquinoline, 2,4-dimethylquinoline, pyrrole, acridine, diquinolyl, diquinolylmethane, dimethyldiquinolyl, β-naphthoquinoline, methylacridine, 3,6-diaminoacridine, phenylacridine, 3,6-dimethyl-2, 7-diaminoacridine ethyl chloride, 3,6-dimethyl-2,7-diethyldiaminoacridine hydrochloride, benzidine, α-naphthylamine, phenyldinaphthacridine, α, β-dinaphthacridine, fluorenenaphthacridine, β,β-dinaphthacridine, α,α-dinaphthacridine, and diphenanthracridine.

They concluded that the inhibitory effect increased with the mol. wt. and also with the introduction of a methyl, phenyl, or amino-group. Thus, in such a series as pyridine-quinoline-acridine the increase in the number of rings in the molecule was accompanied by a regular increase in effect, and in the series pyridine-lutidine-picoline-collidine the introduction of a single additional methyl group increased the inhibiting action of the compound by nearly 25 per cent. Hydroxyl groups decreased the inhibiting action, and the most efficient of all the compounds studied were those containing several alkyl and amino-groups substituted in an acridine nucleus; thus, 3:7-diamino-2:8-dimethyl-acridinum ethochloride and hydrochloride. The addition of a specific inhibitor to an acid electrolyte increased the film resistance, and it is indicated that the protective action is due to some specific property of the observed film and not solely to the increased resistance offered. L. Heilbronn used an inhibitor, a peptone and formol; J. H. Gravell and A. Douty, a thiocyanate; J. H. Gravell, anhydroformaldehydeaniline, thiocarbonilide, or thionex; L. J. Christmann, tetramethyldiaminodiphenyl disulphide; J. G. Vignos, sulphated arylthiazole compounds; and E. I. du Pont de Nemours, a product of the action of an aldehyde and an amine, and carbon disulphide, *e.g.* $CH_3.CO.H$, or $C_6H_5NH_2$ and CS_2. M. Hartmann and W. Klarer used as inhibitors of the reaction the products obtained by condensing aldehydes, ketones, and suitable acid chlorides like phosgene with aromatic amino- or nitro-compounds with subsequent reduction, *e.g.* diaminodiphenylmethane, diaminoditolylmethane, and diaminonaphthylmethane, or the corresponding symmetrical and unsymmetrical, primary or secondary nitrogen-substitution products, *e.g.* 4, 4′-tetramethyldiaminodiphenylmethane. Further, they employed the corresponding products which may be obtained with acetaldehyde, or acetone instead of with formaldehyde; ketones such as 4, 4′-tetramethyldiaminobenzophenone, also the triphenylmethane, or, quite generally, the leuco-compounds of the triarylmethane dyes containing amino-groups, such as leuco-crystal-violet, or leuco-malachite-green, or the corresponding quaternary ammonium bases of all these compounds. T. W. Bartram and D. H. Tomkins, and J. G. Schmidt used a complex aldehyde; L. B. Sebrell, trithioformaldehyde.

G. Walpert found that the rate of dissolution of iron and the electrode in $8N$-H_2SO_4 was depressed by the addition of hydrochloric acid, and the period of induction is augmented. The rate of dissolution of the iron in conc. sulphuric acid is depressed more by the addition of iodides than with bromides, and with bromides more than with chlorides. The effect with dil. sulphuric acid is small. The addition of the aliphatic acids also retards the rate of dissolution, and this in the order: formic acid, acetic acid, propionic acid, and butyric acid. Substances with a high mol. wt., like gelatin and methyl violet, also reduce the speed of the reaction. The phenomena are attributed to the adsorption of the foreign substance on the surface of the metal being dissolved.

The effect of the inhibitor quinoline ethiodide on the evolution of hydrogen from various kinds of iron, and also the cathode potential was studied by E. L. Chappell and co-workers. The results on the evolution of hydrogen from steel in N-H_2SO_4 with different proportions of quinoline ethiodide, at 60°, are indicated in Fig. 339, and the effect on the cathode potential of Armco iron at 25°, in Fig. 340.

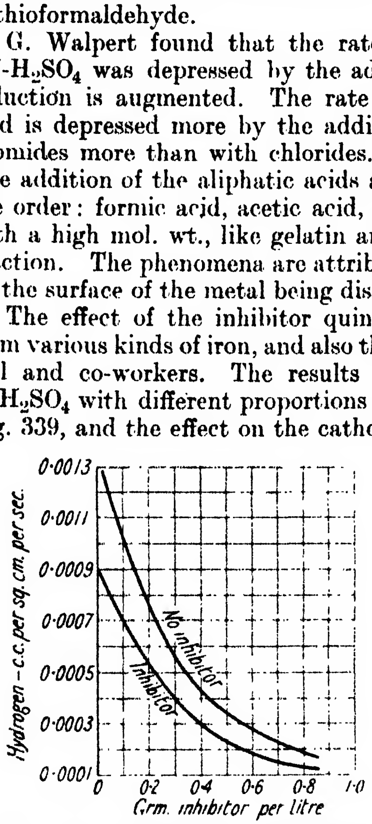


FIG. 339.—The Effect of Inhibitors on the Evolution of Hydrogen.

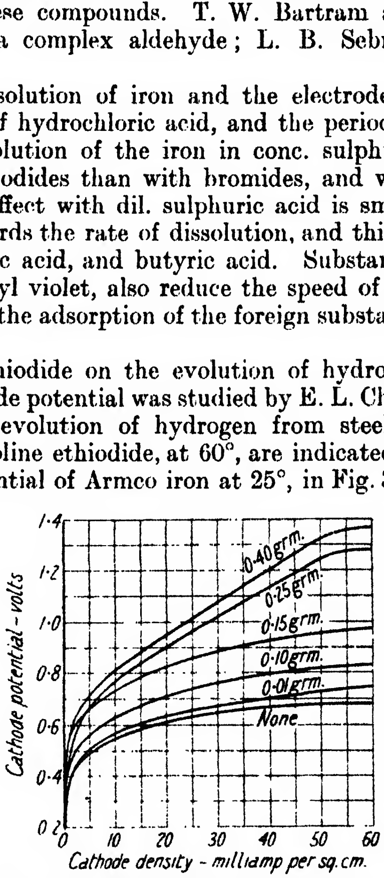


FIG. 340.—The Effect of Inhibitors on the Cathode Potential.

The inhibitor has little effect on the anode potential, and a marked effect on the hydrogen overvoltage. It is therefore concluded that the effect produced is the result of cathode reactions. With a constant density of 10 milliamperes per sq. cm., N-H_2SO_4, and soln. with 0·0 and 0·4 grm. quinoline ethiodide per litre at 25°, the following cathode potentials, E volt, and increases in the overvoltages were observed:

	Armco iron	Rough steel	Polished steel	White cast iron	Annealed malleable	Wrought iron
E { 0·0 . .	0·56	0·38	0·60	0·41	0·46	0·52 volt
E { 0·4 . .	0·80	0·55	0·77	0·57	0·58	0·60 ,,
Increase o.v. .	0·24	0·17	0·17	0·16	0·12	0·08 ,,

E. L. Chappell and co-workers also observed the effect of various inhibitors, 0·70 grm. per litre, on the evolution of hydrogen -*v* c.c. per sq. cm. per minute—with N-H_2SO_4 and steel; as well as the cathode potential, *E* volt, with a current density of 9·1 milliamperes per sq. cm., at 60°.

	None	Sodium cyanide	Picric acid	Bismarck brown	Sodium arsenate	Quinoline ethiodide
E . .	0·388	0·408	0·304	0·428	0·395	0·454
v . .	0·091	0·064	0·061	0·029	0·020	0·020

The effect of alkaloids like brucine on the overvoltage of metals was indicated by J. I. Crabtree, and M. le Blanc; organic quinine and quinoline bases, by A. Mazzucchelli; colloids like gum and gelatine, by N. Isgarisheff and S. Berkmann, and C. Marie and R. Audibert; and arsenious acid, potassium cyanide, hydrogen sulphide, brucine, and quinine, by N. Isgarisheff and E. Koldaeva.

W. Rohn showed that with 10 per cent. cold sulphuric acid, purified, unannealed iron loses 0·06 grm. per sq. dm. in 1 hr., and 1·1 grm. in 24 hrs.; and 21·7 grms. per sq. dm. are lost in 1 hr. in the hot acid. The attack on annealed iron is less vigorous. According to G. J. Burch and J. W. Dodgson, iron in contact with silicon in sulphuric acid of sp. gr. 1·84 hastens the dissolution. The resistance to sulphuric acid offered by iron containing silicon, etc., was discussed by A. Ricevuto, R. Irmann, D. F. McFarland and O. E. Harder, F. Schmitz, L. Aitchison, etc.—*vide* the corrosion of iron and steel. C. E. Fawsitt and A. A. Pain observed that with 5 grms. of steel exposing a surface of 36 sq. cm., at 30°, for 28 days, the average vol. of gas evolved in c.c. per hr. per sq. dcm. of steel surface, and the loss of weight in grams in 28 days, were:

H_2SO_4 . .	97·4	94·0	90·9	89·3	87·9	85·0	80·0 per cent.
Vol. gas no shaking	—	0·27	0·31	0·06	0·28	0·30	2·5 c.c.
Vol. gas shaking .	0·17	1·46	2·07	0·24	0·89	0·89	4·94 c.c.
Loss wt. shaking.	0·099	0·861	1·222	0·140	0·523	0·526	2·915 grms.

According to W. D. Richardson, grey cast iron, containing graphite, is more readily attacked by N-H_2SO_4 than open-hearth iron, but the corrosion of the latter is greatly accelerated if a trace of platinum salt be added so as to produce a little platinum in contact with the iron. The losses in grams per hour, from plates 15 cm. square, at 16°, with open-hearth iron and cast iron, were respectively 0·76 and 8·9 grms. without platinum, and 15·5 and 9·6 grms. with platinum. W. D. Richardson observed that with normal acids at about 16°, the average attack per hour:

	H_2SO_4 (First 20 hrs.)	H_2SO_4 (Second 20 hrs.)	HNO_3 (2 hrs.)
Copper steel (0·1 per cent. Cu) .	0·09 to 0·23	0·00 to 0·03	1·90 to 19·8
Open-hearth iron . . .	0·30 to 0·08	0·02 to 0·05	15·2 to 20·7
Bessemer steel	0·27 to 0·34	0·01 to 0·09	14·7 to 20·5
Puddled iron	0·39 to 1·03	0·06 to 0·86	18·2 to 20·0
Grey cast iron	4·82 to 4·87	3·99 to 5·02	5·0 to 8·8
White cast iron . . .	2·03 to 2·12	1·77 to 2·33	6·5 to 9·9
Malleable iron	1·56 to 2·91	0·98 to 1·36	5·4 to 6·0
Semi-steel	4·06 to 4·18	4·26 to 5·15	5·4 to 7·2
Cast steel	0·66 to 1·03	0·30 to 0·77	1·60 to 16·5

He also found that the action was not stimulated by the presence of copper or silver salts, although O. P. Watts and H. C. Knapp observed that the action of the acid is accelerated by the presence of these salts. O. P. Watts and N. D. Whipple found that the presence of arsenic in dil. sulphuric acid greatly reduces the corrosion for the same reason as that indicated in connection with hydrochloric acid; whilst the presence of hydrogen dioxide hastened the rate of attack. H. Anthes discussed the evolution of arsine under these conditions. For E. Heyn and O. Bauer's observations on the effect of carbon in steel on the corrosion by dil. sulphuric acid, *vide infra*, Fig. 394. C. E. Fawsitt and C. W. R. Powell, from a study of the action of sulphuric acid on iron and steel, concluded that conc. sulphuric acid acts at the ordinary temp. on steel and on some kinds of cast iron, the products being ferrous sulphate and hydrogen with a small quantity of sulphur dioxide. The reaction proceeds more rapidly with rise of temp., and the gaseous products at 180° are sulphur dioxide with occasional small quantities of sulphuretted hydrogen, but no hydrogen. The rate is increased, on the average, about three times for each 10° rise of temp. The rate of reaction depends on the conc. of the acid, but for small dilutions the ratio of hydrogen to sulphur dioxide in the mixture of gases evolved remains almost unchanged. Although the rate of reaction depends to a certain extent on the composition of the sample of iron, as indicated by the large difference between steel wire and pig-iron, an important factor governing the reaction with any one sample appears to be the condition of the surface of the iron. C. E. Fawsitt found that at 30° with 91·5 per cent. acid, steel lost in 4 days 0·068 grm., and if mercury was in contact with the steel, 0·061 grm.; at 25° and with 91·5 per cent. acid, in 11 days the loss was 0·134 grm., and with platinum and aluminium respectively in contact with the steel, the losses were 0·123 and 0·071 grm.; and with 96·3 per cent. acid, at 250°, the loss was 0·048 grm. in 27 days; and if platinum and aluminium were in contact with the steel, the losses were respectively 0·048 and 0·055 grm. C. E. Fawsitt and A. A. Pain found that the differences in the electrochemical behaviour show that no real similarity exists between iron which is slowly dissolving in conc. sulphuric acid and iron rendered "passive" by dipping into nitric acid. The action of the acid produces a form of ferrous sulphate monohydrate on the surface of the iron, which causes the slowing down or cessation of the reaction. In general, increasing dilution of the acid with water results in greater reactivity, but certain anomalies were observed in this respect, notably that 89·3 per cent. acid had considerably less action on the metal than 94 per cent., 90·9 per cent., 87·9 per cent., or 85 per cent. acid. The solvent effect is in all cases noticeably increased by shaking the vessel containing the acid and the metal. F. J. R. Carulla reported that cast-iron nitre-pots withstand the action of sulphuric acid and nitrous and nitric acids in a glowing furnace for months, and sometimes years: J. E. Stead attributed this to the formation of a protecting layer of ferrous sulphate insoluble in the hot, conc. acid. The resistance offered by the silicon-iron and other alloys (*q.v.*) to the action of sulphuric acid was discussed by J. W. Parkes.

J. W. Turrentine, and M. G. Levi and co-workers found that iron dissolves in a soln. of **ammonium persulphate**, forming ferrous sulphate, a portion of which undergoes further oxidation. The reaction was studied by G. Tammann and F. Neubert. O. Aschan and G. V. Petrelius found that with soln. of ammonium, **potassium and sodium persulphates** iron dissolves, forming the complex salts $(NH_4)_2Fe(S_2O_8).6H_2O$, $K_2Fe(S_2O_8).6H_2O$, and $Na_2Fe(S_2O_8).4H_2O$, respectively. J. I. Crabtree and G. E. Matthews observed that iron is attacked by **sodium thiosulphate,** and the photographic fixing-bath is discoloured. E. Beutel and A. Kutzelnigg observed that with a boiling soln. of sodium thiosulphate and lead acetate, iron acquires a sequence of colours from yellow to steel-blue owing to the formation of a film of lead sulphide.

C. F. Burgess and J. Aston found that the presence of 0·017 per cent. of **selenium** in iron reduced the attack by 20 per cent. sulphuric acid, but increased its tendency to atmospheric corrosion. A. E. H. Tutton found that **selenic acid** dissolves iron, forming ferrous selenate and a deposit of selenium which hinders the action of the acid on the metal; no hydrogen is evolved, and the selenium is presumably formed by the reaction: $3H_2+H_2SeO_4=4H_2O+Se$; so that the resultant equation is $3Fe+4H_2SeO_4=3FeSeO_4+Se+4H_2O$. For the action of selenium, *vide* the selenides—**10**. 58, 7. G. Tammann and K. Schaarwächter found that the attack of iron by selenium begins about 200°, and quickly attains a maximum speed. The alloys were studied by H. Fleek, and A. L. Norbury; and the effect of iron on the photoelectric properties, by F. H. Constable and A. F. H. Ward. For the action of **tellurium**, see the tellurides—**11**. 59, 7. G. Tammann and

K. Schaarwächter observed that tellurium begins to attack iron at about 446°, and the action becomes very rapid soon afterwards. N. Ageeff and M. Zamotorin studied the diffusion of tellurium in iron. G. B. Waterhouse and I. N. Zavarine observed that steel with 0·12 per cent. of tellurium has a lower ductility than normal steel. C. F. Burgess and J. Aston discussed the working properties of iron with a small proportion of selenium. Iron decomposes dry **hydrogen selenide,** as well as **hydrogen telluride.** J. B. Peel and P. L. Robinson found that hydrogen selenide reacts with iron at 750°, forming ferrous selenide. V. Lenher found that iron when heated in a sealed tube with **selenium oxybromide** is attacked, forming iron bromide and **selenium monobromide ;** and V. Lenher and C. H. Kao found that the metal is attacked by **selenium monochloride.**

The absorption of **nitrogen** by iron has been discussed in connection with Table XLVII, and also from the point of view of the nitrides—**8.** 49, 12. F. Durau and C. H. Teckentrup [7] showed that the absorption of nitrogen by electrolytic iron is a process of adsorption. T. Graham, and A. Wehrle obtained the gas from iron. One group of observers—E. Baur and G. L. Voerman, G. Charpy and S. Bonnerot, G. J. Fowler, W. Frankenburger and K. Mayrhofer, A. Mittasch and W. Frankenburger, H. Hardtung, W. Herwig, A. Ledebur, E. B. Maxted, P. Oberhoffer and A. Beutell, I. I. Shukoff, J. K. Smith, C. Stahlschmidt, and N. Tschischewsky—could not detect any marked adsorption of molecular nitrogen by iron at temp. ranging up to 800°, and at a press. up to 205 atm.; another group—F. Briegler and A. Geuther, C. Despretz, W. A. Dew and H. S. Taylor, E. Frémy, K. Iwase, E. Martin, E. Jurisch, A. F. Benton and co-workers, E. B. Maxted, W. Moldenhauer and F. Groebe, A. Sieverts, A. Sieverts and P. Beckmann, E. W. R. Steacie and F. M. G. Johnson, H. S. Taylor and R. M. Burns, J. G. Thompson and E. H. Hamilton, H. Wolfram, and F. Wüst and J. Duhr—found that nitrogen is absorbed under these conditions. E. Jurisch inclined to the opinion that the discordant conclusions are due to the iron absorbing nitrogen only at a temp. exceeding 850° ; G. Tammann, to the formation of an impervious film of nitride on the surface of the metal ; and W. Frankenburger and co-workers, to the absorption with pure iron being dependent on its structure, which, in turn, depends on its mode of preparation ; it is further supposed that the nitrogen is absorbed only at particularly active parts of the surface and is thence able to pass to the interior—with commercial iron, the impurities present can take up nitrogen directly, and then deliver it up to the iron. E. Martin's results agree with those of A. Sieverts, Fig. 343, and not with those of K. Iwase. A. Fry's results are shown in Fig. 342. There is another difference in the case of the results of E. Jurisch, and K. Iwase. As indicated previously, **8.** 49, 12, the percentage amount of nitrogen taken up by the metal at different temp. is, according to E. Jurisch :

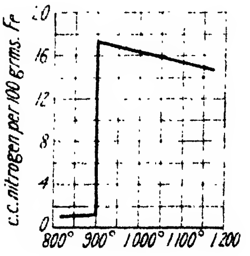


FIG. 341.—The Solubility of Nitrogen in α-Iron.

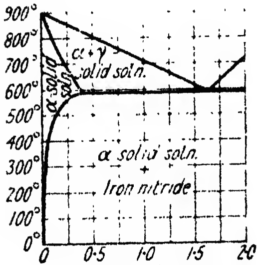


FIG. 342.—The Solubility of Nitrogen in Iron.

	878°	930°	981°	1033°	1084°	1136°
Nitrogen	0·00158	0·02165	0·02103	0·02022	0·01973	0·01885 per cent.

whilst K. Iwase gave :

	620°	722°	852°	940°	980°	1030°
Nitrogen	0·00128	0·00207	0·00220	0·00285	0·00477	0·00687 per cent.

so that in both cases the nitrogen absorbed increases with a rise of temperature up to about 900°, and in the former case the amount taken up beyond 900° decreases with a rise of temp., and increases in the latter case. K. Iwase represented his results by the curve shown in Fig. 343, when the solubility of nitrogen in iron is represented as c.c. of gas at n.p. θ per 100 grms. of metal. The rates of absorption of the gas at 850° and 980° are shown in Fig. 344. The presence of increasing quantities of carbon lowers progressively the solubility of the nitrogen. The corresponding data for the soln. of nitrogen in cast iron are summarized in Figs. 345 and 346. The rate of absorption of nitrogen by iron was also studied by H. Braune, P. Oberhoffer and A. Heger, G. Tammann, and W. Watson; the absorption of the gas was also investigated by L. Cailletet, G. M. Eaton, A. Grabe, L. Jordan and J. R. Eckman, E. Martin, F. Rapatz, A. Sieverts, J. K. Smith, C. E. Stromeyer, B. Tazawa, N. Tschischewsky, G. Valensi, and A. Villachon and G. Chaudron; the absorption of nitrogen by alloy steels, by N. Parravano and A. Scortecci; the absorption of nitrogen in the electric arc between iron electrodes in nitrogen was observed by L. Arons, J. H. Paterson, J. H. Paterson and H. Blair, H. S. Rawdon and co-workers, W. E. Ruder, and E. J. B. Willey; and the absorption of nitrogen during the cathodic spluttering of iron in nitrogen, by W. Frankenburger and K. Mayrhofer, V. Kohlschütter and T. Goldschmidt, V. Kohlschütter and R. Müller, M. Pawloff, and R. Ruer and J. Kuschmann.

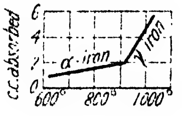


FIG. 343.—The Solubility of Nitrogen in Iron.

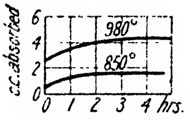


FIG. 344.—The Rate of Absorption of Nitrogen by Iron.

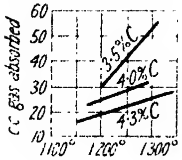


FIG. 345.—The Solubility of Nitrogen in Cast Iron.

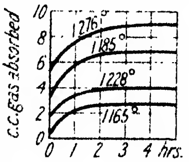


FIG. 346.—The Rate of Absorption of Nitrogen by Cast Iron.

A. Sieverts, and E. Jurisch observed that the quantity of nitrogen, S, absorbed by the metal is proportional to the sq. root of the press., p mm., so that with press. up to 1·5 atm., $S=kp^{\frac{1}{2}}$, where k denotes the coeff. of solubility. C. B. Sawyer, and J. H. Andrew also found the rule to be valid for steel up to 200 atm. press. Molten iron absorbs nitrogen more readily than does the solid, since, according to C. B. Sawyer, when iron is melted in nitrogen under a press. of 1 to 3 atm., the molten metal "spits" during solidification. B. Strauss found that after the solidification of iron which has been melted for half an hour in nitrogen under a press. of 1 atm., the metal retains 0·03 to 0·04 per cent. of nitrogen; F. Adcock observed that iron melted for half an hour in nitrogen at atm. press., and cooled under a press. of 1 to 2 mm., retains 0·02 per cent. nitrogen; C. B. Sawyer, that armco iron, with 1 per cent. of carbon melted and cooled in nitrogen at 1 to 3 atm. press., retains 0·014 to 0·036 per cent. of nitrogen; and J. H. Andrew, molten iron, with 0·16 to 0·6 per cent. of carbon, solidified in nitrogen at 200 atm. press., retains 0·25 to 0·30 per cent. of that gas. K. Jellinek also studied the effect of the press. of the gas on the electrical resistance of the metal; and G. B. Kistiakowsky, the ionization potential of adsorbed nitrogen.

L. Kaul found that when nitrogen acts on heated iron, a state is reached at the γ-point at which nitrogen is fixed by the release of at. energy. Further heating alters the conditions so that the then highly active nitrogen is no longer fixed, and on cooling below the γ-point, the freed energy is again required for cohesion and nitrogen is given up. R. Lenz, and F. Haber did not consider that the nitrogen in electrodeposited iron was derived from the air dissolved in the electrolyte. The subject was discussed by S. Epstein and co-workers. The absorption of nitrogen from air in the manufacture of steel by the Bessemer, or the open-hearth processes was discussed by W. Köster, P. Oberhoffer and co-workers, E. H. Schulz and R. Frerich, C. E. Stromeyer, and H. E. Tholander. The nitriding or nitrogenization of steel, and the case-hardening of steel by nitrogenization were discussed by C. R. Aldon, C. F. Bason, E. Baur and G. L. Voerman, L. E. Benson, H. Braune and C. Bolin, F. Brühl, J. H. Cates, F. L. Coonan, R. J. Cowan, M. Daubois, R. O. E. Davis, G. M. Eaton, J. J. Egan, W. Eilender and O. Meyer, P. H. Emmett and co-workers, S. Epstein, H. A. de Fries, A. Fry, L. Guillet, H. M. Gustafson, O. E. Harder and co-workers, J. H. Higgins, R. H. Hobrock, V. O. Homerberg and co-workers, H. A. de Fries, J. E. Hurst, M. Ishizawa, B. Jones and co-workers, A. B. Kinzel and co-workers, A. B. Kinzel and J. J. Egan, W. Köster, E. Lehrer, H. W. McQuaid and co-workers, H. W. McQuaid and W. J. Ketcham, V. T. Malcolm, W. J. Merten, J. T. Norton, E. Oehman and E. S. Engberg, C. F. Olmstead, A. Osawa and S. Iwaizumi, F. Rapatz, R. G. Roshong, F. W. Rowe, D. Saito and H. Okawa, S. Sato, C. B. Sawyer, F. Schmitz, L. W. Schuster, R. Sergeson, A. Sieverts and F. Krüll, E. A. Sjöstet, J. W. Urquhart, A. E. White and J. S. Vanick, and E. J. B. Willey. T. Nakayama studied the effect of various elements on the nitrogenization of steel.

A. Müller, and H. Krämer thought that the occluded nitrogen in iron is present as nitride, and this view is supported by the X-radiograms of nitrogenized steel by R. Brill, O. Eisenhut and E. Kaupp, G. Hägg, L. R. Ingersoll, A. Osawa and S. Iwaizumi, and A. Pourcel. G. Charpy and S. Bonnerot, W. Frankenburger and co-workers, and N. Tschischewsky have suggested that the nitrogen is combined with the foreign elements associated with the iron. S. Sato said that the nitrogen is present as atomic nitrogen or iron nitride. H. E. Tholander discussed the assumption that the iron is combined with the carbon as iron cyanide; but H. Braune favoured the nitride and rejected the cyanide hypothesis (i) because of the behaviour of nitridized iron towards hydrochloric acid; (ii) A. H. Allen could detect no definite relation between the nitrogen and carbon-content of steel; and (iii) H. Braune, and W. Giesen found that in nitridized steel the cementite is free from nitrogen. In favour of the cyanide hypothesis, there are the observations of J. Kirner, B. Strauss, S. W. Miller, and W. E. Ruder that nitrogen is associated with the carbon of steel. H. Nishimura studied the system: $Fe-N_2-H_2$. For the effect of foreign elements on the absorptions of nitrogen—*vide infra,* the action of ammonia. J. Duhr discussed the absorption of nitrogen by ferroaluminium, ferrotitanium, ferrovanadium, ferrochromium, ferrotungsten, ferromanganese, and phosphor iron. F. Schmitz found that in molten iron, the foreign elements are neutral towards nitrogen. E. J. B. Willey discussed the action of activated nitrogen on iron.

The effect of nitrogen on the equilibrium diagram of iron was discussed by J. H. Andrew, S. Brunauer and co-workers, O. Eisenhut and E. Kaupp, A. Fry, R. F. Mehl and C. S. Barrett, J. Rieber, S. Sato, C. B. Sawyer, L. W. Schuster, B. Strauss, and C. Wagner and W. Schottky—*vide* **8**. 49, 12. The microstructure of nitrogenized iron was discussed by A. Fry, F. Hanaman, O. A. Knight and H. B. Northrup, W. E. Ruder and G. R. Brophy, C. B. Sawyer, B. Strauss, and N. Tschischewsky. H. Braune observed that the effect of nitrogen is to decrease the grain-size of the crystals, and when the nitrogen-content has attained 0·2 per cent., the cellular structure disappears. A system of linear markings is developed and dark pointed needles appear—*vide* iron nitride. H. le Chatelier, and B. Strauss suggested that the needles are Neumann's lines. G. S. Scott observed that twinning occurred in iron carburized with nitrogenous cements, and that nitrogen in steel favoured the γ-state. J. H. Andrew agreed with this and said that Neumann's lines are characteristic of nitrogenized iron. J. Kirner, and B. Strauss observed a constituent resembling pearlite in nitrogenized steel; J. Kirner called it *flavite*—*vide* cementation—and B. Strauss showed that it could be distinguished by heat-tinting, and J. Kirner, by etching with picric acid. S. W. Miller considered that the needles in welded steel were cementite, but G. F. Comstock showed that they are produced by nitrogen, and he recommended the use of an alkaline soln. of potassium ferrocyanide to distinguish nitride from pearlite; W. E. Ruder and

G. R. Brophy used Stead's phosphorus reagent; and A. Fry an alkaline soln. of sodium picrate. The acicular constituent of steel was also studied by J. H. Andrew, W. R. Bean and co-workers, A. A. Blue, H. M. Boylston, H. Braune, H. le Chatelier, E. Colver-Glauert, G. F. Comstock, G. F. Comstock and M. E. Ruder, R. A. Hadfield, F. Hanaman, Z. Jeffries, O. A. Knight and H. B. Northrup, W. Köster, E. F. Law and co-workers, S. W. Miller, H. S. Rawdon and co-workers, W. E. Ruder, W. E. Ruder and G. R. Brophy, C. B. Sawyer, B. Strauss, and N. Tschischewsky. The X-radiograms, and the lattice structure of nitrogenized steel were studied by G. Hägg, S. Epstein and co-workers, S. B. Hendricks and P. R. Kosting, P. D. Merica, S. Epstein, A. Osawa and S. Iwaizumi, E. Lehrer, O. Eisenhut and E. Kaupp, A. Sieverts and co-workers, and R. Brill. W. A. Wood observed that in the case-hardening of steels by nitridization, a surface layer of nitrides is formed with distorted lattices. The sp. gr. was studied by A. Sieverts and co-workers, F. Krüll, and O. Eisenhut and E. Kaupp. The effects of nitrogen on the mechanical properties of iron, observed by N. Tschischewsky and co-workers, were summarized in Fig. 16, **8**. 49, 12; and the subject was discussed by H. L. Buff, T. P. Campbell and H. Fay, A. W. Coffman, R. S. Dean, R. S. Dean and co-workers, C. Despretz, W. Eilender and R. Wasmuht, H. Fay, G. J. Fowler, H. G. Freeland, A. Fry, T. S. Fuller, B. Getzov, A. Grabe, W. T. Griffiths, F. Hanaman, I. E. Kontorovich, O. E. Harder and G. B. Todd, O. Hengstenberg and R. Mailänder, E. C. Herbert, W. Herwig, J. H. Higgins, V. O. Homerberg and J. P. Walstead, J. E. Hurst, J. E. Johnson, W. Köster, R. Mailänder, O. Meyer and R. Hobrock, N. L. Mochel, H. A. Pearson, J. Petren and A. Grabe, F. Savart, F. W. Scott, A. Sieverts and F. Krüll, O. Silvestri, V. N. Svechnikoff, G. Tammann, O. I. Ver and co-workers, and T. Yosiki. A. A. Noyes and L. B. Smith measured the dissociation press. E. Rupp studied the optical properties of the film of adsorbed nitrogen. H. Braune observed that there is an increase of 14·6 microhms per cm. cube in the electrical resistance for 1 per cent. of nitrogen adsorbed by iron. The subject was also studied by F. Hanaman, and E. B. Maxted. The effect of nitrogen on the magnetic properties of iron was discussed by H. Gries and H. Esser, C. Despretz, G. J. Fowler, E. Frémy, W. Köster, E. Lehrer, E. B. Maxted, P. D. Merica, and A. W. F. Rogstadius. The decarburization of iron by heating it in nitrogen was studied by A. Bramley and co-workers, L. Forquignon, H. M. Howe, A. Johansson and R. von Seth, H. von Jüptner, E. Jurisch, J. Kirner, P. Oberhoffer and A. Heger, F. Schmitz, B. Strauss, H. E. Tholander, H. Wolfram, F. Wüst and C. Geiger, and F. Wüst and E. Sudhoff—*vide infra*, cementation. No decarburization occurs at 1050° other than that depending on other gases occluded in steel, and no cyanogen was formed. W. Eilender and R. Wasmuht said that as little as 0·01 per cent. of nitrogen in steel will raise the hardness 15 per cent. S. Sato studied the occlusion of hydrogen by iron nitride; and N. P. Inglis and G. F. Lake, the corrosion of nitrided steel.

The effect of nitrogen on the corrosion of iron by dil. acids was studied by L. Guillet and M. Ballay, who observed that the nitrogenization of steels increased their corrodibility by 5 per cent. (by vol.) sulphuric or hydrochloric acid, with the exception of a steel containing 4·08 per cent. Ni, and 0·91 per cent. Cr, the resistance of which towards the former acid was increased. For the chromium-aluminium steels, cementation had the same effect. O. Hengstenberg observed that the nitrogenization of the alloy steels made them more resistant to corrosion by air and steam, and soln. of copper sulphate. H. H. Gray and co-workers found that the nitrogenization of mild steel rendered it almost insoluble in dil. hydrochloric acid. The resistance to attack by sea-water containing 5 per cent. of 12-vol. hydrogen dioxide, and to a mist from 20 per cent. sodium chloride soln., was increased by nitridation more than by cementation, followed by tempering, especially in the cases of the chromium and aluminium steels. This effect was even more marked with rain-water, especially for nickel steels. Cementation slightly increased the resistance towards 10 per cent. copper sulphate soln., but the nitride steels were scarcely attacked. H. H. Gray and M. B. Thompson found that the higher the initial proportion of carbon in a steel, the greater the loss of carbon during nitrogenization; and the higher the temp. of nitrogenization, the greater the subsequent resistance of the metal towards hydrochloric acid. O. Niezoldi observed that copper is deposited on nitrided steel from soln. of copper sulphate more slowly than it is on ordinary steel. O. Meyer found crucibles of **titanium nitride** attack iron slightly at about 1600°.

According to F. Hatton, nitrogenous organic matter dissolved in water is reduced by spongy iron to form elemental nitrogen. The action of **ammonia** gas on heated iron was considered in connection with the nitride—**8**. 49, 12. F. Durau and C. H. Teckentrup showed that the absorption of ammonia by electrolytic iron is a chemical process. Iron takes up nitrogen from ammonia far more readily than it does directly from nitrogen. G. Gore observed that liquid ammonia does not attack electrolytic iron. W. A. Dew and H. S. Taylor observed that iron at 0°, 110°, 218°, and 305° absorbs respectively 0·175, 0·0669, 0·036, and 0·0084 c.c. of ammonia per gram of metal. N. I. Nikitin and W. I. Sharkoff observed that between −18° and 100°, powdered iron readily absorbs ammonia in accord with the formula $a=kp'/n$. Near the beginning of the nineteenth century, A. B. Berthollet, and L. J. Thénard reported that they could detect no increase in weight when iron is heated in ammonia gas, but C. Stahlschmidt explained this result by assuming that the temp. was too high. J. S. Vanick and co-workers noted the deterioration of steel and wrought-iron pipes in hot gaseous ammonia; and R. Coustal and H. Spindler found that iron anodes are slightly attacked by liquid ammonia. L. J. Thénard, and C. Despretz showed that the presence of iron favours catalytically the thermal decomposition of ammonia. J. A. Almquist and E. D. Crittenden, M. P. Applebey, A. K. Brewer, J. K. Dixon and W. Steiner, A. B. F. Duncan and D. A. Wilson, E. Elöd and W. Banholzer, P. H. Emmett, W. Gluud and co-workers, C. H. Kunsman and co-workers, A. T. Larson and A. P. Brooks, J. S. Vanick and co-workers, E. Winter, P. H. Emmett and S. Brunauer, H. H. Gray, E. Tiede and E. Hay, F. Czopinsky and M. Wojcik, and J. Zawadzky and B. Modrzejewsky discussed iron as a catalyst in the synthesis of ammonia; and P. H. Emmett and S. Brunauer, the poisonous action of water vapour on the iron catalyst. Quite a number of observers—G. T. Beilby and G. G. Henderson, H. L. Buff, G. Charpy and S. Bonnerot, C. Despretz, T. G. Finzel, G. J. Fowler, E. Frémy, F. Hanaman, H. Hardtung, G. G. Henderson and J. C. Galletly, H. Herzer, E. B. Maxted, A. Mittasch and co-workers, H. V. Regnault, F. Savart, C. B. Sawyer, C. Stahlschmidt, A. E. White, and H. Wolfram—noted that when iron is heated in ammonia, nitrogen is absorbed; and N. Tschischewsky gave for the percentage increase in weight at different temp.:

	200°	300°	400°	450°	500°	600°	700°	750°	850°	
N_2 .	0·11	3·09	10·705	11·11	10·36	8·905	4·76	0·535	0·290	per cent.

showing that with finely-divided iron, the optimum temp. is about 450°—Fig. 17, **8**. 49, 12. T. Nakayama obtained analogous results. A. Mittasch and co-workers found that the reaction begins near 200°, and at 300° iron nitride is readily formed. Observations with compact iron were made by G. T. Beilby and G. G. Henderson, G. Charpy and S. Bonnerot, P. H. Emmett and S. Brunauer, F. Hanaman, O. A. Knight and H. B. Northrup, A. Mittasch and co-workers, E. Müller and K. Schwabe, B. Strauss, B. Tazawa, N. Tschischewsky, J. P. Walsted, and H. E. Wheeler. E. Lehrer's observations on the equilibrium conditions in the system: iron–ammonia–hydrogen are summarized in Fig. 347. The α-phase is a solid soln. of nitrogen in α-iron; the γ-phase, a solid soln. of nitrogen in γ-iron; and the γ'-phase, a solid soln., the ϵ-phase, containing iron tetritanitride. J. G. Thompson discussed the best type of steel for resisting attack in plants synthesizing ammonia. R. H. Hobrock, etc., discussed the surface hardening of steels by nitridizing them in ammonia at a suitable temp., and pressure. B. Strauss observed no absorption of nitrogen when ammonia is passed over molten iron. C. Stahlschmidt observed the formation of hydrogen in the reaction between ammonia and iron. J. H. Andrew showed that a large proportion of hydrogen is formed; but E. Colver-Glauert observed only a trace; and G. J. Fowler, F. Hanaman, and E. B. Maxted observed none. The rate of absorption, or diffusion of the nitrogen from ammonia by heated iron, was studied by H. Braune, E. Colver-Glauert, J. Duhr, A. Fry, L. Guillet, E. B. Maxted, T. Nakayama, C. B. Sawyer, G. Engelhardt and C. Wagner, and H. E. Wheeler. C. B. Sawyer showed that the presence of phosphorus in iron affects the nitrogenization of iron; L. Guillet found that the presence of aluminium, silicon, chromium, and molybdenum accelerates the absorption, and they form, along with the iron, stable nitrides, but H. E. Wheeler doubted if these elements form nitrides under these conditions. F. W. Harbord and T. Twyham discussed the action of manganese, but they found no relation between the nitrogen and manganese-content of iron. N. Tschischewsky considered that in addition to manganese, silicon and aluminium may be regarded as carriers of nitrogen, because in nitrogenized ferromanganese, ferroaluminium, and considerable proportions of the nitrides of manganese, aluminium, and silicon are present. W. Frankenburger and co-workers considered that carbon, manganese, chromium, and hydrogen, and B. Strauss, that silicon and chromium, play an important part in the adsorption of nitrogen; T. Nakayama also showed that the presence of aluminium, silicon, titanium, and chromium accelerates the absorption of nitrogen, but copper, manganese, cobalt, and nickel do not favour the absorption. A. Bramely and co-workers found that the presence of carbon retards the action of ammonia so that the amount of nitride formed decreases as the initial conc. of the carbide increases– *vide supra*. A. Fry observed that when heated to 680° in ammonia, the carbon of cementite is all displaced by nitrogen.

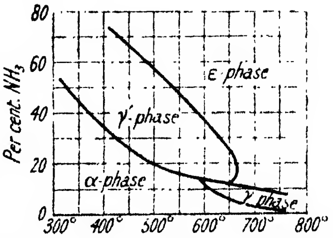


FIG. 347.—The Solid Phases in the System: $Fe–NH_3–H_2$.

P. A. von Bonsdorff observed that air containing traces of ammonia does not favour the rusting of iron. U. R. Evans observed no corrosion of iron over conc. aq. ammonia for 8 days. C. Matignon and G. Desplantes studied the oxidation of metals in the presence of ammonia. The corrosive action of aq. soln. of ammonia on iron is discussed below. W. R. Hodgkinson and N. E. Bellairs studied the action of aq. ammonia; and F. N. Speller, the action of ammonia in refrigerators. F. Schmitz showed that with pieces of 0·06, 0·42, and 0·92 per cent. carbon steel, 20×20×10 mm. with a 4 mm. hole, the losses in conc. aq. ammonia were respectively 0·000, 0·173, and 0·059 per cent. during 180 hrs. J. D. Pennock and D. A. Morton found that conc. aq. ammonia does not rust clean iron, but actually prevents rusting, even in the presence of oxygen or of ammonium carbonate. W. Guertler and T. Liepus observed that iron is not corroded by aq. ammonia in 24 hrs. The action of ammoniacal feed-water for boilers was discussed by M. Tilgner. A. H. White and L. Kirschbraun studied the electrolytic dissolution of nitrogenized iron. K. A. Hofmann and co-workers compared the action of dry hydrogen chloride and **ammonium chloride** vapour on metals at 250° to 350°, and found that the sequence with the former is Fe>Ni>Cu>Ag>Hg, and with the latter Fe>Cu>Ni>Ag>Hg. For the action of soln. of ammonium salts, *vide infra*. F. W. Bergstrom found that a soln. of **ammonium bromide** in liquid ammonia acts on iron in a few months to form $FeBr_2.6NH_3$. A. d'Heureuse observed that molten **ammonium sulphate** and iron yield ammonia, and at a higher temp. sulphur dioxide and ferrous sulphide are formed. M. Lachaud and C. Lepierre noted that a series of complex ferric or ferrosic ammonium sulphates is formed when iron acts on the molten salt; and F. W. Bergstrom said that a soln. of ammonium sulphate in liquid ammonia acts very slowly on iron. F. W. Dafert and R. Miklauz observed a vigorous reaction between iron and molten **lithium nitride.** H. and F. Hanaman found that the effect of heating iron in **hydrazines** is similar to that which occurs with ammonia; and likewise also with **amines,** and **imides.** F. W. Bergstrom found that the action of **potassamide** on iron, if it occurs at all, is extremely slow. F. Ephraim observed no reaction when iron is heated with **sodamide.** T. Curtius and J. Rissom observed that iron dissolves in **hydrazoic acid,** N_3H, forming ferrous azide with the brisk evolution of hydrogen. A. W. Browne and co-workers observed the nitridization of iron when it is used as anode in a soln. of **ammonium azide,** with liquid ammonia as solvent; ferric azide is formed. J. W. Turrentine found that a soln. of **sodium azide** on electrolysis with iron as anode furnishes initially ferric azide; if the soln. is agitated the iron becomes passive. J. T. Nance examined the action of soln. of ammonium chloride; and P. Junius, the vapour of that salt; W. R. Hodgkinson and A. H. Coote, F. Hatton, E. Heyn and O. Bauer, G. Tammann, E. Ramann, E. Weitz and H. Müller, and E. B. R. Prideaux and R. M. Caven, the action of iron on soln. of **ammonium nitrate**—*vide infra* for the effect of soln. of these salts; and the effects of pressure, by E. Berl and F. van Taack, F. Haber, H. Ehrig, A. Kaufmann, L. G. Knowlton, and E. Weitz and H. Müller; and W. R. Hodgkinson and A. H. Coote, the action of fused ammonium nitrate and **ammonium nitrite,** as well as of their aq. soln. O. Baudisch discussed the reduction of nitrites by iron. E. Divers found that iron is not attacked by a soln. of ammonium nitrate in liquid ammonia, but F. W. Bergstrom found that with powdered iron some ferric oxide is formed as well as $Fe(NO_3)_2.4NH_3$ and $Fe(NO_3)_2.6NH_3$. E. Priwoznik observed that iron gradually acquires a black film when immersed in a soln. of **ammonium polysulphide.**

P. Sabatier and J. B. Senderens found that **nitrous oxide** is reduced by iron powder at 170° to form ferrous oxide. F. Durau and C. H. Teckentrup showed that the absorption of nitrous oxide by electrolytic iron is purely adsorption. P. Oberhoffer observed that iron can be nitrogenized by heating it to 200° or 300° in an atm. of nitrous oxide. The rate of attack was studied by E. Schröder and G. Tammann. P. Sabatier and J. B. Senderens found that **nitric oxide** behaves like nitrous oxide at 200°; and F. Emich found iron is nitrogenized by heating it in nitric oxide. F. Durau and C. H. Teckentrup observed that the absorption of nitric oxide by electrolytic iron is a chemical process. According to B. B. Adhicary, when a mixture of nitric oxide and hydrogen is passed over the heated metal, ammonia begins to form at 300°, and the action is rapid at 350°. E. Müller and H. Barck found that decomposition is complete at 500°. The rate of attack was studied by E. Schröder and G. Tammann, and G. Tammann and W. Köster. E. Davy, and J. J. Sudborough found that iron is attacked by **nitrosyl chloride.** P. L. Dulong, and P. Sabatier and J. B. Senderens found that reduced iron decomposes **nitrogen peroxide** at ordinary temp. The metal becomes incandescent and yields ferric oxide. J. A. Almquist and co-workers found steel to be stable in contact with the liquid peroxide. There is also formed nitro-iron, Fe_2NO_2—**8.** 49, 39.

B. Lambert and J. C. Thomson found that cold dil. **nitric acid** has very little action on the purified metal, but when warm, the metal is dissolved. According to H. Gautier and G. Charpy, iron dissolves in 34 per cent. nitric acid at ordinary temp., giving off gas rapidly; the rate of evolution of gas then slackens, until finally only traces of ammonia and nitrogen peroxide are evolved, and ferric nitrate is formed. No gas is evolved with 61 per cent. acid in the cold, but at temp. exceeding 60°, gas is evolved. V. H. Veley and J. J. Manley said that purified nitric acid, freed from nitrous acid and dissolved nitrogen oxides, is without action on purified iron, even at the b.p. According to B. C. Banerji and N. R. Dhar, ferrous salts accelerate the dissolution by forming nitrous acid, which acts as a catalyst, and ferric salts also favour the reaction since they are reduced to ferrous salts. Oxidizing agents retard the reaction by preventing the formation of nitrous acid. C. C. Palit and N. R. Dhar also discussed the action of nitric acid on metals. A. Quartaroli showed that oxidation is a necessary antecedent for the dissolution of metals in nitric acid, and that nitric acid is not an oxidizing agent if no nitrous acid be present, or if substances like carbamide, an amino-acid, or an amide, which destroy the nitrous acid, be present. J. G. Brown studied the rate of the reaction. H. Endo observed that the weights lost by iron, expressed in grams per sq. cm., during 5 hrs'. action at 25°, are:

HNO_3 .	5	10	25	30	35	45	50	55 per cent.
Loss .	0·1021	0·2045	0·5210	0·8356	0·7590	0·0584	0·0233	nil

W. H. Hatfield observed that with cylinders of iron approximately 0·5 in. diam. and weighing 50 grms., in 85 c.c. of acid at 15°, the losses in grms. per sq. cm. in 24 hrs. were:

	Electrolytic iron	Armco iron	English wrought iron	Steel with 0·29 per cent.			
				15°	40°	60°	80°
N-HNO_3 . . .	0·1147	0·1406	0·1263	0·0957	0·0282	0·3215	0·3512
46 per cent. HNO_3 .	0·7261	0·7592	0·6399	0·6766	0·6538	1·3809	1·7278

B. C. Banerji and N. R. Dhar observed that with the 1 : 1 nickel-iron alloy (*q.v.*) the reaction with 5 to 20 per cent. nitric acid is periodic. According to A. J. Hale and H. S. Foster, with plates of 1 sq. dm., at 17° to 20°, and 0·2*N*-HNO_3, with a litre of acid, the losses with cast iron and wrought iron were respectively 2·60 and 1·30 grms. in 4 hrs.; with half a litre of acid per day for 7 days, the losses were respectively 15·4 and 14·5 grms.; and with half a litre of acid for 28 days, respectively 2·5 and 2·0 grms. H. Gautier and G. Charpy observed that at ordinary temp. clean iron wire in nitric acid of sp. gr. 1·21 does not give off any gas, but the metal is slowly attacked with the formation of iron nitrate, ammonia, and nitrogen peroxide, which remain in soln. The percentage losses in acids of different concentration were:

Specific gravity (HNO_3) .		1·28	1·34	1·38	1·48	1·53
Loss	First 2 days . .	0·82	0·75	0·29	0·34	5·80 per cent.
	First 10 days . .	0·59	0·45	0·25	0·33	5·75 ,,

The e.m.f. of the cell Fe : HNO_3 : Pt diminishes rapidly as the conc. of the acid increases from a sp. gr. below 1·21 to higher densities. In the latter case it is about 0·15 volt, and corresponds with the dissolution of the iron, for with circuits of different resistances, different intensities are obtained. By raising the temp., the limit of sp. gr. of the acid giving disengagement of gas and rapid attack is raised. At 60° it is only with concentrations above 1·38 that no disengagement of gas occurs. The limit is also raised by the presence of oxide on the surface of the iron; this is due to local heating caused by the solution of the oxide. If the iron be agitated in the acid until perfectly clean, it then behaves exactly as if the surface had not been coated with oxide. The same effect is produced if the oxide be electrolytically reduced.

W. Rohn found that unannealed iron in contact with 10 per cent. cold nitric acid loses 33·0 grms. per sq. dm. during 2 hrs., and with the hot acid, 40·0 grms. The attack on the annealed metal is rather slower. The subject was studied by W. Guertler and T. Liepus. J. I. Crabtree and G. E. Matthews found that with 5 per cent. acid, iron was corroded at the rate of 2·2 grms. per 100 sq. in. per day. According to F. Schmitz, 0·06, 0·42, and 0·92 per cent. carbon steel specimens, 20×20×10 mm. with a 4 mm. hole, lost respectively 100 per cent. in nitric acid (1 : 1) in 180 hrs., and in the conc. acid, respectively 0·113, 0·352, and 0·353 per cent. The loss with aqua regia was also 100 per cent. J. G. Thompson found that none of the iron alloys was so resistant to 100 per cent. nitric acid as aluminium and its alloys. Of all the iron alloys, a cast iron with 14 per cent. silicon (0·59 per cent. carbon) was the most resistant; one with 12·24 per cent. silicon and 1·17 per cent. carbon was less satisfactory. Molybdenum steel was little better than ordinary steel, but by adding 10 to 15 per cent. of chromium the steel resisted acids up to 68 per cent. HNO_3. Nickel counteracted the beneficent effects of chromium. For other observations, see the corrosion and the passivity of iron and steel.

A. Scheurer-Kestner observed that with nitric acid of sp. gr. 1·034, ferrous and ammonium nitrates are formed; with nitric acid of sp. gr. 1·073, ferrous, ferric, and ammonium nitrates are produced; while with nitric acid of sp. gr. 1·115, only ferric nitrate and no ammonia is formed. W. Heldt found that when ammonia is formed ferrous nitrate is produced, and when no ammonia is developed ferric nitrate is formed. With 32 per cent. nitric acid a hardened steel yields a black mass which slowly dissolves to form a brown soln. The dissolution proceeds more rapidly as the temp. is raised. This furnishes a mode of estimating the temper carbon in steel colorimetrically. Observations were made by H. von Jüptner, and E. Heyn. L. Schneider, and A. Tamm found that steels containing phosphorus yield a soln. containing phosphoric acid. J. M. Ordway observed that the products of the reaction depend on the conc. of the acid, the proportion of acid and metal employed, the degree of purity and the state of subdivision of the iron, and on the temp.; and J. H. Whiteley and A. F. Hallimond, that the products of the action also depend on the cold-work the metal has received, and on the carbon-content—*vide infra*. Y. Yamamoto, J. Hale and H. S. Foster, P. Kötzschke and E. Piwowarsky, and J. Sauvageot and L. Lauprète compared the rate of attack on different forms of iron. H. Endo showed that the rate of attack on 0·1 to 1·3 per cent. carbon steels increases almost linearly with the proportion of carbon. C. F. Burgess and S. G. Engle observed the losses in weight, in grams per sq. inch per hour, with N-H_2SO_4, at 22°, and found (i) 0·3728 grm. for the average with electrolytic iron; (ii) 0·0091 grm. with electrolytic iron heated to 1000° and cooled slowly; (iii) 0·0093 grm. with soft sheet iron low in carbon as used for transformer plates; (iv) 0·0971 grm. with a temper steel used in the manufacture of knife-blades; and (v) 0·0643 grm. with an ordinary grade of cast iron. The subject was studied by S. C. Bate, F. F. Chapman, N. R. Dhar, V. Duffek, H. Endo, L. F. Girardet and T. R. Kou, L. Loskiewicz, N. A. E. Millon, C. C. Palit and N. R. Dhar, W. D. Richardson, F. Schmitz, C. F. Schönbein, J. G. Thompson, and Y. Utida and M. Saito—*vide supra*, hydrochloric and sulphuric acids.

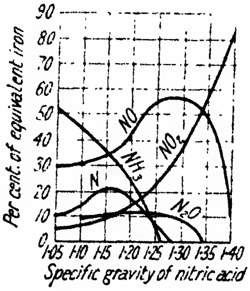


FIG. 348.—Products of the Action of Nitric Acid on Iron.

J. J. Acworth and H. E. Armstrong found that at 9° to 16°, the vols. of gas obtained per gram of metal, with nitric acid of varying concentration, are:

$HNO_3 : H_2O$.	1 : 1(16°)	1 : 2(13°)	1 : 4(10°)	1 : 4(13°)	1 : 8(12°)	1 : 12(9°)
Total . .	8064	5997	5330	5456	5904	5638 c.c.
NO . .	7392	5323	4598	4773	5542	5146 c.c.
N_2O . .	404	375	551	492	202	252 c.c.
N_2 . .	567	299	221	191	160	242 c.c.

The proportion of nitric oxide is relatively large. As the conc. of the acid decreases, the proportion of nitrous oxide at first increases and then diminishes; whereas, with nitric oxide, there is at first a decrease and then an increase. These differences correspond with the behaviour of the dissolved metal. With the 1 : 1- and 1 : 2-acids, the iron dissolves rapidly, producing a pale greenish-yellow liquid; with the 1 : 4-acid, the iron dissolves less rapidly, and the soln. is dark brown, as is also the case with the 1 : 8- and 1 : 12-acids, where the action proceeds still more slowly. It is inferred that by the action of the more conc. acid, the iron is immediately converted into the ferric salt, whereas with a more dil. acid, ferrous salt is first formed, and this is afterwards converted into ferric salt on heating the liquid. The hydrogen displaced in the formation of the ferrous salt is probably more active than that displaced in the formation of the ferric salt; and a similar conclusion follows from the manner in which the nitrous oxide is evolved. The last portion of gas with the 1 : 1- and the 1 : 2-acids is free from nitrous oxide. The mechanism of the reduction of nitric acid by the metals is discussed in connection with nitric acid.

J. J. Acworth and H. E. Armstrong assumed that the direct reduction products are nitrous and hyponitrous acids, hydroxylamine, and ammonia. If the nitric acid is present in large excess, and highly concentrated, the products will be richer in oxygen than where a small proportion of the acid is used. Thus, nitrogen peroxide predominates in the former case, and nitric oxide in the latter case. E. Divers classed iron amongst the metals which yield ammonia, hydroxylamine, hydrazine, or hydrogen. C. Montemartini found that the gases evolved on treating a gram of iron with an excess of 27·5 per cent. nitric acid were :

	NH_3	HNO_2	N_2O	N_2	NO	Total
Grams . .	0·02493	0·00195	0·00422	0·00045	—	0·03553

C. Montemartini said that the nitric oxide formed is of secondary origin, being derived partly from the decomposition of the nitrous acid and partly from the oxidation of the ferrous salts first formed. P. C. Freer and G. O. Higley found that with dil. nitric acid of sp. gr. 1·03 to 1·20, the products are nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, and ammonia in proportions which vary with the conc. and amount of acid employed ; with more conc. nitric acid of sp. gr. 1·35 to 1·40, the products are nitrogen peroxide and nitric oxide. The results are summarized in Fig. 348. The non-ionized acid is supposed to act merely as an oxidizing agent, because the results with silver, copper, and iron were practically the same with conc. nitric acid. Nitrogen peroxide is said to be the first product of the action, and nitric oxide is derived from this by the action of water, because the relative proportions of these two gases vary with the proportion of acid employed. For E. J. Joss's observations on the action of nitric acid on metals, *vide* **8**. 49, 45.

According to J. H. Whiteley and A. F. Hallimond, the gases obtained when nitric acid of different concentrations—grams HNO_3 per 100 c.c.—acts on 0·3 grm. of purified iron at 100° and 500 mm. press., are as follow (the nitrogen peroxide condensed in the receiver was not determined) :

Nitric acid (Grms. per 100 c.c.)	NO	N_2O	N_2	NH_3	Total gas (at n.p. θ)
11·5	32·0	2·5	13·3	14·0	47·5 c.c.
21·5	39·0	2·5	8·0	18·2	49·5 c.c.
22·7	41·0	2·0	8·0	18·3	51·0 c.c.
23·9	49·0	2·0	8·2	14·1	59·2 c.c.
25·1	74·0	2·5	5·5	5·6	82·0 c.c.
26·3	83·0	2·5	5·8	3·0	91·3 c.c.
27·5	87·0	2·5	4·3	2·0	93·8 c.c.
33·5	90·0	1·5	3·5	1·0	95·0 c.c.

There is a very striking discontinuity in the nature of the reaction when the conc. of the acid attains 24 grms. HNO_3 per 100 c.c. Much of the N_2+NH_3 mixture is replaced by a mixture of $NO+NO_2$ as the conc. of the acid changes from 23 to 25 grms. HNO_3 per 100 c.c. The sharp change in the character of the curves becomes less pronounced when a larger excess of nitric acid is employed. The products of the reaction depend on the concentration of the NO_3 as free acid or nitrate, and not on the acidity *per se*. No appreciable change occurred when the press. was reduced from 500 to 200 mm. By lowering the temp. of the reaction from 100° to 45°, the same general results were obtained, but there was an increase in the proportion of nitrogen at the expense of the ammonia. It is assumed that the ammonia combines with the nitrous acid formed in the reaction, and the resulting ammonium nitrite is subsequently decomposed : $NH_4NO_2=2H_2O+N_2$. The nitrous acid can also be formed by the action of nitric oxide on nitric acid : $2NO+HNO_3+H_2O=3HNO_2$. The proportion of nitrogen peroxide which is formed increases with the concentration of the acid, and decreases when the temp. of the reaction is lowered. The variations in the proportion of nitric oxide are dependent on the secondary reactions: $2NO_2+H_2O=HNO_3+HNO_2$, and $3HNO_2=HNO_3+2NO+H_2O$. It is suggested that the nitrous and nitric oxides are the result of the rapid decomposition of an unstable intermediate compound. E. Ramann represented the action of iron on the ferrous nitrate first formed: $4Fe(NO_3)_2+8H_2O+11Fe=4NH_4NO_3+5Fe_3O_4$. When ammonium nitrate acts on iron, nitrosyl-ammonium, NH_4NO, is said to be first formed as an intermediate product. J. H. Whiteley and A. F. Hallimond found that the composition of the nitrogenous gases involved on treating cementite by the method indicated above, was as follows:

Nitric acid (Grams per 100 c.c.)	NO	N_2O	N_2	NH_3
11·5	53·0	7·0	7·8	9·8
16·5	67·0	6·0	7·0	5·1
21·5	81·0	5·0	6·0	3·6
27·5	92·0	4·0	6·7	1·6
33·5	94·0	5·0	4·5	1·8
45·0	88·5	5·0	3·7	0·2

Some complex hydrocarbons, approximating on the average CH_2, are produced; and some of the hydrocarbons are slowly oxidized to carbon dioxide. Taking the weight of iron consumed in producing the ammonia and nitrogen as ordinate, and the conc. of the acid as abscissa, they obtained the so-called reaction curves, Fig. 349, for the effect with pearlitic steels. They found that the reaction curves are in accord with the mixture rule. The reaction curves of quenched steels indicate a high energy-content, and its gradual decrease in tempering.

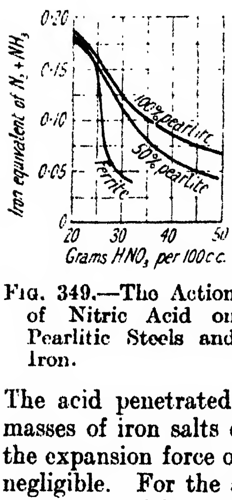


FIG. 349.—The Action of Nitric Acid on Pearlitic Steels and Iron.

Observations on the action of nitric acid on metals were also made by V. H. Veley, E. Divers, E. J. Maumené, J. J. Acworth, A. J. Ewart, C. Montemartini and E. Colonna, J. H. Stansbie, M. Drapier, W. D. Bancroft, E. J. Joss, and A. Klemenc. A. C. Cumming reported the bursting of cast-iron vessels containing a mixture of sulphuric and nitric acids. The metal contained large plates of graphite forming a network *viâ* which the acid could pass within. The acid penetrated the metal to a depth of one-third the thickness, and small masses of iron salts crystallized in the interior. The disruption was produced by the expansion force of the growing crystals, even though corrosion was practically negligible. For the action of conc. nitric acid whereby the iron becomes passive, see the special section on the passivity of iron. A. Quartaroli observed that oxidation facilitates the dissolution of iron in acids. P. Pascal found that for varying proportions of mixtures of nitric and sulphuric acid, there is a concentration between 10 and 20 per cent. of water at which the resistance of steel is a maximum. P. Pascal observed that the addition of 5 per cent. sulphuric acid to nitric acid considerably reduces the activity of the acid. R. C. Griffin observed that the attack on wrought iron, cast iron, and steel by 10 per cent. nitric acid is reduced in the presence of 1 per cent. of formaldehyde. According to L. E. Benson, iron is nitrogenized by heating it in a bath of 85 per cent. sodium nitrate, and 15 per cent. of sodium chloride, at 500°. The action of fused **alkali nitrates** on iron was discussed by E. Frémy, E. Berger, L. Moser, and C. S. A. Tatlock—*vide* the ferrates. A. E. Menke said that molten sodium nitrate with iron filings forms some sodium hyponitrite, but W. Zorn could not confirm this. L. Hackspill and R. Grandadam reported that when alkali nitrates and iron are heated in vacuo, the alkali metal is formed: *e.g.* $KNO_3+2Fe=Fe_2O_3+K+N$. Lithium nitrate does not react in this way. C. B. Gates observed no reaction between iron and molten silver nitrate; and A. Naumann, no reaction with iron and a soln. of **silver nitrate** in benzonitrile. J. A. Jones found that soln. of ammonium, sodium and calcium nitrates develop cracks in mild steel plates owing to their action on the intercrystalline cement. C. F. Bonilla studied the rate of attack by aqua regia.

The action of **phosphorus** on iron has been discussed in connection with the phosphides—**8.** 50, 12. G. Tammann and K. Schaarwächter[8] observed that the attack of iron by phosphorus can be detected at about 360°, and R. Vogel has investigated the effect of phosphorus on the arrests. The reaction was studied by M. V. Ruisakoff and I. N. Buschmakin. J. Percy pointed out that the presence of phosphorus reduces the malleability and strength of iron at ordinary temp., thus making the metal cold-short—*i.e.* brittle when cold. On the other hand, iron which contains enough phosphorus to be cold-short may be quite malleable at a high temp. such as that at which the metal is usually forged and rolled. C. J. B. Karsten said that if less than 0·5 per cent. of phosphorus be present, the quality is not seriously affected; with 0·6 per cent., the iron does not stand the breaking test; with 0·75 per cent., the iron fails under the breaking and bending tests, and its tenacity is low; with 0·8 per cent., the metal is decidedly cold-short. Observations were also made by L. Schneider, J. A. Barr, J. Wagner, B. W. Cheever, and H. von Jüptner. The interpretation of the equilibrium diagram, and the effect of phosphorus on the critical points of iron, were studied by E. Gerecke. J. E. Stead, J. L. Haughton, W. Venator, F. Wüst, K. Heitmann, J. H. Whiteley, P. Oberhoffer and C. Kreutzer, H. Esser and P. Oberhoffer, N. S. Konstantinoff, H. Gontermann, B. Saklatwalla, A. Allison, H. Voss, F. Osmond, H. M. Howe, J. E. Stead, E. Richarme, R. Mitsche, and P. Goerens and W. Dobbelstein examined the effect of phosphorus on the iron-carbon alloys, and their results have been previously described. K. Schichtel and E. Piwowarsky found that phosphorus reduces the solubility of carbon in liquid iron. W. F. Holbrook and co-workers studied the diffusion of phosphorus in molten iron. J. E. Stead showed that the effect of increasing proportions of carbon is to throw free iron tritaphosphide out of soln.:

Carbon .	0	0·125	0·180	0·70	0·80	1·40	2·00	3·50	per cent.
Fe_3P .	0	0·18	0·59	1·00	1·06	1·16	1·18	1·40	..
P in soln. .	1·75	1·37	1·18	0·75	0·70	0·60	0·55	0·31	..

With only 0·18 per cent. of carbon, free phosphide is formed, and the phosphide is then surrounded by pearlite; with 1·4 per cent. of carbon, the eutectic phosphide becomes surrounded by a layer of cementite which increases in thickness as the proportion of carbon increases. The interior has the character of a solidified eutectic. On reheating the mass to 900°, and allowing it to cool slowly, the cementite formed independent cells cutting up the pearlite into a number of small grains. The phosphide eutectic retained its original position and was no longer surrounded by the cementite; the cementite diffused throughout the iron at 900°, but not so the phosphide. When the carbon exceeds 2 per cent., there is evidence of a carbide-phosphide eutectic which contains 6·7 per cent. of phosphorus and 2·0 per cent. of carbon. This was confirmed by F. Wüst. J. E. Stead showed that phosphorus and carbon each require its quota of iron, and the presence of either diminishes the amount of the other simultaneously present in pig-iron; but phosphorus is without influence on the actual conditions of the carbon in pig-iron. This was confirmed by J. T. McKenzie, H. O. von Samson-Himmelstjerna, and K. A. Schreiber. K. Schichtel found that the introduction of phosphorus into the iron-carbon alloys altered the carbon solubility curve, the *SE* line, as indicated in Fig. 350. The effects of phosphorus on the proportion of carbon in the eutectic, and on the eutectic temp., are indicated in Fig. 351. Observations were also made by E. Söhnchen

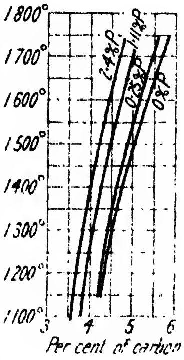


FIG. 350. — The Effect of Phosphorus on the Solubility of Carbon in Iron.

and E. Piwowarsky, M. Künkele, P. Bardenheuer and M. Künkele, H. Schenck, H. S. Rawdon, J. T. McKenzie, H. Sawamura, O. Bauer and K. Sipp, J. H. Higgins, R. Vogel, L. Jordan, F. Fettweiss, F. Sauerwald and W. Hummitzsch, and F. Wüst; whilst R. Vogel and O. de Vries studied the ternary system: Iron–phosphorus–sulphur. P. Goerens and W. Dobbelstein, E. Thews, and O. von Keil and R. Mitsche studied the influence of silicon on the system: Fe–P–C. J. H. Whiteley examined the distribution of the phosphorus in steel between the Ac_1- and the Ac_3-arrest. He concluded:

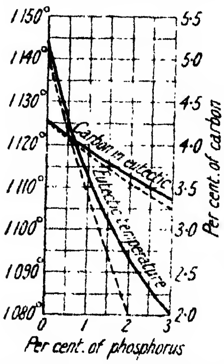


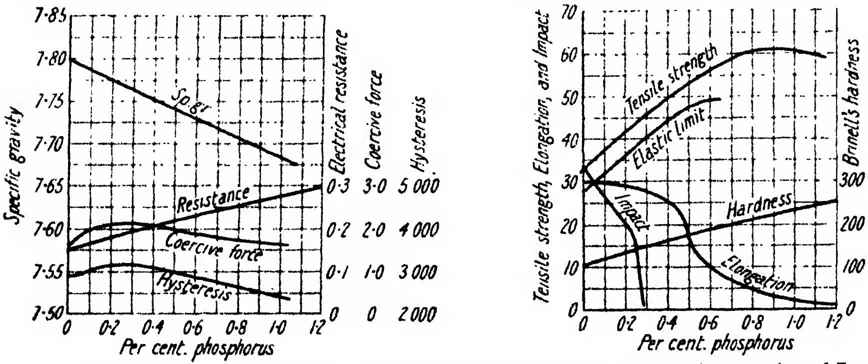
FIG. 351.—The Effect of Phosphorus on the Eutectic Temperature and on the Proportion of Carbon in the Eutectic.

> When ordinary hypoeutectoid steel is heated to, and maintained at, temp. between the critical points Ac_1 and Ac_3, part of the phosphorus contained in the γ-iron diffuses into the adjacent ferrite owing to the fact that, under these conditions, the phosphorus is more soluble in the latter than in the former. With a series of steels in which the phosphorus varied from 0·006 to 0·12 per cent., it is phosphorus which diffuses out of the γ-iron. The lowering of the solubility in the γ-iron is most probably due to the presence of dissolved carbide. At temp. below 650°, phosphorus diffuses extremely slowly in ferrite; above this temp., the velocity gradually increases, and above 800° it is quite rapid, for a diffusion which requires 4 hrs. to complete at 740° is complete in 15 mins. at 830°. The velocity of diffusion of phosphorus in γ-iron also increases with the temp. in a similar manner, but it is never so high as that at which the carbon travels. At or near the Ac_3-arrest the speed of diffusion suddenly diminishes. By heating steels slowly through the critical range, a reticulated structure is produced which is also due to the movement of phosphorus in the γ-iron. The lowest temp. at which this structure is formed depends upon the carbon-content of the steel; with 0·18 per cent. of carbon it was about 820° and with 0·06 per cent. 870°. Owing to the fairly rapid rate at which phosphorus diffuses in γ-iron above 820°, it is possible, by heating sections of steel plates at a temp. just below the Ac_3 point, to remove completely the excess of phosphorus contained in the micro-ghost-line included in the areas occupied by the γ-iron. This treatment does not entirely remove the lines, however, for, although not so pronounced as formerly, they can still be detected by etching, even in samples containing less than 0·02 per cent. of phosphorus. Their presence would appear to be due, therefore, to the uneven distribution of some other substance besides phosphorus.

C. Kreutzer found that the X-radiograms agree with the assumption that with up to 1·7 per cent. of phosphorus, solid soln. are formed; that with increasing phosphorus, the indications of the tritaphosphide becomes stronger, and with 15·58 per cent. phosphorus the tritaphosphide with a tetragonal lattice having $a : c = 1 : 0·3482$ is formed; with 21·5 per cent. phosphorus, the hemiphosphide is formed; and with still more phosphorus, an unknown compound is produced. The subject was studied by F. Rogers, B. Kjerrman, H. Jungbluth, H. Schottky, J. B. Friauf, N. S. Konstantinoff, O. Kuhn, S. B. Hendricks and P. R. Kosting, H. le Chatelier and S. Wologdine, and G. Hägg. The solubility of phosphorus in iron was examined by J. E. Stead, A. E. Cameron, and E. D. Campbell and S. C. Babcock; the microstructure, by J. O. Arnold, J. E. Stead, N. S. Konstantinoff, E. Piwowarsky, B. Saklatwalla, and B. Strauss; the segregation of the phosphorus or phosphide, by P. Oberhoffer, J. W. Bolton, B. W. Cheever, L. Schneider, A. Carnot and E. Goutal, E. Piwowarsky, H. A. Schwartz and A. N. Hird, and J. E. Stead; and the sp. gr. by J. O. Arnold—C. Benedicks' results for liquid iron are indicated above, Fig. 350. F. Roll found that phosphorus partly favours, and partly hinders, the decomposition of the carbide in cast iron; O. von Keil and R. Mitsche, that phosphorus hinders graphitization; and K. Schichtel and E. Piwowarsky, that phosphorus decreases the solvent power of iron for carbon. C. H. Herty, and B. Kjerrman studied the effect of phosphorus on the pearlite interval; W. Bischof and E. Maurer, the distribution of phosphorus between iron and slags; H. Pinsl, Y. Yamamoto, and M. Künkele, the phosphide eutectic in cast iron; and P. Bardenheuer and M. Künkele, A. E. Cameron, and H. Jungbluth and H. Gummert, the effect of silicon on the phosphide eutectic. The effect of phosphorus on the casting shrinkage was studied by W. J. Keep; the diffusion of phosphorus in iron, by A. Fry, and N. C. Marples; the sp. vol., by C. Benedicks and co-workers; the hardness, by N. S. Konstantinoff, B. Saklatwalla, W. Köster, and E. d'Amico; J. J. Porter, and D. Saito and K. Hayashi, the fluidity which increases linearly with the proportion of phosphorus; and the mechanical properties, by C. J. B. Karsten, J. E. Hurst, F. F. McIntosh, F. Wüst and R. Stotz, A. Stadeler, J. S. Unger, N. J. Gebert, A. Müller-Haufe, E. W. Rettew and L. A. Lanning, E. C. Groesbeck, H. H. Beeny, A. E. M. Smith, R. C. Good, M. Hamasumi, F. Fettweiss, A. Wimmer, W. H. Hatfield, H. Ford, R. Moldenke, W. Guertler, E. Touceda, R. H. Smith, B. H. Paul, E. d'Amico, H. M. Howe, J. H. Higgins, G. R. Johnson, J. de Kryloff, E. Maurer and W. Haufe, H. I. Coe, J. E. Johnson, F. Graziani, W. E. Dennison, R. T. Rolfe, F. F. McIntosh, J. E. Fletcher, A. Ledebur, P. R. von Tunner, T. D. West, W. J. Keep, K. Taniguchi, J. E. Hurst, E. Piwowarsky and co-workers, and J. E. Stead. F. F. McIntosh found that the endurance properties and strength of steel increased with the phosphorus-content between 0·01 and 0·10 per cent., without producing a proportional loss in ductility. J. H. Teng found that malleable cast irons having approximately 0·80 to 0·90 per cent. combined carbon; 1·08 to 1·20 per cent. graphitic carbon; 0·200 to 0·210 per cent. silicon; 0·006 to 0·008 per cent. sulphur; no manganese, and variable proportions of phosphorus, had the mechanical properties in tons per sq. in.:

Phosphorus . .	0·010	0·046	0·096	0·144	0·210	0·302	0·412	0·508 per cent.
Yield-point . .	17·20	17·30	17·65	17·90	18·20	18·70	19·20	19·80
Max. stress . .	22·85	22·90	22·54	22·20	22·20	21·56	20·75	19·95
Elongation (4 ins.) .	3·8	3·5	3·5	3·1	3·2	2·9	2·2	0 per cent.
Reduction area .	3·12	3·00	3·10	2·80	2·85	2·00	1·5	nil per cent.
Transverse strength.	3·6	3·67	3·55	3·50	3·40	2·95	2·55	1·80
Deflection . .	0·57	6·57	0·56	0·56	0·53	0·44	0·37	0·18 in.
Angle of bend. .	60°	62°	58°	55°	55°	45°	30°	nil
Brinell's hardness .	175	180	184	193	203	224	253	308

He also found that the Izod test fell from 8·5 ft.-lbs. with 0·06 phosphorus to 3·0 with 0·465 per cent. N. S. Konstantinoff measured the electrical conductivity. The observations of E. d'Amico on the sp. gr., hardness, the mechanical properties, the electrical resistance, and the magnetic properties are summarized in Figs. 352 and 353, where the electrical resistance is expressed in ohms per metre per sq. mm. section; the coercive force is for $B=13{,}000$, and the hysteresis for $B=10{,}000$; the tensile strength and elastic limit refers to kilograms per sq. mm.; and the elongation is in percentages. One per cent. of phosphorus raises the electrical resistance 11·0 microhms per cm. cube. W. M. Hicks found that phosphorus and arsenic decreased the coercive and the hysteresis loss of iron. The subject was studied by F. Goltze, H. F. Parshall, and J. H. Partridge.



Figs. 352 and 353.—The Effect of Phosphorus on the Mechanical Properties of Iron.

According to R. Finkener, the general opinion is that phosphorus makes steel less resistant to corrosive influence, although C. Diegel did not find this to be the case with plates of iron exposed for sixteen months to sea-water in Kiel harbour. The results showed that the losses in weight per sq. dm. were :

P .	10·01	0·09	0·23	0·45	0·84	0·85 per cent.
Loss .	7·00	6·10	5·71	5·48	5·16	4·93 grms.

The resistance was ascribed to the formation of an iron phosphide which is not so readily corroded as iron. The experiments of E. Heyn and O. Bauer with iron containing larger proportions of phosphorus than those employed by C. Diegel, were very irregular. This is attributed to the unequal distribution of the phosphide favouring galvanic action. The subject was studied by L. Tronstad and J. Sejersted. H. Endo, Fig. 354, observed the losses in grams per sq. cm. during 5 hrs'. exposure at ordinary temp. from alloys with 0·35 to 0·45 per cent. of carbon and

Phosphorus .		0·75	1·35	1·81	3·10	6·84	12·17 per cent.
Loss	H_2SO_4 .	0·02688	0·03274	0·04255	0·03904	0·02478	0·00832
	HCl .	0·02388	0·02366	0·02566	0·01737	0·00847	0·00351
	HNO_3 .	0·06422	—	0·04642	0·05170	0·03177	0·02605

W. S. Calcott and co-workers, and M. Merlub-Sobel observed that the **phosphorus chlorides** readily attack iron ; and A. Granger found that in the vapour of **phosphorus trifluoride, trichloride,** and **tribromide,** iron phosphide is formed ; the metal is also attacked by **phosphorus iodide,** P_2I_4. A. Sieverts found that iron is dissolved by a soln. of **sodium hypophosphite.** H. Schackmann and W. Krings represented the action with **phosphorus pentoxide** by the equation: $5\ Fe+P_2O_5 \rightleftharpoons 5FeO+2P$. According to E. Erlenmeyer and O. Heinrich, a 48 per cent. soln. of **phosphoric acid** rapidly dissolves finely-powdered iron with the evolution of gas and the formation of a green liquid thought to contain $Fe(H_2PO_4)_2$. W. Rohn observed that cold, 10 per cent. phosphoric acid dissolves 0·27 grm. per sq. dm. from purified unannealed iron, and 0·14 grm. from the annealed metal; whilst the hot acid dissolves 5·77 grms. from the unannealed metal and 12·3 grms. from the annealed metal. According to P. R. Kosting and C. Heins, with 0·5 in. discs of armco iron and 50 per cent. phosphoric acid after an hour's action, the loss in weight was 0·13 grm. ; and with the addition of 0·49 per cent. arsenic oxide, 0·00 grm. ; with 0·75 per cent. HCl, 0·04 ; with 0·75 per cent. pyridine, 0·10 per cent. ; with 0·45 per cent. HF, 0·14 per cent. ; with 0·27 per cent. H_2SiF_6, 0·14 per cent. ; with 0·75 per cent. H_2SO_4, 0·16 per cent. ; with 1 c.c. of pine oil per 100 c.c. of soln., 0·05 per cent. ; and with 1 c.c. of mucilage per 100 c.c., 0·06 per cent. V. K. Pershke and co-workers studied the resistance to the acid of iron alloys containing copper, lead, aluminium, and zinc. Those with copper were best. R. L. Jenkins and co-workers found that the presence of about 0·1 per cent. of furfuraldehyde and 0·003 per cent. potassium iodide inhibits the action of 75 per cent. phosphoric acid on iron. The action of phosphoric acid on iron and its alloys was studied by F. Clarkson and H. C. Hetherington, R. Finkener, J. H. Gravell, J. Heimann, V. K. Pershke and co-workers, P. R. Kosting and C. Heins, A. M. Portevin and A. Sanfourche, M. V. Ruisakoff and I. N. Buschmakin, and M. Wunder and B. Janneret.

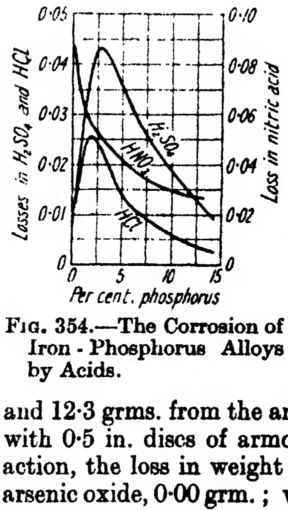


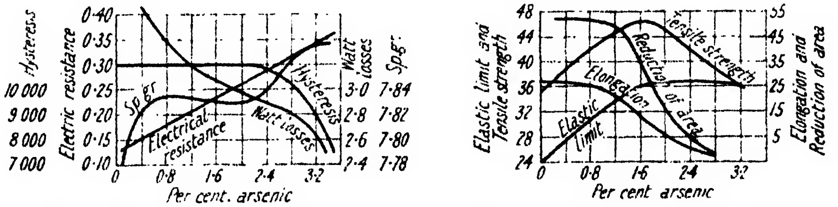
Fig. 354.—The Corrosion of Iron - Phosphorus Alloys by Acids.

A method for protecting the surface of iron and steel from rusting was developed by T. W. Coslett,[9] and hence called *coslettizing*. The metal is coated with a basic iron phosphate by treating it with a dil. soln. of phosphoric acid to which some iron filings have been added to control the action. W. I. Oeschger modified the process by adding the oxide of some metal of the third, fourth, or fifth groups. In one modification, manganese dioxide is added to T. W. Coslett's soln. in order to accelerate the action by removing hydrogen from the metal surface. The patent was assigned to the Parker Co., and hence the process is called *parkerizing*. The subject was discussed by W. H. Allen, E. M. Baker and co-workers, E. L. Blassett, O. W. Roskill, J. Cournot and co-workers, L. E. Eckelmann, F. Kolke, L. C. Morrow, M. T. Murray, E. Rackwitz, and J. W. Wunsch.

The effect of **arsenic** on iron was discussed in connection with the iron arsenides—**9**. 51, 10. G. Tammann and K. Schaarwächter[10] observed that the attack of iron by arsenic begins at 420° and increases rapidly with a rise of temp. K. Friedrich gave the equilibrium diagram for the system: Fe–As. The alloys were discussed by O. Bauer, P. Blum, A. Carnot and E. Goutal, H. J. French and T. G. Digges, W. Guertler, W. N. Hindley, C. J. B. Karsten, E. Kordes, P. E. McKinney, J. Marchal, W. Mathesius, E. Maurer and W. Haufe, M. Merle, P. Oberhoffer, F. Osmond, and J. Weeren. C. F. Burgess and J. Aston found that alloys with 4 per cent. arsenic forge well, machine easily, and weld in the electric welder. With high arsenic, dull forging heats are not suitable. J. E. Stead found that 4 per cent. of arsenic had no marked influence on the working properties; while P. Blum said that 4 per cent. of arsenic makes steel brittle; and F. W. Harbord and A. E. Tucker found that the presence of 1·4 per cent. of arsenic does not make the metal red-short. F. Osmond added that arsenic raises the temp. at which the arrest A_3 at 855° occurs in the cooling curve, and makes the point less distinct; while it has no effect on the arrests A_2 and A_1, and it thus resembles the action of silicon—*vide infra*, the action of copper; and for P. Oberhoffer and A. Gallaschik's observations, *vide* **9**. 51, 10. J. Liedgens found:

Arsenic . . .	0·3	0·7	1·4	1·9	2·5	3·3	3·5 per cent.
Upper arrest, A_3	855°	859°	848°	—	—	—	—
Lower arrest, A_1	678°	659°	658°	655°	650°	639°	630°

Observations were made by A. E. Cameron, and P. E. McKinney. G. Hägg studied the X-radiograms of these alloys. J. O. Arnold measured the sp. gr. of the alloys. J. Liedgens' observations on the sp. gr., the mechanical properties, the electrical resistance, and the magnetic properties are summarized in Figs. 355 and 356. P. E. McKinney, and O. Bauer studied the mechanical properties of these alloys. The tensile strength and elastic limit are expressed in kilograms per sq. mm.; the elongation and reduction of area in percentages; the electric resistance, in ohms per metre per sq. mm. sectional area; the hysteresis, in ergs per c.c. C. F. Burgess and J. Aston also found that the magnetization of iron is improved by the presence of arsenic. The results for the magnetization, or magnetic induction, B, of alloys of iron and arsenic—unannealed, annealed at 675° and 1000°, and quenched from 900°—for magnetic fields of intensity H gauss, are given in Table XLIX, while the results for the coercive force ($H_{\max.}$=200), and retentivity ($H_{\max.}$=200) are given in Table L. "S" refers to Swedish iron, and "El" to electrolytic iron forged. Observations were also made by W. M. Hicks, E. K. Smith and H. C. Aufderhaar, and E. Maurer and W. Haufe.



FIGS. 355 and 356.—The Effect of Arsenic on the Mechanical, Electrical, and Magnetic Properties of Iron.

P. Berthier observed that arsenic alloys with iron are more readily corroded than iron alone. E. Heyn and O. Bauer's experiments appeared to support this state-

TABLE XLIX.—MAGNETIZATION OF IRON-ARSENIC ALLOYS.

Arsenic (per cent.)	$H=10$				$H=100$			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°
S	9,500	10,000	10,850	8,400	17,450	18,000	17,200	—
El	13,100	10,000	13,350	11,800	18,850	18,850	18,200	18,150
0·29	10,500	13,200	10,800	11,200	18,350	18,550	17,850	17,950
0·43	7,000	7,800	10,400	8,100	17,800	18,100	17,250	17,600
0·92	6,200	6,250	11,950	12,600	17,950	18,550	17,950	18,250
1·81	8,300	11,850	12,600	10,300	17,950	18,750	18,150	18,250
3·56	12,400	14,200	12,300	13,450	17,950	18,750	17,950	18,000
3·86	13,850	15,050	14,850	13,600	17,600	18,650	17,850	18,100
4·14	13,300	14,200	14,650	--	18,200	18,450	18,150	--

TABLE L.—COERCIVE FORCE AND RETENTIVITY OF IRON-ARSENIC ALLOYS.

Arsenic (per cent.)	Coercive force				Retentivity			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°	Not annealed	Annealed at 650°	Annealed at 1000	Quenched from 900°
S	5·5	4·8	3·9	5·0	11,400	12,700	9,000	8,500
El	5·5	6·2	5·1	2·5	12,300	13,800	10,000	8,000
0·29	6·5	5·5	4·5	4·0	12,400	14,600	9,900	10,800
0·43	8·2	8·0	5·5	4·3	12,700	12,700	9,400	8,600
0·92	9·5	9·2	5·3	3·0	12,700	14,700	12,300	9,500
1·81	5·9	5·0	3·7	3·0	10,300	12,200	8,900	8,600
3·56	4·5	4·0	2·7	2·7	11,000	13,400	8,600	8,900
3·86	4·0	3·5	2·0	2·1	12,100	13,000	6,500	8,600
4·14	5·0	3·3	2·3	--	10,800	12,300	8,900	—

ment, but they were not satisfied with the results. C. F. Burgess and J. Aston observed that with electrolytic iron alloyed with arsenic :

Arsenic . .	0	0·292	0·430	0·915	1·810	3·862	4·141	5·362%
Acid corrosion .	1·300	0·448	0·815	0·405	0·131	0·086	0·102	0·144
Atm. corrosion .	0·499	0·405	0·343	0·425	0·352	0·312	0·361	0·306

the acid corrosion refers to the loss in grams per sq. dm. when immersed in 20 per cent. sulphuric acid for an hour ; and atmospheric corrosion to the loss in kgrms. per sq. metre per year when exposed to the weather for 162 days from July to February. The resistance to atm. corrosion is about the same as for electrolytic iron. L. Lindet noted that the presence of **arsenic trioxide** retards the corrosion of iron—*vide infra*—and C. F. Burgess and S. G. Engle, and E. Heyn and O. Bauer made a similar observation with arsenic trioxide in sulphuric acid. E. Heyn and O. Bauer's results with 1 per cent. sulphuric acid are illustrated in Fig. 357, taking the result with no arsenic trioxide present as the standard. The addition of 0·0069 grm. reduced the attack to one-third. H. Anthes observed the formation of arsine when arsenical sulphuric acid acts on iron. Observations were made by W. N. Hindley, and A. E. Cameron and G. B. Waterhouse—*vide supra*, sulphuric acid. When iron is allowed to stand in contact with anhydrous **arsenic trichloride**, L. Kahlenberg and J. V. Steinle found that some arsenic separates out; at 100°, there is a feeble reaction. They

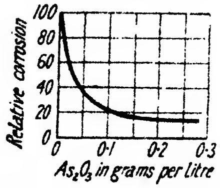


FIG. 357.—The Effect of Arsenic Trioxide on the Attack of Iron by Dilute Sulphuric Acid.

also observed no separation with **arsenic tribromide.** The effect of hydrochloric acid on the corrosion of iron by arsenic trichloride was studied by H. E. Patten.

G. Tammann and K. Schaarwächter [11] observed that **antimony** begins to attack iron at about 610°, and the rate increases rapidly with rise of temp. C. J. B. Karsten found that 1 per cent. of antimony acts very injuriously on iron; 0·144 per cent. made bar iron so cold-short as to be worthless. L. J. Thénard observed that an alloy of antimony with twice its weight of iron, sparks when it is filed. The equilibrium diagram was studied by N. S. Kurnakoff and N. S. Konstantinoff—*vide* **9**. 52, 9. G. Tammann and W. Salge studied the residue left after treating the alloy with an acidified soln. of ammonium persulphate. P. Goerens and K. Elligen observed that the temp. of the primary separation of austenite from molten pig-iron, and the solidification temp. of the eutectic, are lowered by antimony; the temp. of the pearlitic change is not affected; and the magnitude of the recalescence decreased as the proportion of antimony was increased. G. Hägg studied the X-radiograms. E. K. Smith and H. C. Aufderhaar, and A. M. Portevin found that antimony affected the mechanical properties like arsenic does. A. L. Norbury, and H. J. French and T. G. Digges studied some of the alloys. C. F. Burgess and J. Aston said that the alloys of antimony seem of no value as a magnetic material. The alloys are difficult to work. W. Guertler, and P. Oberhoffer discussed the alloys, and A. Lotti observed that iron pans are corroded by molten lead containing antimony and copper. H. E. Patten studied the corrosion of iron by **antimony pentachloride** in the presence of hydrochloric acid. The reduction of antimony from soln. of **antimony salts** has been previously discussed—**9**. 52, 6. The reaction was studied by J. Thiele.

C. J. B. Karsten found that 1 per cent. of **bismuth** had little effect on the quality of the iron, but the metal did not work so well; C. F. Burgess and J. Aston examined this subject. The alloys were discussed in connection with the bismuthides—**9**. 53, 7. G. Hägg studied the X-radiograms. C. F. Burgess and J. Aston found 2 per cent. of diamagnetic bismuth improved the ferromagnetism of iron; otherwise, the alloys furnished no features of particular interest. For the action of antimony, *vide* the antimonides, **9**. 52, 9; and bismuth, *vide* the bismuthides, **9.** 53, 7. P. Oberhoffer discussed the alloys. N. Ageeff and M. Zamotorin studied the diffusion of bismuth in iron. E. K. Smith and H. C. Aufderhaar found that bismuth softens and decreases the strength of cast iron. The reduction of bismuth from soln. of **bismuth salts** has been previously discussed—**9**. 53, 5. F. E. Brown and J. E. Snyder found that **vanadyl trichloride,** $VOCl_3$, does not act on iron either at ordinary temp. or at the b.p.

S. Konobejewsky [12] discussed the solid soln. of iron in graphite; the solid soln. of carbon in iron has been previously discussed. G. Tammann and K. Schaarwächter observed that **carbon** begins to attack iron at about 1145°. H. Trapp discussed the mechanism of the attack of iron by carbon. For the action of carbon, *vide infra*, corrosion; cementation; the allotropic forms of iron; the carbides, **6**. 39, 20; and *vide supra* for the effect of carbon on the physical properties of iron. F. Fischer and H. Bahr studied the carbides; and W. F. Holbrook and co-workers, the diffusion of carbon in molten iron. A. Rossel, and A. Rossel and L. Franck found that when iron is heated with **calcium carbide** in air some iron nitride, and calcium oxide are formed. O. Meyer studied the action of **silicon carbide, chromium carbide,** and **molybdenum carbide** on iron, and found the metal is attacked at temp. approximating 1500°. The absorption of **methane** by iron is indicated in connection with Table LI. G. Charpy and S. Bonnerot said that when iron is heated in contact with graphite it does not become carburized at 950° unless at least traces of oxygen or of a carbon oxide are present, but F. Giolitti and co-workers do not agree. W. Hempel, and F. Osmond found that the diamond reacts with iron at 1160°, and sugar-charcoal and graphite at about 1400°. According to R. Schenck, the action of methane can be represented by the equation $3Fe+CH_4=Fe_3C+2H_2-35{,}811$ cals., where

$CH_4 = C + 2H_2 - 21{,}368$ cals. The relative proportions of the gases at different temp., and under atm. press., in the system: $CH_4 \rightleftharpoons C + 2H_2$, are:

	310°	445°	580°	680°	710°	720°	740°
CH_4 . . .	99·20	77·00	36·65	16·82	13·00	11·95	10·90
H_2 . . .	0·80	23·00	65·35	83·18	87·00	88·05	98·10

and in the system: $3Fe + CH_4 \rightleftharpoons Fe_3C + 2H_2$:

	310°	360°	445°	580°	680°	710°	720°
CH_4 . . .	—	98·30	95·70	59·80	22·70	15·23	12·07
H_2 . . .	trace	1·70	4·30	40·20	77·30	87·77	87·93

The results are plotted in Fig. 358. The two curves intersect at 720°. The reaction was studied by T. Watase, and F. Eisenstecken—*vide* cementation. The reaction was studied by A. Johansson and R. von Seth, E. D. Campbell, M. Mayer and V. Altmayer. F. Durau and C. H. Teckentrup found that the absorption of methane by iron is purely adsorption, and similarly with methane, **ethane**, and **propane**. H. S. Taylor and R. M. Burns observed that at 25°, 100°, and 218°, one vol. of iron absorbs respectively 0·25, <0·05, and <0·05 vol. of **ethylene.** The reaction was studied by R. N. Pease and H. S. Taylor, and W. Ipatéeff and N. Kliukvin. A. Magnus and R. Klar studied the absorption of ethylene by pyrophoric iron; and F. Durau and C. H. Teckentrup found the adsorption of ethylene is purely an adsorption process, and similarly with **propylene.** H. Hollings and R. H. Griffith studied the adsorption of hydrocarbons. H. Moissan and C. Moureu observed that finely-divided iron catalytically decomposes **acetylene** into its elements, and at the same time forms a trace of a condensation product of acetylene. The action of acetylene on metals was also discussed by H. Reckleben and J. Scheiber, W. R. Hodgkinson, E. Tiede and W. Jenisch, and J. F. Durand and M. Banos. U. Hofmann and E. Groll observed that the solid phase produced when benzene vapour acts on iron at 700° contains carbon, iron, and principally cementite. S. I. Levy and R. Defries studied the corrosive action of **turpentine** on iron. U. Hofmann and E. Groll found that at 700°, **benzene** passed over iron furnishes carbon and cementite. S. P. Uspensky and N. I. Laduizhnikova observed a loss of 10 mgrms. per sq. cm. by 8 months' exposure of iron to motor benzene. E. W. Kanning and O. W. Brown studied the catalytic decomposition of **kerosene** by iron.

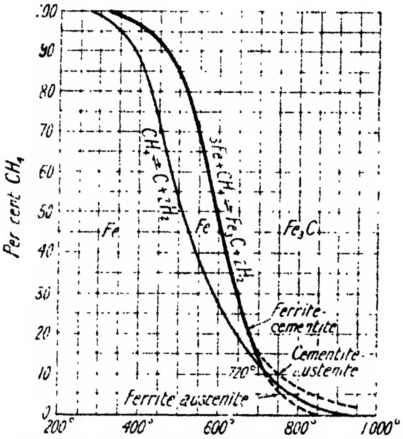


FIG. 358.—Equilibrium Curves for the System with Methane and Iron.

For the absorption of **carbon monoxide** by iron, *vide* Table LI. A. F. Benton and co-workers, K. Iwase, F. Rapatz, and A. Villachon and G. Chaudron also discussed the subject. F. Durau and C. H. Teckentrup showed that the absorption is purely an adsorption process. According to H. S. Taylor and R. M. Burns, one vol. of iron absorbs 0·70, 0·20, and 0·10 vol. of carbon monoxide respectively at 25°, 110°, and 218°. A. Stoffel said that the pentacarbonyl which is formed is adsorbed by the iron, and it forms a protective film on the surface of the metal. N. Parravano and C. R. del Turco found that deoxidizing agents in steel reduce the occluded carbon monoxide; and they also usually reduce carbon monoxide and dioxide at high temp. K. A. C. Elliott studied the oxidation of cystein and thioglycollic acid with iron catalysts. P. Farup discussed the catalytic action of iron ores in reducing carbon monoxide. R. N. Pease and L. Stewart compared the catalytic activity of iron, nickel, cobalt, copper, and silver on the hydrogenation of ethylene ; S. Kodama, C. M. Loane, and H. Ritter studied the catalytic action of iron in the synthesis of oils, etc. R. Yoshimura, A. Jaeger, J. H. Jones and co-workers, S. Kodama and K. Fujimura, R. N. Pease and H. S. Taylor, P. Rischbieth, H. Tropsch and A. von Philippovich, O. Warburg, O. Warburg and W. Brefeld, and R. Yoshimura, the activation of charcoal catalysts by iron ; O. Baudisch and L. A. Welo, the formation of a blue colour with benzidine hydrochloride and hydrogen dioxide, and the growth of the *Bacterium lepisepticum* ; and M. C. Boswell and C. H. Bayley, the action of ceric oxide as a promoter of the catalytic activity of iron. B. S. Srikantan compared the atomic energy and efficiency of iron as a catalyst.

H. F. Coward and P. G. Guest compared the ignition temp. of gases by heated metal bars, and found that iron did not give comparable results. H. C. Greenwood, and A. Johansson and R. von Seth, studied the surface decarburization of steel by heating it in carbon dioxide. N. Parravano and C. R. del Turco found that the deoxidation of steel reduces the amount of absorbed carbon monoxide, and that the usual deoxidizing agents, employed in the steel industry, reduce both carbon monoxide and dioxide at high temp. H. St. C. Deville observed that carbon monoxide, like hydrogen, can diffuse through red-hot iron ; and a similar observation was made by T. Graham. According to C. Decroly, at atm. press., carbon monoxide does not diffuse through a steel tube of 3·5 mm. thickness at 800° and at 1000°. L. Cailletet found that the gases which escape from cast iron in a state of fusion contain some carbon monoxide as well as hydrogen and nitrogen. T. Graham obtained the gas from meteoric iron. P. A. Klinger found that electrolytic iron with 0·03 per cent. of carbon contained 0·0075 per cent. CO and 0·0078 per cent. CO_2, and after heating to redness in carbon monoxide, contained 0·0050 per cent. CO, and 0·0059 per cent. CO_2 ; while with electrolytic steel with 1·2 per cent. of carbon and containing 0·0050 per cent. CO and 0·0108 per cent. CO_2, after heating to redness in carbon monoxide, contained 0·0044 per cent. CO and 0·0138 per cent. CO_2. Observations were made by V. Lombard, H. C. H. Carpenter and C. C. Smith, N. Nikitin, and A. Villachon and G. Chaudron. With the molten metals, P. A. Klinger found the results indicated in Table LI. P. D. Merica discussed the effect of absorbed gas on the magnetic properties.

TABLE LI.—THE EFFECT OF THE ABSORPTION OF CARBON MONOXIDE BY MOLTEN IRON.

		Before			After saturation with CO			
	C per cent.	O per cent.	CO per cent.	CO_2 per cent.	C per cent.	O per cent.	CO per cent.	CO_2 per cent.
Electrolytic iron .	0·04	0·002	0·0525	0·0079	0·03	0·022	0·0450	—
Siemens-Martin's basic steel . .	0·47	0·008	0·0463	0·0059	0·44	0·023	0·1538	—
Crucible steel . .	0·37	0·035	0·0637	—	0·26	0·022	0·1400	—
Crucible steel . .	0·72	0·002	0·0575	—	0·60	0·021	0·1337	—

The formation of iron carbonyls by the action of carbon monoxide on finely-powdered iron at about 120° was discussed in connection with the carbonyls—5. 39, 27. T. Bahr observed that at 400° to 600°, some substances similar to humic acid are formed along with the carbon. J. Garnier inferred from the luminosity of the flame of furnaces in the manufacture of iron and steel, and from the nature of the flue-dust, that volatile compounds of iron and carbon monoxide are formed in the furnace ; and H. Morton, in manufacturing gas. A. Villachon and G. Chaudron considered that in molten iron, some carbon monoxide is dissolved as a carbonyl.

V. Falcke, A. N. Guntz, H. Nippert, H. Nishimura, and H. J. van Royen found that iron reacts with carbon monoxide at about 600°, forming ferrous oxide and carbon. The reactions were discussed in connection with the blast-furnace. R. Schenck found the equilibrium conditions in the reaction: $2CO \rightleftharpoons C+CO_2$:

	450	480°	500°	580	640°	700	800°
CO . .	2·0	3·5	5·0	11·75	35·5	59·0	86·1 per cent.
CO_2 . .	98·0	96·5	95·0	82·25	64·5	41·0	13·9 ,,

and for the reaction: $3Fe+2CO \rightleftharpoons Fe_3C+CO_2$:

	480°	500°	580°	640°	680	700°
CO . . .	12·12	15·50	32·36	47·80	58·86	64·00 per cent.
CO_2 . . .	87·87	84·50	67·64	52·20	41·14	36·00 ,,

The results are plotted in Fig. 359 along with an approximation for the reaction: $2CO+Fe_3C \rightleftharpoons Fe_3C_2+CO_2$. There are also many other side-reactions, *e.g.* $Fe_3C+4CO_2 \rightleftharpoons 3FeO+5CO$, discussed L. Gruner, W. Leybold, H. C. H. Carpenter and C. C. Smith, V. Falcke, S. Hilpert and T. Dieckmann, A. Gautier and P. Clausmann, etc.—in connection with the different iron oxides (*q.v.*), and with the reactions in the blast-furnace (*q.v.*). J. E. Stead discussed the action of blast-furnace gases on iron. W. P. Fishel and J. F. Wooddell observed more carbon dioxide is formed with iron in carbon monoxide than corresponds with the equilibrium value at 800° to 1100°. U. Hofmann discussed the form of the carbon or graphite deposited on iron at 900°. According to A. Gautier and P. Clausmann, when a mixture of moist carbon monoxide and hydrogen is passed over iron at 250° to 300°, formaldehyde, as well as a fatty substance of m.p. 35°–36°, can be detected in the products of the reaction; and L. Vignon observed that methane is formed between 500° and 1000°. H. Remy and H. Gönningen, H. Remy, J. V. Vaughen and W. A. Lazier, A. Bramley and H. D. Lord, W. Gluud and R. Schönfelder, E. Audibert and A. Raineau, K. Fujimura, T. Watanabe, and H. Tutiya studied the catalytic decomposition of carbon monoxide by iron.

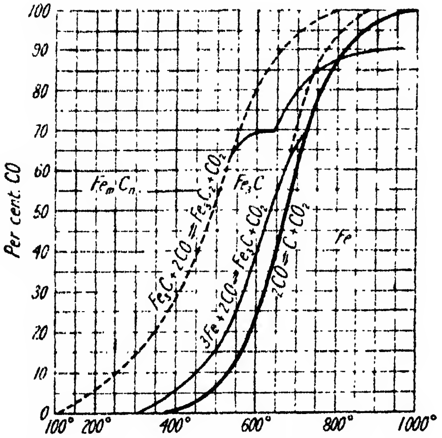


FIG. 359.—Equilibrium Curves for the System with Carbon Monoxide and Iron.

According to G. Tissandier, at 1000°, iron in an atm. of carbon monoxide forms ferrous oxide; and in an atm. of **carbon dioxide** at 900°, ferrous oxide is formed, while at 1200°, ferrosic oxide is produced. The reaction is discussed in connection with the respective iron oxides. B. Beer discussed the absorption of carbon dioxide by iron, see Table LII. F. Durau and C. H. Teckentrup showed that the

TABLE LII.—ACTION OF CARBON DIOXIDE ON IRON.

	Before				After saturation with CO_2			
	C per cent.	O per cent.	CO per cent.	CO_2 per cent.	C per cent.	O per cent.	CO per cent.	CO_2 per cent.
Electrolytic iron .	0·04	0·002	0·0525	0·0079	0·03	0·020	0·0375	—
Siemens-Martin basic steel .	0·47	0·008	0·0463	0·0059	0·35	0·018	0·1063	—
Crucible steel .	0·37	0·035	0·0637	—	0·27	0·025	0·1262	—
Crucible steel .	0·72	0·002	0·0575	—	0·49	0·018	0·1912	0·0039

absorption process is purely one of adsorption. A. Magnus and B. Klar, and N. I. Nikitin found that carbon dioxide is strongly absorbed by pyrophoric iron even at ordinary temp.; and a chemical action occurs at 500°; and R. Ruer and J. Kuschmann, that 100 grms. of reduced iron powder absorbed 5 mgrms. of carbon dioxide. P. P. Fedotéeff and T. N. Petrenko observed that the action of carbon dioxide at 1000° to 1100° resembles the action of steam—*vide supra.* H. S. Taylor and R. M. Burns found that a little carbon dioxide—less than 0·05 vol. per vol. of metal—is absorbed at 25° and 110°. F. G. Finzel observed that a sample of non-pyrophoric iron adsorbed more carbon dioxide than did a sample of pyrophoric iron. P. P. Fedotéeff and T. N. Petrenko studied the oxidation of iron by carbon dioxide at 1000° to 1100°, and found that the composition of the product varies continuously from ferrous to ferrosic oxide. Observations on the action of carbon dioxide at a high temp. were also made by F. von Bacho, G. Neumann, P. A. Klinger, W. H. Hatfield, and C. B. Marson and J. W. Cobb. H. Tutiya observed the formation of no new compound in the catalysis of the decomposition of carbon monoxide by iron, the reduction proceeds $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe_3C$.

In 1774, T. Bergman observed that iron dissolves in water holding carbon dioxide in soln. J. Tillmans and B. Klarmann found that oxygen-free water, containing carbon dioxide in soln., dissolves iron until its water has attained a $H^{\cdot}$-ion conc. of 10^{-7}. The rate of dissolution depends on the velocity of flow, the time of contact with the pipes, the size and nature of the pipes, and the $H^{\cdot}$-ion conc. of the water. The presence of iron tends to form a supersaturated soln. of ferrous carbonate, the solubility product of $FeCO_3$ being $2{\cdot}7 \times 10^{-10}$. Water with less than 100 mgrms. of H_2CO_3 does not attack iron pipes to any great extent; but with more conc. soln. or carbonic acid, the attack is marked. Carbonic acid, although a very weak acid, can act appreciably on iron; with an excess of carbon dioxide in the absence of air, the reaction is symbolized: $2H_2O+2CO_2=H_2(HCO_3)_2$; and if an excess of iron be present, $Fe+H_2CO_3=H_2+FeCO_3$. G. T. Moody observed that 250 c.c. of a sat. soln. of carbon dioxide in water at one atm. press. dissolved after:

	20 hrs.	56 hrs.	96 hrs.	26 days
FeO per litre	0·2546	0·3771	0·8172	2·139 grms.

The soln. was colourless in the absence of air; but when air was present, the mixture was coloured by the ferrous carbonate, and ferrous and ferric hydroxides in varying proportions. This reaction was also studied by G. Just, R. Girard, A. Bramley and H. D. Lord, and G. W. Whitman and co-workers—*vide infra,* Fig. 360. W. Leybold, and B. Klarmann discussed the solubility of iron in carbonic acid—*vide infra.* According to A. Schleicher and G. Schultz, the relative corrosion factors for wrought iron and cast iron in soln. of carbonic acid are, respectively, 100 and 273 in the absence of air, and 100 and 152 in the presence of air. H. Henecka, and E. Müller and H. Henecka found that carbonic acid under a

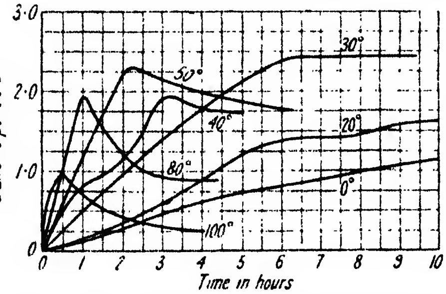


FIG. 360.—The Effect of Temperature on the Solubility of Iron in Carbonic Acid.

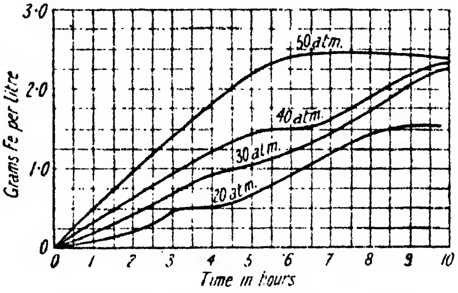


FIG. 361.—The Effect of Pressure on the Solubility of Iron in Carbonic Acid.

high press. dissolves iron to form easily-soluble ferrous hydrocarbonate; the equilibrium constant for the reaction $Fe+2H_2CO_3=Fe(HCO_3)_2+H_{2gas}$, is $K=[Fe(HCO_3)_2]/H_2CO_3]^2$, or $K=1{\cdot}2\times10^3$. There is also the reaction $Fe(HCO_3)_2 \rightleftharpoons FeCO_3+CO_2+H_2O$. H. Henecka's observations on the rate of soln. of iron in water saturated with carbon dioxide at 50 atm. press., and at temp. between 0° and 100°, are summarized in Fig. 360, and the rate of soln. of iron in water saturated with carbon dioxide at 30° and 20 to 50 atm. press., in Fig. 361—*vide infra*, ferrous hydrocarbonate. W. Leybold observed that water sat. with carbon dioxide at atm. press. in 10 weeks dissolved 1·058 grms. of iron. According to A. Bruno, the vigorous shaking for thirty-six to forty hours of a steel bottle containing water and iron-filings in an atm. of carbon dioxide causes the whole of the carbon dioxide to be replaced by hydrogen according to the equation: $CO_2+H_2O+Fe=FeCO_3+H_2$. If a glass vessel is used, this reaction is accompanied by the absorption of part of the carbon dioxide by the alkali of the glass. Further, a mixture of iron-filings, water, and nitrobenzene yields aniline just as if a strong acid were employed. P. Petit found that when water containing 638 mgrms. of calcium carbonate per litre dissolved in carbon dioxide, but neutral to phenolphthalein, is brought in contact with finely-powdered iron, more than half the carbonate is precipitated, and iron is dissolved. Water sat. with carbon dioxide will dissolve as much as 500 mgrms. of iron per litre, with liberation of an eq. quantity of hydrogen. The iron is converted into ferrous carbonate, and if the soln. is exposed to air, ferric oxide is precipitated. The water of the Moselle was found to dissolve 3·15 mgrms. of iron per litre; if previously treated with a current of carbon dioxide for a few minutes, it dissolved 200·6 mgrms.; but if mixed with lime-water until slightly alkaline to phenolphthalein, it dissolved no iron at all. J. V. Emmons, and A. Johansson and R. von Seth studied the surface decarburization of steel by heating it in carbon dioxide. P. A. von Bonsdorff observed that rusting does not occur in an atmosphere containing traces of carbon dioxide provided the conditions are such that no water can deposit on the metal. U. R. Evans found that iron and steel rusted a little particularly along the small grooves left by the emery treatment when exposed to water vapour alone; and carbon dioxide did not produce any great acceleration in the corrosion of iron and steel, though it appeared to favour the rusting.

A. Bolis observed that the loss suffered by cast iron in contact with boiling **carbon tetrachloride** for 10 hrs. is inappreciable; the metal acquires a dark coating which preserves it from further attack. If the carbon tetrachloride is saturated with moisture, the metal is appreciably attacked by the boiling liquid. A mixture of carbon tetrachloride with one-third its vol. of water caused cast iron to lose about 5 per cent. of its weight in the course of 10 hrs.' boiling. The subject was investigated by A. E. Wood and co-workers, E. V. Zappi, H. W. Doughty, A. W. Smith, A. Bolis, J. R. Crocker, H. E. Pattèn, S. G. Sastry, J. Milbauer, L. Vernitz and A. Kudinova, and F. H. Rhodes and J. T. Carty. T. Midgley and A. L. Henne found steel resists the action of **carbon difluorodichloride** at 175°. J. Formanek found that the action of carbon tetrachloride during 8 months is negligibly small; but with **trichloroethylene** and **tetrachloracetylene,** the action is small but perceptible; J. Milbauer observed that the presence of ethyl alcohol increases the rate of attack by boiling carbon tetrachloride. H. E. Patten observed no action occurs with iron and **chloroform,** or **ethyl chloride.** F. Durau and C. H. Teckentrup observed that the absorption of chloroform by iron is purely an adsorption process. J. G. Tapley and co-workers, H. R. S. Clotworthy, B. R. Parkinson, and J. B. Peel and P. L. Robinson found that when iron is heated in the vapour of **carbon disulphide,** at 1000°, impure ferrous sulphide is formed. M. Delépine and L. Ville investigated the action of **carbonyl chloride** on iron. J. Tapley and co-workers, J. F. G. Hicks, and B. R. Parkinson discussed the corrosive action of **hydrocyanic acid** in town gas on the conveying pipes (*vide infra*); and G. P. Gray and E. R. Hulbert, the action of hydrocyanic acid on various metals, most of which promote the decomposition of liquid hydrogen cyanide. The action of **cyanogen,** and of **cyanides** on iron has been discussed in connection with the cementation process. F. Durau and C. H. Teckentrup found that the absorption of cyanogen by electrolytic iron is a chemical process. V. E. Hillman and E. D. Clark, H. Braune, H. Fay, W. Giesen, J. E. Johnson, and J. K. Smith studied the nitrogenization of iron by means of cyanides. M. Berthelot observed no reaction between iron and cyanogen in a sealed tube at 100°; at 300° some iron cyanide is formed without the evolution of nitrogen, and at 500°, free nitrogen and some polymerization products are formed. H. Braune noted that the reaction with cyanogen is very slow at 600° to 700°, but rapid at 1000°. L. Hackspill and R. Grandadam found that iron reacts with the alkali cyanides in vacuo at 600° in accord with the equation: $2NaCN+Fe=2Na+N_2+$Iron carbide; L. Hackspill did not get the corresponding result with lithium cyanide. W. Heike, and A. Vournasos did not observe any reaction between iron and fused potassium cyanide. L. Elsner observed that at ordinary temp. iron dissolves in a soln. of potassium cyanide, and hydrogen is evolved; and C. Reichard said that cyanogen is given off. M. Centnerszwer and J. Szper, and E. F. Kern observed that iron is dissolved in the electrolysis of soln. of potassium cyanide—*vide supra*, the passivation of iron. A. Brochet and J. Petit studied the action of soln. of potassium cyanide on metals under the influence of an alternating current. F. W. Bergstrom observed that a soln. of **ammonium cyanide** in liquid ammonia, with iron, forms a complex $(NH_4)_4[FeCy_6]nNH_3$; with mercuric cyanide, and with **ammonium thiocyanate,** under similar conditions, there is a very slow reaction; and with **mercuric thiocyanate,** the complex $Hg(CyS)_2.4NH_3$ is formed. When iron is heated with **potassium thiocyanate** it forms potassium ferrocyanide. N. Tananajeff and G. Tkatschenko found that an aq. soln. of the salt dissolves iron, forming ferrous thiocyanate. A. Brochet and J. Petit found that iron dissolves in a soln. of **potassium cyanate,** hydrogen is evolved, and potassium ferrocyanide is formed.

H. Adkins and W. R. Peterson found that **methyl alcohol** is oxidized to form aldehyde, using iron or iron-molybdenum as catalyst. W. Ledbury and E. W. Blair, and E. W. Blair and co-workers observed that a 10 per cent. soln. of **formaldehyde** readily reacts with iron in a sealed tube at 155°. Hence the danger of iron apparatus in the distillation of formalin. H. Will and F. O. Landtblom found iron and steel are not attacked by a dil. soln. of formalin, but a conc., 40 per cent. soln. readily attacks iron—possibly owing to the presence of some formic acid; W. Löb noted that a 20 per cent. soln. of formaldehyde slowly attacks iron. G. Batta found that the presence of a little formaldehyde in acids facilitates the dissolution of iron. H. Tropsch and O. Roehlen studied the catalytic decomposition of formaldehyde by iron, and A. Schellenberg, and H. Tropsch and A. Schellenberg, by **methanol.** J. Malmejac studied the action of 95 per cent. **alcohol** on iron; and the action of absolute alcohol on the metal was studied by L. Lindet, E. Boulanger, E. Heinzelmann, K. R. Dittrich, and M. Wawrziniok. S. P. Uspensky and N. I. Laduizhnikova found that with commercial ethyl alcohol, iron lost 29·9 mgrms. per sq. cm. in 9 months, and with commercial methyl alcohol, 43·6 mgrms. per sq. cm. in the same time; whilst with the vapour of commercial methyl alcohol, 7 mgrms. per sq. cm. were lost in 9 months' and with refined methyl alcohol, 6·7 mgrms. per sq. cm. in the same time. With **acetone,** iron lost 9·8 mgrms. per sq. cm. in 8 months. C. Dufraisse and R. Horclois studied the catalytic effect of iron on various organic compounds, sodium sulphate, etc.; and S. Swann, the electro-reduction of ketones at iron cathodes.

A. Hébert studied the action of **organic acids** on iron. A. Scheurer-Kestner, and K. A. Hofmann and G. Bugge found iron dissolves in **formic acid,** producing ferrous formate. H. J. Prins found that the attack is hastened if nitrobenzene be present. J. H. G. Monypenny found that mild steel lost 0·33 mgrm. per sq.

cm. per hr. in 10 per cent. formic acid. J. C. G. de Marignac observed that when iron is allowed to stand in contact with **acetic acid** for a few weeks, crystals of ferrous acetate are formed. The dissolution of iron by vinegars, and the corrosion of iron in the acetic acid industry, was observed by B. Franz, C. Luckow, A. Steinmetz, and W. Hoffmann; and H. Wieland and W. Franke studied the speed of rusting in dil. acetic acid. P. A. von Bonsdorff, and N. A. Bouchkoff noted the rapid corrosion of iron in the vapour of acetic acid and air. S. Leet noted the graphititis of cast-iron retorts in the distillation of vinegar—*vide infra*. According to W. Rohn, cold, 10 per cent. acetic acid dissolves in 24 hrs. 0·14 grm. per sq. dm. from the unannealed metal, and 0·21 grm. from the annealed metal at ordinary temp.; and with the hot acid, in 1 hr., 0·79 grm. was dissolved from the annealed, and 0·76 grm. from the unannealed metal. F. Schmitz observed that with steels containing 0·06, 0·42, and 0·92 per cent. of carbon, 20×20×10 mm. with a 4 mm. hole, the losses with 80 per cent. acetic acid were, respectively, 0·700, 0·584, and 0·886 grm. in 180 hrs. The action of acetic acid on iron was also studied by M. Ballay, W. Guertler and T. Liepus, A. Jouve, G. W. Whitman and R. P. Russell, P. Bardenheuer and K. L. Zeyen, P. Kötzschke and E. Piwowarsky, O. Kröhnke, and M. L. Hamlin and F. M. Turner. According to W. H. Hatfield:

				Steel			
	Electrolytic iron	Armco iron	Wrought iron	0·39 per cent. C	0·92 per cent. C	Steel 11·75 per cent. Mn	Cast iron 3·3 per cent. C
Wine vinegar . .	0·0061	0·0053	0·0139	0·0044	0·0042	0·0397	0·2640
Acetic acid, 33 per cent..	0·0128	0·0133	0·2810	0·2072	0·1697	0·0999	0·6693
Citric acid, 5 per cent. .	0·0106	0·0163	0·1943	0·2025	0·1843	0·0965	0·1950

J. H. G. Monypenny found that the losses of mild steel in mgrms. per sq. cm. per hour with 5, 15, and 33 per cent. acetic acid were, respectively, 0·067, 0·105, and 0·115; and with glacial acetic acid, 0·124. H. J. Prins found that the dissolution of iron in acetic acid is accelerated by the presence of nitrobenzene. The effects with various alloy steels (*q.v.*) were studied by J. H. G. Monypenny, W. H. Hatfield, O. K. Parmiter, H. S. Rawdon and A. I. Krynitsky, A. Fürth, and M. L. Hamlin and F. M. Turner. G. Arth observed that in dil. acidic soln. of **alkali acetate,** and a low current density, iron goes into soln., but at higher current densities the metal becomes passive. F. Wüst and N. Kirpach found the average losses per sq. cm. per hour with iron in an agitated 40 per cent. soln. of **monochloroacetic acid** were 0·10 mgrm. in the first 24 hrs., 0·16 mgrm. in the second 24 hrs., 0·14 mgrm. in the third 24 hrs. A. Renard observed that **propionic acid** dissolves iron, forming pale green crystals of the ferrous salt.

According to A. Hébert, **stearic acid,** and other fatty acids, when heated with iron to 350°, form ketones which decompose at that temp. The reaction was studied by A. Mailhe, T. H. Easterfield and C. M. Taylor, and G. Schicht and A. Grün, who assumed that the formation of a ferrous salt precedes the formation of the ketone. W. Singleton found that steel is corroded after standing 1000 hrs. at 80° in contact with stearic acid, whilst **oleic acid** at 60° and 80° did not corrode the metal. C. B. Gates obtained a similar result with oleic acid, but A. Gunn and E. F. Harrison found that at ordinary temp. iron is perceptibly attacked during a prolonged contact with oleic acid, and the acid is coloured dark red or brown. M. Welwart made analogous observations. E. Marazza said that wrought iron resists attack by the fatty acids better than steel or cast iron—*vide infra*, greases, and oils. Stainless steel was found by J. H. G. Monypenny to resist attack by oleic acid at ordinary temp. and at 60° for prolonged periods of time. C. B. Gates found that copper is precipitated by iron from a soln. of copper oleate, or from fused **copper palmitate, stearate,** or **margarate.** O. F. Hunziker and co-workers studied the action of **lactic acid** and milk on iron. F. Schmitz found that with **citric acid** (1 : 2) and samples of iron, 20×20×10 mm., containing 0·06, 0·42, and 0·92 per cent. of carbon, when the test-pieces had a 1 mm. hole, the losses were respectively 0·195, 0·370, and 1·842 per cent. in 180 hrs.; W. H. Hatfield's observations with 5 per cent. citric acid are indicated above. K. K. Järvinen also studied this subject. J. H. G. Monypenny found mild steel lost 0·260 mgrm. per sq. cm. per hour in 6 per cent. citric acid. T. N. Morris and J. M. Bryan noted that traces of a salt of tin inhibit the corrosive action of citric acid. V. Duffek, and A. Jouve studied the corrosive action of **tartaric acid**—*vide infra.* J. H. G. Monypenny found that mild steel lost, respectively, 0·062 and 0·14 mgrm. per sq. cm. per hour in normal and in 25 per cent. tartaric acid. A. Jouve studied the corrosive action of **oxalic acid.** O. Bauer and W. Mecklenberg observed that dil. oxalic acid has a mild action on iron and it forms a protective film of ferrous oxalate on the metal. J. H. G. Monypenny found that mild steel in a normal soln. of oxalic acid lost 0·036 mgrm. per sq. cm. per hour, and F. Wüst and N. Kirpach observed that the losses in mgrm. per sq. cm. per hour in cold sat. soln. of oxalic acid were 0·052 during the first 24 hrs., 0·070 during the second 24 hrs., and 0·060 during the third 24 hrs. V. Duffek studied the action of oxalic acid. F. W. Bergstrom observed that a soln. of **ammonium oxalate** in liquid ammonia acts very slowly on iron. R. Girard studied the attack by **carbolic acid** or **phenol**—*vide supra,* hydrochloric acid. J. H. G. Monypenny found that mild steel loses 0·005 mgrm. per sq. cm. per hour when in contact with 5 per cent. carbolic acid. F. Zetzsche and co-workers observed that the hydrogen of the OH-groups of some phenols can be replaced directly by iron when the soln. also contains some water. D. Müller, R. E. Lyons and L. T. Smith, G. Bunge, H. Kast, L. Loskiewicz, J. Saposchnikoff, and F. W. Richardson examined the action of **picric acid** on iron. According to H. Pomeranz, the nitro-groups of picric acid, in hydrochloric acid soln. in contact with iron, are reduced to amino-groups; the ferrous picrate first formed is rapidly oxidized to ferric picrate. F. Wüst and N. Kirpach found that the losses in mgrm. per sq. cm. per hour in a cold, sat. soln. of picric acid were 1·20 in the first 24 hrs., and 0·70 in the second 24 hrs.; after that, a protective film appeared on the metal. *Vide supra,* the etching of iron by picric acid and picrates, discussed by H. H. Shepherd, J. H. G. Monypenny, and Société Grauer et Weil. J. B. Trommsdorff observed that iron is very slightly soluble in an aq. soln. of **benzoic acid**; and S. Barilari, that **salicylic acid,** with iron filings, develops a little hydrogen, very slowly at ordinary temp. and more rapidly when warmed. F. Zetzsche and co-workers added that the evaporation of the soln. furnishes ferrous salicylate. W. J. Clark found that **gallic acid** forms ferrous gallate in contact with iron—*vide infra,* inks. M. Schirmonsky, and St. Reiner studied the action of **naphthenic acid** on iron.

According to S. Micewicz, **nitrobenzene** is readily reduced to aniline by powdered iron, and in an aq. soln. of magnesium chloride—the compound $2C_6H_5NH_2.MgCl_2.6H_2O$ is said to be formed at an intermediate stage of the reaction. S. G. Sastry, and H. W. Doughty examined the corrosion of metals by **organic halides.** L. Luuyt noted that soln. of **sugar** attack iron. According to D. Klein and co-workers, if iron is heated with a soln. of cane-sugar in a sealed tube at 115° to 125°, it is strongly attacked, and hydrogen is evolved. Some ferrous acetate is formed. Similar results were obtained with **invert-sugar** and **maltose,** but **glycerol** and **mannite** acted more slowly. J. H. Gladstone, C. Kosmann, A. Lodin, L. Kayser, J. H. G. Monypenny, D. Klein and A. Berg, I. McNiece, and K. K. Järvinen studied the corrosive action of soln. of sugar on iron at ordinary temp. If air is excluded, no action occurs. M. L. Hamlin and F. M. Turner found that **molasses** slowly attacks iron. J. A. N. Friend and co-workers, W. H. Hatfield, and J. H. G. Monypenny discussed the action on iron of organic colloids and **foodstuffs.**

P. H. Emmett and R. W. Harkness studied the catalytic decomposition of **azomethane, dimethylhydrazine,** and **ethylamine** by iron. L. Vignon, J. T. Wood, T. L. Phipson, and L. Manstetten examined the corrosive action of **tannin** on iron plates. J. I. Crabtree and G. E. Matthews observed that **hydroquinone,** and

pyrogallol developing baths are discoloured by iron; and they, and also E. Eule, examined the action of other photographic soln. on the metals. A. Benedicenti and S. Rebello-Alves found that powdered iron unites with the **protein** when shaken with a soln. of egg-albumin or blood serums. According to H. Handowsky, the oxidation of **leucine** is not affected when a 0·5 to 1·0 per cent. soln. is shaken in air or oxygen with ferrous sulphate, ferrosic oxide, ferric oxide hydrosols, and a mixture of iron and iron oxide obtained by heating the oxalate. Iron obtained by the hydrogen reduction of the oxide effects the oxidation of leucine with the production of carbon dioxide, ammonia, and isovaleraldehyde (isolated as the nitrophenylhydrazone). **Glycine, alanine, valine, tyrosine, histidine, formyl-leucine, and glycyl-leucine** are similarly oxidized by the reduced iron, yielding substances which give a positive fuchsine-sulphurous acid reaction. The oxygen uptake with leucine is never more than 19 per cent. of that required for complete combustion; and the oxidation is inhibited by hydrocyanic acid. When the heated reduced iron is cooled in nitrogen a black iron powder is obtained which has no oxidizing action on leucine, but if the inactive iron is reheated for some time and subsequently cooled in hydrogen, the oxidizing power is regenerated. Consequently, it is not the iron but the hydrogen dissolved in it which effects the oxidation of amino-acids, and the "active" hydrogen reacts with oxygen to give hydrogen peroxide which is catalytically decomposed on the surface of the iron. Similarly, animal charcoal loses its power to catalyze the oxidation of leucine when heated and cooled in nitrogen, but regains this power when reheated and cooled in hydrogen. The *active iron* was studied by O. Baudisch and L. A. Welo, and by A. Simon and K. Kötschau. It gives a blue colour in contact with an alcoholic soln. of guaiacum resin and hydrogen dioxide; and it also gives a blue colour with a soln. of benzidine—*vide* ferrous salts. J. C. Elgin and co-workers studied the effect of iron and nickel catalysts on the sulphur **naphthas** and **petroleums**; and K. A. C. Elliott, and N. W. Pirie, the catalytic action of iron in the oxidation of **cysteine,** and **thioglycolic acid.**

The corrosion of iron by the by-products in the manufacture of coal-gas was discussed by E. Donath,[13] P. Parish, W. E. Dennison, and A. R. Warnes and W. S. Davey; **coal-tar,** by F. J. R. Carulla; coal-tar fractions, by A. R. Warnes and W. S. Davey, U. Ehrhardt and G. Pfleiderer, W. A. Damon, W. E. Dennison, and F. Fischer; **liquid fuels**—gasoline, etc.—by E. K. O. Schmidt, S. H. Diggs, and K. R. Dietrich. According to A. R. Warnes and W. S. Davey, the dissociation of ammonium chloride, ammonium sulphide, ammonium hydrosulphide, ammonium cyanide, and the subsequent action of the dissociation products upon the iron are the chief causes of the corrosion, the rate of the action being probably increased by electrochemical conditions. Strain may have contributed towards corrosion by producing a certain amount of molecular instability in portions of the iron plates, thus rendering those parts more easy of attack. The final products into which the corroded iron is converted are chiefly ferrous sulphide and ammonium ferrocyanide. Ammonium chloride exerts a more corrosive action upon the iron than ammonium sulphide. The corrosive effects of **oil refining products** were studied by O. N. Edgar, G. Egloff, G. Egloff and J. C. Morrell, R. Lind, W. R. Finney and H. W. Young, R. R. Matthews and P. A. Crosby, R. V. A. Mills, H. F. Perkins, D. E. Pierce, H. Schmidt, F. W. L. Tydemann, and R. E. Wilson and W. H. Balke. B. Bleyer and J. Schwaibold determined the corrosion of iron by **tea** and **coffee** at 75° in grams of metal per sq. m. in 24 hrs., and found the losses to be:

Time	10″	1′ 10″	5′ 10″	42′ 30″	2·5 hrs.	5 hrs. 40′	22 hrs. 40′
Tea	42·5	42·5	35·0	18·0	15·0	6·3	5·0
Coffee	16·3	17·5	15·0	11·3	5·5	4·5	5·0

The corrosion of iron by coffee vapours was studied by R. Evans. G. N. Quam[14] found chrome-steel suffered no perceptible loss after 30 mins'. contact with **milk.** The corrosion of iron by **beer** was studied by J. Brand, L. Nathan, and H. Seyffert;

wood, by F. C. Calvert, and P. Rohland; flour **paste,** by T. Thomson; by **inks,** by O. Bauer and W. Mecklenberg; by **gunpowder,** by E. H. Schulz, and A. Wright; by **tanning liquors,** by A. Gansser, and M. P. Balfe and H. Phillips; by **india-rubber,** by C. O. Weber, and W. Thomson and F. Lewis; by **paper,** by P. Klemm; and by **perspiration,** by W. J. Huff, and H. E. Yerbury.

Corrosion may be hindered or inhibited by **grease** which acts by preventing water from coming in contact with the metal and thus suppressing one of the conditions necessary for corrosion. Thus grease may be associated with water in the form of an emulsion. Many forms of grease and oil are really salts of organic acids. Thus, olive oil is a glyceryl oleate which forms glycerol and oleic acid when hydrolyzed by water. The glycerol was found by D. Klein and A. Berg[15] to have no action on iron, but the organic acids slowly attack the iron, forming, say, ferrous oleate, which is decomposed by the oxygen of the air to form hydrated ferric oxide and oleic acid. E. A. Cowper emphasized the deleterious effects of the conversion of common grease into acid grease in boilers; and J. Stingl, and F. J. Rowan, the corrosive effects produced by the introduction of greasy water into boilers. The action of lubricating oils on metal was discussed by S. Aisinmann, A. H. Allen, P. T. Bruhl, P. Cuypers, J. Dewrance, S. Reiner, E. Donath, W. R. Finney and H. W. Young, M. Cook and U. R. Evans, C. Fichandler, J. A. N. Friend, J. E. Hackford, H. von der Heyden and K. Typke, W. J. Huff, A. F. Meston, W. Singleton, H. Schmidt, H. G. Smith, H. Spurrier, C. W. Volney, and H. J. Young; and of liquid fuels, by K. R. Dietrich. H. von der Heyden and K. Typke discussed the action of transformer oils in iron; R. E. Wilson and W. H. Balke, and H. F. Perkins, the corrosion of iron in oil refineries; E. K. O. Schmidt, M. Wawrziniock, and H. J. Young, the corrosive effect of motor oils; F. G. Hoffmann, the corrosive action of tar and benzene vapours; Wo. Ostwald, benzene; and F. Schuster, naphthalene and the protective action of tetralene, $C_{10}H_{12}$.

The **drying oils** employed in the manufacture of paint exert very little solvent action on iron. W. H. Watson's observations on the marked effect of linseed oil in 24 hrs. are so different from those of W. Marcey, and J. A. N. Friend, that it is probable that the oils he employed were very impure. W. Marcey observed no action during 3 days' exposure of iron to linseed oil, and J. A. N. Friend observed no action with raw linseed oil, poppy oil, and tung (or Chinese wood) oil when alternately heated to 100° and cooled for 12 days; also when the iron was exposed to the action of the oil for 5 months. The metal always remained bright. With boiled linseed oil, the metal was dulled in every case, and the slight loss through the solution of the iron was more or less counterbalanced by the gain due to oxidation. L. L. Steele studied the effect of iron soaps on the drying of linseed oil. W. Marcey found that with 10 days' exposure to the action of **non-drying fatty oils,** there was a loss of 0·0025 grm. with 2·1830 grms. of iron with olive oil; and with this as an arbitrary standard of 100, the solvent action with sperm oil was 48; with neatsfoot oil, 44; with cotton-seed oil, 36; with castor oil, 28; with lard oil, 20; with almond oil, 16; and with rape oil, none. R. M. Corelli studied the action of castor oil on several metals. A. E. Tucker found that with 500 c.c. of oil acting on iron for 26 hrs., the following amounts of metal dissolved: sperm oil, 0·0370 grm.; lard oil, 0·0120 grm.; olive oil, 0·0314 grm.; castor oil, 0·0034 grm.; valvoline, nil; cylinder oil of sp. gr. 0·921, trace; and lubricating oil of sp. gr. 0·915, a trace. I. J. Redwood found the following percentage losses of metal during 12 months' action at atm. temp. with mineral lubricating oil, 0·02693; olive oil, 0·17187; rape oil, 0·04418; tallow oil, 0·20603; lard oil, 0·11111; cotton-seed oil, nil; sperm oil, 0·09210; whale oil, 0·12279; seal oil, 0·01539. Signs of rusting occurred with the tallow, lard, cotton-seed, and seal oils. D. Holde also examined the action of some lubricating oils on plates of iron 30 mm.×4 mm. in an autoclave at 10 atm. press. for 2, 4, and 6 hrs., with light mineral oil the losses were respectively, 3, 3, and 4 mgrms.; with heavy mineral oil, 4, 4, and 4; with raw rape-seed oil, 0, 5, and 41; with refined rape-seed oil, 1 to 15, 12·5 to 66, and 118 to 205; and with tallow, 0, 21, and 168. R. M. Corelli examined the action of castor oil on metals; S. Macadam, and C. Engler, the action of petroleum, and paraffin oils; G. Egloff, oil-refining products; and Wo. Ostwald, the action of benzol. A. Boutaric and R. Amiot measured the adhesion of lubricating oils to iron.

For the action of **silicon,** *vide* the silicides—**6.** 40, 13; and *vide infra*, Fe-Si alloys. F. Osmond[16] observed that as the proportion of silicon increases, the conversion of α- to β-iron is retarded, and with 2 per cent. of silicon, the conversion is practically zero; the arrest in the cooling curve A_2 at 730°—720° takes place at 710°—700°; and the arrest A_1 at 660°—650° is raised to 710°—700° —*vide infra*, the silicon steels. H. Hanemann found carburized iron reduced silica from **fireclay** crucibles to silicon. L. Troost and P. Hautefeuille observed a siliceous rock rapidly attacked cast iron at an elevated temp. A. Becker and H. Salmang did not observe any reaction with **glass** and iron of a high degree of purity at 1450°, although with ordinary iron containing carbides and silicides there is a reaction. U. R. Evans found that a soln. of **sodium silicate,** like other alkaline soln., retards the corrosion of iron. E. Vigouroux represented the reaction with **silicon tetrachloride** at a high temp.: $SiCl_4+4Fe=Fe_2Si+2FeCl_2$. The reaction was studied by G. Rauter, and H. E. Patten. H. zur Strassen applied the mass law to the action of iron on **nickel silicate**: $Fe+NiSiO_3 \rightleftharpoons Ni+FeSiO_3+7{\cdot}6$ to 9·5 Cals., and found that for the equilibrium constant in $[Fe][NiSiO_3]=K[Ni][FeSiO_3]$, $K=6{\cdot}53\times10^{-3}$ at 750° K., and $7{\cdot}25\times10^{-3}$ to $7{\cdot}44\times10^{-3}$ for $T=1840°$ K. W. Heike represented the reaction with **ferrous silicate**: $3Fe+FeSiO_3 \rightleftharpoons 3FeO+FeSi$. G. Tammann and H. Bohner observed that iron precipitates 58 per cent. of the nickel from the slag, $CaO.NiO.2SiO_3$. O. Ruff and R. Ipsen observed that at a red-heat, **titanium tetrafluoride** is reduced by iron; and L. Lévy, that **titanium tetrachloride** is not decomposed by iron at a red-heat. H. E. Patten observed that iron is not corroded by **stannic chloride**. For the action of **boron,** *vide* the borides **5.** 32, 4. Iron containing boron was found by F. Osmond to behave like iron with carbon in that the arrest A_3 is lowered from 855° to 805°, and partly at 735° to 725°, or becomes coincident with A_2—*vide infra*, the action of copper. H. Moissan found that **boron trichloride** acts on iron at a red-heat, forming ferrous chloride and ferroboron.

The action of iron on the **metals** is discussed in connection with the alloys and intermetallic compounds. K. A. Hofmann and H. Hiendlmaier[17] found that iron is readily attacked by burning **potassium.** W. G. Imhoff, E. J. Daniels, and C. Diegel found that molten **zinc** at galvanizing temp. readily attacks cast and malleable iron, and that the presence of chromium and nickel does not make the metal more resistant; R. Perrin said that interpenetration occurs when steel is heated in contact with **bronze**; R. Genders, with **brass**; and C. E. Schwartz, with **lead.** L. Hackspill observed that at 1400°, under a press. of 0·1 mm., **lithium oxide** is reduced by iron to form lithium. G. Tammann and E. Kordes found that **copper oxide** can react with iron in the solid state, at 610°, and B. Garre observed that when a mixture of powdered iron and copper oxide is compressed and heated to 700°, the tensile strength rises from 7·0 to 46·8 kgrms. per sq. cm., and it is supposed there is a diffusion from iron to copper oxide and conversely. J. E. Stead also found that cupric oxide is reduced by iron at 780° to form copper. H. Moissan found that molten **calcium oxide** rapidly attacks iron. According to G. Tammann, G. Tammann and E. Kordes, and D. Balareff, iron reacts with **lead oxide** in the solid state at 460°. G. Tammann and E. Kordes observed that **tungstic oxide** reacts with iron at 300° to 340°. L. A. Hallopeau found that molten **lithium tungstate** dissolves iron. M. Billy found that **ferric oxide** is reduced to a lower oxide when heated with iron; **ferrosic oxide** under similar conditions reacts at 570°, and the reaction was studied by L. B. Pfeil. B. Garre found that **nickel oxide** reacts with iron at 640°, and the reaction was studied by J. E. Stead. H. zur

Strassen represented the action of nickel oxide on iron by the equation: $Fe+NiO=Ni+FeO+6{\cdot}4$ to 14·2 Cals.

The early workers, J. L. Gay Lussac and L. J. Thénard, H. St. C. Deville, and H. Debray observed that at an elevated temp., iron reduces the **alkali hydroxides** to the corresponding metal. L. Hackspill and co-workers observed that iron displaces the alkali metals, excepting lithium, from sulphates and arsenates at their m.p.; from thiocyanates at 650°; from borates and phosphates at about 1400°; and from the aluminates at the m.p. of iron. Lithium is formed from the oxide or silicate at 1300°. Potassium sodium and lithium hydroxides are reduced: $2Fe+3KOH\rightleftharpoons Fe_2O_3+1\frac{1}{2}H_2+3K$, the reaction with potassium hydroxide begins at 500°, and at 600° to 650°, 70 to 80 per cent. of the hydroxide is reduced to metal, they also obtained potassium and sodium by heating the alkali hydroxide with iron and coke.

A. Scheurer-Kestner found that fused alkali hydroxide rapidly attacks iron, particularly under the influence of pressure wrought iron is more rapidly attacked than cast iron. C. E. Groves found that solid potassium hydroxide, with 5 per cent. of water, and fused at a gentle heat, attacks steel readily under conditions where the action of sodium hydroxide is much less. W. Venator observed that different kinds of iron—cast iron, wrought iron, steel, and forged iron—were strongly attacked by boiling soda-lye, and hydrogen was given off. Commercial sodium hydroxide was employed, and pieces of metal of 32 sq. cm. surface area and weighing nearly 50 grms., were submerged in the alkali. The alkali was contained in a silver vessel which exerted no electrolytic action on the iron. The following losses were observed, under similar conditions:

	Fused NaOH		80 per cent.-lye	46 per cent.-lye	20 per cent.-lye
	400°	350°	200°	150°	150°
Cast iron . . .	0·1969	0·1568	0·3680	0·0345	0·0000
Wrought iron . .	0·1660	0·0348	—	0·1928	0·0723
Steel	0·2072	0·0193	0·1422	0·1322	0·0133

The results show that the action of the fused alkali is intensified by a rise of temp.; the effect of dilution is to reduce the action on cast iron so that with a 20 per cent. soln. at 150° no perceptible action was observed. According to M. le Blanc and O. Weyl, fused potassium hydroxide attacks iron appreciably between 550° and 660°, but evidence that potassium or hydrogen are formed is lacking; in the case of fused sodium hydroxide between 400° and 720°, the evolution of hydrogen and the formation of water were taken by M. le Blanc and L. Bergmann to prove that a compound $Fe(ONa)_n$ is formed. The dehydration of sodium hydroxide which occurs at 400°, and the stability of the products at temp. up to 720°, show that the formation of water cannot be due to the simple reaction: $2NaOH=Na_2O+H_2O$. The action of fused alkali hydroxides on different forms of commercial iron was studied by R. Rossberg, C. Föhr, and A. Scheurer-Kestner. W. Hentschel observed that at a red-heat iron does not act on sodium hydroxide with up to 1 per cent. of water, but if 1 to 4 per cent. of water is present, the action is turbulent, but the action is mild at temp. below a red-heat. A. Thiel and H. Luckmann noted that with 25 grms. of iron powder and $0{\cdot}01N$-NaOH, at ordinary temp., 0·01 c.c. of hydrogen is evolved per hour. The subject was studied by J. Woost, and F. Haber and L. Bruner. J. M. van Bemmelen and E. A. Klobbie said that the primary reaction is the formation of sodium ferrite, $Na_2O.Fe_2O_3$. St. Meunier noted the formation of a ferrate when the fused alkali hydroxide attacks the metal in air. The action of fused sodium hydroxide on iron and steel was also discussed by W. Dittmar, T. Wallace and A. Fleck, H. Ostermann, H. Brunck and C. Graebe, A. Fry, J. A. Jones, J. H. Andrew, H. E. Balsford, M. L. Hamlin and F. M. Turner, J. L. Everhart, and H. F. Whittaker.

A. Payen, and A. Wagner found that dil. alkali-lye retarded the rusting of iron at ordinary temp., and G. Lunge found that while a 10 to 20 per cent. soln. of soda-lye has a slight action, a 50 per cent. soln. attacks the metal strongly. E. Heyn and O. Bauer found a maximum attack occurs with a conc. of 0·0025 mols. per litre, or 0·1 grm. per litre; as the conc. of the soln. increases, the action is lessened, so that with 1 grm. per litre there is scarcely any action at all. F. N. Speller and C. R. Texter did not get a maximum in the curve; within the limits 0·005 to 1·05 grm. per litre, *i.e.* in the p_H interval 8·4 to 12·8, the corrosion decreases with the alkalinity of the soln. G. W. Whitman and co-workers suggest that the maximum with experiments in open vessels is due to the action of atmospheric carbon dioxide. The formation of a protective skin on the metal was discussed by F. Haber and F. Goldschmidt, and W. R. Dunstan and J. R. Hill—*vide supra,* passivity.

The action of soln. of alkali hydroxides is discussed in connection with the corrosion of iron and steel. J. A. N. Friend observed that the corrosion of wrought iron or steel in dil. soln. of the alkali hydroxides, like $0·02N$-NaOH or $0·02N$-NH_4OH is prevented, and cast iron acquires a thin film of a bronze-coloured oxide. T. Turner found that whilst acids attack the ferrite and leave the graphite, cementite, and phosphide of cast iron, conc. alkali-lye leaves the ferrite and attacks the carbide of a pearlite. J. C. Poggendorf, F. Haber, and W. Pick showed that when iron is made the anode in alkali-lye, cast iron is more readily attacked than other forms of iron, and that when iron is boiled gently in conc. soda-lye, ferrous oxide passes into soln., and on exposure to air, ferric oxide is precipitated—*vide infra,* the ferrites. If iron is made the anode in a conc. soln. of soda-lye or potash-lye, using a low current density—say, 0·001 amp. per sq. cm.—alkali ferrate is formed. Soda-lye acts more rapidly than potash-lye because of the greater solubility of sodium ferrate. At 100°, A. Thiel and H. Luckmann found that 0·01 to $0·1N$-NaOH attacks iron less than does distilled water, and the reaction rapidly slackens as a protection skin is formed on the metal. In an autoclave at 200°, the protective oxide film is continuously dissolved. E. Berl and F. van Taack found that at 1000 atm. press. and 310°, a maximum attack occurs with $0·02N$-NaOH (0·8 grm. per litre). E. Berl and co-workers found that soda-lye with 0·5 to 5·0 grms. per litre and at press. up to 50 atm. exerts only a small action on iron, but the action increases with rising temp. and press.; soln. with 100 to 400 grms. of sodium or potassium hydroxide per litre have a deleterious action on the mechanical properties of iron. The presence of atm. oxygen does not strengthen the attack by conc. alkali-lye. With 10 grms. of powdered iron, after 16 hrs.' action, at 50 atm. press.:

NaOH . .	0·55	1·15	2·17	3·0	5·4	11·80 grms. per litre
Hydrogen .	60	100	170	175	370	550 c.c.
Fe . .	99·01	99·28	99·32	99·07	99·12	98·10 per cent.
FeO . .	0·17	0·37	0·34	0·50	0·52	1·32 ,,

No ferric oxide is formed. With lye containing 1·15 grms. per litre:

Pressure .	30	50	80	100	150	200 atm.
Hydrogen .	Small	100	240	270	320	410 c.c.
Fe . .	99·48	99·30	99·38	98·70	97·25	91·08 per cent.
FeO . .	0·13	0·10	0·10	0·29	0·82	7·25 ,,
Fe_2O_3 . .	—	—	—	—	0·11	0·82 ,,

The variations in the degree of oxidation with press. and conc. of lye are plotted in Fig. 362. The reaction can be symbolized by $Fe+NaOH+H_2O=HO.Fe.ONa+H_2$, followed by $HO.Fe.ONa+H_2O=Fe(OH)_2+NaOH$; or $Fe+2NaOH+H_2O=HO.Fe(ONa)_2+1\frac{1}{2}H_2O$, followed by $HO.Fe(ONa)_2+2H_2O=Fe(OH)_3+2NaOH$. W. Dittmar, G. Zirnite, C. H. Cribb and F. W. F. Arnaud, M. V. Pershke and L. Popova, J. L. Everhart, F. N. Speller and C. R. Texter, H. F. Whittaker, C. E. Stromeyer, P. D. Merica, M. L. Hamlin and F. M. Turner, J. H. Andrew, F. Lyon, E. Heyn and O. Bauer, and A. J. Hale and H. S. Foster examined the effect of aq. soln. of the alkali hydroxide on iron. The utilization of the facts in alleviating the attack of water on boilers was discussed by R. Baumann, E. Berl and co-workers, R. E. Hall and co-workers, G. Neumann, S. W. Parr and F. G. Straub, A. Splittgerber, F. G. Straub, R. Stumper, A. Thiel and co-workers.

F. Schmitz found that with 0·06, 0·42, and 0·92 per cent. carbon steel, 20×20×10 mm. with a 4 mm. hole, the losses in potash-lye (1 : 2) were 0·000 per cent. during 180 hrs.' attack. J. A. Jones observed that cracks develop in mild steel plates in soln. of potassium hydroxide, and this was attributed to the action of the alkali on the intercrystalline cement—*vide infra*. T. Geuther discussed the formation of hydrogen by heating powdered iron with **calcium hydroxide.** E. Heyn and O. Bauer found that calcium hydroxide, even in dil. soln., passivates iron, and they observed no maximum in the curve representing the effect of varying the concentration of the soln. The retarding action of calcium hydroxide soln. was discussed by C. Bücher, and M. Groeck. St. Meunier found that in the presence of calcium, barium, or magnesium oxide, iron forms a ferrate when heated in air with sodium hydroxide. W. Heike studied the reaction with **manganese oxide :** $Fe+MnO \rightleftharpoons FeO+Mn$. W. Krings and H. Schackmann studied the equilibrium in this system at 1550° to 1560°, and observed that $K=[Mn][FeO]/[Fe][MnO]$ is 0·0032 when concentrations are taken in percentages.

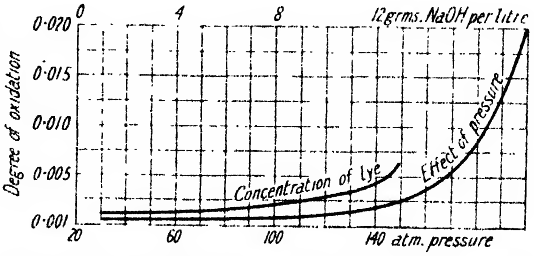


FIG. 362.—The Effect of Pressure and the Concentration of the Soda-Lye on the Oxidation of Iron.

The corrosive action of soln. of many **metal salts** is discussed in connection with the corrosion of iron and steel—*vide infra*. H. Krause[18] studied the colouring of fused salts by iron and its alloys. T. Peczalsky found that iron increases in volume and electrical resistance if it be heated in the presence of salts, although no reaction occurs. L. Hackspill and R. Grandadam observed that when iron and **alkali fluorides** are heated in vacuo to 1000°, a reaction : $Fe+2KF=FeF_2+2K$ takes place. The reaction with sodium fluoride was tried industrially for the preparation of sodium by the Société d'Electrochimie. L. Hackspill and R. Grandadam found that with the **alkali chlorides**—potassium, rubidium, cæsium, and sodium chlorides—the reaction is symbolized : $Fe+2KCl=FeCl_2+2K-115\cdot9$ Cals. L. Hackspill did not obtain the corresponding result with lithium chloride. M. E. Chevreul observed that sodium and potassium chlorides are decomposed by iron in a moist atmosphere. A. Sanfourche observed no reaction between molten or vaporized sodium chloride. A. M. Portevin, and L. Hackspill and E. Schwarz studied the decarburization of iron by the alkali chlorides, whilst L. Hackspill and R. Grandadam observed that **alkali bromides,** and **alkali iodides** behaved like the corresponding chlorides towards iron. F. Streintz observed that iron has no action on potassium iodide test paper.

A. E. Dolbear found that **potassium sulphide** at a red-heat is reduced by iron to form potassium. E. Heyn and O. Bauer found that iron rusts in dil. soln. of **sodium sulphide,** but not when the concentration exceeds $0\cdot1N$-Na_2S. G. Lunge observed a black film is formed on the iron dipped in conc. soln. of the sulphide. B. Garre observed no reaction when iron is heated with solid **sodium sulphate,** but A. Gorgeu observed a brisk evolution of sulphur dioxide when iron is added to the molten salt ; sodium oxide and sulphite, and a double sulphide of sodium and iron are formed, but with a more protracted heating the sulphide and sulphite disappear. When the product is washed with water, ferrosic oxide remains. The reaction was studied by A. d'Heureuse, and A. Stromeyer. According to F. Projahn, iron in the absence of air, reacts with the heated sulphate, in accord with the probable equation : $Na_2SO_4+3Fe=Na_2O+FeS+Fe_2O_3$; and L. Hackspill and R. Grandadam represented the reaction in vacuo by the equation : $2Na_2SO_4+3Fe=Fe_2O_3+2FeS+5O+4Na$. The reaction occurs at 900°, and with potassium sulphate, at 1000°. There is an intermediate formation of ferrous sulphate ; L. Hackspill did not observe the reaction with lithium sulphate. The Société d'Electrochimie proposed to utilize the reaction for the preparation of sodium. O. Pettersson and A. Smit, and M. Websky observed that in the reaction with steel, **potassium hydrosulphate** forms ferric sulphate, oxidizes the carbon to carbon dioxide, and leaves the graphite untouched. L. Hackspill and R. Grandadam found that in vacuo the **alkali carbonates** react with iron in accord with $2Na_2CO_3+2Fe=Fe_2O_3+CO_2+CO+4Na$. Almost all the sodium carbonate is reduced in 2 hrs. at 1000°. B. Garre observed that solid sodium carbonate reacts with iron at a high temp., and E. Deiss, that powdered iron reacts with the molten salt. J. E. Fletcher studied the action of **sodium carbonate** on cast iron.

According to J. J. Berzelius, an aq. soln. of **copper chloride** extracts all the iron from cast iron leaving behind the whole of the carbon mixed with copper. R. Böttger found much heat is developed when anhydrous cuprous or **cupric chloride** is reduced with powdered iron and wetted with water, and G. Tammann observed a vigorous reaction when iron is added to molten cuprous chloride; and the reaction was studied by C. B. Gates. According to W. Eidmann, iron reduces a soln. of cupric chloride in acetone; and, according to A. Naumann, and E. Alexander, a slow reaction occurs with a soln. of cupric chloride in ethyl acetate. The precipitation of copper from soln. of **copper salts** by iron has been discussed in connection with copper—**3**. 21, 3. Observations on the subject were made by R. M. Caven, and G. L. Oldbright and co-workers. The precipitation has been used in a wet process for the extraction of copper. J. C. Essner found that the structure of the iron employed exerts a marked influence on the form of the copper obtained, so that by selecting suitable iron it is possible to obtain the reduced copper in a fibrous or granular condition. The formation of a mud of hydrated ferric oxide is prevented by the presence of a little sulphuric acid. With dil. soln. of copper salts F. Mylius and O. Fromm, and G. Tammann observed that some hydrogen may be developed, and the iron is associated with the precipitated copper. J. B. Senderens found that the deposition of copper from soln. of cupric nitrate, by iron, is rather slow at ordinary temp., with soln. of medium concentration the gases evolved contain 80 per cent. of nitrogen peroxide and 20 per cent. of nitrogen with some nitric oxide at the beginning; the precipitated copper contains some ferric hydroxide, and the soln. contains ammonium and ferrous nitrates. D. Tommasi found that the precipitation from soln. of cupric chlorate is only partial; J. B. Senderens, that no copper is precipitated from soln. of the acetate; and C. B. Gates, that copper is precipitated by iron from soln. of copper salts of many organic acids.

H. Forestier observed that the rate of dissolution of 99·86 per cent. iron immersed for 10 mins. in a 2 to 12 per cent. soln. of cuprous chloride at 15° increases with the magnetic field up to 4500 to 5000 gauss, after which it remains constant. The rate of dissolution is tripled for 2 per cent. soln., but the stimulating effect of the magnetic field decreases with the conc. of the reagent up to 8 per cent., and then remains approximately constant. Copper sulphate soln. act similarly but the effect is less marked, possibly owing to the formation of a protecting layer of copper. T. Andrew found that magnetized iron dissolves in a soln. of cupric chloride about 3 per cent. more quickly than the same iron not magnetized; and C. M. Kurtz and R. J. Zaumeyer studied the subject. A. A. Blair discussed the dissolution of steel in a soln. of copper sulphate, and E. Goutal, by feebly acidified soln. with 40 per cent. potassium cuprous chloride. K. Ulsch utilized the reduction of nitrites or nitrates to ammonia by an iron-copper couple for the determination of these salts in soln.; and D. Tommasi also reduced chlorates to chlorides. The iron-copper couple was obtained by the action of *ferrum hydrogenio reductum* on a soln. of copper sulphate. The decomposition of **cuprous sulphide** by iron was studied by O. Reuleaux; and B. Garre found that **cupric sulphide** is reduced at 400°, and that the thermal value of the reaction is 11·4 Cals. F. P. Treadwell observed that in the presence of powdered iron, the sulphides, insoluble in dil. acids, in a current of carbon dioxide, and at a dull red-heat, form ferrous sulphide. According to

J. J. Berzelius, **silver chloride** is reduced when in contact with cast iron under water acidified with hydrochloric acid; and C. J. B. Karsten said that the iron is dissolved, leaving a residue of silver and graphite, and iron carbides. C. B. Gates studied the reaction. The reduction of **silver salts** by iron was discussed in connection with silver—**3.** 22, 5. G. Tammann found that iron acts slowly on molten silver chloride. C. J. B. Karsten, and J. Percy studied the reduction of molten **silver sulphide** by iron. J. B. Senderens observed that unworked iron is far more active in precipitating silver from dil. soln. of silver nitrate than is the case with worked iron. The difference is attributed to a difference in the physical condition of the different forms of iron. W. Heldt said that the precipitation from silver nitrate soln. is slower the more conc. the soln. Steel acts more slowly than iron. The silver separates more slowly from ammoniacal than from neutral soln., and some ferric salt is formed. J. B. Senderens added that iron goes into soln. faster than the silver is precipitated, and some nitrites are formed. The reaction was also discussed by J. S. de Benneville, and by N. Schilow. F. Mylius and O. Fromm, and G. Tammann found that the precipitated silver always contains some iron. V. Lenher studied the precipitation of gold from soln. of **gold chloride** by iron. F. Mylius and O. Fromm, and G. Tammann found that the gold is always contaminated with iron.

A. M. Portevin, and L. Hackspill and E. Schwarz discussed the decarburization of iron (*q.v.*) by the **alkaline earth chlorides.** C. B. Gates said the molten calcium chloride does not act on iron. A. d'Heureuse observed that the **alkaline sulphates** at a red-heat react with iron, forming ferrous sulphide, and ferrosic and ferric oxides. R. Finkener, and G. Hilgenstock obtained with calcium sulphate at a white-heat in an evacuated tube, ferrous sulphide and lime. F. Martin and O. Fuchs observed that in a current of nitrogen, calcium sulphate reacts with iron at 750°, strontium sulphate at 850°, and barium sulphate at 950°, forming respectively $3CaO.2Fe_2O_3$, $2SrO.Fe_2O_3$, and $BaO.Fe_2O_3$. According to L. A. Bhatt and H. E. Watson, when the mixture $3CaSO_4+8Fe$ is heated in a current of nitrogen at 950°, for 5 hrs., 46·6 per cent. of the original sulphur remains as $CaSO_4$; 13·9 per cent. forms $CaS+FeS$; 28·2 per cent. as SO_2; 2·5 per cent. as SO_3; and 8·6 per cent. as sulphur. An excess of silver retards the reaction. F. Hundeshagen observed the formation of magnesium ferrite when iron acts on **magnesium chloride** melted in its water of crystallization, but B. Garre observed no reaction with anhydrous magnesium chloride at a high temp. For the action of aq. soln. of magnesium chloride on iron, *vide infra.* S. Micewicz found that the speed of decomposition of aq. soln. of sodium, potassium, calcium, and magnesium chloride increases in the order named. T. Petitjean recommended reducing **magnesium sulphide** by iron in order to prepare magnesium, but F. G. Reichel did not succeed with the process. A. Mourlot said that at a dark red-heat magnesium sulphide is not decomposed by iron. B. Garre studied the reaction between iron and **magnesium sulphate** at an elevated temp.

C. J. Reed, and W. M. Camp found that iron is attacked only slightly by a soln. of **zinc chloride,** in contrast with the attack by a soln. of sodium chloride. N. N. Jefremoff and J. M. Jakimez found that ferrosilicons are more resistant. G. Tammann studied the action of iron on molten zinc chloride. C. A. Graumann found that metallic iron in a reducing atmosphere attacks **zinc sulphide,** forming iron sulphide and zinc. H. Heinrichs observed that a mixture of **cadmium sulphate** and iron in a crucible at 900° yields a mixture of cadmium and ferrous sulphides. R. Varet observed the slow reduction of soln. of **mercuric chloride** to mercurous chloride by iron; and R. Böttger noted that with a boiling soln. some mercury or amalgam is formed. E. Alexander, and A. Naumann found that iron precipitates ferrous and mercurous chlorides from a soln. of mercuric chloride in ethyl acetate; W. Eidmann, and A. Naumann obtained a similar precipitate from a soln. in methylal; and A. Naumann, from a soln. in benzonitrile; R. Varet observed that iron produces no change in a soln. of mercuric chloride in pyridine, but if water is added, and the soln. warmed, mercury, mercurous chloride, and oxidized iron are formed. W. Guertler and T. Liepus noted that a 1 : 500 soln. of mercuric chloride is unstable in contact with iron. The reaction was studied by V. Majer. G. F. Hildebrandt found that when iron is heated with **mercuric sulphide**, mercury and ferrous sulphide are formed.

F. C. Calvert and R. Johnson observed that iron aluminides are formed when **aluminium chloride** is passed over red-hot iron. T. Petitjean recommended reducing **aluminium sulphide** with iron in order to prepare aluminium, but F. G. Reichel did not succeed with the process. L. Hackspill observed that when heated with iron in vacuo, **alkali aluminate** furnishes the alkali metal.

The reduction of tin from soln. of **tin salts** by the addition of iron has been previously discussed—**7**. 46, 5. N. W. Fischer found that tin is not usually precipitated by iron from soln. of stannous chloride, and the reduction of stannic to stannous salts was discussed by C. Tookey, J. Attfield, W. L. Clasen, etc., with dil. acidic soln. A. Thiel and K. Keller, and J. Thiele found that some tin may be precipitated. B. Schultze added that tin is slowly and completely precipitated from neutral soln. if ferrum reductum be employed as reducing agent. Air should be excluded. The subject was discussed by N. Bouman, and J. M. Kolthoff. According to A. Thiel and K. Keller, the fact that when iron is added to a soln. of the chlorides of tin and antimony, only antimony is precipitated, is in contradistinction to the position of iron and tin in the electrochemical series. Tin is actually precipitated, but only in very minute quantity, forming a very thin protecting layer of a tin-iron alloy on the surface of the iron. Iron dissolves much less rapidly in an acid if a tin salt is present. If iron is introduced into a vessel containing a conc. electrolyte, and tin in the lower part, and a more dil. electrolyte free from tin in the upper part, the iron becomes covered with crystals of tin where it dips into the conc. electrolyte, but remains free from tin if immersed completely in either the conc. or the dil. soln. G. Tammann found that iron slowly acts on molten stannous chloride. H. Biltz and V. Meyer found that iron is strongly attacked by the vapour of stannous chloride ; H. E. Patten found that iron is not affected when placed in liquid stannic chloride or in a hydrochloric acid soln. of that salt. The Chemische Fabrik Buckau reported that in the cold, the vapour of stannic chloride warms up iron, particularly if some chlorine be present ; the metal becomes very hot if the temp. at the start be 100°. chlorine alone begins to act on iron at about 300°. The reduction of lead from soln. of **lead salts** by iron was discussed in connection with lead—**7**. 47, 3. G. L. Oldbright and co-workers observed that lead is precipitated from a soln. of lead chloride by iron, but D. Tommasi, and H. Schiff noted that lead chlorate soln. are not so reduced. L. Taricco observed that lead is deposited on iron from alkaline soln. of lead cyanide. G. Tammann observed that some lead separates when iron acts on molten lead chloride. The decomposition of lead sulphide by iron was studied by J. Fournet, J. Percy, W. Guertler, and H. von Jüptner. B. Garre said that the reaction occurs at 390°, and that the thermal value of the reaction is 2·2 Cals. N. W. Fischer found that at a red-heat iron and carbon reduce **lead sulphate** to lead. G. Tammann and E. Kordes found that solid lead sulphate and iron react vigorously. The reaction begins at 540°, and the thermal value of the reaction is less than 11 Cals.

F. A. Abel and W. A. Deering found that conc. soln. of **chromic acid** dissolve steel. The kinetics of the dissolution of iron by chromic acid were studied by R. G. van Name and D. U. Hill. According to W. R. Dunstan and co-workers, iron can be kept bright in a soln. of chromic acid for 10 years, but W. Moody found that there is a slow dissolution ; and R. G. van Name and D. U. Hill observed that with chromic acid in the presence of an excess of sulphuric acid, iron is rapidly corroded. J. A. N. Friend found that dil. soln. of chromic acid had no perceptible action on cast iron during 14 years' exposure in sealed tubes. U. R. Evans observed that with soln. containing *n* mols. per litre of the acids, the average losses in weight during 6 hrs. at 14°, were :

H_2SO_4 .	0·05	0·05	0·05	0·05	*Nil*	0·02	0·05	0·09
CrO_3 .	*Nil*	0·005	0·01	0·02	0·01	0·01	0·01	0·01
Loss .	9·7	25·9	42·7	77·9	0·2	38·2	42·7	55·8

So that chromic acid, in virtue of its strong oxidizing and weak base-dissolving properties, produces passivity by the formation of a protective film when present alone, but stimulates corrosion in the presence of sulphuric acid. The subject was discussed by E. Heyn and O. Bauer, G. W. Heise and A. Clemente, and P. Rohland—*vide infra*. E. Heyn and O. Bauer, H. Endo, P. Rohland, and G. P. Vincent studied the action of **potassium dichromate** soln. on iron; and E. Berl and F. van Taack observed that under a high pressure, soln. of the dichromate attack iron more strongly than do soln. of **potassium chromate.** Some reduction occurs, and the liquid becomes alkaline. *Vide infra*, for the action of chromates and dichromates on the corrosion of iron. H. Endo observed that iron can be kept in 0·002 to 0·1*M*-soln. of **potassium permanganate** for a year without being perceptibly attacked, but corrosion occurs in 10 hrs. in a 0·0002*M*-soln. R. Vogel and H. Baur, and E. C. Krekel studied the reaction between iron and **manganese sulphide** and noted that the mixtures show an eutectic point—*vide infra*, iron-manganese alloys.

According to F. E. Brown and J. E. Snyder, molten **ferrous chloride** attacks iron; and H. Heinrichs studied the reaction between iron and **ferrous sulphate.** C. F. Schönbein observed that iron precipitates an oxide from soln. of ferrous chloride or sulphate. The action of iron on soln. of ferric salts was studied by T. E. Thorpe, H. Schild, and M. Troilius. According to J. C. Essner, dil. soln. of **ferric sulphate** when treated with iron yield ferrous sulphate; and the basic ferric sulphate precipitated by iron from soln. of copper sulphate reacts with iron: $3Fe_2(OH)_4SO_4+Fe=3FeSO_4+4Fe(OH)_3$. O. Collenberg and S. Bodforss, and R. G. van Name and D. U. Hill studied the rate of dissolution of iron in a soln. of ferric alum in the presence of 0·01*M*- to 5·0*M*-H_2SO_4; and observations were made by J. Napier. O. P. Watts and N. D. Whipple found that the presence of arsenic retarded the rate of attack. The corrosion of iron by water containing iron salts in soln. was studied by A. E. Menke, and N. R. Dhar. W. Spring found that a conc. soln. of **ferric chloride** has little action on iron, but the metal readily dissolves in a dil. soln. R. G. van Name and D. U. Hill studied the rate of dissolution of iron in a soln. of ferric chloride in the presence of 0·1*M* and 0·5*M*-HCl; and observations were made by J. Napier, and H. F. Whittaker. O. P. Watts and N. D. Whipple found that the presence of arsenic slows down the rate of attack. H. Pauling obtained a cell with electrodes of iron and carbon in a conc. soln. of ferric chloride. The e.m.f. is 0·9 volt; and the cell is cheap and free from smell. A constant flow of ferric chloride through the cell can be maintained so as to ensure depolarization. F. W. Küster represented the reaction: $2Fe^{\cdots}+Fe=3Fe^{\cdot\cdot}$. Owing to the carbon impurities in the iron, local action like the main reaction must occur. The iron dissolves as ferrous chloride, not as ferric chloride, since when the iron plate is immersed in a soln. of sodium chloride, and the carbon plate in a soln. of ferric chloride, and the current is allowed to pass for some time, the soln. in the vicinity of the iron plate contains ferrous salt alone, without a trace of ferric salt. B. Garre observed that the reaction between iron and **nickel sulphide** begins at 380°, and that the thermal value of the reaction is 5·7 Cals. F. Mylius and O. Fromm observed that platinum precipitated from soln. of **platinum salts** readily alloys with the iron. O. Ruff and F. W. Tschirch found that the vapour of **osmium octofluoride** strongly attacks iron.

Some reactions of analytical interest.—The salts of bivalent and tervalent iron, respectively **ferrous salts** and **ferric salts,** behave as if they were salts of two totally different elements. Neither series of salts gives any precipitate when treated with **hydrochloric acid,** nor does the acidic soln. of either salt give any precipitation of an iron compound when treated with **hydrogen sulphide.** If the soln. of ferrous salt is dilute and neutral, a small amount of ferrous sulphide may be precipitated; and, according to J. L. Gay Lussac,[19] C. C. Grischow, R. Winderlich, and H. W. F. Wackenroder, soln. acidified with some of the weaker acids—carbonic, oxalic, citric, tartaric, acetic, succinic, formic, and benzoic acids—may give an incomplete precipitation of ferrous sulphide. In the case of acetic acid, for example, there are presumably balanced reactions involving the dissolution of ferrous sulphide, and its conversion of the sulphide into acetate: $FeS+2HC_2H_3O_2 \rightleftharpoons Fe(C_2H_3O_2)_2+H_2S$, and the escape of hydrogen sulphide as a gas, allows more ferrous sulphide to pass into soln. to preserve the balance. By adding to the soln. a considerable excess of alkali acetate, the balance is disturbed owing to the decreased solubility of the sulphide. Ferric salts are reduced to ferrous salts by hydrogen sulphide with the separation of sulphur: $2FeCl_3+H_2S=2FeCl_2+2HCl+S$. The sulphur appears as a milk-white or bluish turbidity. According to H. Rose, a small proportion of sulphuric acid is produced in soln. of the chloride, but not with soln. of the acid acetate; and in ferric salts of the weaker acids, *e.g.* the acetate, H. W. F. Wackenroder observed that some hydrated ferric sulphide may be precipitated if the acid is not in excess; and also from soln. of ferric salts of one of the strong acids if a large excess of sodium acetate be present. Iron is completely precipitated from soln. of ferrous salts by **ammonium sulphide:** $FeCl_2+(NH_4)_2S=2NH_4Cl+FeS$; the precipitate is readily soluble in acids with the evolution of hydrogen sulphide. If very dil. soln. are employed, green colloidal ferrous sulphide is formed; it coagulates to a black precipitate on long standing, or in the presence of ammonium chloride. According to H. N. Stokes, **ammonium polysulphide** will give a precipitate containing ferric sulphide. Ammonium sulphide with ferric salts gives a precipitate of ferrous sulphide and sulphur: $2FeCl_3+3(NH_4)_2S=6NH_4Cl+2FeS+S$, but with an excess of soln. of yellow ammonium sulphide, J. J. Berzelius said that ferric sulphide is precipitated. Similar results are obtained with alkali sulphides on soln. of ferrous and ferric salts; and the precipitate is insoluble in an excess of the reagent, but H. N. Stokes added that with alkali sulphides the precipitate is always ferric sulphide. According to J. Roth, an aq. soln. with one part of iron in 100,000 parts of water gives a black precipitate with ammonium sulphide; with 1 : 200,000, a dark green mixture is produced; with 1 : 400,000, greyish-green; and with 1 : 800,000, a greyish-green colour in a few minutes. F. Jackson found that ammonium sulphide enables one part of ferrous or ferric iron in 128,000 to be detected. Acidic ferrous salt soln. give no precipitate with **ammonium thioacetate,** but with alkaline soln., ferrous sulphide is precipitated; soln. of ferric salts are reduced to ferrous salts by this reagent.

Ferrous salts, in neutral soln., give an incomplete precipitation of white ferrous hydroxide when treated with **ammonia.** If ammonium salts be present, *e.g.* in chloride soln., a soluble complex salt, $(NH_4)_2FeCl_4$, is formed so that if sufficient ammonium chloride be present, ammonia gives no precipitate with soln. of ferrous salts. If the soln. be exposed to air, it becomes turbid, green, and finally brown or black from the precipitation of brown, hydrated ferric or ferrosic oxide (*q.v.*). **Alkali hydroxides** give a complete precipitation of ferrous hydroxide from ferrous salt soln., and the precipitation is only partially prevented by the presence of ammonium salts. According to J. Roszkowsky, non-volatile organic acids, sugar, etc., retard or inhibit the precipitation of ferrous salts by ammonia or alkali hydroxides. F. Jackson found that 1 : 8000 of ferrous iron could be detected by precipitation with ammonia, or alkali hydroxides. Ammonia, or alkali hydroxide soln. with ferric salts give a precipitate of brown, gelatinous, hydrated ferric oxide (*q.v.*): $FeCl_3+3NH_4OH=3NH_4Cl+Fe(OH)_3$, which is soluble in acids. According to J. Roszkowsky, non-volatile organic acids, sugar, etc., inhibit or hinder the precipitation of hydrated ferric oxide by ammonia or alkali-lye owing to the formation of complex salts. G. C. Wittstein said that hydrated ferric oxide is slightly soluble in conc. alkali-lye, but L. Schaffner showed that this is a mistake; the ferric oxide is only in "a state of fine mechanical suspension." F. Jackson observed that the precipitation occurs with ammonia in soln. with ferric iron 1 : 16,000, and with sodium hydroxide 1 : 32,000.

Ferrous salts give a white precipitate when treated with an **alkali carbonate:** $FeCl_2+Na_2CO_3=2NaCl+FeCO_3$; the ferrous carbonate rapidly oxidizes in air; with ferric salts, a brown, basic carbonate is precipitated, which, in a boiling soln., is hydrolyzed to hydrated ferric oxide. According to J. N. von Fuchs, F. von Kobell, W. Schopper, and H. Demarçay, the **alkaline earth carbonates,** and **manganous, zinc, magnesium, and cupric oxides** precipitate hydrated ferric oxide from cold soln. of ferric salts, but not so with soln. of ferrous salts unless boiling. The reaction with zinc oxide is symbolized: $2FeCl_3+3ZnO+3H_2O=3ZnCl_2+2Fe(OH)_3$; and similarly also with **mercuric oxide.** According to C. H. Pfaff, **sodium phosphate** with ferrous salts precipitates white ferrous phosphate, and the reaction is sensitive to 1 : 1,000; while with ferric salts, yellowish-white ferric phosphate is precipitated sensitive to 1 : 1500; ferrous salts with **sodium arsenate** give a white precipitate sensitive to 1 : 1000; and ferric salts, a white precipitate sensitive to 1 : 20,000.

According to J. von Liebig, ferric salts in cold, neutral soln. of **alkali acetates or formates** give a brown coloration: $FeCl_3+3NaC_2H_3O_2=3NaCl+Fe(C_2H_3O_2)_3$; and on boiling the soln. the iron is precipitated: $Fe(C_2H_3O_2)_3+2H_2O=2HC_2H_3O_2+Fe(OH)_2(C_2H_3O_2)$, the precipitated basic acetate redissolves as the soln. cools, or when the precipitate is washed with cold water. The basic acetate process was discussed by J. W. Mellor. The presence of organic oxy-acids—like tartaric, citric, and malic acids—and of polyhydric alcohols—like glycerol, erythritol, mannitol, and sugars—prevent these reactions because they form complex salts. C. H. Pfaff observed that **alkali succinates and benzoates** give light reddish-brown precipitates with ferric salts sensitive to 1 : 5000 provided an excess of acid is not present. Ferrous salts give a yellow coloration with **oxalic acid** and acid alkali oxalates, and on standing a yellow precipitate is formed; with **alkali oxalate** the yellow precipitate is formed at once; ferric salts give a yellow colour with oxalic acid, but no precipitation. Ferrous salts do not give a coloration or a precipitate with **tincture of galls;** but in air or in the presence of ferric salts a violet-black or purple colour is developed. According to C. H. Pfaff, and J. Roth, the precipitation occurs with ferric chloride with a concentration of the ferric salt of 1 : 120,000; a bluish-black coloration is produced with a dilution of 1 : 200,000; a greenish-blue with 1 : 400,000; and a greenish-blue on standing a few minutes with a dilution of 1 : 800,000. P. Harting said that the limit of the reaction with ferric sulphate is 1 : 300,000. If one of the stronger acids is present no precipitation occurs unless alkali acetate is present. O. Lutz found that if a few drops of a soln. of **protocatechuic acid,** and then an excess of sodium carbonate be added to a soln. of an iron salt, an intense red coloration occurs sensitive to 1 : 10,000,000; the presence of ordinary inorganic or organic acids does not interfere with the test. The reaction was studied by H. Hlasiwetz and co-workers, and R. F. Weinland and K. Binder. G. von Knorre, and M. von Ilinsky and G. von Knorre observed that **nitroso-β-naphthol,** dissolved in 50 per cent. acetic acid, gives a voluminous, green precipitate with dil. soln. of ferrous salts; and a voluminous, brownish-black precipitate with ferric salt soln. H. Kofahl, I. Bellucci and A. Chiucini, J. Papish and L. E. Hoag, C. Meineke, L. L. de Koninck, E. A. Atkinson and E. F. Smith, and F. C. Mathers studied the reaction. K. W. Charitschkoff found a soln. of **naphthenic acid** in light petroleum gives a reddish-brown soln. with ferrous salts—the petroleum extracts the iron from aq. soln.—ferric salts must be first reduced to ferrous salts. P. Slawik found that a most sensitive reaction for ferrous salts is to add tartaric acid to a drop of a ferrous salt soln., then 1 c.c. of alcoholic **dimethylglyoxime,** then an excess of ammonia, when an intense red coloration is produced which disappears by atm. oxidation, but is restored by reducing agents. The reaction was studied by L. Tschugaéeff, L. Tschugaéeff and B. Orelkin, R. Nakaseko, P. N. van Eck, M. Matsui, E. J. Kraus, and W. Vaubel. A faint rose-red is perceptible with a dilution of 1 : 1,600,000. J. Dubsky and M. Kuras found that 1 c.c. of a 1 per cent. alcoholic soln. of **di-iso-nitrosoacetone** added to 5 c.c. of a ferrous salt soln. gives an intense blue. The colour develops in 2 hrs., with 0·00001*N*-soln., and in 3 hrs. with 0·000001*N*-soln. G. von Knorre observed that 2, 4-**dinitrosoresorcinol** gives a green colour or a green precipitate with ferric salt soln., and in feebly acidic or feebly alkaline soln. of ferrous salts, a green colour. The reaction was studied by M. L. Nichols and S. R. Cooper, W. R. Orndorff and M. L. Nichols, and M. Goldstück. The ammonium salt of **phenylnitrosohydroxylamine**—or **cupferron**—gives a red precipitate of a complex ferric salt with acidic soln. of ferric salts. The reaction was studied by E. H. Archibald and R. O. Fulton. O. Baudisch, O. Baudisch and V. L. King, I. Bellucci and A. Chiucini, J. Brown, H. Biltz and O. Hödlke, E. Ferrari, R. Fresenius, G. E. F. Lundell, G. E. F. Lundell and H. B. Knowles, H. Nissenson, A. Pinkus and F. Martin, K. Schröder, and H. Weber. P. Cazeneuve found that a soln. of **diphenylcarbazide** in benzene, when shaken with a soln. of a ferric salt, gives a peach-red coloration. A. W. Gregory estimated that the violet colour, produced when an acetic acid soln. of **salicylic acid** is added to ferric chloride in soln. with sodium acetate, is sensitive to 1 : 50,000. The reaction was first reported by R. Piria, and studied by A. Almén, R. Böttger, E. Brücke, A. Conrady, A. Dollfus, M. Frehse, J. E. Gerock, A. Hantzsch and M. Singer, M. Konowaloff, O. Langkopf, H. Marty, P. Nicolardot, S. Pagliani, L. Rosenthaler, A. Sagaidatschin and M. Rawitsch, E. Schaer, E. F. Smith, J. Traube, A. Vogel, R. F. Weinland and A. Herz, H. Weiske, and J. Wolff. H. B. Pulsifer utilized, for colorimetric determinations, the red colour produced by ferric salts with **acetyl acetone.** R. Berg recommended **o-oxyquinoline derivatives** as a precipitant.

A soln. of **potassium cyanide** and a ferrous salt give a reddish-brown precipitate soluble in excess to form potassium ferrocyanide ; with a ferric salt soln., potassium ferricyanide is formed in an analogous way. Ferrous salts with **potassium ferrocyanide,** in the complete absence of air, give a white precipitate of ferrous ferrocyanide or ferrous potassium ferrocyanide, in air, a pale blue colour is due to oxidation to ferric ferrocyanide (Prussian blue) ; with ferric salts under similar conditions, an intense blue precipitate of Prussian blue is formed. C. H. Pfaff said that the reaction is sensitive to 1 : 100,000 ; P. Harting, to 1 : 420,000 ; and F. Jackson, 1 : 64,000. Ferrous salts with **potassium ferricyanide** give a dark blue precipitate of Turnbull's blue ; and with ferric salts, only a brown coloration is developed. Ferrous salts give no coloration with **potassium thiocyanate ;** but with ferric salts a blood-red coloration is produced: $FeCl_3+3KSCy \rightleftharpoons Fe(SCy)_3+3KCl$. The reaction is reversible, and the ferric thiocyanate can be extracted with ether. C. H. Pfaff added that the coloration is sensitive to 1 : 20,000 ; A. Wagner, 1 : 1,600,000 ; E. C. Smith, 1 : 8,000,000 ; and J. Roth added that with 1 : 25,000 the colour is red ; with 1 : 200,000, orange ; with 1 : 800,000, pale orange ; and with 1 : 1,600,000, a scarcely perceptible yellow. The coloration cannot be recognized in the presence of an excess of alkali acetate ; organic oxy-compounds—*e.g.* tartaric acid—in neutral soln., not in acid soln. ; and mercuric chloride destroys the coloration. The subject was studied by E. Kahane. Ferric salts give an intense blue colour with **potassium molybdenocyanide.**

A. Richaud and M. Bidot said that a sky-blue coloration is produced with ferrous salts, not ferric salts, when treated with a soln. of **sodium phosphatotungstates,** acidified by hydrochloric acid, and the liquid then made alkaline with sodium hydroxide, but A. Popesco showed that other reducing agents produce the same coloration. If a ferrous salt soln. is treated with an excess of conc. sulphuric acid, and a crystal of **potassium nitrate** is introduced, a brownish-red ring is produced which, according to L. Blum, enables a ferrous salt to be detected in the presence of a ferric salt—*vide* nitric oxide. According to E. Lenz, with ferrous salts, **sodium thiosulphate** gives no precipitation ; while ferric salts are coloured violet and finally reduced to ferrous salts without precipitation.

According to N. W. Fischer,[20] **zinc** precipitates from neutral soln. of ferrous chloride or sulphate a mixture of ferrous hydroxide and metal if air be excluded ;

otherwise, a mixture of ferric hydroxide and metal. J. A. Poumarède obtained a similar result, but not E. F. Anthon. H. N. Warren observed that **magnesium** precipitates iron mixed with the hydroxide from soln. of the acetate, and by this means iron can be separated from chromium. D. Vitali stated that when a soln. of a ferric salt is treated with magnesium, flecks of hydroxide are formed, and these are gradually reduced to the metallic state.

The physiological action of iron salts.—In the first century of our era some medicinal uses of iron were described by Pliny, in his *Historia naturalis* (**34**. 44). In classical times there was a general belief that iron lent its strength to the body, and later on this belief was reinforced by the association of iron with the planet Mars. Mars was assumed to control the blood, and accordingly "iron" was employed to strengthen and purify the blood. In the Middle Ages several writers—*e.g.* J. L. Bausch[21]—discussed the therapeutics of iron compounds. The medicinal use of iron increased during the sixteenth and seventeenth centuries, and the therapeutic reputation of iron was supported by its curative effect on chlorosis or green sickness; and by its helpful action in counteracting the effects of excessive blood-letting so generally practised in that period. Iron was also a general remedy for cachexia and ill-health. The popularity of iron led to an increase in the number of available preparations as a knowledge of chemistry increased, and a number of secret preparations appeared in the eighteenth century—*vide infra*, iron chlorides. To-day it is estimated that over 600 preparations are available for medicinal purposes! The physicians of the seventeenth and eighteenth centuries thought so highly of the curative properties of iron that H. Boerhaave could say: *In ferro est aliquid divinum.*

The action of iron salts on the animal organism was discussed by G. C. Gmelin[22] in 1825—*vide supra,* the occurrence of iron—and by A. J. Clark. The iron salts have no particular action on the unbroken skin, and when applied locally to the abraded skin, sores, and the mucous membranes, ferric salts are powerful astringents because they coagulate albuminous fluids. The administration of iron in health has very little action on the blood. If iron be injected subcutaneously or directly in the veins, it may cause gastro-intestinal irritation and paralysis. The iron administered during hæmorrhage does not influence the hæmoglobin of the blood. The ferric salts act as local hæmostatics and arrest severe hæmorrhage by coagulating the blood and plugging bleeding vessels. The iron salts have a styptic taste, and may blacken the teeth and tongue owing to the formation of iron sulphide from the sulphur in the food and the "tartar" of the teeth. Ferric salts are converted in the stomach into chloride—maybe also a little ferrous chloride is formed—by the action of the hydrochloric acid there present. The iron salts thus have an astringent action in the stomach. As the iron salts pass into the intestine, the contents of which are alkaline, hydrated iron oxide or carbonate is formed which probably remains in soln. owing to the presence of organic substances. Lower down the intestine, the sulphur compounds, nascent hydrogen, and other readily oxidized products of decomposition convert the iron into ferrous sulphate and tannate—the tannic acid being derived from the vegetable matter of the food—and these ferrous compounds are eliminated as such with the fæces which are thereby turned black. The oxide, sulphide, and carbonate of iron are non-astringent. If an excess of iron in the form of an astringent preparation is administered, the excess has a constipating effect, since it is not acted on in the stomach and intestine. F. Wohlwill observed that iron causes capillary hyperæmia of the alimentary canal, and the accompanying nervous symptoms indicate a direct action on the central nervous system. W. Schürmann and T. Baumgärtel observed that ferric chloride precipitates red corpuscles from the blood of normal oxen or sheep. L. Massol and M. Breton found that the injection of a milligram of ferrous sulphate in the brain of a guinea pig did not cause death. H. W. Armit studied the toxic action of iron carbonyl.

The total iron in the adult body, amounting to about 3 grms., is derived from the food; about 2 grms. of this iron is combined in the hæmoglobin; and more than half the remainder is stored as a reserve in the spleen, liver, lymphatic glands, and marrow. The rest of the body contains about 5 mgrms. of iron per kilogram, and this is important because the respiration of every cell in the body depends on the small traces of iron it contains.

C. G. Lehmann, and others found that men starving for long periods excreted 8 mgrms. of iron daily, and this corresponds with a wastage of body tissue. G. von Wendt, and W. Lintzel agree that with diets adequate in amount, but poor in iron alone, the iron excretion is not more than 2 to 5 mgrms. daily—*vide supra*, occurrence of iron. About a milligram of iron is eliminated in the urine of man per diem, and this remains nearly constant under all circumstances. An excessive elimination may follow subcutaneous injection or excessive absorption from the intestine, and some may be eliminated through the intestinal membranes.

The amount of iron required in the food in order to maintain a balance is comparatively small. About 20 mgrms. per diem is usually considered sufficient; but W. Lintzel and co-worker observed that a mixed daily diet only contains about 10 to 14 mgrms. of iron, and probably less than this is needed by an adult on a mixed diet. Most of the iron is present in the meat, and in green vegetables. The iron contents, in mgrm. per 100 grms., of some foods rich in iron are—liver, 15; spinach, 5; and meat, 2 to 5; and in some foods poor in iron—cow's milk, 0·2; white flour, 1·5; and potatoes, 1·2—*vide supra*, occurrence of iron. The poverty of iron in cow's milk explains the nutritional anæmia of bottle-fed babies. M. Blauberg observed that a breast-fed human infant of 5 months retained 10 mgrms. of iron daily, and that this represented about 70 per cent. of the total amount supplied with the milk.

Ruminants, feeding on grass, etc., growing on soils with a low proportion of "iron," acquire a wasting disease, which, in New Zealand, is called *bush sickness*, and, in Kenya, *nakuruitis*. These diseases are characterized by arrested growth, and by excessive anæmia, which is ultimately fatal unless the animals are supplied with "iron" in some suitable form. Accordingly, B. C. Aston called the disease *iron starvation*. The subject was discussed by J. B. Orr. W. Lintzel found that a deficiency of iron arrested the growth of young rats; and J. P. McGowan and A. Crichton, that young pigs became œdematous, and frequently died suddenly—a post-mortem showed fatty degeneration of the heart and liver. Hence, while a deficiency of iron may cause anæmia, it may have serious deleterious effects on various tissues of the body.

According to G. von Bunge, the iron reserves in the liver and spleen play an important part in the blood formation of infant animals, and, added A. J. Clark, in many cases new-born animals have large iron reserves in their liver, and, although they receive but little iron in their mother's milk, yet by drawing on these reserves, they can avoid anæmia. W. Lintzel showed that a calf, for example, starts with a rich iron store in its liver, and hence does not suffer from the fact that cow's milk contains very little iron. On the other hand, young pigs, and human infants have only a moderate iron store, but receive a better iron supply from their mother's milk. Naturally, when a human infant is fed on cow's milk it tends to become anæmic, because it has no large iron store and receives very little iron in its food.

G. von Bunge doubted whether inorganic salts of iron can be absorbed directly from the alimentary canal. He supposed that the only iron absorbed is present in the food as organic salts, but the presence of inorganic salts of iron in the alimentary canal favours the absorption of the organic iron by combining with and precipitating any sulphur as iron sulphide, thus preventing the sulphur from decomposing the organic iron salts. The hypothesis was disproved by E. Abderhalden, and S. Tartakowsky, who showed that inorganic iron hastens the formation of hæmoglobin in adult animals rendered anæmic by repeated bleeding whilst supplied with food deficient in iron. G. H. Whipple and co-workers also showed that iron salts administered in sufficiently large doses definitely increased the rate of formation of hæmoglobin. E. B. Hart and co-workers found that nutritional anæmia in young rats was not cured by the administration of iron alone, but was cured if a small amount of copper was simultaneously given. This subject was studied by I. J. Cunningham, E. B. Hart and co-workers.

According to W. H. White, soln. of iron salts are antiseptic. The effect of iron on vegetation was studied by J. L. Lassaigne. F. C. Calvert found that dil. soln. of ferrous sulphate do not prevent bacterial or fungoidal growths in albumin. C. Richet observed that at 16° to 20°, a soln. of 0·24 grm. of ferric chloride per litre will hinder the development of bacteria, and 0·014 grm. per litre will kill marine fishes in 48 hrs. L. Nathan found that black iron is active in checking the fermentation of apples, and beer-wort, whilst polished iron has but a slight action. L. Nathan and co-workers showed that iron is very injurious to the fermentation of fruit musts and beer-wort. A. Chassevant and C. Richet observed the toxic action of iron salts on lactic fermentation.

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§ 24. The Corrosion of Iron and Steel

> Nature, in conformity with her usual benevolence, has limited the power of iron, by inflicting upon it the punishment of rust.—Pliny (6. 40).

The tendency of ordinary iron to rust on exposure to air is inherent in its nature; and A. S. Cushman,[1] in discussing *The Conservation of Iron*, said that the rusting is essentially a process of slow combustion which is annually burning up an untold and unknown quantity of this precious metal. No partnership between industry and Nature will ever again reclaim the iron that has fallen away to rust. D. M. Buck considered that the annual charge due to the corrosion of iron and steel is between £17,000,000 and £23,000,000; but R. A. Hadfield estimated that the annual cost of wastage due to the rusting of the world's iron and steel is probably well over £500,000,000. W. S. Johnston estimated that 2 per cent. of iron and steel is lost per annum by corrosion. The cause and prevention of rusting is therefore a subject of surpassing importance unless we are to be mere passive spectators of this enormous loss. The subject was discussed by J. T. Milton, R. J. McKay, E. H. Schulz, W. Wiederholt, E. H. Schulz and R. Kühnel, C. H. Desch, B. D. Saklatwalla, E. Maass, and W. H. Creutzfeldt. Quite a number of books have been published on the rusting of iron; and the *Reichsausschuss für Metallschutz* publishes a journal, *Korrosion und Metallschutz*, devoted to this subject. The special works are:

Lc. E. Andes, *Der Eisenrost, seine Bildung, Gefahren, und Verhütung*, Wien, 1898; London, 1918; J. Newman, *Metallic Structures: Corrosion and Fouling and their Prevention*, London, 1896; J. A. N. Friend, *The Corrosion of Iron and Steel*, London, 1911; A. S. Cushman, *The Corrosion of Iron*, Washington, 1907; A. S. Cushman and H. A. Gardner, *The Corrosion and Preservation of Iron and Steel*, New York, 1910; A. A. Pollitt, *The Causes and Prevention of Corrosion*, London, 1923; O. F. Hudson, *Iron and Steel: An Introductory Textbook, with a Section on Corrosion by G. D. Bengough*, London, 1921; U. R. Evans, *The Corrosion of Metals*, London, 1926; F. N. Speller, *Corrosion: Causes and Prevention*, New York, 1926; A. Sang, *Corrosion of Iron and Steel*, New York, 1910; M. P. Wood, *Rustless Coatings: Corrosion and Electrolysis of Iron and Steel*, New York, 1904; A. H. Sexton, *The Corrosion and Protection of Metals with special reference to the Preservation of Engineering Structures*, Manchester, 1906; *Engg.*, **82**. 467, 1906; G. de Lattre, *Protection des métaux contre la corrosion*, Paris, 1927; C. Frémont, *Essais de corrosion des fers et des aciers*, Paris, 1927; *Essais des fers et des aciers par corrosion*, Paris, 1910; L. C. Wilson, *Corrosion of Iron—A Summary of Causes and Preventative Measures*, New York City, 1915; W. H. Creutzfeldt, *Korrosion forschung vom Standpunkte der Metallkunde*, Braunschweig, 1924; *Stahl Eisen*, **48**. 228, 1928; W. S. Calcott, J. C. Whetzel and H. P. Whittaker, *Corrosion Tests and Materials of Construction for Chemical Apparatus*, New York, 1923; M. L. Hamlin and F. M. Turner, *The Chemical Resistance of Engineering Materials*, New York, 1923; M. Ragg, *Vom Rost und vom Eisenschutz*, Berlin, 1928; W. Palmaer, *The Corrosion of Metals*, Stockholm, 1929; J. H. Gibboney, *Proc. Amer. Soc. Testing Materials*,

29. 13, 1930 ; E. Maass, *Rost und Rostschutz*, Berlin, 1925 ; N. van Patten, *Bibliography of Corrosion of Metals and its Prevention*, Kingston, 1924 ; W. H. J. Vernon, *A Bibliography of Metal Corrosion*, London, 1928 ; E. Liebreich, *Rost und Rostschutz*, Braunschweig, 1914 ; H. G. Haase, *Säure- und alkalifestes Gusseisen*, Düsseldorf, 1927 ; R. Schäfer, *Rostfreie Stähle*, Berlin, 1928 ; J. G. H. Monypenny, *Stainless Iron and Steel*, London, 1926 ; O. Kröhnke, E. Maass and W. Beck, *Die Korrosion unter Berücksichtigung des allgemeinen Materialschutzes*, Leipzig, 1929 ; P. Kotzschke, *Ueber die Korrosion und des Rosten von unlegiertem und legiertem Gusseisen*, Düsseldorf, 1928 ; H. Suida and H. Salvaterra, *Rostschutz und Rostschutzanstrich*, Wien, 1931.

There have been numerous discussions on the corrosion of iron and steel—*e.g.* W. van W. Scholten,[2] A. Matagrin, G. Masing, V. Sallard, C. O. Bannister, A. M. Portevin, etc. Methods for measuring the corrosion of metals were described by G. D. Bengough [3] and co-workers, W. H. J. Vernon, E. K. O. Schmidt, etc. ; and microscopic tests, by C. H. Desch [4] and co-workers.

According to U. R. Evans and G. D. Bengough,[5] the term *abrasion* denotes friction between one solid body and another resulting in change of shape or removal of material from one or both sides ; *corrosion* means the chemical or electrochemical action of a liquid or gas on the surface of a metal resulting in a passage from the elementary to the combined state ; and *erosion* denotes the removal of material from some part of a surface by means of abrasion, by capillary action, or otherwise, without a change of composition at the moment of removal although changes may occur afterwards. Both abrasion and erosion may operate on either metal or scale. J. A. N. Friend used the term erosion to designate corrosion such as that induced by acids when a more or less soluble product is formed which exposes the underlying metal to attack ; and *surrosion* for that type of corrosion which results in the production of insoluble oxide or rust which clings to the unattacked metal ; and W. H. J. Vernon used the term surrosion for cases where the total action is quantitatively represented by the increase in weight of the specimen.

The action of water on iron.—Some observations on this subject have been discussed in connection with the chemical properties of iron. B. D. Saklatwalla [6] noted that the condensation of gases on the surface of metals would tend to impart surface activities that would depend on the degree of adsorption. When iron is covered by a thin layer of water, and exposed to air, hydrated ferric oxide is formed, but with a thicker layer of water, F. Wöhler found that hydrated ferrosic oxide is produced. The water carries oxygen from the air to the iron. M. M. Hall, and N. J. B. G. Guibourt found that iron powder, out of contact with air, does not decompose thoroughly boiled water, though a feeble evolution of hydrogen may occur at 50° to 60°, and ferrosic oxide be formed. J. A. Wanklyn and L. Carius found that iron reduced by hydrogen gives no hydrogen when heated with purified water at 50° to 60° ; and R. Lenz said that electrodeposited iron, re-heated to redness in vacuo, rapidly oxidizes in contact with boiling water, the water is decomposed and the hydrogen which is formed is absorbed by the iron. E. Ramann also said that finely-divided iron slowly decomposes boiling water ; thus, 12 c.c. of hydrogen were obtained by boiling 10 grms. of iron—reduced in hydrogen—in water for an hour ; he also noticed that the glass containing vessel was corroded when the boiling was continued for several days. J. A. N. Friend also observed that the reaction between iron and boiling water occurs about one-fourth as quickly in a copper vessel as it does in a glass vessel. M. M. Hall, and N. J. B. G. Guibourt said that if the iron be in contact with electronegative substances like ferric oxide, or mercury, it can decompose water under conditions where it otherwise would not do so. The case is as different with iron *en masse*, as it is with, say, pyrophoric iron and ordinary iron in air.

The action of water on iron was discussed early last century by J. Keir, C. Becker, C. Girtanner, J. B. Trommsdorff, N. J. B. G. Guibourt, M. Meyer, R. Adie, J. Spennrath, M. Traube, and M. M. Hall ; and later by E. A. and L. T. Richardson, J. Rothe and F. W. Hinrichsen, A. Bobierre, K. Hasegawa and S. Hori, W. R. Dunstan and co-workers, W. H. Walker and co-workers, A. S. Cushman, V. Andström, E. Heyn and O. Bauer, W. Palmaer, W. R. Whitney, A. Wagner, W. P. Mason, W. van Rijn, H. W. Clark and S. D. Gage, R. S. Weston, M. Kernbaum, V. M. Isnardi, W. P. Jorissen, A. W. Stuart, J. W. Cobb and G. Dougill, O. Bauer and E. Wetzel, G. D. Bengough and co-workers. W. A. Bradley, A. B. Bradley, D. Geoghegan, P. J. Thibault, J. W. Shipley and co-workers,

J. Tillmanns and co-workers, R. E. Wilson, J. R. Baylis, F. N. Speller and C. R. Texter, G. M. Enos, H. Klut, M. Heegewaldt, T. Steel, A. T. Stuart, G. J. Burrows and C. E. Fawsitt, W. R. Fleming, C. F. Hickethier, and K. Inamura.

There is the electrolytic theory of corrosion which is independent of the ionic hypothesis and all that is implied by the term " ions." The ionic theory is the electrolytic theory with the theory of ions as a subsidiary hypothesis. The theory of ions is another story. Here, it is convenient to regard the two theories of corrosion as the same, but expressed in different ways. According to the **ionic hypothesis** advocated by W. R. Whitney,[7] F. N. Speller, F. W. Hinrichsen, H. Endo and S. Kanazawa, H. Friedmann, E. K. Rideal, W. J. Sweeney, G. Bresch, J. W. Shipley and I. R. McHaffie, W. Palmaer, W. T. Hall, W. G. Whitman, T. Fujihara, C. F. Burgess, W. H. Walker and co-workers, and A. S. Cushman and co-workers, it is assumed that water and air are sufficient to cause rusting. The action of an acid on iron is represented as an exchange of electric charges between the $\mathrm{H}^{\cdot}$-ions of the acid, and the neutral atoms of the metal which then pass into soln. as metal ions. Water is supposed to be slightly ionized: $\mathrm{H_2O} \rightleftharpoons \mathrm{H}^{\cdot}+\mathrm{OH}'$, and when a metal is immersed in this liquid, it is assumed that the electric charges are transferred from the $\mathrm{H}^{\cdot}$-ions to the iron atoms so that the water in the vicinity of the metal has $\mathrm{Fe}^{\cdot\cdot}$-ions, and OH'-ions corresponding with a dil. soln. of ferrous hydroxide. If oxygen has access to the latter, the ferrous hydroxide is oxidized to hydrated ferric oxide, and deposited as rust. The de-electrified $\mathrm{H}^{\cdot}$-ions form molecular hydrogen. In order to establish this hypothesis it was necessary to demonstrate that iron passes into soln. under these conditions, and, as indicated elsewhere, this has not been satisfactorily done. The tendency of iron to pass into soln. in water depends on (i) the so-called solution pressure, and (ii) on the solubility product $[\mathrm{Fe}^{\cdot\cdot}][\mathrm{OH}']^2$. The reaction $\mathrm{Fe}+2\mathrm{H}^{\cdot}=\mathrm{Fe}^{\cdot\cdot}+\mathrm{H_2}$ is in equilibrium when $k_1=[\mathrm{Fe}^{\cdot\cdot}][\mathrm{H}^{\cdot}]^2 \cdot 67\times10^{-14}$, or since for water at 18°, $[\mathrm{H}^{\cdot}][\mathrm{OH}']=0{\cdot}56\times10^{-14}k_2$, $[\mathrm{Fe}^{\cdot\cdot}][\mathrm{OH}']^2{:}\ 2{\cdot}1\times10\ ^{14}$. This assumes that the ferrous hydroxide is completely ionized in soln. As indicated later, the value for the solubility product of ferrous hydroxide is not accurately known. If the solubility product $[\mathrm{Fe}^{\cdot\cdot}][\mathrm{OH}']^2$ be less than k_1, some hydroxide will be precipitated before equilibrium is attained. One of the values for the solubility product, $1{\cdot}9\times10^{-14}$, is very near the value of k_1. W. J. Sweeney found that the solubility product is $10^{-18\cdot8}$. A. L. McAulay and G. L. White studied the effect of the $\mathrm{H}^{\cdot}$-ion concentration on the potential of the iron- *vide supra*—and H. O. Halvorson and R. L. Starkey calculated that the relations between the $\mathrm{H}^{\cdot}$-ion conc. and the ferrous or ferric ions held in soln.—parts per million—are:

p_{H} . .	3·0	4·0	5·0	6·0	7·0
$[\mathrm{Fe}^{\cdot\cdot}]$ . .	270	2·70	0·027	$0{\cdot}0_3 27$	$0{\cdot}0_5 27$
$[\mathrm{Fe}^{\cdot\cdot\cdot}]$ . .	$6{\cdot}1\times10^{-1}$	$6{\cdot}1\times10^{-2}$	$6{\cdot}1\times10^{-5}$	$6{\cdot}1\times10^{-8}$	$6{\cdot}1\times10^{-11}$

The driving force of the reaction $2\mathrm{Fe}+\mathrm{O_2}+2\mathrm{H_2O}=2\mathrm{Fe(OH)_2}$ is equal to the difference of the potentials $\epsilon'=\frac{1}{4}RT \log \{[\mathrm{O_2}]/[\mathrm{OH}']\}^4$ and $\epsilon''=\frac{1}{2}RT \log \{[\mathrm{Fe}^{\cdot\cdot}]/[\mathrm{Fe}]\}$, so that if $[\mathrm{Fe}^{\cdot\cdot}][\mathrm{OH}]^2=k$, and $[\mathrm{Fe}]$ is constant, $\epsilon'-\epsilon'=\frac{1}{4}RT \log \{[\mathrm{O}^2]/k^2\}$. M. Randall and M. Frandsen calculated the free energy to be —2·28 Cals., indicating that the reaction, $\mathrm{Fe}+2\mathrm{H_2O}=\mathrm{Fe(OH)_2}+\mathrm{H_2}$, can progress at 25°.

According to M. Mugdan, the potential of iron immersed in various salt soln. varies considerably with the nature of the dissolved salt. Since the dissolved salts cannot be supposed to take part in the reaction, this should not be the case. The phenomena can be regarded only as further instances of a metal assuming a more or less passive condition. Thus, iron can dissolve with the elimination of hydrogen in soln. of chlorides, bromides, iodides, fluorides, sulphates, perchlorates, and nitrates, whilst in soln. of the salts of weak anions (chlorate, acetate, hydroxide, cyanide, chromate, and permanganate), the reverse occurs. The different potentials show that the rusting in one case and not in the other is due to some modification of the iron impressed on it by contact with the soln. The fact that many of the salts, in soln., which do not attack the iron are reducing agents, speaks against the passivity being due to a layer of oxide. W. J. Sweeney showed that a small decrease of free energy occurs when iron is attacked by water to form ferrous hydroxide in the absence of oxygen; and K. Murata studied the thermodynamics of the phenomena. W. D. Bancroft gave a bibliography of the ionic theory of corrosion and discussed the available data.

As the ions pass from the metal into soln., an eq. number of hydrogen ions are discharged on the electrode so as to form a hydrogen electrode. As the conc. of the metal ions in the soln. increases, the potential of the combination: Metal : Metal ions, becomes nobler; and conversely, as the H -ion conc. of the soln. becomes less, the potential of the hydrogen electrode becomes more basic. The solubility product of the metal hydroxide is limited by a change in the conc. of the metal ions, and the $H^{\cdot}$-ion conc., and this limits the value of the potential. With base metals like zinc, the limiting value of the potential of the metal electrode and the hydrogen electrode cannot be attained at atm. press., and, in consequence, the action of water on these metals does not come to a standstill; but with iron, when air is excluded, no reaction occurs. The hydrogen potential with a decreased press. becomes nobler, and there must be a press. less than the atmospheric, at which the limiting potential is attained, and the reaction between iron and water can come to a standstill. Since the potential of iron against a sat. soln. of ferrous hydroxide was given by F. Förster as $-0{\cdot}54$ volt—W. Palmaer gave $-0{\cdot}57$ volt—the potential of the hydrogen electrode is $E=-0{\cdot}29 \log\{p/[H^{\cdot}]^2\}$, where the gas press. of the hydrogen is p, and the $H^{\cdot}$-ion conc. is $[H^{\cdot}]$, or, according to W. G. Whitman and co-workers, $[H^{\cdot}]=2{\cdot}5\times10^{-10}$. Then, by substitution and simplification, $p=0{\cdot}25$ atm., or 190 mm. Hg (approximately).

G. Schikorr found that the press. generated by the hydrogen in the action of water on iron (with 0·18 per cent. of carbon, and notable amounts of other impurities) is very much greater than this. For instance, at about 20°:

	0	23	51	82	113	148	days
Press. (mm.) . .	8	163	414	550	633	748	mm.
	0	24	79	104	156	236	days
Press. (atm.) . .	1	1·2	2·3	2·7	4·0	5·8	atm.

This is taken to mean that other factors are concerned in the reaction. Ferrous hydroxide can act on water at 200° producing hydrogen and ferrosic oxide; and W. Traube and W. Lange found that when a gel of ferrous hydroxide is heated with spongy palladium, hydrogen is developed, and ferrosic oxide is formed. Again, J. Preuss observed that powdered iron boiled in water with hydrated ferric oxide produces a black powder, and hydrogen is evolved; and F. Wöhler showed that the black powder is ferrosic oxide, and that the reaction can be symbolized: $Fe+2FeO(OH)=Fe_3O_4+H_2$. R. Stumper also showed that hydrogen is developed in the reaction between rust and iron. G. Schikorr showed that the hydrated ferric oxide does not attack the iron directly, rather is it reduced to hydrated ferrosic oxide, and some ferrous hydroxide passes into soln. The dissolved ferrous hydroxide attacks the iron. The rate of formation of hydrogen in this reaction is proportional to the cube root of the press. Raising the temp. from 25° to 35° doubles the rate of formation of hydrogen. The attack on dense, compact iron is comparatively slow.

Purified water free from air was reported by M. M. Hall,[8] C. J. B. Karsten, J. F. Westrumb, J. Persoz, and R. Mallet to have no action on iron at a temp. below the b.p. of water; and R. Adie reported that he kept iron in water, entirely free from dissolved air, for six months without its showing any sign of attack. B. Lambert and J. C. Thomson showed that commercial iron will dissolve under these conditions. W. R. Whitney found that purified water and purified iron sealed up in flasks, so that the contents were free from oxygen and carbon dioxide, could be kept an indefinitely long time without the iron undergoing any perceptible change; but when air was admitted, the water rapidly became cloudy owing to the formation of metal oxide. It was therefore inferred that a portion of iron must previously have passed into soln. J. A. Collins, J. F. G. Hicks, A. S. Cushman, M. Traube-Mengarini and A. Scala, and W. H. Walker and co-workers described modified experiments in agreement with the assumption that purified water can dissolve purified iron. A. S. Cushman estimated that the solubility of iron in purified air-free water is 0·0006 to 0·00117 grm. per litre. W. R. Fleming, and W. R. Dunstan and co-workers were unable to confirm W. R. Whitney's conclusion; and H. Nordensen, and J. A. N. Friend raised the objection that it is quite probable that the precautions taken by W. R. Whitney, and the others were not sufficient to remove all the residual gas carbon dioxide and oxygen from the water, and from the walls of the containing vessels, so that a trace of iron may have passed into soln. as carbonate. This is supported by W. Scoresby's observation that air cannot be removed from water by merely boiling, since water which has been thoroughly boiled furnishes bubbles of gas on freezing; and A. Leduc's calculation that at least 1 c.c. of gas remains in a litre of water which has been thoroughly boiled. A large portion of this gas is probably carbon dioxide. The fair inference from the observations is that iron is very slightly soluble in ordinary water, or well-boiled water when air or free oxygen is excluded; but it cannot seriously be claimed that the solubility of iron in water, quite free from dissolved gases, has been adequately demonstrated.

The action of damp air on iron.—J. P. Barruel[9] said that he kept electro-deposited iron for many years in a cupboard in which acid vapours were continually present, and yet it presented not the faintest trace of rust; but there is some mistake, for J. Percy said that such iron rapidly rusts when exposed to the joint action of air and moisture. In 1782, S. Rinman observed that dry air does not corrode iron, but moist air does. Hence, he inferred that " rust must be formed by some kind of acid, which, in the presence of moisture, will exert a dissolving, attacking, or corroding influence. . . . Other less noble metals seem likewise to be partially corroded by moist air." J. Spenrath, and others also noted that iron does not rust in dry air. S. Rinman also added that in accord with C. W. Scheele's theory of the nature of air, in a confined space, the good air (oxygen) is absorbed by the rusting drillings of pig-iron. P. A. von Bonsdorff also observed that iron remains unaltered in damp air provided no liquid water is deposited on the metal; similar results were obtained in damp air containing ammonia and carbon dioxide. These observations were confirmed by W. R. Dunstan and co-workers; they enclosed pieces of 99·94 per cent. iron, free from occluded gases, in tubes containing dry and moist oxygen, dry and moist carbon dioxide, and a mixture of moist carbon dioxide and oxygen. No visible action occurred in a set of tubes maintained at a constant temp.; while in a similar set kept at ordinary temp., no visible action occurred in the tubes containing dry oxygen, and dry and moist carbon dioxide; but copious rusting occurred in the tubes containing moist oxygen, and a mixture of moist oxygen and carbon dioxide. In the tubes kept at ordinary temp., there are fluctuations in which the conditions favour the deposition of moisture. Consequently, it is not the water vapour in the atmosphere which evokes the rusting of iron; for if the temp. be above the dew-point, iron initially free from rust does not corrode. A. C. Hanson, W. S. Patterson, and J. C. Hudson observed the rate of corrosion is fastest in the presence of water, and this is attributed to the greater condensation of moisture.

F. C. Calvert observed that in some cases no oxidation occurred on exposing iron to moist oxygen, that in the light of W. R. Dunstan's results, it is probable that no corrosion took place when no moisture condensed on the metal. M. Meyer, P. A. von Bonsdorff, F. von Hutten, and J. Spenrath previously observed that iron does not change in moist air provided no liquid condenses on the surface of the metal. W. M. Thornton and J. A. Harle regarded the attack by the deposited moisture as a kind of electrolysis. J. C. Hudson measured the vap. press. of the moisture in air required for the deposition of films of moisture, and found, with iron, this critical press. is near the saturation point. The rusting of iron in an apparently dry atmosphere, the so-called *dry corrosion*, was discussed by W. H. J. Vernon, U. R. Evans, and G. D. Bengough and J. M. Stuart—*vide supra*, the action of oxygen on iron—*cf.* Fig. 330. E. A. and L. T. Richardson, W. G. Whitman and E. L. Chappell, W. F. Robertson, J. Aston and C. F. Burgess, V. V. Kendall and E. S. Taylerson, E. I. Duirmont, and C. E. Reinhard, discussed the rate of the atmospheric corrosion of iron. Experiments on the action of superheated steam at 186° were made by F. Hanaman, and the subject merges into the equilibrium relations between iron, the iron oxides, and steam discussed below.

The corrosion of iron exposed to the atmosphere is affected by climatic conditions—large diurnal variations of temp., etc., discussed by O. Hähnel, and U. R. Evans; by the presence of foreign gases—*e.g.* sulphurous gases, discussed by J. F. Barkley, U. R. Evans, J. Rothe and F. W. Hindrichsen, P. Siedler, and W. Wislicenus—*vide supra*; hydrogen chloride, by U. R. Evans—*vide supra*; gases from manure heaps, etc., by M. Meyer, and P. A. von Bonsdorff; by the presence of dust—*e.g.* soot—by W. H. J. Vernon; and by the elements associated with the iron, by K. Arndt, J. A. Aupperle, O. Bauer, H. Böringer, J. Aston and C. F. Burgess, A. S. Cushman, G. M. Enos, U. R. Evans, H. Fischer, J. A. N. Friend, L. E. Gruner, R. A. Hadfield, E. A. and L. T. Richardson, W. Rosenhain, F. N. Speller, G. Tammann, and H. Wölbling.

T. Bergman,[10] in 1773, observed that water saturated with aerial acid corrodes and dissolves metallic iron. In F. C. Calvert's experiments, dry oxygen, dry carbon dioxide, a dry mixture of carbon dioxide and oxygen, and a dry mixture of oxygen and ammonia did not corrode iron; in three experiments with moist oxygen, corrosion occurred in only one case; with the mixture of moist oxygen and ammonia, no oxidation occurred; and in all cases where moist carbon dioxide was present, the corrosion was very marked. G. Wetzlar, and A. Payen found that iron does not rust in water containing alkaline substances—*e.g.* in aq. soln. of potassium hydroxide of sodium carbonate, or of ammonia, even though the soln. be dilute. M. M. Hall also observed that iron does not rust in water containing magnesia or lime, and he discussed what he called *the concealed agency of carbonic acid* in determining the oxidation of iron by water. A. Payen inferred that the preservative effect of the alkaline soln. does not, in all probability, arise from their power of withdrawing carbon dioxide from the water, because iron is corroded even under thoroughly boiled water in contact with air free from carbon dioxide. In view of these results, and of F. C. Calvert's observation, no carbonic acid, no corrosion, F. C. Calvert and A. C. Brown developed **the acid theory of corrosion** in which it was assumed that the action is primarily the result of an attack by an acid, usually carbonic acid. It was supposed that the carbonic acid reacts with the iron to form ferrous carbonate, $FeCO_3$, or possibly ferrous hydrocarbonate, $Fe(HCO_3)_2$, and the liberated hydrogen unites with the dissolved oxygen to form water. The ferrous carbonate is then oxidized by dissolved oxygen to form hydrated ferric oxide, or rust. The liberated carbon dioxide then attacks a fresh portion of iron, and the cycle begins anew, so that a small amount of carbon dioxide in the presence of water and oxygen can convert, catalytically, an indefinitely large amount of iron into rust. The inhibition of rusting by alkaline soln. was attributed to their power of neutralizing traces of free acid.

The acid hypothesis has assumed several forms. T. Fujihara said that water and air free from carbon dioxide form a protective film on iron electrolytically, and once this film is formed, carbon dioxide is necessary to produce rusting. The removal of the protective film by the carbon dioxide exposes a fresh surface to attack. N. M. Gariloff and co-workers interpreted the effect of carbon dioxide on iron as follows:

The iron in contact with air and water acquires a film of ferrous oxide; this is oxidized to ferric oxide, which is gradually reduced by the iron, and the metal below is simultaneously oxidized. In contact with water containing carbonic acid, the superficial film of ferrous oxide dissolves and ferrous hydrocarbonate is oxidized to hydrated ferric oxide. After a long period under a soln. of ferrous hydrocarbonate in the presence of carbon dioxide the iron is almost passive, but the activity is regained by shaking the iron so as to detach the protective film of hydrated ferric oxide. Corrosion is specially favoured at a low temp., in an atm. with not more than 5 per cent. of oxygen and not less than 14 to 15 per cent. of carbon dioxide.

J. H. Paul assumed, without proof, that the carbonic acid reacts: $Fe+CO_2+H_2O=FeCO_3+2H$; and on hydrolysis of the ferrous carbonate, ferric oxide, carbonic and formic acids are formed: $2FeCO_3+2H_2O=Fe_2O_3+H.COOH+H_2CO_3$, and the carbonic acid is free to attack more iron, while the formic acid attacks the metal: $Fe+2H.COOH=Fe(H.COO)_2+2H$, and some formate is reduced to formaldehyde by the nascent hydrogen: $2Fe(H.COO)_2+4H=Fe_2O_3+3H.COH+H.COOH$. The formaldehyde escapes from the system while the formic acid reacts with more iron. H. E. Armstrong's modification is indicated below. The acid hypothesis was fashionable for a good many years; but investigators began to inquire: Is the presence of an acid necessary for the corrosion of iron?

Observations on the action of carbonic acid on iron and its alloys were made by V. Andström, E. E. Basch, G. Bresch, G. Bruhns, C. Chorower, W. T. Clous, A. S. Cushman, E. Donath and A. Indra, W. R. Dunstan and co-workers, F. Ensslin and F. Buschendorf, T. Fujihara, J. A. N. Friend, R. Girard, O. Haehnel, A. C. Hanson, C. von Hauer, E. Heyn and O. Bauer, J. F. G. Hicks, K. Inamura, B. Klarmann, H. Klut, J. M. Kolthoff, O. Kröhnke, W. Leybold, H. Lührig, B. G. McLellan, A. A. Markson and P. Fritz, G. T. Moody, J. E. Orloff, J. D. Pennock and D. A. Morton, P. Petit, J. Rothe and F. W. Hinrichsen, E. Sauer, J. T. Saunders, K. Scheringa, J. W. Shipley and I. R. McHaffie, H. J. Smith, J. Spennrath, W. A. Tilden, J. Tillmans and co-workers, J. B. Trommsdorff, J. Ville, W. H. Walker, G. W. Whitman and co-workers, W. R. Whitney, R. E. Wilson, and B. G. Worth—*vide* H-ion concentration of natural waters, and also the action of coal-gas on iron.

The work of W. R. Dunstan and co-workers, W. A. Tilden, and J. F. G. Hicks shows that the presence of carbon dioxide, or other acidic substances, is not necessary for the corrosion of iron, nor did J. F. G. Hicks find that moist oxygen rusts iron more quickly if carbon dioxide be present. V. Andström showed that the quantity of iron removed by corrosion in water is independent of the proportion of dissolved carbon dioxide; and is proportional to the amount of dissolved oxygen. The ratio of iron to oxygen corresponds with Fe_3O_4; and the dissolved iron is present as $Fe(HCO_3)_2$. When very little oxygen is present, and the soln. contains a large proportion of carbon dioxide, corrosion proceeds very slowly. Hence, it is inferred that rusting principally is due to the action of oxygen, probably with the intermediate formation of hydrogen dioxide. The subject was discussed by T. Fujihara. The deleterious effects produced by the products of combustion of coal, formerly attributed to carbon dioxide, are now considered to be produced by the oxides of sulphur. U. R. Evans said:

> The corrosive qualities of carbon dioxide have been exaggerated in the past, and probably the damage attributed to carbon dioxide has really been due to sulphur dioxide or hydrogen chloride. If water is allowed to condense in droplets on iron, some of them develop rust, whilst others (which do not happen to rest on a weak point) remain clear; this is true whether carbon dioxide is present or absent, and the clear drops may be dried up in a current of carbon dioxide without developing rust; hydrogen chloride vapours quickly produce rusting. A soln. of carbonic acid causes at first slight corrosion of the hydrogen-evolution type, but the p_H rapidly rises and the formation of hydrogen ceases; the ferrous bicarbonate produced yields ferric hydroxide at the water-line, and this obstructs diffusion of oxygen and prevents attack of the oxygen-absorption type. In effect, therefore, a soln. of carbonic acid is not dangerously corrosive; but it must be remembered that the presence of excessive free carbonic acid in a hard natural water may prevent the deposition of calcium compounds which would otherwise bring the action to a standstill.

The action of aerated water on iron.—W. R. Dunstan and co-workers found that provided liquid water, oxygen, and iron are brought into contact, rusting will occur even in the absence of carbonic or any other acid. K. Inamura obtained similar results. W. A. Tilden also said that commercial iron, liquid water, and oxygen are alone sufficient for the production of rust; carbonic acid is not necessary, but when present it hastens the reaction. E. Heyn and O. Bauer, and A. S. Cushman came to the same conclusion.. B. Lambert and J. C. Thomson prepared iron of a high degree of purity. If platinum vessels were used in place of iridium as a container for the ferric oxide during its reduction to iron, the product always corroded at the places where it had been in contact with the platinum. T. W. Richards and G. P. Baxter had previously observed that iron always contained some platinum when prepared under these conditions. B. Lambert and J. C. Thomson inferred that thoroughly purified iron does not undergo visible oxidation in contact with purified water and purified oxygen, but that a small trace of impurity in the iron is sufficient to cause oxidation under exactly the same conditions even if the impurity be not of an acidic nature or likely to produce an acid during the reaction. The conclusions were discussed by J. A. N. Friend, T. M. Lowry, H. Richardson, J. Meehan, W. R. Dunstan, C. E. Stromeyer, W. A. Davis, H. E. Armstrong, W. D. Bancroft, and G. T. Moody. There is the difficulty in removing air and carbon dioxide from the liquids, and from the inside surfaces of the glass containing vessels; and the fact that commercial iron and steel invariably contain foreign substances like sulphur, phosphorus, etc., which, on exposure to air, readily oxidize to produce acids where their presence may not have been suspected. The contention that the conclusion is invalid because the carbon dioxide clings to glass vessels and other substances so tenaciously that it cannot be effectively removed except by washing with alkali-lye or some other drastic treatment, has perhaps led some *excolare culicem, camelum autem glutire.* U. R. Evans said:

> It is not clear, however, why, if the residual carbon dioxide is supposed to have remained clinging tenaciously to the glass in these very careful experiments, it should have been considered capable of promoting the rusting of iron. In some of J. A. N. Friend's iron experiments, not only the glass, but also the metal was washed with caustic alkali, a substance which is distinctly tenacious in clinging to metallic substances, and which is notably prejudicial to corrosion. J. A. N. Friend found no rusting when normal sodium hydroxide has been used to wash the iron, but he found that iron rusted after treatment with $\frac{1}{50}N$-sodium hydroxide (followed by washing with water)—a fact which he attributed at the time to the small quantity of carbon dioxide which is capable of existing in equilibrium with alkali of that concentration!

J. Tillmans and B. Klarmann said that the carbonic acid dissolves the iron in accord with the equation $Fe+2CO_2+2H_2O \rightleftharpoons Fe(HCO_3)_2+H_2$; and H. J. Smith observed that a definite concentration of carbon dioxide in the soln. is necessary to keep the hydrocarbonate in soln., and he found that this concentration, the cube root of the carbon dioxide in soln., is proportional to the concentration of the dissolved iron, or $[Fe^{\cdot\cdot}]=K(CO_{2\text{dissolved}})^{\frac{1}{3}}$. With natural calcareous waters, part of the dissolved carbon dioxide is free carbonic acid, and part is present as calcium hydrocarbonate, $Ca(HCO_3)_2$. J. Tillmans and co-workers designate the carbon dioxide so fixed as *zugehörigen* or *attached carbonic acid*, and the unattached carbon dioxide in soln. as *aggressive carbonic acid.* E. Müller and H. Henecka studied the effect of pressure, and found that the action of the soln. on iron is thereby augmented. J. Tillmans observed that if a natural water has a $H^{\cdot}$-ion concentration between $0{\cdot}2\times10^{-7}$ and $0{\cdot}4\times10^{-7}$ it does not have a deleterious effect on iron.

According to W. H. Johnson, iron which has been dipped in acid for the removal of scale after heating becomes brittle, and the brittleness is lost if the metal be subsequently stored for any length of time. A. Ledebur made similar observations all tending to show that adsorbed hydrogen was the source of the brittleness. Similarly, J. H. Andrew observed that when iron is immersed for some time in a sat. soln. of sodium hydroxide at 100°, wrought iron becomes brittle owing to the absorption of hydrogen, but if the immersion is continued a longer time, the metal becomes tough again. The initial brittleness is attributed to the more rapid absorption of hydrogen by the amorphous, intercrystalline layer than by the crystals themselves, and the resulting expansion forcing the crystals apart, and weakening their cohesion. When the hydrogen has had time to diffuse into the crystals themselves, the intercrystalline strains are relieved, and the brittleness disappears.

Again, according to J. A. N. Friend, when electrolytic iron foil is immersed in conc. soln. of potassium or sodium hydroxide for several weeks, and, after a thorough washing, allowed to corrode in water, the water becomes contaminated with potassium or sodium salts; and W. H. Perkins obtained similar results with soln. of ammonium, lithium, and barium hydroxides. Here, again, it is supposed that minute quantities of the alkali penetrate the metal between the crystals of ferrite, viâ the pores in the intercrystalline cement. The subject was also discussed by C. A. Edwards, R. S. Williams and V. O. Homerberg, H. van de Loo and co-workers, F. Hundeshagen, P. W. Evans, H. Kriegsheim, S. E. Langdon and M. A. Grossman, A. Ledebur, E. Liebreich, H. L. Hess, L. H. Marshall, V. H. Hillman, C. J. Morrison, H. Sutton, P. Longmuir, P. D. Merica, S. W. Parr and co-workers, H. F. Rech, F. G. Straub, A. Pomp and P. Bardenhauer, B. Neumann, D. Splittgerber, H. E. Wallsom, M. Werner, R. S. Williams and V. O. Homerberg—*vide supra*, the action of alkali-lye on iron. F. C. Lea, F. G. Straub, M. Majima, and M. Okochi studied the embrittling action of hydrogen in electrodeposited iron. This is not the same as the embrittling of metals by contact with chemical agents discussed by C. H. Desch, and J. A. Jones.

G. T. Moody found that pieces of iron can be exposed to the combined action of purified air and water without forming rust; and where the metal rested in contact with the glass, a slight corrosion occurred in the course of a few days, presumably due to a reaction between the metal and the glass—silicic acid. No corrosion occurred when the ends of the pieces of metal which came in contact with the glass were protected by acid-free paraffin wax. The metal in some cases was washed with chromic acid to remove from the surface of the iron only those constituents which would otherwise yield acids on exposure to water and oxygen. G. T. Moody found that when carbonic acid is entirely excluded, no interaction takes place between oxygen and iron in the presence of water. Under such conditions, oxygen alone is unable to endure oxidation of the metal, but as soon as air containing its normal quantity of carbon dioxide is admitted, vigorous rusting occurred. W. H. Walker and co-workers confirmed the results of G. T. Moody's experiments made without the use of chromic acid; but W. R. Dunstan could not do so, and he assumed that the alkali dissolved from the glass inhibited the corrosion of the metal in G. T. Moody's experiment. W. H. Walker and co-workers, W. A. Tilden, and J. A. N. Friend said that the chromic acid employed by G. T. Moody may have rendered the metal passive; H. B. Baker was unable to make iron indifferent towards ordinary water by treatment with dil. soln. of chromic acid; and G. T. Moody observed that (i) the iron was not passive when and where it came in contact with the containing glass tube, and (ii) that rusting began when ordinary air was allowed to enter the tubes. This would not have occurred had the metal been passivated. J. A. N. Friend concluded that his modifications of the experiments demonstrated "in a remarkably clear and decided manner that pure water and air combined are without visible action on pure iron." The demonstration is by no means complete. In order to adapt a colloidal theory of corrosion of rusting, J. A. N. Friend said that iron dissolves in water as ferrous ions, and that these are rapidly converted into a hydrosol of ferrous hydroxide. He also said that the fact that weakly alkaline soln. of many salts readily induce corrosion, disposes of the idea that an acid must necessarily be present in the free state. The evidence is a remarkable testimony to the influence of predisposing opinions on judgment. The ionic theory of corrosion enables its disciples to show experimentally that purified iron will corrode in contact with a soln. of oxygen in purified water because the water is slightly ionized, and the metal can pass into soln. as ferrous iron-ions with the liberation of hydrogen: $Fe+2H^{\cdot}+2OH'=Fe^{\cdot\cdot}+2OH'+H_2$. The ferrous hydroxide present in soln. is oxidized in the presence of oxygen to form rust. On the other hand, the acid theory of corrosion enables its supporters to show experimentally that corrosion cannot take place under these conditions, but that an acid, or something which can play a similar rôle, must be present. The chemical form of the dress which the acid theory assumes has been described by A. C. Brown—*vide supra*; but it may also be attired electrochemically.

The electrochemical nature of the process of rusting in general.—In 1819, an anonymous writer—assumed to be L. J. Thénard—and R. Mallet expressed the opinion that rusting is an electrochemical phenomenon; and H. Davy probably held the same opinion; while M. Faraday persistently emphasized the electrochemical nature of chemical reactions. A. de la Rive stated that the fact that iron does not rust in moist air if no water is deposited on the surface proves that the oxidation of a metal in air is not merely the result of a direct combination:

> Actually, a more complicated phenomenon occurs, that is, a voltaic action; the metal decomposes the water on account of a local voltaic action which is aided by the presence of dissolved oxygen acting on the hydrogen formed. The presence of carbonic acid facilitates the action inasmuch as it renders the water a better conductor.

The idea was utilized by T. Ericsson-Aurén, and T. Ericsson-Aurén and W. Palmaer; while W. Palmaer said that:

> If in the acid soln. a depolarizer for hydrogen is present, that is, a substance which may successively oxidize the hydrogen formed, it is evident that the counter e.m.f. of the local element diminishes, and the dissolution of the metal is facilitated. Direct evidence of this was supplied by J. M. Weeren, who, however, interpreted the phenomenon another way.

H. E. Armstrong emphasized his belief that that hypothetical substance pure water is not an electrical conductor. The presence of a trace of "electrolyte" is necessary for electrical conduction. He said: The rusting of iron can occur either in a circuit from which oxygen is absent, or in one in which it is present. In the one case, when iron - coupled with an electronegative conductor—is brought in contact with an acid soln., it is dissolved as a ferrous salt—say, as ferrous hydrocarbonate: $Fe+2H_2CO_3=Fe(HCO_3)_2+H_2$, or, in the case of dil. soln., as ferrous hydroxycarbonate: $Fe+H_2O+H_2CO_3=Fe(OH)(HCO_3)+H_2$. When the ferrous salt in soln. is brought in contact with oxygen, it is converted into a ferric salt, and rust is formed by the hydrolysis of this salt. The action may be represented diagrammatically: $2Fe(OH)(HCO_3)+(O+H_2O)=2Fe(OH)_2(HCO_3)$, followed by $Fe(OH)_2(HCO_3)+H_2O=Fe(OH)_3+H_2CO_3$. The rust may be formed by the condensation of several simple molecules, attended by a more or less complete dehydration of the hydrated ferric oxide. Here the rust is formed in *solution*, as it were, away from the iron. This is demonstrated by the following experiment due to G. T. Moody:

> The lower end of a glass cylinder was packed with ordinary iron-wire nails, then the nails covered with water to the depth of an inch or two after placing above them a disc of white filter-paper. On observing the cylinder at intervals, it was seen that the nails undergo little, if any, perceptible change, but that rust gradually separates out from the liquid and settles on the paper disc above them.

H. E. Armstrong continued: In the second case, when oxygen is present together with an acid in a soln. bathing an iron surface, it is included in the circuit of change, and acts as a depolarizer, and no hydrogen is then evolved. Initially, when no ferrous salt is present, the interaction may be represented: $Fe+2H_2CO_3+O_2=Fe(HCO_3)_2+H_2O_2$; and when a ferrous salt is also present, some may be included in the circuit of change and converted into ferric salt: $Fe+2H_2CO_3+H_2O_2+2Fe(HCO_3)_2=Fe(HCO_3)_2+2Fe(OH)(HCO_3)_2$—*vide infra*, for the hydrogen dioxide theory of corrosion. In other words, while iron dissolves as ferrous salt, ferrous salt which has been produced previously is converted into a basic ferric salt; in the final stage this latter salt is acted upon by water and converted into rust and acid, the which acid is then available to dissolve a further quantity of iron. It is to be supposed that when, in presence of oxygen, the hydrogen displaced by iron in dissolving is oxidized effectively in the primary circuit (entirely to water) a large additional amount of energy is developed in the circuit, so that the electromotive force is raised about 1½ volt beyond that of a single fluid iron-acid cell. The part oxygen plays is therefore a very important one in so far as it is included in the primary circuit in which corrosion is effected. It is well known that when iron has once begun to rust in air, corrosion proceeds more rapidly, the rust appearing to promote attack. There is little doubt that this is in some measure due to the fact that the finely-divided oxide serves to attract and condense moisture. It has been supposed that the rust also promotes corrosion by its electro-negative character. It may be doubted whether ferric oxide itself has much influence on this account, but inasmuch as the electronegative impurities in steel are set free as corrosion proceeds, it is easy to understand that as these accumulate on the iron surface they may well exercise a considerable influence in lowering the resistance in the circuit of change by increasing the area of the electronegative element.

The electrochemical nature of rusting, from one point of view, has been indicated in connection with the ionic hypothesis of rusting. In its present form it has been called the *local element theory of rusting*, and it was discussed by K. P. Grigorowitch,[11] W. M. Thornton and J. A. Harle, F. Goudriaan, W. Guertler and B. Blumenthal, A. Thiel, J. Eckell, F. Förster, E. Heyn and O. Bauer, T. Fujihara, W. D. Bancroft, G. Chaudron, G. V. Akimoff, S. Rachwal, U. R. Evans, F. N. Speller and co-workers, and G. D. Bengough and co-workers—*vide infra*. The electrochemical phenomena—*vide infra*, electromotive force of iron—associated with the corrosion of metals were studied from the point of view of the anode and cathode by U. R. Evans, W. R. Fleming, W. W. H. Gee, G. Gore, G. Grube, A. Günther-Schulze, R. Hadfield and E. Newbery, E. Liebreich, C. Michalke, D. Reichinstein, E. K. Rideal, E. P. Schoch, and A. Thiel; anodic corrosion due to an externally applied e.m.f., by A. J. Allmand and R. H. D. Barklie, H. Beeny, F. Bergius and P. Krassa, W. R. Cooper, J. Eckell, W. W. H. Gee, J. L. R. Hayden, R. Kremann, B McCollum and G. H. Ahlborn, R. Saxon, E. P. Schoch and C. P. Randolph, W. M. Thornton and J. A. Harle, and G. R. White; and overvoltage or overpotential in relation to corrosion phenomena, by C. W. Bennett and J. G. Thompson, J. I. Crabtree, E. Denina and G. Ferrereo, H. J. T. Ellingham and A. J. Allmand, U. R. Evans, C. Hambuechen, N. Isgaricher and S. Berkmann, M. Knobel, M. Knobel and D. B. Joy, E. Liebreich, E. Liebreich and W. Wiederholt, D. A. MacInnes, F. Meunier, W. R. Mott, E. Newbery, T. Onoda, J. W. Richards, and O. P. Watts and co-workers.

According to U. R. Evans and co-workers, the electric currents flowing between the anodic and cathodic portions of a corroding metal are equivalent to the corrosion produced, not only (*a*) in cases when the anodic and cathodic areas consist of different metals, but also (*b*) in cases where the whole specimen consists of one metal, the anodic and cathodic areas being determined by differences in oxygen-concentration, so that *the problem of corrosion velocity resolves itself into a study of the electrochemical factors which determine the strength of this current.* Owing to polarization, the cathodic and anodic potentials tend to approach one another as the current flowing is increased. The strength of the current can never exceed the value which would cause the two potentials to meet. This sets a limiting value for the corrosion-rate under any particular conditions, which can never be exceeded, however low the resistance of the circuit is made; the current-strength cannot be obtained by assuming a fixed value for the e.m.f. and dividing this by the resistance. There is an approximation to " equipotential conditions " at fairly high concentrations, but the anodic and cathodic potentials remain far apart in dil. soln., where, owing to the low sp. conductivity, an appreciable residual e.m.f. is needed to force even the small corrosion-current round the circuit. It is possible that in certain cases the part of the circuit between the anodic circuit and the anodic tubulus may have an appreciable resistance; this may occur, for instance, (1) when the primary skin has only occasional weak points (as on stainless steel), (2) if the anodic surface becomes covered with an undissolved layer of the anodic product (which may conceivably occur with ordinary iron or steel in conc. soln.). In most cases, the polarization which limits the corrosion-rate, occurs at the *cathodic area*, and is due to *limitations in the rate of oxygen-supply.* Cathodic polarization curves, under controlled conditions of oxygen-supply, have been traced for a number of metals. These curves end at high potentials in a horizontal branch which serves to indicate the law governing the ratio of anodic and cathodic areas. When corrosion starts at a weak point in the invisible film covering the surface of a metal, *the area undergoing attack extends (or contracts) until the cathodic current density on the part remaining unattacked is equal to the "protective value"*; the current flowing under these conditions will define the rate of corrosion. The protective value is the current density which will cause any incipient attack on a weak point within the area in question to lead to the precipitation of rust so close to the surface as to seal the defect.

The rapid action of acid on commercial zinc is connected with the presence of impurities which exist as a separate phase; a perfectly homogeneous metal, or a one-phase solid soln., may dissolve more slowly or more quickly than the pure metal. An impurity which exists as a separate phase will assist corrosion if it be nobler than the dominant metal and has a smaller overvoltage. Using a figure of speech, when two metals are in contact and conjointly exposed to chemical influence during long periods of time, one metal sacrifices itself to ensure the other's preservation. Actually, one metal acts as anode and the other metal as cathode. Thus, there may be a rapid local attack on iron railings fixed in position by lead where iron is the sacrificial metal. In the case of iron in aerated water, ferrous iron may at first dissolve leaving an equivalent amount of hydrogen as a polarizing film on the surface of the metal. Oxygen removes this layer. Hence, iron should dissolve faster when it is in contact with a more electronegative metal like platinum, for the hydrogen would preferably collect on the platinum plate rather than on the iron. G. J. Burrows and C. E. Fawsitt[12] found this to be the case. Thus, iron lost 0·218 per cent. when alone and 0·399 per cent. when in contact with platinum for 17 days; and respectively 0·286 and 0·504 during 35 days. O. P. Watts and H. C. Knapp cited an extraordinary case of a yacht constructed of the non-corroding monel metal, with a steel stem, keel, stern post, and rudder-frame. Before the vessel had made a single voyage, the steel parts were rendered useless by corrosion—the steel acted as anode, and the monel metal as cathode. On ships, steel is very liable to corrode in contact with brass, bronze, or other copper alloy. J. B. Hartley reported that brass had the power to preserve cast and wrought iron from attack by sea-water, but E. Davy, and C. F. Schönbein doubted the statement, and R. Mallet said a more destructive practice than the use of this supposed preserver can scarcely be conceived or more fatally applied. E. Heyn and O. Bauer observed that contact with brass had very little influence on the corrosion of cast iron. H. Davy in his paper on the preservation of the copper sheathing of ships by using zinc as the sacrificial metal, stated that cast or wrought iron can be preserved by using zinc or tin as sacrificial metals. H. Davy was wrong with regard to tin, because A. van Beck, M. Meyer, G. J. Mulder, and E. Davy showed that iron acts as sacrificial metal and preserves tin, but zinc will preserve both iron, and tin. A. van Beck said that H. Davy was misled by observing that tin is positive to iron in atm. air, but the relations are reversed when the couple has been for half an hour in sea-water. In the tinning of iron, described by E. Trubshaw, and P. Flower the iron (sacrificial metal) is covered with a thin layer of tin. The iron is protected from corrosion only so long as the tin coating remains intact; once the iron is exposed, rusting proceeds more quickly than if the tin were absent. F. Ulzer showed that the tin surface usually breaks down at a number of isolated points, and not in continuous patches. This shows that the tin surface contains a number of pinholes. M. F. von Wurstemberger discussed what he called the selective corrosion of metals; the dissolution of iron in acids, and the rusting of iron in contact with other metals. A. Stansfield observed that in electrolytic iron, which is considered to be pure and homogeneous, local action may occur because of the different orientations of the atoms in different grains, so that even if the metal is homogeneous, local action can occur through differences in the crystals of the metals, and differences in the concentration of the oxygen in different parts of the same metal.

Anodic corrosion due to local e.m.f.—*e.g.* the corrosion of "tinned" iron—galvanic couples, and concentration cells were discussed by T. Andrews, J. Aston, R. Auerbach, O. Bauer and O. Vogel, G. D. Bengough and co-workers, L. H. Callendar, H. Cassel, M. Centnerszwer and M. Straumanis, G. Chaudron, G. C. Clifford, H. J. Donker and R. A. Dengg, J. W. Cobb, C. Bach, J. T. Corner, E. Cumberland, A. S. Cushman, H. E. Davies, P. Debye, C. H. Desch, C. M. van Deventer, J. Eckell, U. R. Evans and co-workers, J. Farquharson, R. H. Gaines, W. W. H. Gee, W. Guertler and B. Blumenthal, H. H. Hanson and W. K. Lewis, E. S. Hedges and J. E. Myers, E. Heyn and O. Bauer, A. L. Hughes, W. E. Hughes, W. P. Jorissen, K. Kieper, E. F. Kohman and N. H. Sanborn, G. von Knorre, R. H. Lueck and H. T. Blair, A. L. McAulay and F. P. Bowden, R. J. McKay, C. L. Mantell and W. G. King, E. Maurer, P. D. Merica, W. Palmaer, T. E. Perks, A. Phillip, F. H. Rhodes and E. B. Johnson, W. Schmid, E. C. Sherman, J. W. Shipley, A. Sinclair, M. Straumanis, A. T. Stuart, R. Stumper, G. Tammann and F. Neubert, F. Tödt, W. H. J. Vernon, F. Ulzer, W. H. Walker and co-workers, G. C. and M. C. Whipple, W. G. Whitman and co-workers, and W. G. Whitman and R. P. Russell. The increased corrosion of iron by segregations was discussed by C. V. van Brunt, W. H. Walker, and G. R. Woodvine and co-workers. The effect of graphite in cast iron on corrosion was discussed by O. Bauer and co-workers, U. R. Evans, P. Kötzschke and E. Piwowarsky, E. Liebreich and W. Wiederholt, H. Nipper and E. Piwowarsky, W. Palmaer, J. W. Shipley and I. R. McHaffie, F. N. Speller, R. Stumper, and A. Thiel and co-workers; the effect of slag and non-metal inclusions in iron, by C. Benedicks and H. Löfquist, H. le Chatelier and B. Bogitsch, J. W. Cobb, C. H. Charles, H. D. Hibbard, C. E. Homer, E. F. Law, P. Oberhoffer and co-workers, L. T. Richardson, and R. S. Weston; and gas inclusions, by O. Bauer, and M. Schromm. J. Walter, M. Rudolph, O. Gross, W. Bennett, and U. R. Evans attributed the corrosion of rivet-heads in boilers, and at discontinuities in metal coatings to electrolytic action.

H. Davy was right with respect to zinc, as was shown by E. Davy, W. H. Pepys, M. Meyer, the 1840 patent of S. Sorel for "zincking" or galvanizing iron with zinc, and the 1791 patent of G. le R. de Jeaucourt for preserving metals from rust by covering them with an alloy of zinc, bismuth and tin. The subject was discussed by W. H. Walker. G. von Knorre observed that iron in contact with the noble metals and alloys is strongly attacked, whereas in contact with zinc it becomes inert. The feasibility of zinc as a protector for iron ships has been discussed by R. Mallet, and B. Bell; and its use for protecting boilers from acidic feed-water, by G. Richardson, and W. Parker.

G. Gallo, and others have shown that the greater the difference of potential of iron and a soln. with which it is in contact, the more readily does rusting occur. O. Bauer and O. Vogel, and E. Heyn and O. Bauer measured the electrochemical series of the metals in a 1 per cent. soln. of sodium chloride, at 18°, and found the approximate order: Mg, Mn, Zn, Fe, Cd, Al, Te, Pb, Sn, Si, Sb, W, Cu, Bi, Mo, Ni, Ag, Hg, Te, Cr, Au, Pt, $C_{\text{graphite}}+$; and H. Diegel found the corrodibility of some metals in sea-water to be: Zn, Al, Fe, Sn, Al—and Sn bronzes, Cu, Phosphor-bronze+. E. Davy found that iron in contact with *copper* in soln. of electrolytes is corroded, and the subject was studied by E. Davy, H. Diegel, O. Bauer, and O. Vogel, H. Cassel, U. R. Evans, E. Heyn and O. Bauer, G. von Knorre, and W. G. Whitman and R. P. Russell. O. Bauer and O. Vogel found that iron in contact with *silver* is corroded, and similar results were obtained with iron in contact with *gold*, and the reaction was studied by W. S. Landis. O. Bauer and O. Vogel observed that the iron is protected when in contact with *magnesium* in soln. of electrolytes; iron in contact with *zinc* is also protected, as was observed by O. Bauer and O. Vogel, W. R. Dunstan, U. R. Evans, C. Lindet, M. Meyer, and W. H. Walker and co-workers. O. Bauer and O. Vogel, and U. R. Evans observed that iron is also protected when in contact with *cadmium*. O. Bauer and O. Vogel found that iron is incompletely protected when in contact with *aluminium*. The reaction was studied by A. T. Stuart, and H. Bauermeister. The rusting of iron in contact with *tin* is accelerated, and the reaction was studied by O. Bauer and O. Vogel, U. R. Evans, R. H. Lueck and H. T. Blair, and M. Meyer—*vide infra*. O. Bauer and O. Vogel, F. Enslin and F. Buschendorf, U. R. Evans, and H. H. Hanson and W. K. Lewis found that the corrosion of iron is accelerated when that metal is in contact with *lead*. O. Bauer and O. Vogel also found that iron is more susceptible to corrosion when it is in contact with *bismuth*. R. Irvine reported that when wrought *iron* is in contact with cast iron, the former metal is preferentially corroded. A. Schleicher and co-workers found that iron is attacked when in contact with passive wrought iron, rusty cast iron, clean wrought iron, passive cast iron, and clean cast iron, and this order is the order electrochemically. Oxidized iron is positive to clean iron. The subject was discussed by E. Heyn and O. Bauer, and G. von Knorre. O. Bauer and O. Vogel found that the corrosion of iron is favoured by contact with *nickel*, and the reaction was studied by U. R. Evans, W. Schlötter, and O. P. Watts and P. L. de Verter. A. Brochet and J. Petit found that the corrosion of iron is favoured by contact with *platinum* in soln. of potassium cyanide. Iron becomes passive in contact with platinum—*vide supra*, the passive state of iron.

The corrodibility of iron in contact with various alloys depends, as in the case of single metals, on the position of the alloy in the electrochemical series. O. Bauer and O. Vogel found that in a 1 per cent. soln. of sodium chloride, at 18°, the e.m.f. after 120 hrs. ranges from −1·5 volts with *magnesium-zinc alloys* ; −1·480 volts with *magnesium-aluminium alloys* ; −1·115 volts to −0·980 volt with *magnesium-zinc-aluminium alloys* ; −1·026 volts with *zinc-aluminium-copper alloys* ; −1·012 volts with *zinc-tin alloys* ; −0·936 volt with *zinc-aluminium alloys* ; from −0·763 to −0·577 volt with *aluminium-copper alloys* ; from −0·762 to −0·759 volt with *cast iron* ; −0·744 volt with *steel* ; −0·707 volt with *Wood's alloy*—that is, Bi : Pb : Sn : Cd as 50 : 25 : 12·5 : 12·5—percentages by weight ; −0·581 volt with 25 per cent. *nickel-steel* ; −0·483 volt with *lead-antimony alloys* ; from −0·418 to 0·401 volt with *tin-antimony-copper alloy* ; with *brass* :

Copper . . .	40·4	48·4	51·9	70·2	77·8	92·3 per cent.
E.m.f. . . .	−0·401	−0·359	−0·322	−0·236	−0·212	−0·193 volt

from −0·170 to −0·146 volt with *tin-copper alloys* ; −0·154 volt with *phosphor-bronze*—0·493 per cent. phosphorus and 5·69 per cent. of tin ; and −0·100 volt with *nickel-copper alloy* with 49·27 per cent. of copper. Observations were also made by O. Bauer, G. von Knorre, G. C. Clifford, and O. P. Watts and H. C. Knapp. W. P. Jorissen observed that the attack on iron with brass containing 33·4 per cent. of copper was less than with brass with 36·9 per cent. of copper.

In connection with the corrosion of the iron by organic acids in fruit juices preserved in "tinned cans," E. F. Kohman and N. H. Sanborn studied the electrochemical relations of tin and iron. They found that at concentrations eq. to 0·75 per cent. malic acid, tin is distinctly cathodic in acetic, malonic, and succinic acids, only slightly cathodic in malic acid, and distinctly anodic to iron in citric acid. Addition of apple pomace to acetic, malonic, and succinic acids reverses the condition and the tin becomes anodic, a further protection to iron being also induced by the presence of tin in soln., which raises the cathodic polarization on iron. In hydrochloric and sulphuric acids of conc. ranging from 0·05 to 20 per cent., tin becomes increasingly more anodic to iron with increasing conc. of acid even when the metals are not in electrical contact, and corrosion of tin is very greatly increased with metallic contact, due to galvanic action. The potential conditions are influenced chiefly by the $H^{\cdot}$-ion conc. and negligibly by the conductivity of the soln. The results agree with those of commercial practice in which the more acid fruits produce little perforation of the container, although less acid fruits—*e.g.* black cherries, in the juice of which tin is only mildly anodic to iron—cannot be canned successfully because of the hazard of corrosion. The subject was discussed by C. L. Mantell, E. Nehring, P. and E. Nehring, O. Carrasco and E. Sartori, A. Pellerin and E. Lasausse, E. Gudeman, E. F. Kohman and N. H. Sanborn, and T. N. Morris and J. M. Bryan. R. H. Lueck and H. T. Blair observed that in approximately 0·2*N*-soln. of various acids having p_H ranging from 0·81 to 2·98, iron dissolves with evolution of hydrogen but tin is unattacked. With an iron-tin couple, hydrogen is evolved but the rate of evolution is always less than that from uncoupled specimens of iron. With a citric-malic acid soln. of $p_H=2·98$ this protective action of tin on iron is exhibited when the soln. is aerated as well as when it is kept sat. with hydrogen or nitrogen. Corrosion is most rapid in the aerated soln., but in all cases it is the tin which dissolves more rapidly from the couple. Cadmium coupled with iron protects it to a similar extent, but the cadmium dissolves more rapidly than tin under the same conditions. As just indicated, the e.m.f. of cells of the type Fe | canned foods | Sn shows that, although tin is definitely cathodic to iron on open circuit, on short-circuiting, the e.m.f. falls rapidly and changes sign, the tin becoming the anode. The removal of either electrode and exposing it to air gives it a more noble potential. With similar cells using iron and cadmium electrodes, the latter is always the anode and the e.m.f. changes very little on short-circuit; using tin and cadmium, cadmium is again always anodic, but the e.m.f. falls notably on a closed circuit and recovers gradually when the circuit is opened. In a diaphragm cell containing a citric-malic acid mixture buffered to $p_H=3·5$, with the iron electrode in a soln. sat. with oxygen or hydrogen, the tin electrode always becomes the anode whether the soln. into which it dipped is kept saturated with oxygen or with hydrogen or not treated with gases at all. But with no gas passed through the soln. around the iron, the tin is always cathodic if the soln. into which it dipped is kept sat. with oxygen or with hydrogen. The addition of hydrogen dioxide to the soln. around the tin also keeps it cathodic to the iron. These results are related to the high hydrogen overvoltage of tin compared with that of iron; the tin becomes polarized and then hydrogen is more readily liberated at the iron. The abnormal tendency of canned fruits to cause the perforation of the tin container is possibly due to the presence of mild oxidizing agents which cause the microscopic areas of exposed iron to become anodic to the surrounding tin.

The speed of the reaction between iron and the ambient medium—say, a corrosive acid—is determined by the rate at which the film of liquid in contact with the metal is saturated, and on the rate at which the solute diffuse into the surrounding medium. This so-called *diffusion theory of dissolution* was studied by E. Bruner, L. Bruner and St. Tolloczko, W. Nernst, A. A. Noyes and W. R. Whitney, W. Palmaer, W. G. Whitman and co-workers, and R. P. Russell and co-workers.

W. R. Dunstan and J. R. Hill consider that when air and water alone fail to produce rusting, the iron has been made passive by the process of purification, and that carbon dioxide destroys the passivity and inaugurates rusting. The normal rusting process is a result of the direct action of oxygen dissolved in water upon the iron—ferrous hydroxide is first formed and this subsequently oxidizes to the ferric condition. Substances in soln. which inhibit rusting are supposed to do so by making the iron passive—*e.g.* oxidizing agents like alkali chromates, dichromates, permanganates, iodates; and potassium sodium hydroxides, etc.—and some of these substances—*e.g.* potassium dichromate—have found industrial application as anti-rusting agents.

Iron of a high degree of purity was found by H. Kreusler, A. Skrabal, A. Neuburger, J. A. N. Friend, and B. Lambert to be comparatively inactive. Industrial iron is impure, and not physically homogeneous; while natural water always contains electrolytes. Hence, local currents may be generated on the surface, and as a result the metal may be dissolved in one place and give off hydrogen in another, so that the impurities act as centres of corrosion. The oxygen dissolved in the water acts as a depolarizer for the cathodic hydrogen. M. Centnerszwer and M. Straumanis demonstrated the existence of these local currents; and F. Tödt, that the corroding surface of iron consists of local elements of active and passive metal. E. Pietsch and co-workers observed that distilled water alone does not attack homogeneous surfaces of iron, but with heterogeneous surfaces rusting commences between the grains. O. P. Watts found that a " busy rail "—that is, a rail in regular use—is electropositive to an "idle rail" and so is less liable to rust. Similarly, cold-worked metal is electropositive to the unworked metal.

In the case of iron and steel there may be many different phases—graphite, carbide, phosphide, oxide, sulphide, etc.—and the distribution of anodic and cathodic areas on the surface of the metal can be explored by the so-called *ferroxyl indicator* suggested by W. H. Walker and co-workers, and A. S. Cushman and H. A. Gardner. The soln. or jelly, containing potassium ferricyanide, and phenolphthalein, becomes blue where the iron acts as an anode, and passes into soln. as a ferrous salt, while it becomes pink where the iron acts as cathode and alkali is liberated. The test was discussed by H. S. Rawdon, W. van W. Scholten, U. R. Evans, S. Kyropoulos, J. W. Cobb, W. Blum and C. F. Thomas, and K. Pitschner. R. E. Wilson observed that the potassium ferricyanide in the indicator may act as oxidizing depolarizer when no sensible increase in the conc. of the OH′-ions occurs, and the cathode areas are then recognizable by the disappearance of the yellow colour of the ferricyanide. A. S. Cushman described the preparation of the ferroxyl indicator as follows:

> A 1·5 per cent. soln. of agar-agar is first made by dissolving a weighed quantity of powdered agar-agar in the requisite amount of water. This soln. is boiled for 1 hr., fresh water being added to replace that lost by evaporation. It is then filtered while hot, and 2 c.c. of standard phenolphthalein indicator added to every 100 c.c. of soln., after which it is brought to a perfectly neutral condition by titration with a 0·1*N*-soln. of potassium hydroxide, or hydrochloric acid, as the case may be. The addition of 7 c.c. of a 1 per cent. soln. of potassium ferricyanide to every 100 c.c. of soln. is then made, and the ferroxyl reagent while still hot is ready to use. Enough of the reagent should be poured into a dish just to cover the bottom and the dish floated in cold water until the agar-agar has jellied. A clean sample of iron is then placed on this bed of jelly and covered with the hot soln. After the final addition of agar-agar the dish should not be removed until thoroughly cooled. While the colours sometimes show up immediately, they usually require from 12 to 24 hrs. to attain their most perfect development. The mounts may be preserved for many months by keeping the surface of the agar-agar covered with alcohol.

L. Aitchison observed that compact iron consists of crystals of ferrite, separated by an amorphous cement; the soln. press. of the cement must differ from that of the ferrite, so that when immersed in water, a difference of potential will be set up which must lead to corrosion. If the cement is positive to the ferrite, the cement will be corroded, and conversely. When steels are attacked by dil. acids, J. O. Arnold and A. A. Read—*vide supra,* sulphuric acid—showed that the ferrite passes into soln. while the carbides are not attacked but remain in their original form. The irregularity in the composition of a piece of iron and steel produced by segregation, etc., was discussed by R. H. Gaines, J. W. Cobb, and W. Marriott; and the pitting produced by local galvanic action due to surface impurities—traces of cinder, slag, sulphide, oxide, etc.—by C. Bach, N. Barnaby, O. Bauer, U. R. Evans, G. Gallo, B. Garre, W. W. H. Gee, E. Heyn and O. Bauer, S. Kyropoulos, V. B. Lewes, J. T. Milton and W. J. Larke, W. Palmaer, W. Parker, H. F. Richards, L. T. Richardson, A. Schleicher and G. Schultz, C. J. Smithells, R. Stumper, W. H. Walker and W. K. Lewis, G. C. and M. C. Whipple, and W. H. White—*vide infra.* As emphasized by U. R. Evans, this does not necessarily mean that impure metals have a greater tendency to corrode than purer metals.

R. Stumper found that the corrosion of iron is considerably increased when the metal is in contact with iron sulphide, and in the case of galvanic contact, the corrosion is more than twice as great. R. Mallet explained the greater corrosion of thin pieces of cast iron in sea-water by showing that thin castings cool more quickly and more irregularly than thick ones so that they are more likely to be less homogeneous. Consequently, when immersed in sea-water the number of local voltaic couples is proportionally increased, and the corrosion is thus augmented. The difference was most marked with grey, or graphitic, cast iron, and least marked with the white varieties. U. R. Evans observed that local electrolytic action may occur owing to the local abrasion of surface layers. Where the corrosion product is loose and flocculent, the abraded portion is often cathodic, and no local action occurs, but when the film is thin and highly protective, the abraded portion will be anodic, and corrosion on that part will be intensified. Similarly, local currents may be produced by the same metal, one part greased and one part not greased. G. A. Tomlinson discussed the corrosion of steel surfaces in contact.

B. Martell, and W. Denny mentioned puzzling cases of corrosion which have occurred when old iron structures have been patched up with new material. Pliny, in the first century of our era, mentioned such a case in his *Historia naturalis* (**36**. 43), for he said that the iron chain across the river Euphrates at Zeugma (Mesopotamia) was repaired by introducing new links, but the new links gathered rust under conditions where the remainder of the old links were free from rust. R. Mallet found that in sea-water, grey cast iron in contact with white cast iron corroded with the greater velocity, so that white cast iron was protected by the grey cast iron. T. Andrews found that the potential difference in volts between cast iron and wrought iron, in sea-water, is 0·030 volt in favour of cast iron for 233 days out of 300, and during that time, the cast iron was less corrodible than wrought iron ; but the potential difference varies from day to day, so that in some cases the potential difference is reversed, and he found in one case the potential difference is —0·011 volt, so that wrought iron having the higher potential was least attacked for 66 days out of 300. The adhesion of rust, and the heterogeneity of the metal are known to affect the difference of potential. E. Heyn and O. Bauer also found that the contact of steel with cast iron reduced the corrosion of steel. Hence, the contact between steel and cast iron may augment corrosion and be a source of danger. J. A. N. Friend mentioned a serious accident in the Portsmouth Dockyard owing to the abnormally rapid corrosion of wrought iron in contact with cast iron. Errors may occur in experimental work when one metal plate is placed above another in the corroding liquid, for the one plate may prevent a certain amount of oxygen diffusing to the other plate, and thus reduce corrosion independently of any galvanic action. V. B. Lewes mentioned a possible case of galvanic activity when plates of the same metal but at different temp. form couples ; and T. Andrews, *vide supra*, when plates of strained and unstrained metal are in contact—the unstrained metal is electropositive to the strained metal. The galvanic action between different kinds of iron was discussed by J. Farquharson, H. Diegel, H. S. Munroe, W. Parker, A. Ledebur, A. Sang, H. M. Howe, etc.

The galvanic activity between strained and unstrained pieces of the same iron was discussed by T. Andrews, W. M. Barr and R. W. Savidge, C. F. Burgess, U. R. Evans, C. Hambuechen, E. Heyn and O. Bauer, K. Mandi, T. W. Richards and G. E. Behr, W. Spring, W. H. Walker and C. Dill, etc.—*vide infra*. F. Osmond and J. Werth found that the cold-worked metal dissolves faster than does the unworked metal in salt soln. P. A. von Bonsdorff, C. F. Burgess, U. R. Evans, J. A. N. Friend, P. Goerens, H. Hanemann and C. Lind, W. Charpentier, E. Heyn, R. Kremann and R. Müller, D. J. McAdam, T. W. Richards and G. E. Behr, R. P. Russell and co-workers, and M. Werner made observations on this subject. According to B. Garre, the rate at which iron dissolves in dil. sulphuric acid increases directly with the number of twists to which the metal has been subjected, and the rate of dissolution of iron is greater after bending than before. H. S. Rawdon also noted that intercrystalline corrosion is favoured by high stresses. As indicated below, H. Endo observed that the loss by corrosion in dil. sulphuric acid is almost proportional to the amount of deformation by tensile stresses ; the loss also increased with torsion, and, in general, the attack is greatest where the twist is greatest ; and the loss also increases with the load of compressive stresses. J. A. N. Friend found that, as a rule, unstressed iron corrodes more quickly than iron which has been deformed by stretching, twisting, or compression—*vide infra*, corrosion fatigue. The slower the rusting of busy iron in comparison with idle iron—*e.g.* railway lines—was discussed by J. A. N. Friend, O. Bauer, and A. S. Cushman and H. A. Gardner.

A. C. Brown,[13] O. Brown, and J. Aston and co-workers observed that iron coated with freshly-formed rust, which has had no chance to dry, is always anodic to the bare metal, so that the rust promotes electrolytic effects equal to or surpassing those factors generally considered to be of marked importance. There is sometimes a reversal of the current between anodic rust and the cathodic metal. The change in the polarity of freshly-formed wet rust is attributed to unpreventable local action on relatively large electrode surfaces. Dry rust tends to reverse its initial cathodic character and to behave like fresh wet rust after varying periods of immersion. The reversal of the polarity in the drying of wet rust is attributed to a change in the degree of hydration, to the adsorption of gases from the atmosphere, or to the formation of an oxide or other compound of iron in contact with the metal surface. The effect of rust on the surface of the metal was discussed by J. Aston, O. Bauer, E. L. Chappell, U. R. Evans, J. A. N. Friend, F. Goudrian, E. Heyn, O. Kröhnke, R. Kremann and R. Müller, E. Maass and E. Liebreich, E. A. and L. T. Richardson, W. D. Richardson, A. Schleicher and G. Schultz, G. C. Schmidt, J. Spennrath, J. Stapenhorst, W. A. Tilden, W. H. Walker, G. C. and M. C. Whipple, and H. Wölbling. L. H. Callender showed that a boundary film solid, liquid, or gas—tends to form on a metal whenever the film has a higher potential than the metal itself. E. L. Chappell, and T. Fujihara discussed the rôle of rust-films in the corrosion of metals. According to G. A. Tomlinson, the rusting which occurs when the two pieces of steel have been rubbed together is not due to the crushing of the surfaces of contact and so producing minute particles of powder which oxidize rapidly, but he considers that the phenomenon is a result of molecular cohesion produced by pressure.

J. Aston showed that the reason wet rust promotes further rusting is not due to its acting as a cathode, but rather because it acts as a diaphragm the same as the interposition of wet cloth, or filter paper between two metals. J. Aston said:

> The underlying feature appears to be the relative access of oxygen to the surface of the electrodes. The electrolyte (moisture) must reach both; then that to which oxygen has the more free access becomes the cathode, and the other is the anode. If two bare iron electrodes are separated by a partition of porous earthenware, parchment, etc., either may be made the cathode by bubbling air into this compartment, and not into the other. Wet rust or similar coating upon one electrode plays the rôle of a diaphragm permeable to the moisture, but preventing or slowing down the oxygen penetration. Anodic soln. of the underlying iron results, with oxidation and precipitation as greenish ferrous hydroxide. This colloid, migrating outwards under the directive influence of the current, is in turn oxidized to ferric hydroxide nearer to the exposed surface of the rusted anode. The effect of rust and oxygen is well illustrated by local rusting of an iron sheet which has air bubbling up one strip or zone. Contrary to general expectation, the zone supplied with air remains clear, whilst the adjoining parts are anodic and become coated with rust.

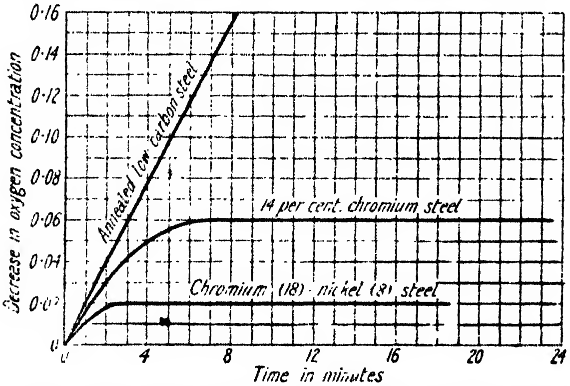


FIG. 363.—Initial Rates of Corrosion of Ordinary and Alloy Steels.

According to H. O. Forrest and co-workers, the corrosion of iron and other metals in, say, aerated water is attended by the formation of more or less protective films of hydrated oxide on the surface of the metal. The metals which are usually considered to resist corrosion, like ordinary iron and steel, are initially attacked in a similar manner, but so-called resistors of corrosion form a very resistant and protective surface film. The differences in the resistance of, say, ordinary mild steel and stainless steel is attributed solely to differences in the physical and mechanical properties of the films. Fig. 363 represents the rates of attack of these steels expressed in terms of the rates at which oxygen is consumed in c.c. per sq. dm. Corrosion starts in all cases but ends very quickly as the protective film is formed. This is shown by the flattenings of the curve corresponding with zero corrosion. The curve for the low-carbon steels begins to flatten after a longer period of time, but the film is here not so resistant as in the case of the two alloy steels.

In 1830, E. Marianini found that momentary currents can be produced between two zinc electrodes immersed in water, simply by lifting one of them into the air and replacing it; and E. Warburg, and W. Kistiakowsky showed that an electrical current may be generated by variations in the conc. of the oxygen in the soln., and by variations in the conc. of the salts in soln. in contact with different parts of the metal. U. R. Evans made a special study of the electrical currents set up by the **differential aeration** of metals. In what he called the key experiment, a cell was made with two sheets of the same iron as electrodes; one of which was placed in a porous cell of parchment; the electrolyte was 0·5N-KCl; the electrodes were connected with a milliammeter. Air was bubbled against the iron plate in the outer compartment. The milliammeter then showed that the aerated electrode was the positive pole or cathode, and the unaerated electrode was the negative pole or anode; the current was provided by the consumption of metal from the unaerated electrode, since the unaerated electrode loses more weight than the aerated electrode. If the current be tapped from a plate of metal immersed vertically in a soln. of potassium chloride exposed to air, a current flows between the upper aerated zone at the top, and the unaerated portion below. The general results indicate that the corrosion of metals like iron, zinc, and lead by a soln. of a salt like sodium chloride is an electrochemical process; for it involves (i) the production of an electric current; (ii) the production of a soluble metal salt—ferrous chloride—at the anodic or unaerated places; (iii) the production of sodium hydroxide at the cathodic or aerated places; and (iv) the precipitation of an insoluble hydroxide—*e.g.* ferrous hydroxide—where the products from the cathodic and anodic zones meet. The white ferrous hydroxide darkens rapidly, and it may appear green on the lower surface and brown on the upper surface. This is illustrated by U. R. Evans' study of the corrosion of a dry horizontal sheet of polished iron by a drop of a soln. of sodium chloride resting on it. After some minutes, a precipitate of ferrous hydroxide begins to appear, not at the edge, but in a circle running round the drop a short way within the margin—Fig. 364. The precipitate is at first white, and after a time it becomes brown, and extends as a membrane until it passes over the top of the drop. A sample of liquid taken from the clear outer ring is strongly alkaline, and free from iron salts, while a sample abstracted from the interior, by means of a fine capillary tube, contains ferrous chloride but no free alkali. Oxygen is more easily renewed at the edge than near the centre of the drop, so that metal under the outer rim of the drop acts as cathode and alkali hydroxide is formed, whereas in the interior unaerated portion the metal suffers anodic attack and ferrous chloride is formed. Along the surface of contact of the alkali hydroxide and ferrous chloride soln., a ring of white ferrous hydroxide is formed, which by further oxidation changes to rust-brown hydrated ferric oxide. Corrosion occurs only in the central portion of the drop. Hence, U. R. Evans concluded that corrosion is likely to persist most readily in places where oxygen has least access, provided the inaccessible places are not far removed from places to which oxygen can freely penetrate. He illustrated the principle of differential aeration by the

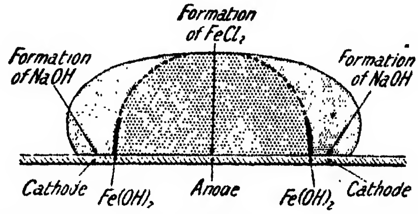


FIG. 364.—Vertical Section illustrating the Corrosion of Iron by a Drop of a Solution of Sodium Chloride.

case of a minute cavity in a plate of metal immersed horizontally just below the surface of a soln. of sodium chloride. Oxygen will not be so quickly supplied to the liquid within the cavity as it is to liquid over the plane surface of the metal. Hence, the metal about the cavity becomes anodic, and the aerated portion outside becomes cathodic. The phenomena occurring in the case of the drop are repeated under another guise—Fig. 365. The general result is that the corrosion is concentrated upon a small anodic area within the cavity, and pitting results. The drop method of studying corrosion was employed by U. R. Evans, T. Fujihara, and T. S. Fuller; and the principle of differential aeration was discussed by E. Maass and E. Liebreich, E. Herzog and G. Chaudron, F. Tödt, E. Liebreich, D. W. Smith and R. F. Mehl, and H. Cassel and T. Erdey-Gruz.

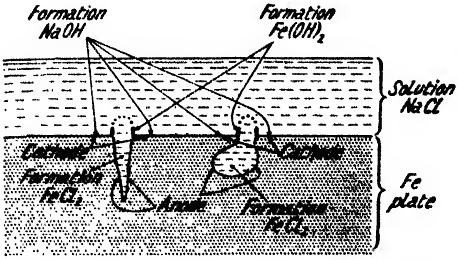


FIG. 365.—Vertical Section illustrating the Formation of a Couple of Pits in Iron immersed in a Solution of Sodium Chloride.

A. Payen noted the localized oxidation at what he called oxidized points. The corrosion of iron is thus due to the formation of local *oxygen concentration cells*. The amount of corrosion depends on the supply of the corroding agent to the cathodic areas where it acts as a depolarizer, but the metal is attacked in the anodic areas. At the cathodic surface, $6H'+1\cdot5O_2=3H_2O+6\oplus$; at the anodic surface, $2Fe+4OH'=2Fe(OH)_2+4\ominus$; and in the corrosion product, $2Fe(OH)_2+2HO'=2Fe(OH)_3+2\ominus$, the resultant reaction being $3H_2O+1\cdot5O_2+2Fe=2Fe(OH)_3$. The theory was discussed by R. E. Wilson, J. Aston, R. J. McKay, W. G. Whitman and co-workers, and F. N. Speller. The localized forms of corrosion known as pitting and perforation are usually the most serious forms of corrosion. Many pounds of iron might be lost by a boiler through uniform surface corrosion without any particular harm, but a small proportion lost by pitting might perforate the plate; or, as A. S. Cushman expresses it, just as a chain is no stronger than its weakest link, so also a piece of iron in service may be ruined and discarded even if more than 99 per cent. of its mass and surface is still in good condition. The subject was discussed by J. R. Baylis, C. Benedicks, S. C. Britton and U. R. Evans, E. Englesson, U. R. Evans and C. W. Borgmann, J. A. N. Friend, G. N. Huntley, E. Liebreich, G. Mehrtens, J. Mitchell, E. Pietsch and E. Josephy, G. Schikorr, E. H. Schulz, A. Thiel and W. Ernst, W. Thomson, F. Tödt, G. C. and M. C. Whipple, A. Winstanley, and F. Wurtzemberger. D. F. Calhane and A. L. Gammage found that a small proportion of iron in nickel plates forms with nickel a series of galvanic couples, and these after long exposure to the atmosphere cause rusting.

J. T. Milton and W. J. Larke,[14] and S. Rachwal noted that iron with a heterogeneous structure is more prone to corrosion than when the structure is more homogeneous. C. Frémont and F. Osmond discussed corrosion along Hartmann's and Luder's lines—*vide supra*. The *annealing* of cold-worked iron makes it less corrodible, and, according to E. Heyn and O. Bauer, the influence is perceptible even when the metal has been heated to 100°. The subject was discussed by H. Altpeter, M. Delbart, P. Goerens, H. Hanemann and C. Lind, and J. H. Whiteley and co-workers. C. Chappell found that *quenched steel* is more corrodible than steel which has been quenched and then annealed, and that the effect depends on the temp. of corrosion; J. Driesen observed a maximum between 350° and 400°, and a minimum between 100° and 200°. The subject was discussed by V. Duffek, H. Endo, W. Köster, and S. Whyte.

Observations on *the effect of grain-size* on the corrosion of metals are often complicated by the simultaneous presence of other factors, so that the evidence is sometimes conflicting. P. T. Bruhl, and S. W. Smith considered that a small grain-size favoured the attack. J. P. Sparrow, S. Whyte, W. H. J. Vernon, and N. S. Kurnakoff and A. N. Achnasaroff said that a fine structure resists attack better than does a coarse structure; R. J. Anderson and co-workers, and G. D. Bengough and R. May added that whilst the effect of the grain-size is small, corrosion is less with a small grain-size than with a large one; and J. H. Whiteley and A. F. Hallimond could detect no difference in the reaction curves of annealed iron having widely different grain-size with nitric acid. Observations on the subject were made by H. Hanemann and C. Lind, W. R. Fleming, R. G. Guthrie, C. Irresberger, G. Rittler, A. Schleicher, G. Schleicher, G. Schumann, and S. Whyte. Some of the results of C. Chappell with sea-water for 116 days are summarized in Fig. 366—*vide infra*. The preferential corrosion between the crystals—*intercrystalline corrosion*—was studied by H. S. Rawdon, D. Hanson, and J. A. Jones. L. Aitchison concluded that *the twinning of the crystals* is likely to hasten the corrosion of any metal showing a tendency to be attacked.

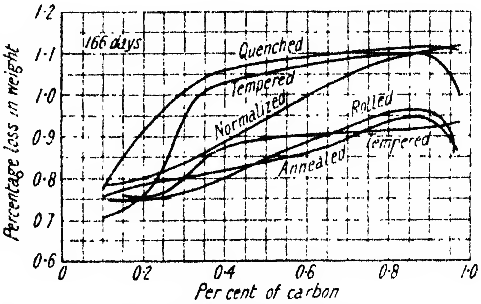


FIG. 366.—The Effect of Heat-treatment on the Corrosion of Iron.

K. Arndt[15] showed that the physical condition of the exposed surface is an important factor affecting its corrodibility. R. Pflücker emphasized the favourable influence of polishing on the resistance to rusting; and U. R. Evans, the unfavourable influence of surface abrasion. A highly polished surface is less liable to corrode than a rough-filed, more or less porous mass. The latter will rust under conditions where the former will remain bright, because moisture may condense in the interstices of the rough surface, and evaporate slowly. So also are the coarser grained varieties of cast iron more corrodible than the finer grained varieties. The interstices between the strands of a wire cable behave as pores, and allowing condensed water to lodge therein greatly accelerate the speed of corrosion, so that, as M. T. Murray showed, a cable may appear outwardly sound and strong, and be internally rotten. O. Bauer discussed the influence of blobs and pores in the metal on rusting; and H. S. Rawdon, etc.—*vide supra*—the intercrystalline corrosion of metals. Observations on the influence of surface conditions on corrosion were made by L. Aitchison, G. D. Bengough and co-workers, L. H. Callender, U. R. Evans, C. E. Fawsitt, W. Fraenkel and G. Tammann, B. Garre, P. Goerens, H. Hauschild, E. Liebreich, E. Liebreich and F. Spitzer, L. R. Luce, E. Newbery, W. Rosenhain and co-workers, G. M. Schwab and E. Pietsch, G. Tammann, H. S. Taylor, W. H. J. Vernon, and G. Walpert; the intercrystalline corrosion of metals was studied by H. S. Rawdon; and observations on the surface phenomena, by U. R. Evans, H. Euler, W. H. Hatfield, I. Langmuir, C. Marangoni and P. Stefanelli, D. Ruff, B. D. Saklatwalla, and G. A. Tomlinson. The favourable effect of the skin produced during the casting of the metal in resisting the corrosion of cast iron was noted by H. G. Haase; and the unfavourable influence of spheroids of cementite in the rim, by R. G. Guthrie. J. Wulff found that the form of the test-piece has an influence on the corrosion; and A. M. Portevin found that the attack is dependent on the curvature of the surface.

The **porosity of metals** has been long recognized. In 1620, Francis Bacon, in his *Novum organum* (London, 2. 45, 1620), demonstrated the porosity of lead by compressing water in a hermetically sealed vessel until "the water, impatient of further pressure, exuded through the solid lead like a fine dew"; and in 1667, the Accademia del Cimento reported, in the *Saggi di naturali esperienze* (Firenze, 1667), a similar result with gold. At the beginning of last century, F. Clement placed a turned and bored cylinder of cast iron within a copper cylinder and filled the intervening space with molten tin. On cooling, some of the tin had squeezed through the cast iron, and appeared like a fine, filamentous wool lining the interior. E. H. Amagat observed a similar result with mercury—*vide* iron amalgams. P. W. Bridgman found that when mercury is pressed on to the surface of steel, some mercury penetrated the pores of the steel, and made it rotten, owing to the formation of an iron amalgam (*q.v.*). J. Smithson observed that tin could be forced by pressure through cast iron. The penetration occurred only when the strain was expansive and thus tended to open the pores; a compressive strain, such as that caused by pressing on the outside of a steel ball, closed the pores and prevented penetration. During the ocean survey, by the officers of the United States Navy, it was observed that thick, hollow, glass balls, sunk to great depths in the ocean for an hour or two, became more or less filled with water. No cracks or breakages could be detected microscopically, and the inference made was that water had been forced by the enormous ocean press.—5 to 6 tons per sq. in.—through the pores of the glass. This will prove to be a very important fact if it be confirmed. A. Jouve has also observed the permeation of sulphuric acid in the pores of vessels of cast iron with a high proportion of silicon; whilst G. Tammann and H. Bredemeier forced by press. a soln. of dye into the interior of specimens of metal; and M. Juncker proposed to reduce the corrodibility of cast iron by forcing under press. linseed oil into its pores. Observations on the porosity of metals were also made by J. Dewrance, U. R. Evans, J. A. N. Friend, W. H. Perkins, E. Piwowarsky and H. Esser, and W. M. Thornton—*vide supra*, the sp. gr. of iron. B. Garre discussed the pores formed when the metal is twisted or bent.

The capillary channels, discussed by L. Guillet and co-workers, are thought to follow the edges of the original crystal grains—*vide infra*, surface oxidation. U. R. Evans considered that the corrosion in capillaries is also due to differential aeration, and not to capillary action assumed by L. McCulloch. In cast metals, therefore, as pointed out by U. R. Evans, the corrosion in cavities will tend to dig downwards into the metal and enlarge the cavities, producing pitting, sponginess, and penetration; while in worked metals, corrosion will tend to pass below the surface layer in a direct parallel to the surface, enlarging the original capillary channels, causing the surface layer to peel off in flakes, or rise in blisters, or split into flakes and appear rotten. As observed by C. Chappell, and others—*vide supra*—cavities are also likely to occur where the iron contains inclusions of slag, scoria, etc., so that corrosion is often found to penetrate deeply around the edges of inclusions, and to follow slag lines in the metal. W. H. J. Vernon emphasized the effect of atm. dust in favouring the corrosion of iron exposed to the atmosphere. Unfiltered air produced rusting under conditions where polished plates remained bright in air filtered through cotton-wool. Here, the speck of dust may lead to the retention of a film of moisture between the grain of dust and the underlying metal, and the conditions will then be established for the anodic corrosion described by U. R. Evans. When the rust is produced as a precipitate, well away from the metal, and afterwards settles on the metal, it forms a flocculent layer with no great adhesive power; and, as E. L. Chappell showed, when the whole surface is completely covered, it will act as a protector by hindering the diffusion of oxygen to the metal.

The effect of oxygen in corrosion has been treated from one point of view in connection with the action of aerated water; and the subject has been also discussed by W. D. Bancroft, J. M. Bryan, G. Chaudron, G. L. Cox and B. E. Roetheli, W. H. Creutzfeldt, W. R. Dunstan and J. R. Hill, H. Endo and S. Kanazawa, U. R. Evans and co-workers, H. O. Forrest and co-workers, E. C. Groesbeck and L. J. Waldron, J. C. Hudson, K. Inamura, B. Lambert and J. C. Thomson, A. R. Lee, A. L. McAulay and F. P. Bowden, J. McBride, T. N. Morris, C. Moureau and C. Dufraisse, E. Naumann, G. Paris, W. S. Patterson, J. G. A. Rhodin,

W. D. Richardson, B. E. Roetheli and co-workers, J. Rothe and F. W. Hindrichsen, G. Schikorr, C. F. Schönbein, F. N. Speller, G. Tammann and W. Köster, F. Tödt, W. H. J. Vernon, W. H. Walker, W. K. Weller, W. G. Whitman and R. P. Russell, W. R. Whitney, and H. Wölbling—*vide infra.* G. Paris, E. Naumann, and J. W. Cobb and G. Dougill attributed the extensive rusting in hot-water-pipe systems to the oxygen dissolved in the water. W. A. Bradbury found that the corrosive effects of water are due to the dissolved air and carbon dioxide, and that magnesium chloride alone, usually represented as acting $MgCl_2+Fe+2H_2O=Mg(OH)_2FeCl_2+H_2$, does not so act at atm. press. when cold or hot. The prevention of the corrosion of hot-water pipes by de-aeration of the water was discussed by F. N. Speller, C. R. Texter, J. R. Baylis, O. Kröhnke, and F. Meyer.

When a plate is immersed horizontally below the surface of a soln. of sodium chloride, lines, spots and rings of the hydrated oxide appear on the surface; these are formed about the openings of the pores; in time, the centres of the rings fill in, humps of hydrated oxide extend over the pore openings, and the flocculent rust spreads irregularly until the whole surface is covered. The blanket of hydrated oxide shields the metal from oxygen, and the whole surface will become anodic, but the corrosion will be slow, since the presence of oxygen is not needed at the anodic portions, yet access of oxygen is necessary at the cathodic areas. If the blanket of hydrated oxide is removed from part of the surface by movements of the liquid, slow corrosion will continue over the blanketed portion. On the lower surface of the plate the removal of the hydrated oxide may occur by sedimentation, so that blanketing does not occur, and corrosion continues in the pores. With plates placed vertically in the liquid, there is the tendency of the hydrated oxide to spread downwards from each pit, and the fact that the upper portions are more accessible to oxygen than the lower portions. The lower, less aerated part is therefore anodic to the upper, aerated portion. The lower portion is therefore corroded first, while the upper portion, near the level of the soln., remains clear. The corrosion may begin in pits or cavities, forming what A. Payen called *les tubercules ferrugineaux*, and extending downwards, developing into streamers, or, as A. Payen called them, *les formes vermiculaires*. F. H. Rhodes and E. B. Johnson found that in the case of a municipal gas-holder, the attack occurred along a horizontal zone between 4 in. and 3 ft. below the level of the sealing water. There was no evidence of attack at or just below the water-level. In this case the reducing action of the coal-gas may have helped to lessen the oxygen concentration of the parts below the surface of the water. In some cases, the aerated, cathodic zone may resist corrosion for a time, even when the distribution of the oxygen has become uniform; and U. R. Evans attributed this to the formation of a film of oxide which is more protective than a film formed by exposure to dry air. This film of oxide may become thick enough to give interference tints.

According to J. R. Baylis, tuberculous deposits form an impervious coating where soluble iron from the interior comes into contact with dissolved oxygen. If the water has $p_H=8\cdot5$ the iron forms an impervious coating of crystalline iron oxide in a few months. Pits are often found under tubercles, and negative ions, such as sulphate and chloride ions, are concentrated in these: the overlying tubercles may contain over 1 per cent. of these salts. A. L. McAulay and F. P. Bowden measured the potential between metal and liquid at different parts of a surface both during corrosion, and afterwards when removed from the liquid. The value on the cathodic zone varied slightly from that on the anodic zone. Using $0\cdot1N$-NaCl, against a normal calomel electrode, the anodic portion near the bottom had a potential of $-0\cdot520$ volt, and near the water-line of the cathodic portion, $-0\cdot380$ volt.

Iron is less quickly attacked by distilled water than it is by a soln. of potassium chloride, sulphate, or nitrate; and with water, the direct product of anodic corrosion is ferrous hydroxide, which is sparingly soluble in water. The corrosion of the metal by a drop of distilled water follows very much the course of that illustrated by Fig. 364; but with water distinctly alkaline, where the solubility of ferrous hydroxide is greatly reduced, U. R. Evans showed that an insoluble, protective film will be produced which will grow until the potential of the parts inaccessible to oxygen approaches the value of the aerated part, the current will cease to flow, and corrosion will cease. This agrees with the general observation that iron immersed in alkaline liquids containing oxygen usually remains bright, and passive.

Some factors influencing the rate of corrosion.—Although in the local anodic corrosion of iron, access of oxygen where the actual corrosion occurs is not necessary, yet oxygen must be present at the cathode portions to act as depolarizer. Hence, considering the whole system, the attack on the metal is dependent on the proportion of dissolved oxygen; and if the proportion of dissolved oxygen in the water could be reduced the rate of corrosion would be reduced. C. Chappell found that for low-carbon steels, the amount of corrosion is proportional to the time of immersion. With respect to the velocity of corrosion, except for very short intervals of time, the extent of the corrosion is not proportional to the time of exposure to the corroding influence. These results, however, were not obtained with one piece of metal, but rather by the use of a series of plates which were all corroding at the same rate. J. A. N. Friend, therefore, measured the absorption of oxygen by a piece of rusting iron, and obtained the results shown in Fig. 367, where the slope of the curve at any given time measures the velocity of the reaction. The attack is more rapid in the early stages of rusting; and as the time of exposure is more prolonged, the rate decreases and becomes more nearly proportional to the time. Here, the metal was fairly pure, and the experimental conditions constant, but under working conditions, this is not the case; and, as emphasized by G. Schumann, the problem is rather complex. According to I. D. van Giessen, open, steel equalizing tanks in waterworks are subject to severe corrosive conditions, since the top layer of water rarely changes, there being but a single bottom connection; the effect is worst on the inside portion facing the south, as this receives the full heat of the sun, and is besides alternately wet and dry. O. Kröhnke, and K. Arndt found that cast iron at first corrodes as rapidly as steel, but afterwards it resists corrosion far better than the other metals. This is in accord with general experience. The following are K. Arndt's data:

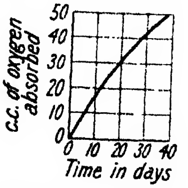


FIG. 367.—The Absorption of Oxygen by Rusting Iron.

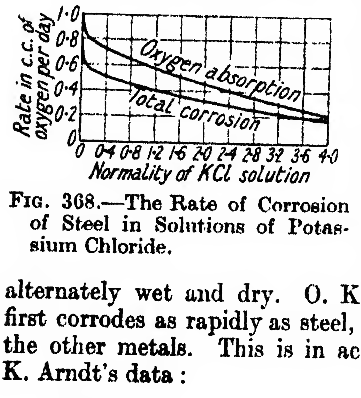


FIG. 368.—The Rate of Corrosion of Steel in Solutions of Potassium Chloride.

Time		1	3	5	10	20	30	43 days
Oxygen absorbed	Cast iron .	13	24	30	45	59	73	95 c.c.
	Mild steel .	13	32	45	63	108	156	213 ,,
	Weldless tube .	5	8	30	109	198	293	389 ,,

G. D. Bengough and co-workers compared the rate of absorption of oxygen and the total corrosion of steel with a soln. of potassium chloride of different concentrations, and the results are summarized in Fig. 368.

Water from mountain streams in showery districts was found by F. J. Rowan [16] to be highly oxygenated, and to be particularly corrosive; and R. Mallet made a similar observation with respect to the corrosive power of rain-water. E. Heyn and O. Bauer found that the relative corrosion of three plates of the same metal immersed in distilled water, in water in which a block of charcoal was suspended, and in water with powdered wood charcoal sprinkled on the surface, was respectively as 100 : 68 : 20. The charcoal acted by reducing the supply of oxygen to the metal. According to J. A. N. Friend, corrosion is not proportional to the area of the exposed surface, because once corrosion has started, oxygen may be absorbed more rapidly than can be supplied to the metal by mere diffusion through the water; and the rate of corrosion will bear some relation to the exposed surface area of the metal, because the supply of oxygen to the metal is determined by the rate of diffusion of the oxygen, and this is determined by the area of the surface to which the oxygen has access. Similarly, also a film of oil on the surface of water helps to reduce the supply of oxygen to the metal; the extent of the protection is determined by the rate at which the oil can absorb oxygen from the air, and deliver it to the water beneath. R. Mallet showed that thick iron plates corrode less rapidly than thin plates; and A. S. Cushman, that doubling the thickness of a plate usually more than doubles its life. W. H. J. Vernon observed that the rate of corrosion of copper was affected by the area but not by the thickness of the plates.

R. Mallet showed that the depth to which an iron plate is immersed in still water will greatly influence its rate of corrosion, because once the oxygen in the vicinity of the plate is used up, the plate is dependent for further supplies on the rate at which oxygen can diffuse downwards from the surface; and this will be slower the greater the depth of the submerged iron. E. Heyn, and E. Heyn and O. Bauer also found the following losses due to corrosion with iron plates immersed in still water:

Time . . .		8	15	22	29 days
Depth	5 cm. . .	0·0268	0·0480	0·0731	0·0783
	28 cm. . .	0·0244	0·0450	0·0628	0·0766
	50 cm. . .	0·0206	0·0364	0·0606	0·0788

As the time of exposure increases, the difference in the rates of corrosion at various depths becomes less marked. This was attributed to the slow reduction of the rust by the iron at the lower depths: $Fe+Fe_2O_3=3FeO$, in accord with the fact that the proportion of ferrous oxide at the greater depths was larger. In air, the partial press. of the oxygen has little influence on the rate of corrosion, because the surface of the metal is being continually swept by fresh gas. The case is different in deep wells where the temp. is more uniform, and the access of fresh air is more difficult. The rate of corrosion of iron submerged in water is dependent on the solubility of the oxygen in water, and this is largely dependent on the partial press. of the gas. Hence, W. H. Walker and co-workers found the following losses due to rusting of iron submerged in water with variable percentages of oxygen in the atmosphere above:

Oxygen . . .	18·2	21·8	28·0	64·5	72·1	97·0 per cent.
Loss by corrosion .	0·018	0·021	0·031	0·057	0·064	0·086

The action of oxygen on corrosion by water was discussed by J. W. Shipley and co-workers, F. Tödt, W. G. Whitman and co-workers, G. Bresch, W. van W. Scholten, J. N. D. Heenan, U. R. Evans, W. R. Whitney, M. Traube, E. Heyn and co-workers, W. H. Walker and co-workers, J. Spennrath, V. Duffek, A. L. McAulay and F. P. Bowden, J. Tillmans and co-workers, J. W. Cobb and G. Dougill, J. R. Baylis, J. A. N. Friend, G. N. Huntley, G. D. Bengough and co-workers, and E. Liebreich. G. Schikorr found that the rate of corrosion in water with the oxygen gas under press. between 0·2 and 5·0 atm. showed a maximum at about 1 atm. press. L. E. Jackson observed a rapid corrosion of iron in a refrigerator plant due to the high oxygen-content of the cold water.

When water is in motion, it will usually contain a high proportion of oxygen provided it is shallow, and the atmosphere has free access to its surface. M. B. Jamieson found that the corrosion in street water-mains is proportional to the amount of water passing through them. E. Heyn and O. Bauer found that a gentle flow of the water increases the corrosion 8-fold; but with still higher velocities, the corrosion is less. Thus:

Cast iron	Velocity	0	6·6	36	240 litres per hr.
	Corrosion loss	0·0350	0·2971	0·2912	0·1470 grm.
Steel	Velocity	0	15	50	350 litres per hr.
	Corrosion loss	0·0566	0·1357	0·0826	0·0377 grm.

J. A. N. Friend employed still higher velocities. The following results were obtained by exposing for 22 to 25 hrs. iron foil—$3\times0{\cdot}5$ sq. cm. in area, and approximately 0·35 grm. in weight—to water with a velocity V ft. per hr.; the loss in weight is expressed in mgrms. per hour:

V	0	540	570	4200	9000	13,000	30,000
Loss	0·082	0·188	0·177	0·054	0·029	0·032	0·034
	Rust			Streams of rust	Traces of rust		No rust

It is assumed that the resistance to corrosion in water at a high velocity is due to the water sweeping away some catalyst which assists the metal to corrode; and that without this catalyst the metal dissolves as postulated by the ionic theory, with such a small velocity that it is almost passive. The catalyst, said J. A. N. Friend, is supposed to be the hydrosol of ferrous oxide. R. F. Passano and F. R. Nagley studied the subject.

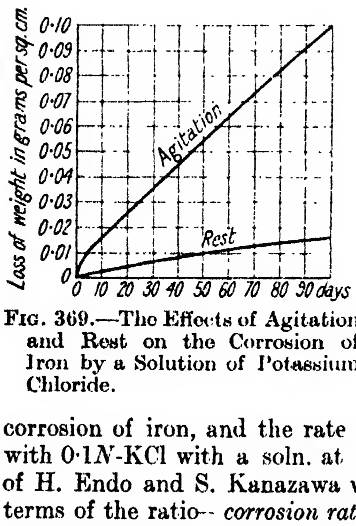


FIG. 369.—The Effects of Agitation and Rest on the Corrosion of Iron by a Solution of Potassium Chloride.

J. Aston, R. J. McKay, U. R. Evans, and H. Endo and S. Kanazawa showed that when iron rusts under water, the area to which oxygen has the freer access becomes cathodic, and the areas shielded from oxygen become anodic. The presence of dissolved oxygen was shown by R. Adie, J. Aston, W. D. Bancroft, A. S. Cushman, H. Endo and A. Kanazawa, U. R. Evans, M. M. Hall, K. Inamura, H. A. D. Jowett and E. Goulding, R. J. McKay, R. Mallet, J. W. Shipley and I. R. McHaffie, W. G. Whitman and R. P. Russell, W. H. Walker and co-workers, and W. R. Whitney—*vide supra*—to favour the corrosion of iron, and the rate of corrosion is favoured by agitation as indicated with 0·1N-KCl with a soln. at rest, and a soln. aerated by stirring. The results of H. Endo and S. Kanazawa with soln. of various salts and acids expressed in terms of the ratio—*corrosion ratio*—of the losses in weight of a specimen when the soln. is aerated by a current of oxygen, and by a current of hydrogen,

Concentration		0·1M-	0·05M-	0·02M-	0·01M-
Corrosion ratio	NaCl	2·8	2·2	1·4	1·3
	KCl	2·7	2·3	1·6	1·4
	K_2SO_4	2·9	2·5	1·4	1·2
	KNO_3	1·2	1·3	1·6	1·2
	$KAl(SO_4)_2$	—	2·2	1·2	1·0
	$BaCl_2$	2·6	2·1	1·6	1·3

Concentration		95	50	20	5	1	0·5 per cent.
Corrosion ratio	H_2SO_4	1·0	1·5	4·2	14·1	—	—
	HCl	—	—	—	15·4	—	70·4
	HNO_3	—	1·1	—	—	1·5	—

H. Endo and S. Kanazawa, adopting the ionic hypothesis, assumed that the corrosion of the iron takes place in two stages: First, a small quantity of the iron passes into soln. as ferrous ion and an equivalent amount of hydrogen is deposited on the surface of the metal as molecular hydrogen: $Fe+2H^{\cdot}+2OH'\rightleftharpoons Fe^{\cdot\cdot}+2OH'+H_2$, or $Fe+2H_2O\rightleftharpoons Fe(OH)_2+H_2$. Second, when oxygen is introduced into this system, the ferrous hydroxide is oxidized to ferric hydroxide, $4Fe(OH)_2+O_2+2H_2O=4Fe(OH)_3$, and the molecular hydrogen is oxidized and so removed from the surface of the iron.

The corrosion of iron by moving liquids was also examined by E. Heyn, G. D. Bengough and R. May, M. Drapier, J. A. N. Friend and co-workers, W. Beck, M. B. Jamieson, J. Tillmans and co-workers, W. R. Whitney, R. P. Russell and co-workers, J. N. D. Heenan, F. N. Speller and V. V. Kendall, M. Straumanis, J. F. Thompson and R. J. McKay, R. J. McKay, and W. G. Whitman and co-workers. S. S. Cook studied water-hammer corrosion, and attributed it to the favourable influence of the motion of the metal surfaces; and C. A. Tomlinson, the corrosion of two, hard steel surfaces subjected to relative motion under load. R. Auerbach observed that differences in the rate of flow of an electrolyte may set up differences of potential on a surface of iron, and he studied the effect of the flow of the liquid in capillaries.

Iron corrodes most rapidly when it is alternately wet and dry—*e.g.* the water-line of iron ships, bridge columns, etc.

R. Mallet found that raising the **temperature** up to a maximum of 79° to 88° favours corrosion. E. Heyn and O. Bauer found a maximum at 60° in one case, and at 80° in another. J. A. N. Friend and co-workers, E. Ramann, I. H. Woolson, A. Lodin, W. van Rijn, E. Heyn and O. Bauer, A. Thiel and H. Luckmann, O. Bauer and co-workers, G. M. Enos, J. R. Baylis, and F. N. Speller also made observations on the subject. The effect of temp. is the resultant of two opposing influences. There is, first, the acceleration of the speed of the reaction by a rise of temp., and second, the retardation of the corrosion owing to the decreasing solubility of oxygen, etc., in water with a rise of temp. A maximum effect will therefore be obtained at some critical temp. which, according to the observations of H. Endo, Fig. 370, occurs between 60° and 70°. This agrees with the previous observation of E. Heyn and O. Bauer. The degree of corrosion in Fig. 370, refers to results expressed in relation to the corrosion at 20° taken as unity. The observed losses in weight in grams per sq. cm. during 30 days were:

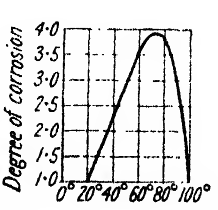


FIG. 370.—The Influence of Temperature on the Corrosion of Iron.

	20°	30°	40°	50°	60°	70°	80°	90°	100°
Loss .	1·00402	0·00605	0·00885	0·01209	0·01405	0·01612	0·01530	0·01410	0·00563

C. H. Cribb and F. W. F. Arnaud, and J. A. N. Friend found that the corrosion is less in darkness than in **light,** with distilled-water, tap-water, river-water, and soln. of various compounds—magnesium chloride, sodium carbonate, hydrocarbonate, and hydroxide, and calcium hydroxide. H. E. Armstrong suggested that the effect might be due to a difference in temp. rather than to the action of light *per se*, but J. A. N. Friend found that light is still active when the effect of temp. is eliminated. H. Endo and co-workers obtained the results summarized in Fig. 371. During the exposure, 11 of the 50 days were cloudy. C. Benedicks and R. Sundberg observed that stainless steel is not quite so much attacked by a soln. of ferrous sulphate, in a photo-cell, in light as it is in darkness. In general, however, light favours the corrosion of metals. The subject was discussed by H. S. Allen, G. Athenasiu, R. Audubert, W. D. Bancroft, W. Beck, G. D. Bengough and O. F. Hudson, S. S. Bhatnagar and co-workers, T. W. Case, W. W. Coblentz and co-workers, H. Endo, G. M. Enos, J. A. N. Friend and co-workers, O. Hähnel, M. Kimura, A. Leighton, J. Nordensen, C. C. Palit and N. R. Dhar, W. H. J. Vernon, and W. P. Wood. According to W. Beck, exposure to **radium radiations** reduces **corrosion.**

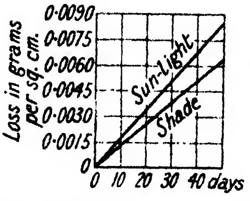


FIG. 371.—The Influence of Light on the Rate of Corrosion of Iron.

R. H. Gaines[17] emphasized the need for reckoning with certain bacterial organisms as an influence favourable to corrosion. The work of iron-bacteria was discussed by D. Ellis, R. Grant and co-workers, and C. Tonami. The effect of sulphides due to the action of bacteria and other forms of life or organic matter on sulphates or decaying organic matter was studied by R. Irvine, P. Agostini, G. D. Bengough and R. May, S. H. Ellis, A. Molteni, and E. V. Smith and T. G. Thompson. C. Darwin showed that worms may excrete acidic fluids; B. Schorler observed the same thing with respect to the *Gallionella ferruginea*; and A. Molteni observed that the humic acid of decaying plants, and the acidic fluids exuded or excreted from some plants, earthworms, and micro-organisms have a marked action on iron structures embedded in soils. The subject was discussed by R. H. Gaines, A. Beythien, O. Adler, and E. Raumer—*vide infra*, limonite.

W. L. Dudley [18] buried iron pipes in various kinds of soil and found the corrosion about half as fast in the case of pipes conveying coal-gas, as it was with pipes conveying no gas. The *corrosion of iron by coal-gas* is usually attributed to the presence of impurities—hydrocyanic acid, carbon disulphide, carbon dioxide and oxygen. J. A. N. Friend noted that water saturated with coal-gas is about two-thirds as active as water alone in the attack on iron buried in moist soils, not exceptionally acidic. The subject was discussed by W. Bertelsmann, A. Bolzinger, H. G. Colman, W. D. Davidson, W. E. Dennison, F. Firth, G. M. Gill, I. Ginsberg, J. T. Haddock, T. Holgate, H. M. Howe, W. Leybold, J. McLeod, G. Masing, R. V. A. Mills, L. Monk, E. Ott and F. Hinden, J. Parker, B. R. Parkinson, F. H. Rhodes and E. B. Johnson, B. Richardson, J. Rollison, R. H. Ruthven, J. G. Taplay and co-workers, C. H. S. Tupholme, C. E. Williams, and R. E. Wilson. In agreement with B. Richardson, and C. E. Williams, J. F. G. Hicks showed that the hydrocyanic acid plays a subsidiary part, for the moist oxygen and carbon dioxide initiate the corrosion. The hydrocyanic acid accelerates the corrosive action, and it plays a most important part, as is indicated by the curves, Fig. 372, showing the rates of corrosion in the presence of moist gases. The speed is greatest when hydrocyanic acid is present. The final product of the action in the case of coal-gas mains is prussian blue. It is estimated that there is thus produced 10 tons of prussian blue per annum in the gas mains of Portland City. No corrosion was observed with dry air, dry oxygen, or dry carbon dioxide.

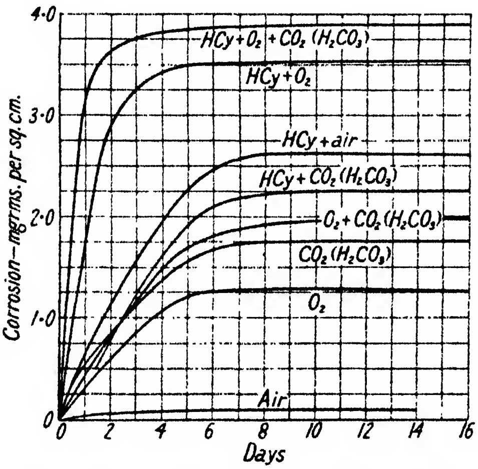


FIG. 372.—Corrosive Action of Moist Gases.

The *corrosion of iron buried in soils* was discussed by F. O. Anderegg and R. V. Achatz,[19] K. Arndt, W. Beck and K. Jacobsohn, F. L. Bassett, F. Besig, L. G. E. Bignell, G. Blanchart, M. J. Blew, O. Bauer and E. Wetzel, J. R. Bradshaw, E. A. Cross, A. S. Cushman, R. O. E. Davies, I. A. Denison, W. L. Dudley, F. Ensslin and F. Buschendorf, S. Ewing, H. O. Forrest, M. Freund, R. H. Gaines, A. F. Ganz, I. D. van Giessen, J. de Graaff, M. Gutierres, F. Haber and P. Krassa, O. Haehnel, R. B. Harper, M. Horioka and M. Iwasa, H. D. Holler, R. Irvine, R. Krzizan, R. J. Kuhn, C. Lepierre, K. H. Logan, K. H. Logan and co-workers, B. McCollum and K. H. Logan, P. Medinger, A. Molteni, G. Murdoch, V. Nagreeff, M. R. Pugh, A. Romwalter, R. P. Russell and W. G. Whitman, R. H. Ruthven, S. G. Sastry, J. E. Schipper, E. H. Schofield and L. A. Stenger, W. B. Schulte, G. N. Scott,

E. R. Shepard, J. W. Shipley and co-workers, E. S. Simpson, E. O. Slater, W. N. Smith and co-workers, W. N. Smith and J. W. Shipley, D. Spataro, F. N. Speller, L. A. Stenger, G. Theim, W. Wark, C. H. Webb, A. Weber, J. R. Weinlinger, and R. E. Wilson. O. Bauer and E. Wetzel observed that cast iron plates 10×2·5×2 cm., during 15 months' exposure lost 6·23 grms. in distilled water; 7·61 grms. in tap-water enriched with calcium sulphate; 10·38 grms. in clay sat. with distilled water; 10·20 grms. in clay sat. with tap-water enriched with calcium sulphate; 5·62 grms. in sand sat. with distilled water; and 6·36 grms. in sand sat. with tap-water enriched with calcium sulphate. F. Hanaman studied the rusting of iron buried in moist sand. J. R. Weinlinger found that an iron gas-pipe which had been in the ground for 25 years was in an excellent state of preservation. For iron embedded in cement and concrete, *vide infra*.

If stray electric currents from tramways, etc., can pass, the iron and soil act as electrodes decomposing moisture into hydrogen and oxygen; and the latter at once attacks iron to form rust. Consequently, iron embedded in concrete is not immune from attack. V. J. Nicholas[20] found that the electrolytic corrosion of structural and reinforcing steel embedded in concrete takes place at the anode. Even neat cement is no protection. The cathode is not affected by oxidation. Cement or concrete immersed in brine will crack when carrying an electric current to or from embedded steel. Concrete conducts electricity electrolytically and not like a metal, its electric resistance being an inverse function of the percentage of sand. It is found that even 0·1 ampere continuously flowing is sufficient to cause the destructive results indicated. The subject is of more direct interest to the electrical engineer. It has been the subject of numerous papers.

H. Hayden studied the effect of an alternating current on the electrolytic corrosion of iron in soln. of salts of sodium, potassium, and ammonium, and in natural and artificial soils; and B. McCollum and G. H. Ahlborn worked with plates immersed in a light clay soil kept moist with a 0·5 per cent. soln. of sodium carbonate. A. J. Allmand and R. H. D. Barklie observed that the superposition of alternating on a direct current increased the corrosion of iron in alkaline soln., and in sub-soil drainage liquor, saturated with carbon dioxide. The presence of chlorides favoured corrosion using a direct current. When an alternating current was employed, a change in the conc. of the alkali in the electrolyte had no particular influence, but the lowering of the current frequency produced an increased corrosive effect, and it is probable that the discharge of $H^{\cdot}$-ions during the cathodic impulse activates the iron by decreasing the oxygen content in the surface layer of metal. The effect of alternating current superposed on direct current was a marked increase in corrosion, and where an anode remained passive either at direct current intensity of 0·125 amp. per sq. cm. or at an alternating current intensity of 0·375 amp. per sq. cm. and 400 frequency, the anode became definitely yellow in two minutes under the combined effect. A high alternating : direct current ratio (more than two) was favourable to corrosion, as was also an increase in current density and low frequency.

The nature of rust.—According to F. N. Speller,[21] films are formed on metals by passivating agents, and rust-resisting alloys, like high-chrome iron, and stainless steel probably owe their resistant qualities to the formation of stable films, so that the life of these metals is more directly dependent on the stability of the film than on the initial tendency of the metal to corrode. This self-protection is more fully developed with some metals than it is with others. A. Ackermann observed the rusting of small particles of iron, iron wire, and spongy iron under the microscope. The forms taken up by the rust depend in the first place on the formation of ferric hydroxide. This colloidal substance assumes forms and passes through the formation processes which are very like the forms and processes which occur in organized nature. Non-rigid threads are formed which grow like organic fibres and which move and change their form when subjected to changes in the external conditions—for example, temperature. Under certain conditions, cell-formation is exhibited, which externally, at least, is similar to organic cell-formation. Drops of a solution of ferric hydroxide possess properties which are otherwise only found in organic cells. They exhibit a solid or semi-solid enclosing semi-permeable membrane or cell-wall, an adhering colloidal layer, and a nucleus. Such drops grow, become broader, and divide in exactly the same manner as is observed in the division of organized cells.

A very great number of analyses of rust have been reported. In analyses by W. R. Dunstan and co-workers of rusts collected from an iron apparatus rusted in the laboratory, and from an iron railing exposed for 30 years to air within 20 yards of the sea, the composition approximated to the limit $Fe_2O_3.H_2O$; but there was about 0·2 per cent. of ferrous carbonate present in the former case, and about 3·25 per cent. of ferrous oxide in the latter case. Both samples contained 1·01 to 1·17 per cent. of hydrogen. This all agrees with F. Wöhler's observation that iron beneath a thin layer of water forms hydrated ferric oxide, but with a thicker layer of water, hydrated ferrosic oxide is produced. Here the transfer of oxygen from air to iron takes place more slowly, and it is inferred that ferrous oxide or hydrated ferrous oxide is the first product of the action, and that this is oxidized to form hydrated ferric oxide, which, uniting with the unchanged ferrous oxide, forms hydrated ferrosic oxide, which, if formed at all, may be regarded as an intermediate stage in the process of oxidation. R. Stumper, for example, found that a 1-day-old rust had 45·3 per cent. FeO, a 5-day-old rust had 22·7 per cent. FeO, and a 15-day-old rust had 9·5 per cent. FeO. He found for $FeO : Fe_2O_3 : H_2O$, 1 : 2 to 20 : 2 to 30. F. C. Calvert observed rust containing 92·9 to 93·10 per cent. Fe_2O_3; 5·8 to 6·2 per cent. FeO; 0·6 to 0·9 per cent. $FeCO_3$; 0·12 to 0·19 per cent. SiO_2; 0·295 per cent. $CaCO_3$; with traces of ammonia. F. M. Stapff observed that the rust on some nails 2000 years old, found in the mines of Mazarron in Murcia, Spain, consists of a mixture of limonite and magnetite. G. T. Moody obtained the following results with half a dozen samples of rust collected from the unpainted interior of some iron flushing-tanks in common use:

Fe as Fe_2O_3 .	55·73	51·12	64·60	65·13	68·89	67·46 per cent.
Fe as FeO .	32·86	36·57	25·74	25·66	23·18	24·40
Fe as $FeCO_3$.	11·40	12·31	9·66	9·21	7·93	8·14

The proportion of calcium carbonate was inappreciable. The proportion of ferrous oxide present in the rust appears to depend on its age, and on the permeability of the rust for oxygen. A. Liversidge found that rust always contained more or less ferrosic oxide. W. Thörner, and P. Longmuir observed that rust collected in railway tunnels had 0·3 to 4·2 per cent. of sulphur expressed as H_2SO_4, and samples collected in the open had 0·8 to 5·5 per cent. H_2SO_4. E. Wilson observed some ferrous sulphide on iron exposed to a London atmosphere. E. K. Rideal found 1·81 per cent. of ferric sulphate in samples collected in the open country, and 7 to 9 per cent. in samples collected from London railway stations.

R. Kattwinkel, and F. Drexler found that the ultimate products of rusting are usually γ-FeO(OH) or Fe_3O_4. F. Drexler said that the formation of α-FeO(OH) or γ-FeO(OH) depends on the chemical nature of the nucleus about which the rust forms. The physical structure of the rust depends on the structure of FeO(OH), and the colour is determined by the grain-size. This subject is discussed in connection with ferric hydroxide, FeO(OH). According to G. Schikorr, the mechanism of rusting may thus be explained: in air-free water a black film is formed, $Fe+2H_2O=Fe(OH)_2+2H$; in the absence of air α-FeO.OH sol reacts with iron to form Fe_3O_4 or a green sol, $FeO.OH+H=Fe(OH)_2$; the green sol reacts with the FeO.OH to produce the green ferrite $Fe(OH)_2.FeO.OH$, or with an excess to form Fe_3O_4, and finally the latter is oxidized to γ-FeO.OH. C. Carius observed the presence of magnetite in rust produced by the corrosion of iron in acidified water, and dried at room temp.; and γ-FeO.OH, in rust obtained in water with $p_H=5{\cdot}5$ to 6·5, and the X-ray spectral lines of γ-FeO.OH decrease in intensity with increasing alkalinity. J. Cates also identified rust with

γ-FeO(OH). J. Huggett said that in the prolonged exposure of iron to aerated water, a mixture of magnetite and rust is first formed, and then lepidocrocite appears. H. O. Forrest and co-workers found the composition of the rust film is dependent on the H'-ion concentration of the liquid near the metal surface, and on the ionic concentration in the liquid film. With oxygenated distilled water, the film is granular magnetic oxide, provided the diffusion of ions from the liquid film to the main body of the soln. proceeds slowly or non-uniformly, whereas with a uniform, rapid ionic diffusion, the film is mainly gelatinous hydrated ferric oxide. The formation of graphite during the attack by water, etc., on cast iron is discussed in connection with sea-water—*vide infra.* R. Richter, and J. Percy mentioned the presence of crystallized silicon in the residue from cast iron; and W. A. Tilden, iron silicide. J. G. Donald observed that there is a loss of carbon during the rusting of pig-iron.

The effect of rust on the corrosion of iron and steel was discussed by R. C. McWane and H. Y. Carson, E. L. Chappell, and J. Aston. W. S. Patterson, and W. H. J. Vernon observed that rust increased the speed of corrosion of iron, and that a certain critical humidity of the atmosphere must be exceeded before the acceleration occurs. J. C. Hudson did not find an abnormal change in the deliquescence of rust at some critical humidity, possibly, said W. H. J. Vernon, because the samples used by J. C. Hudson had already passed through the critical stage. W. S. Patterson and L. Hebbs, however, did observe a critical stage with rust scraped from the metal. The microscopic structure of rust was investigated by A. Ackermann. R. A. Hadfield observed no deterioration in the tensile strength of mild steel, and wrought iron after being immersed in sea-water for five years.

The by-products of rusting.—The production of hydrocarbons was discussed in connection with the carbides—**5.** 39, 20. Reports on the formation of ammonia during the rusting of iron, by A. Chevallier, etc., are discussed in **8.** 49, 15; but R. Mallet said that too much stress cannot be laid on the alleged reports because rust, in common with other porous bodies, greedily absorbs ammonia and many other gaseous substances from the atmosphere—*vide infra,* the action of soln. of ammonium nitrate. U. R. Evans said that the true expansion in rust formation cannot be calculated from the sp. gr. of the components, but it is certain that a considerable expansion force is exerted when iron changes into rust. He discussed the apparent vol. of rust sludges; and A. Ackermann, colloidal rusts.

T. Fujihara found that the uncorroded iron outside a drop of water on a polished surface of iron is protected by a film of ferrous hydroxide—*vide* Fig. 364. The product of the action is protective. The more rapid the initial corrosion, the less the final effect. The formation of protective films in the rusting and corrosion of metals was studied by W. G. Whitman and co-workers, V. Kohlschütter and E. Krähenbühl, F. N. Speller, W. D. Bancroft, G. R. White, C. H. Desch, J. Bresch, W. H. J. Vernon, U. R. Evans, E. M. Enos and R. J. Anderson, J. R. Baylis, and E. L. Chappell.

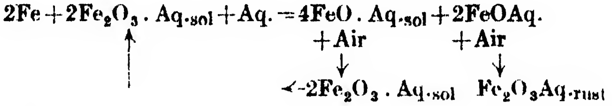
C. F. Schönbein[22] observed that **hydrogen dioxide** is formed when iron amalgam is shaken with water, and this was confirmed by M. Traube, and H. Wieland and W. Franke. The maximum amount is formed in about a minute. It is assumed that the reaction proceeds in accord with the scheme: $Fe+2H_2O=Fe(OH)_2+H_2$, followed by $4Fe(OH)_2+O_2=2(Fe_2O_3.H_2O)+2H_2O$, with hydrogen dioxide an intermediate product resulting from the action of bivalent iron and molecular oxygen: $Fe+O_2+2H_2O=Fe(OH)_2+H_2O_2$. The cycle of reactions is completed by $Fe+H_2O_2=Fe(OH)_2$; and $2Fe(OH)_2+H_2O_2=Fe_2O_3.H_2O+2H_2O$. W. Palmaer said that the formation of hydrogen dioxide in the rusting of iron is due to a side reaction, not an essential part of the process. E. Pietsch and co-workers discussed the subject. No hydrogen dioxide fs iormed in acidic soln., but in alkaline soln. the amount formed increases with the p_H value, *i.e.* with conc. of the OH'-ions. The production does not depend on the occluded hydrogen of the amalgam;

ferrous hydroxide is first produced, and this is further oxidized more slowly than the metal. The presence of hydrocyanic acid retards the autoxidation; and the velocity of oxidation is about ten times as fast in the presence of leucine as it is in water. The acceleration depends on the conc. of the amino-acid. Glycine, alanine, and asparagine act similarly. Salts like sodium sulphate or copper sulphate accelerate the autoxidation of iron. The oxidation is inhibited if the iron be rendered passive by treatment with potassium hydroxide, ferricyanide, chromate, or permanganate. The presence of hydrogen acceptors like quinone, methylene blue, ethyl peroxide, and dithiodiglycollic acid, causes iron to rust in the presence of purified water in an atm. of nitrogen. The presence of sodium or copper sulphate accelerates the action of quinone.

According to a modification of M. Traube's scheme of oxidation, by W. R. Dunstan and co-workers, hydrogen dioxide is formed as an intermediate stage in the rusting of iron: $Fe+H_2O=FeO+H_2$, and $2H+O_2=H_2O_2$, followed by $2FeO+H_2O_2=Fe_2O_2(OH)_2$(rust). Two mols. of dioxide are supposed to be formed by the oxidation of 2 atoms of iron to ferrous oxide, and only 1 mol. of hydrogen dioxide is required to oxidize the ferrous oxide to rust. The excess of hydrogen dioxide is now supposed to oxidize the uncorroded iron, $Fe+H_2O_2=FeO+H_2O$, and $2FeO+H_2O_2=Fe_2O_2(OH)_2$. The inhibitory action of alkalies and chromic acid is attributed to their power of decomposing hydrogen dioxide. W. R. Dunstan and co-workers said that the failure to detect hydrogen dioxide in the oxidation of iron, when its presence could be detected in the case of all other metals which were tried, does not exclude the possibility of its momentary formation—*vide supra*, for H. E. Armstrong's modification of this theory. F. Haber and co-workers, and V. Andström also favoured this hypothesis, but against the hydrogen dioxide theory of corrosion, G. T. Moody argued that a dil. soln. of hydrogen dioxide does not attack iron, but is catalytically decomposed by that metal. W. R. Dunstan and co-workers must have used impure hydrogen dioxide. L. J. Thénard observed that the metal has no action on *eau oxygène*. O. and A. Dony could not detect any traces of hydrogen dioxide, even though, according to the theory, twice as much is produced during the initial oxidation of the iron to form ferrous oxide as is required to convert the latter into rust. G. T. Moody showed that substances which destroy hydrogen dioxide do not necessarily inhibit the rusting of iron—*e.g.* potassium iodide; and E. Divers said that substances which destroy hydrogen dioxide need not necessarily prevent its formation—*e.g.* ferrous sulphate rapidly destroys chlorine, but does not prevent the formation of chlorine from manganese dioxide and hydrochloric acid. W. D. Bancroft reported that in alkaline soln., hydrogen dioxide is decomposed by iron.

When iron has once begun to rust, the subsequent progress of the disease proceeds more quickly even though the temp. be above the dew-point, and under conditions where bright iron would remain unaffected for an indefinitely long time. F. Kuhlmann [23] suggested that the rust acted catalytically as an oxygen carrier; but F. von Hutten, F. C. Calvert, A. Wagner, A. C. Brown, J. A. N. Friend, and H. Bauerman favour the hypothesis that rust is very porous, and hygroscopic, and it becomes charged with liquid water which fills its pores and evaporates very slowly. Hence, corrosion can occur in a damp atmosphere under conditions where bright iron would not be affected. J. Aston showed that wet rust is anodic to bare iron, whilst dry rust is cathodic; wet rust has a high electrical resistance. A compact layer of fired rust thus tends to protect the metal below, but favours anodic attack in the iron immediately around; while flocculent, wet rust favours the corrosion of the metal immediately below. This it does by shielding the affected part from oxygen, and rendering it anodic, so that corrosion is confined to a limited area; the surrounding part is cathodic and hence does not rust—*vide supra*, J. Aston. According to R. J. McKay, the rust accelerates the action in two ways: (i) oxygen is removed by its reaction with ferrous hydroxide; and (ii) iron is removed by precipitation which would retard the reaction and set up a counter e.m.f. in the oxygen concentration cell. J. Aston also showed that the anodic effect produced by wet rust is obtained with other colloidal hydroxides—*vide infra*, colloids.

J. A. N. Friend suggested a modification of F. Kuhlmann's hypothesis in that he considered that the action of rust in promoting further rusting may be due to the presence of the hydrosol of iron which acts as an oxygen carrier as it passes alternately between the ferrous and ferric states. Hence, the modified hypothesis is called **the colloidal theory of corrosion.** The hypothesis is represented schematically:



$$\begin{tikzcd}[column sep=small] 2\mathrm{Fe}+2\mathrm{Fe_2O_3}.\mathrm{Aq}_{\cdot sol}+\mathrm{Aq}.= & 4\mathrm{FeO}.\mathrm{Aq}_{\cdot sol} \arrow[d, "+\mathrm{Air}"] & +2\mathrm{FeOAq}. \arrow[d, "+\mathrm{Air}"] \\ & 2\mathrm{Fe_2O_3}.\mathrm{Aq}_{\cdot sol} \arrow[ul, dashed] & \mathrm{Fe_2O_3Aq}_{\cdot rust} \end{tikzcd}$$

Those salts which favour rusting are supposed to peptize the colloid, and those which inhibit rusting—*e.g.* chromates—are supposed to flocculate the colloid. Against this, U. R. Evans said that chromates also stop the corrosion of other metals—*e.g.* magnesium—which exist in only one state of oxidation; and W. G. Whitman and co-workers showed that the effects of salts on the rate of corrosion do not vary concomitantly with the stability of colloidal iron hydroxide. While J. A. N. Friend said that the destruction of the colloidal iron hydroxide by chromates leaves the iron passive, U. R. Evans considers that the chromate acts by putting a protective film on the anodic portions of the iron and so stops the attack. B. Lambert and J. C. Thomson's work makes it very doubtful if iron hydroxide is needed to start the corrosion, although once started, the presence of the colloidal hydroxide may accelerate the corrosion. The action of electrolytes on the coagulation of the hydrosol is said to resemble their action on the rusting of iron both as regards concentration, and temp.; the retarding influence of alcohol is attributed to its dehydrating action on the colloidal ferric hydroxide; the inhibitory action of arsenious acid or its salts—observed by L. Lindet, G. N. Huntly, etc.—is attributed to the adsorption of arsenic trioxide by the colloidal ferric hydroxide, which prevents it taking part in the sequence of changes just mentioned. Exposure to radium rays retards corrosion by coagulating the hydrosol of ferric hydroxide. G. Schikorr pointed out (i) that the alleged similarity between the action of electrolytes on the coagulation of the hydrosol of ferric oxide and the corrosion of iron does not obtain because in the range of lower concentrations, where the differences in the coagulating action of electrolytes is most marked, there is no corresponding agreement in the rusting process. (ii) The basic assumption: $FeO_{sol}+Air=Fe_2O_{3sol}$ is not confirmed by observation, for under the action, of air, the FeO_{sol} is flocculated as a higher oxide. (iii) The fact that there is maximum corrosion for medium speeds of flow—for the speed of rusting increases to a maximum value in the neighbourhood of 1 atm. as the oxygen press. rises—is satisfactorily explained by other theories but not so by the colloidal theory. The colloid theory was discussed by W. Beck, W. Beck and F. von Hessert, G. Schikorr, T. N. Morris, G. D. Bengough, G. D. Bengough and J. M. Stuart, J. M. Stuart, U. R. Evans, S. G. Sastry, J. K. Wood, J. A. N. Friend and co-workers, W. J. Huff, N. Isgarischer and S. Berkmann, and W. D. Bancroft.

As shown by J. C. Thresh,[24] W. R. G. Atkins, W. Weintraud, and many others, natural waters from peaty districts contain several organic acids derived from decaying vegetation, etc. Water from mining areas may contain sulphuric acid (*q.v.*); and the water of canals and rivers in industrial areas may contain acids and salts derived from discharges of waste liquors. The destructive qualities of water are in many cases related to their acidity which is usually represented in terms of the H'-ion concentration. R. E. Wilson, and F. N. Speller classified waters, arbitrarily, in terms of their acidity: *Acidic waters* have their H'-ion conc., p_H below 4·3, and they rapidly corrode the iron with the evolution of hydrogen even in the absence of the depolarizer oxygen; *neutral waters* have a value for p_H between 4·3 and 10, and they cause rusting in the presence of oxygen; and *alkaline waters* have a p_H-value over 10, they usually act slowly on metals and if the protective film is broken down, as might occur if chlorides are present, local attack may occur. According to W. G. Whitman and co-workers, there is a close relation between the **acidity,** or **H˙-ion concentration,** of the water and the rate at which it can corrode iron. The curves in Fig. 373 refer to water flowing at the rate of 3 ins. per sec., *A* refers to water with 5 c.c. of oxygen per litre, and *B*, to water with 1 c.c. per litre. The results show that with both acidic and alkaline soln. the corrosion varies with p_H, but there is an intermediate range of p_H-values where the rate of corrosion is independent of the acidity, and is represented in the diagram by the vertical portion of the curves. As the proportion of oxygen in the water is reduced, the vertical portion of the curve is reduced, until finally, when no oxygen is present, the velocity falls off continuously as the acidity decreases. This is illustrated by Fig. 374, due to J. W. Shipley and I. R. McHaffie. With water flowing in pipes, the proportion of dissolved oxygen in the water in contact with the metal may become small, so that, as J. R. Baylis showed, corrosion can be controlled by regulating the p_H-value of the water, for, in the absence of oxygen, the speed of attack falls continuously with increasing values of p_H.

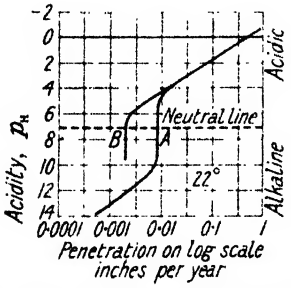


FIG. 373.—The Effect of the Acidity of Solutions on the Velocity of Corrosion (Oxygen present).

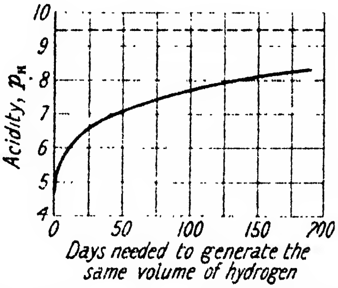


FIG. 374.—The Effect of the Acidity of Solutions on the Velocity of Corrosion (Oxygen absent).

According to J. W. Shipley and co-workers, iron dissolves in purified water, freed from carbon dioxide, when the p_H-value attains 9·4, but not so with higher values. Ordinary purified water has a p_H-value of 7·0 in virtue of the reaction $H_2O \rightleftharpoons H^{\cdot} + OH'$. If OH′-ions eq. to $10^{-4\cdot6}$ mols. per litre be added, the value $p_H = 9\cdot4$ is attained, and this is near the concentration of (OH)′-ions which reddens phenolphthalein. It is inferred by J. F. G. Hicks that the primary cause of corrosion is the dissolution of iron in water, and that this occurs before any chemical action starts. Metallic iron dissolves in an adherent film of water until the resulting soln. of ferrous hydroxide has a value $p_H = 9\cdot4$; the presence of oxygen insures a maximum e.m.f. and acts as an accelerator for the system: $Fe_{solid} \rightleftharpoons Fe_{soln.} + 2HOH \rightleftharpoons Fe(OH)_2 + H_2$. The oxygen removes the ferrous hydroxide by oxidization to less soluble ferric hydroxide, and the hydrogen is also removed by oxidation or depolarization. The presence of carbon dioxide removes ferrous hydroxide by converting it to less soluble carbonate, and it forms carbonic acid, the H˙-ion of which favours corrosion. Indeed, so long as any agent is present capable of removing ferrous hydroxide and hydrogen with sufficient rapidity to prevent the saturation of the adherent water, with respect to ferrous hydroxide and hydrogen, corrosion will occur. R. Girard found that the H˙-ion potential at which corrosion commences is greater with weak acids than it is with strong acids; a film of iron hydroxide appears in acidic soln. when the H˙-ion potential is 3·5. O. B. J. Fraser and co-workers found the maximum in the H˙-ion concentration curve corresponds with the maximum rate of corrosion in sulphuric acid of different concentrations. J. R. Baylis observed that in no case of water corrosion was a concentration of 3 p.p.m. (parts per million) of dissolved iron found in a soln. free from oxygen in which p_H was between 8 and 9. Soluble iron in water with an excess of dissolved oxygen is oxidized faster when $p_H=9·0$ than when $p_H=6·0$. With a concentration of 50 p.p.m., at $p_H=8·0$ less than 0·1 p.p.m. of soluble iron dissolves in the absence of oxygen; about 1·0 p.p.m. when $p_H=7·5$; and about 4 p.p.m. when $p_H=7·0$. With p_H less than 7·0 the proportion of soluble iron increases rapidly.

The effect of the $H^{\cdot}$-concentration of water on corrosion, etc., was discussed by W. R. G. Atkins, J. R. Baylis, W. Blum, W. M. Clark, S. Gottlieb, R. F. Greenfield and G. C. Baker, R. E. Hall and A. R. Mumford, F. Hannan, W. D. Hatfield, J. A. Heymann and A. Massink, E. Imbeaux, I. M. Kolthoff, E. Naumann, W. Olszewsky, S. Rachwal, J. T. Saunders, J. W. Shipley and co-workers, K. Sonden, H. T. Stern, H. Thiesing, J. Tillmans, and W. G. Whitman and co-workers; the effect of acids, and mine waters on the corrosion of iron, by O. Bauer, C. F. Burgess and S. E. Engle, F. C. Calvert and R. Johnson, R. Gans and co-workers, E. Heyn and O. Bauer, A. Ledebur, G. Lunge, R. J. McKay, M. T. Murray, W. D. Richardson, A. Thiel, K. Wagemann, and W. G. Whitman and R. P. Russell; and the effect of soln. of alkalies, by J. H. Andrew, F. Auerbach and H. Pick, R. Baumann, C. H. Cribb and F. W. F. Arnaud, P. W. Evans, A. Fry, G. W. Fuller, I. D. van Giesen, P. Krassa, H. Kriegsheim, G. Lunge, W. Nover and D. Splittgerber, S. W. Parr and co-workers, F. N. Speller and co-workers, D. Splittgerber, T. Steel, C. E. Stromeyer, A. Thiel, A. Vogel, M. Werner, R. S. Williams and V. O. Homerberg, and R. E. Wilson. R. Varet discussed the action of salts dissolved in organic solvents on the metals.

R. E. Wilson said that (i) Strongly alkaline waters have $p_H=10$ and upwards and the $H^{\cdot}$-ion concentration plays here a minor part for protective films are formed on the metal; (ii) Feebly alkaline natural waters have $p_H=9·5$ to 4. The $H^{\cdot}$-ion concentration is not here of importance because the rate of attack depends on the concentration of the oxygen in soln. and the rate of diffusion of the products of the reaction; and (iii) Acidic waters with $p_H=4$ downwards. The overvoltage of hydrogen, the concentration of the $H^{\cdot}$-ions, and the nature of the local galvanic elements are of importance. W. G. Whitman and co-workers represented the effect of variations in the $H^{\cdot}$-ions concentration on iron at 22° and 40°, by the curves in Fig. 375.

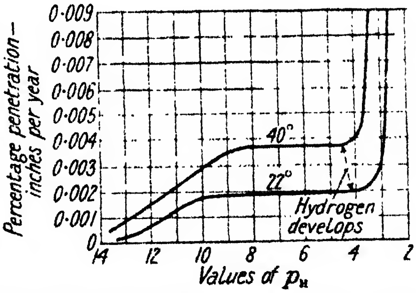


FIG. 375.—The Influence of $H^{\cdot}$-ion Concentration on the Corrosion of Iron.

J. F. Chittum pointed out that the corrosion of iron in air will vary with the p_H-value of the soln. He assumed that ordinary iron is passive, and active iron is the result of a chemical reaction—*vide infra*, passivity. (1) In alkaline soln. where the value of p_H ranges from 9·0 to 12·0, the iron dissolves as (*a*) $Fe+2H_2O \rightarrow FeO_2+4H^{\cdot}+4\oplus$, and a ferrate is formed in soln. as the higher oxide dissolves; where oxygen is not available (*b*) $FeO_2+3H^{\cdot}+2\oplus \rightarrow Fe(OH)^{\cdot}+H_2O$, and where oxygen is available (*c*) $Fe+3H_2O \rightarrow FeO_3''+6H^{\cdot}+4\oplus$. On account of the reaction (*d*) $Fe(OH)^{\cdot}+\frac{1}{2}O_2 \rightarrow FeO_2+H^{\cdot}$, there is a tendency for the formation of the electrode (*b*) over the whole surface; but the reaction (*d*) can establish a state of equilibrium with (*b*) leaving (*c*) to operate where the concentration of oxygen is greatest. Under these conditions, with some other secondary but related reactions, little corrosion occurs; the initial rate of corrosion is about the same as in neutral soln.; and the rate of corrosion rapidly falls to zero, or in extreme cases produces pitting. (2) When the p_H-value lies between 6·0 and 9·0, the iron readily corrodes; the higher oxide dissolves to form a ferrate. As in the preceding case, the differential effect of reaction (*d*) produces an electrolytic cell, with (*c*) as anode and (*b*) as cathode. There is sufficient polarization at the cathode to cause the reaction (e) $Fe+H_2O\rightarrow Fe(OH)+H^{\cdot}+2\oplus$ to be established and the potential is then reversed to produce a corrosion cell in which (c) is the cathode, and (e), the anode. This cell produces the intermittent direct current of corrosion. The ferrate is replenished on the surface of the cathode by the diffusion of the hydroxyferrous ions, and oxidation proceeds in accord with (d). Under these conditions, with other secondary but related reactions, oxidizing agents reduce the rate of corrosion; a low-frequency alternating current superposed on a direct current favours the anodic corrosion of iron; differential aeration effects are marked; oxygen is used in the process of corrosion; and the soln. is made alkaline in the corrosion process up to $p_H=9{\cdot}0$. (3) In soln. where the value of p_H lies between 4·0 and 6·0, iron corrodes rather more quickly than when p_H lies between 6·0 and 9·0. The higher oxide is produced, and being but slightly soluble soon saturates the soln. Owing to reaction (d) a polarization cell with anode (a) and cathode (b) is produced; and when the hydroxyferrous electrode is established, the potential is reversed and a corrosion cell is established with cathode (a), and anode (e) is established. But the electrode (f) $H_2\rightarrow 2H^{\cdot}+2\oplus$ is established and another corrosion cell is established with anode (e) and cathode (f). In this range of p_H-values the potential of the first cell is small, and the potential of the second cell is the greater. Consequently, more corrosion is produced by the second cell. The hydrogen produced at the cathode of the second cell is oxidized with necessary difficulty as the p_H-value of the soln. decreases, and on account of the increasing stability of the ferrous ions, the oxygen does not have so great a tendency to react with ferrous iron to produce ferric oxide. In this case, oxidizing agents slightly increase the rate of corrosion, hydrogen begins to be evolved when p_H lies between 4·0 and 5·0, dependent on the nature of the metal; and general corrosion occurs rather then pitting. (4) With soln. having p_H between 1·0 and 4·0, iron corrodes rapidly and with a greatly increasing rate as the value of p_H diminishes. The difference between this case and the preceding one is that the potential of the cell with (e) as anode and (f) as cathode and that of the cell with (e) as anode and (a) as cathode continually increases as the value of p_H decreases. Here the rate of corrosion is greater than is the case with other values of p_H; hydrogen gas is evolved; and ferrous ions attain a high concentration in the soln.

J. W. Shipley and co-workers found that in the absence of oxygen, the rate of corrosion is proportional to the negative p_H-value of the soln. to $p_H=9{\cdot}4$; and no hydrogen is evolved with soln. more alkaline than $p_H=9{\cdot}4$. The potential of the cell $Fe\,|\,Fe^{\cdot\cdot},H^{\cdot}\,|\,H_2$ should be proportional to the $H^{\cdot}$-ion conc. until $p_H=9{\cdot}0$; and in more alkaline soln., the potential should be independent of the $H^{\cdot}$-ion conc., and should be of the order 0·16 volt. The potentials calculated for slightly acid soln. are greater than they should be to account for the slow dissolution of iron. J. F. Chittum assumes that the first action of iron is to produce a higher oxide *vide infra*, passivity—and that as a result of other reactions the final corrosion cell is $Fe+H_2O+H^{\cdot}\rightarrow Fe(OH)^{\cdot}+H_2$, which has an e.m.f. approaching zero when $p_H=9{\cdot}0$, and this agrees with the results of J. W. Shipley and co-workers.

In the corrosion at a water-air surface in soln. with p_H less than 9·0, there is established an electrolytic cell in which (a) in the surface is anode, and (c), some equivalent electrode, is the cathode. The decreased polarity of the surfaces establishes the anode (a) in the surface film. The fact that the anodic potential of this electrode is greater than that of any other iron electrode in air accounts for the fact that surface corrosion is very important. In more alkaline solutions the boundary potential between the surface film and the main body of the soln. is built up until little surface corrosion occurs in these solutions.

The action of salt and other solutions on corrosion.—The presence of salts in water in contact with iron may have a marked influence on the rate of corrosion. Numerous observations have been made on the action of soln. of various salts on iron. The results with salts of the heavy metals, and ammonium salts, as well as of salts of the oxy-acids, etc., have been indicated in connection with the chemical properties of iron. Effects with some common salts were reported as follow:

Potassium fluoride.—A. W. Chapman.[25] *Sodium chloride.* R. Adie, O. Bauer and co-workers, W. S. Dudley, H. Endo, J. A. N. Friend and co-workers, U. R. Evans and T. P. Hoar, R. H. Gaines, F. Haber and F. Goldschmidt, K. Inamura, S. Micewicz, M. Mugdan, V. K. Perschke and G. I. Tschufaroff, A. Thiel and H. Luckmann, and A. Wagner. The effect of pressure on the results was studied by O. Bauer and co-workers, E. Berl and F. von Taack, and J. A. N. Friend. *Potassium chloride.*—H. Endo, K. Inamura, S. Micewicz, U. R. Evans and T. P. Hoar, and A. Wagner. *Ammonium chloride.* E. Heyn and O. Bauer, J. T. Nance, and A. Wagner—*vide supra*, the chemical properties of iron. *Potassium iodide.*—E. Pietsch and co-workers. *Sodium sulphate.* O. Bauer and co-workers, E. Berl and F. von Taack, H. Endo, J. A. N. Friend and co-workers, E. Heyn and O. Bauer, K. Inamura, U. R. Evans and T. P. Hoar, A. Thiel and H. Luckmann, and A. Wagner. *Potassium sulphate.*—H. Endo, J. A. N. Friend and co-workers, E. Heyn and O. Bauer, K. Inamura, and A. Wagner. *Potassium aluminium sulphate.*—H. Endo. *Ammonium sulphate.*—E. Heyn and O. Bauer, and A. d'Heureuse—*vide supra*, the chemical properties of iron. *Sodium nitrate.*—H. Endo, J. A. N. Friend and co-workers, and E. Heyn and O. Bauer. *Potassium nitrate.*—H. Endo. *Ammonium nitrate*—*vide supra*, the chemical properties of iron. *Sodium and potassium carbonates.*—R. Adie, E. Bosshard and R. Pfenninger, C. H. Cribb and F. W. F. Arnaud, J. A. N. Friend and co-workers, E. Heyn and O. Bauer, C. F. Hickethier, A. Wagner, and F. Westhoff. *Sodium phosphate.*—W. R. Dunstan and co-workers, H. Endo, E. Heyn and O. Bauer, and A. Krefting; and the effect of pressure, by E. Berl and F. von Taack. *Calcium chloride.* R. Girard, E. Heyn and O. Bauer, C. F. Hickethier, P. Medinger, S. Micewicz, W. Palmaer, and G. Zelger. *Barium chloride.*—H. Endo, J. A. N. Friend and co-workers, E. Heyn and O. Bauer, and V. Zemlyanitznin and P. Dobrovolsky. *Calcium nitrate.*—W. Vaubel. *Magnesium chloride.*—O. Bauer and co-workers, E. Bosshard and R. Pfenninger, W. R. Bradbury, H. Endo, F. Fischer, F. Halla, E. Heyn and O. Bauer, S. Micewicz, H. Ost, J. Pfeifer, A. Wagner, and P. West; the effect of pressure, by E. Berl and F. von Taack. *Magnesium sulphate.*—J. A. N. Friend and co-workers, and E. Heyn and O. Bauer.

As observed by G. Wetzler, M. M. Hall, and A. Payen, iron may be kept an indefinitely long time in soln. of potassium, sodium, or an alkaline earth hydroxides, or in aq. ammonia without corrosion, provided the concentration of the solvent be large enough; and iron is corroded in sat. soln. of potassium nitrate or sulphate more slowly than in water, owing, it was assumed, to the liquid dissolving less air than in the case of water alone. A. J. Hale and H. S. Foster found that the action of 0·2*N*-soln. of the following salts on wrought iron and cast iron, between 17° and 20°, per sq. dm. of metal, was represented by the following losses in 7 days using half a litre of soln. per day:

0·2*N*-soln	.	$MgCl_2$	NaOH	$CaCl_2$	NaCl	NH_4OH	Na_2CO_3
7 days	Cast iron	0·85	0·00	0·20	0·10	0·00	0·00
	Wrought iron	0·85	0·00	0·30	0·25	0·00	0·00
7 days	Cast iron	0·45	0·00	0·17	0·32	0·18	0·00
	Wrought iron	0·41	0·00	0·26	0·24	0·00	0·00

According to L. McCulloch, of a number of small particles of electrolytic iron isolated from one another, only a certain proportion will rust in the presence of air, moisture, and sodium chloride. The smaller the particles, the greater the proportion which is "passive," but if the particles are in contact with one another they all rust. Again, in a soln. of ammonia and ammonium chloride pieces of soft iron may either dissolve readily or remain unattacked. "Passivity" in this soln. is produced by heating until temper colours appear, or often merely by cleaning with coarse emery and exposing to the air. The metal is activated by contact with zinc or active iron in the soln. or by cathodic treatment at a sufficiently negative potential. Any of these activating agencies will also cause mill-scale or ferrous oxide to dissolve in this soln., so that the observed passivity of iron is ascribed to a superficial oxide film.

At the beginning of our era, Pliny, in his *Historia naturalis* (31. 19), mentioned the corrosion of iron by the waters of a river in Thessaly; and numerous observations have since been made on the corrosive action of soln. of different salts, and of mineral waters on iron—*e.g.* by E. Berl and F. von Taack, H. G. Denham, H. E. Bellamy, W. B. Lewis and G. S. Irving, U. R. Evans, R. Adie, V. K. Perschke and G. I. Tschufaroff, F. Auerbach and H. Pick, W. D. Bancroft, W. M. Barr and R. W. Savidge, O. Bauer and co-workers, K. Inamura, H. Baucke, C. F. Burgess and S. G. Engle, R. Girard, C. G. Fink and C. M. Decroly, K. Konopicky, M. Scheelhasse, G. D. Bengough and co-workers, F. C. Calvert and co-workers, C. H. Cribb and F. W. F. Arnaud, A. S. Cushman, G. K. Davis, J. B. Dodds, W. R. Dunstan, F. Förster, W. A. Fowler, J. A. N. Friend and co-workers, A. Fry, A. F. Ganz, B. Garre, J. Grossmann, H. C. Haak, A. J. Hale and H. S. Foster, M. M. Hall, E. S. Hedges, M. Heegewaldt, E. Heyn, E. Heyn and O. Bauer, O. F. Hunziker and co-workers, K. Inamura, G. Jüngst, F. Körber and A. Pomp, A. Krefting, O. Kröhnke, O. Lasche and W. Kieser, A. Ledebur, L. Lindet, G. Lunge, E. Maass and W. Wiederholt, R. Mallet, P. Medinger, A. E. Menke, W. Menzel, G. T. Moody, M. Mugdan, J. T. Nance, S. W. Parr and F. G. Straub, W. Peters, P. Petit, J. Persoz, R. Pfenninger, D. Phillips, A. Pomp, P. N. Raikow, W. Ransom, W. D. Richardson, H. Rinne, J. K. Roberts and co-workers, P. Rohland, F. J. Rowan, E. Schulz, J. B. Senderens, R. Stumper, K. Taussig, A. Thiel and H. Luckmann, W. Thomson, M. Usener, M. Vogt, J. H. Vogel, A. Wagner, W. G. Whitman and R. P. Russell, etc.

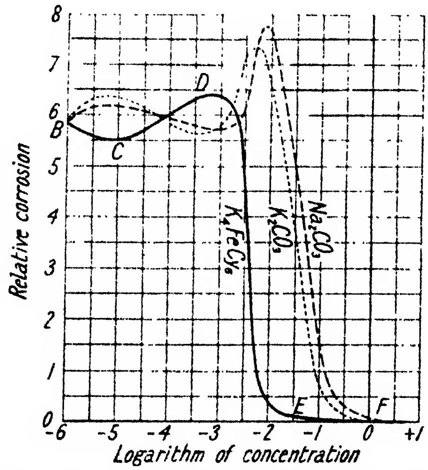


FIG. 376.—Corrosive Action of Solutions of Potassium Ferrocyanide, and Alkali Carbonates.

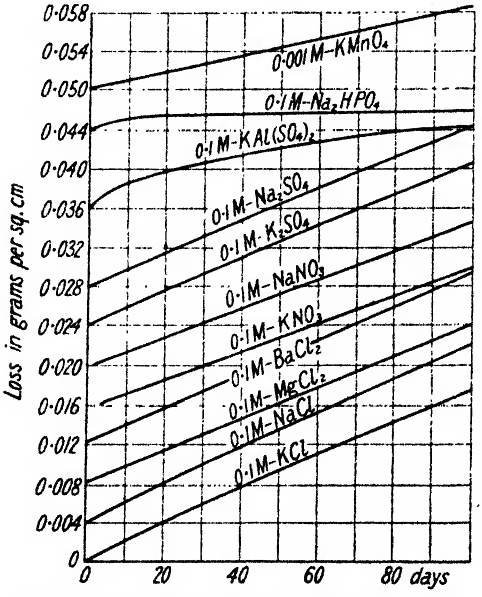


FIG. 377.—The Action of Salt Solutions on the Corrosion of Armco Iron.

U. R. Evans represented the speed of corrosion, dx/dt, for dil. soln., by $dx/dt=k_1(C_0-k_2x)_1$, where k_1 and k_2 are constants; C_0= the initial concentration of the electrolyte; and x, a measure of the corrosion. J. A. N. Friend found that for a concentration, m, of the salt, the rate of corrosion, C, is related to the solubility of oxygen, β; and to the rate of dissolution of oxygen, R, by $C_m=\beta_m R_m$.

H. Endo's observations on the corrosive effect of salt soln. containing 0·1 mol per litre are summarized in Fig. 377. The armco iron in 0·1M-soln. of potassium chromate, dichromate, perchlorate, and permanganate was bright and free from rust during 3 yrs.' exposure; in other soln., the corrosion increased proportionally with the time. With soln. of sodium hydrophosphate, and potash-alum, the corrosion was rapid at first, and then gradual, and finally, as the surface of the iron became coated with a film, corrosion ceased.

In 1845, R. Adie discovered that sat. soln. of potassium or sodium ferrocyanide, ferricyanide, cyanide, carbonate, perchlorate, and permanganate help to resist corrosion. K. Inamura showed that the corrosion with salt soln.—potassium and sodium chlorides and sulphates—increases with increasing concentrations below 0·1*M*. H. Endo also studied the influence of the concentration and found for sodium and potassium chlorides, and sulphate the following losses in grams per sq. cm., and the corrosion ratios—that is, the ratio of the loss in weight of iron in the salt soln. to its loss in distilled water:

NaCl	Conc. .	0	0·1	1·0	2·0	3·0	4·0	5·0	6·0
	Loss .	0·00075	0·00105	0·00097	0·00074	0·00068	0·00037	0·00032	0·00022
	Ratio .	1·0	1·4	1·3	1·0	0·8	0·5	0·4	0·3
KCl	Conc. .	0	0·1	1·0	1·5	2·0	2·5	3·0	3 5
	Loss .	0·00074	0·00112	0·00096	0·00089	0·00077	0·00068	0·00052	0·00044
	Ratio .	1·0	1·5	1·3	1·2	1·05	0·95	0·70	0·60
Na_2SO_4	Conc. .	0	0·1	0·2	0·5	0·6	0·8	0·9	1·0
	Loss .	0·00077	0·00100	0·00095	0·00085	0·00079	0·00058	0·00050	0·00046
	Ratio .	1·00	1·30	1·25	0·10	1·02	0·75	0·65	0·60
K_2SO_4	Conc. .	0	0·1	0·2	0·3	0·4	0·6	0·8	1·0
	Loss .	0·00077	0·00112	0·00093	0·00086	0·00069	0·00062	0·00049	0·00039
	Ratio .	1·00	1·30	1·20	1·05	0·90	0·80	0·64	0·50

There is thus a maximum in the curves where the corrosion is greatest, and larger than that of water; the corrosion then diminishes to less than the value for water; and there is a particular concentration of the salt soln. where the value is the same as that of water, and when the corrosion ratio is unity. H. Endo added that the actual corrosion is a result of two opposing influences. One is due to the solubility of oxygen in water. In dil. soln., where the solubility of oxygen is nearly the same for water, the rate of corrosion increases with an increase in concentration of the salt, but with more conc. soln., where the solubility of oxygen is reduced progressively with increasing concentration of the soln., the corrosion will be reduced. The maximum with the salts under consideration is near 0·1*M*.

According to E. Heyn and O. Bauer, the behaviour of soln. of potassium ferrocyanide is typical of that of many others. *B*, Fig. 376, represents the effect with distilled water; the concentration is expressed in mols per litre. In some cases, with small proportions of salt, say 0·001 to 0·1 grm. per litre, there is a slight retardation, *BC*. Many salts—*e.g.* sodium and potassium carbonates—exhibit no such retardation. As the proportion of salt increases, the corrosive effect increases, *CD*, to a maximum, *D*, which is usually much greater than the effect with distilled water. This represents what has been called *critical concentration*. Subsequent increases in the proportion of salt rapidly depress the activity of the soln. until it reaches what is called a *limiting concentration* at a point, *E*, where corrosion practically ceases; and subsequent increases in the conc. of the soln., *EF*, have no effect on corrosion, for the iron may be kept in contact with these soln. for an indefinite period without corrosion.

According to E. Heyn and O. Bauer, and J. A. N. Friend, the critical and limiting concentrations of a number of salts, expressed in grams per litre, are respectively as follow: *potassium ferrocyanide*, with wrought iron, 0·1, and 1 to 2; and with purified iron, 0·2, —; *potassium ferricyanide*, wrought iron, 0·1, and 1 to 2; *potassium permanganate*, wrought iron, 0·1, and 0·1 to 1·0; *potassium carbonate*, wrought iron, 1·0, and 1 to 10; *potassium iodate*, wrought iron, 0·01, and 0·1 to 1·0; *potassium cyanide*, wrought iron, 0·1, and 0·1 to 1·0; *potassium bromate*, wrought iron, 0·1, and 0·1 to 1·0; *potassium chlorate*, wrought iron, 0·1, and 74·5; *calcium chloride*, steel, 1·27, and 510; *sodium sulphide*, steel, 0·1, and 100; *sodium hydrocarbonate*, wrought iron, 1·0, and 1 to 10; *sodium carbonate*, wrought iron, 1·0, and 1 to 10; *borax*, wrought iron, 0·1, and 1 to 10; *sodium hydrophosphate*, wrought iron, 1·0, and 1 to 10; *ammonium hydrophosphate*, wrought iron, 0·01, and 1·0 to 10; *ammonium acetate*, wrought iron, 0·01, and 0·1 to 1·0; *chromic acid*, wrought iron and pure iron, limiting conc. 0·01 to 0·05; *potassium chromate*, wrought iron, 0·01 to 0·1; and *potassium dichromate*, wrought iron and pure iron, 0·01 to 0·1.

C. H. Cribb and F. W. F. Arnaud showed that the corrosive action of soln. of sodium carbonate is nearly twice as great at 100° as it is at room temp. Ammonium hydrophosphate here acts normally up to its limiting concentration, and before the soln. is saturated, corrosion begins again; but it is not rusting in the ordinary sense, because the metal becomes covered with gas-bubbles, and finally acquires a greyish-green deposit. In the case of soln. of potassium chlorate, calcium chloride, and sodium sulphide, *E* and *F* almost coincide and the limiting conc. is a sat. soln. of the salt. There are no critical conc. with a few salts—*e.g.* chromic acid and its two potassium salts. The slow soln. observed by E. Heyn and O. Bauer with very conc. soln. of chromic acid, and potassium dichromate may be due to the presence of manganese in the iron, for, as A. S. Cushman showed, manganiferous irons are slightly soluble in these soln., but no effect can be observed with pure iron during the course of a few weeks.

Ammonium salts are very corrosive, and of the three tried by E. Heyn and O. Bauer, Fig. 378, the nitrate is the most active, and it is ammonium nitrate which is produced in thunderstorms, and washed down by rain. The rain-water soln., of course, is very dilute, but the concentration increases as the liquid evaporates. Soln. of these ammonium salts were found to attack iron both in the presence and in the absence of air. The ratios: Loss in the absence of air: loss in the presence of air, for the nitrate, sulphate, and chloride are respectively 0·92, 0·17, and 0·023. The activity of the salts is much greater when the temp. is raised. J. A. N. Friend and P. C. Barnet observed that a sat. soln. of ammonium sulphate is less corrosive than distilled water at 6°, but at 18° it is much more corrosive. L. Santi found that iron drillings are attacked by a boiling soln. of ammonium chloride: $Fe+2NH_4Cl = FeCl_2+2NH_3+H_2$; observations on the action of ammonium chloride soln. were also made by J. T. Nance; E. B. R. Prideaux and R. M. Caven made a similar observation with respect to ammonium nitrate; and W. R. Hodgkinson and A. H. Coote, with respect to soln. of ammonium nitrate and nitrite. W. Vaubel observed that while ammonium nitrite is almost without action on iron, ammonium nitrate makes a very effective attack; hydrated ferrous and ferric oxides are formed, and some iron passed into soln. as a complex salt. Ammonium nitrate, said W. Vaubel, is very generally present in common water in contact with iron, for this metal will reduce a portion of the dissolved nitrates to ammonia; the same process, namely, the reduction of the nitrate radicle to ammonia, occurs in the action of ammonium nitrate on iron, the latter undergoing oxidation. The rusting is assisted by the increased activity of oxygen at the attacked spot, and also by the action of the water itself, which, it is stated, in the presence of ammonium nitrate will act on iron, forming iron oxide and hydrogen, especially if the temp. is slightly raised. R. Droste showed that under ordinary conditions, nitrates are reduced by iron to ammonia without forming any appreciable proportion of nitrite. A. A. Bonnema showed that ferrous oxide and hydroxide in contact with air give rise to a certain amount of nitrite. If, as is quite possible, nitrate is produced in the same manner, W. Vaubel added that it is clear that for the rusting of iron only a minimal quantity of an ammonium salt need be present, for the ammonium nitrate could then be easily formed. F. Hanaman discussed the action of soln. of ammonium sulphate.

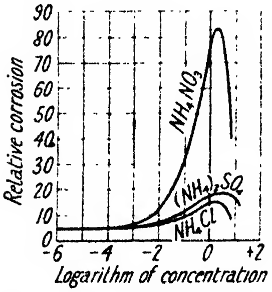


FIG. 378.—The Corrosive Action of Solutions of Ammonium Salts.

There is another series of salts whose sat. soln. are incapable of inhibiting corrosion, and in this sense it can be said that the limiting conc. is imaginary, and that *F* lies to the left of *E*, Fig. 376. These salts therefore show only a critical conc. E. Heyn and O. Bauer, and J. A. N. Friend and J. H. Brown obtained the following results:

Potassium chloride with wrought iron, 50; with purified iron, 5; *potassium sulphate* with wrought iron and purified iron, 10; *potassium nitrate* with purified iron, 1 to 15; *sodium* *chloride*, wrought iron, 10 ; and purified iron, 5 ; *sodium sulphate*, wrought iron and purified iron, 10 ; *sodium nitrate*, wrought iron, 0·1 ; purified iron, 50 ; *calcium hydrocarbonate*, wrought iron, 0·14 ; *calcium sulphate*, wrought iron, 2·034 ; *calcium sulphide*, steel, 0·0014 ; *barium chloride*, wrought iron, 100 ; purified iron, 10 ; *ferrous sulphate*, wrought iron, 100 ; *arsenic trioxide*, wrought iron, 0·064 ; *magnesium chloride*, wrought iron, 100 ; purified iron, 20 ; *magnesium sulphate*, wrought iron and purified iron, 10 to 50 ; *manganese sulphate*, wrought iron, 0·1 ; *ammonium thiocyanate*, wrought iron, 0·01 ; *ammonium chloride*, wrought iron, 100 ; *ammonium sulphate*, wrought iron, 200 ; and *ammonium nitrate*, wrought iron, 500. I. Wasilewsky and W. Bardzynsky discussed the corrosive action of a soln. of ammonium nitrate ; and V. K. Pershke and G. I. Tschufaroff, the corrosive action of potassium salts on cast iron.

The corrosive actions of soln. of potassium and sodium chlorides and sulphates, and of potassium nitrate, by J. A. N. Friend and J. H. Brown, are illustrated by Fig. 379. They show that the corrosive action of conc. soln. of the chlorides is less than that of water alone. This was noticed by R. Adie in 1845, and he explained the results by G. Wetzler's assumption that the solubility of oxygen in brine soln. is less than it is in water alone. F. J. Rowan cited an example where the life of boilers was much greater when run with a higher proportion of sea-water with the fresh water, than when a small proportion of sea-water was used. J. A. N. Friend and J. H. Brown noticed that while at 10°, a soln. of sodium chloride has a critical conc. whose corrosive action is greater than that of distilled water at the same temp., yet at 21°, in agreement with E. Heyn and O. Bauer, the reverse is the case ; and at 14°, the corrosive action is the same as that of distilled water. Hence, a soln. may be less corrosive than distilled water in the tropics and more corrosive in temperate climes ; a similar difference may be shown in summer and winter. E. Heyn and O. Bauer's results with sodium chloride soln. are summarized in Fig. 380, where the concentrations are expressed in mols per litre. The action is nearly twice as great at 40° as it is at 18° ; at 80°, the action with the more dil. soln. attains a maximum. A. Payen, R. Girard, K. K. Järvinen, and L. Aitchison made some observations on this subject. H. Beeny found that the amount of iron which passes into soln. as Fe··-ions when used as anode in a 0·2 per cent. soln. of sodium chloride agrees with the quantity of electricity generated, and it is hence inferred that the corrosion is entirely electrochemical. A. W. Chapman found that *potassium fluoride* below 0·8*N*-conc. act like potassium chloride, but, unlike soln. of the chloride, above that conc. the metal is not corroded. This is attributed to the formation of a protective film of a fluoride or complex fluoride on the surface of the metal. The attack by soln. of potassium fluoride is inhibited by the presence of sodium carbonate or chromate in concentration less than is needed for the chloride. This is attributed to the fluoride being less able to penetrate the protective film formed by the inhibitor. R. Adie, and J. A. N. Friend and J. H. Brown

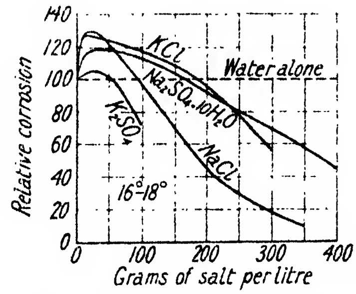


FIG. 379.—The Effect of Aqueous Solutions of Salts on the Corrosion of Iron.

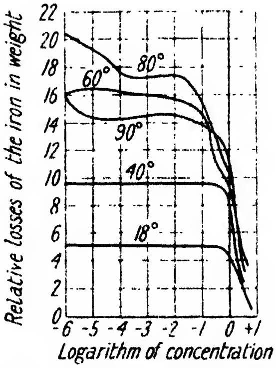


FIG. 380.—The Effect of Temperature on the Corrosive Action of Solutions of Sodium Chloride.

showed that at the temp. of the room, and in the absence of air, soln. of the alkali sulphates and chlorides exert no corrosive action on iron. The results for the alkali nitrates are shown in Fig. 381. P. Rohland observed that whilst most chlorides accelerate the rate of corrosion of iron in water, chromic chloride acts in the converse way, due, it is assumed, to "a transitory separation of chromium by the iron." G. R. White studied the electrolytic corrosion of iron as anode in soln. of sodium chloride, sulphate, nitrate, acetate, and tartrate.

Rain-water, particularly after thunderstorms, contains nitric acid or nitrates, and sewage water also contains nitrites and nitrates. The action of soln. of nitrates on iron was also examined by J. B. Senderens, and J. A. Jones. W. Vaubel found that soln. of the alkali nitrates are not nearly so active as ammonium nitrate; and that soln. of the alkali nitrites are almost without action on iron. F. Hanaman studied the action of soln. of sodium chloride, potassium carbonate, and ammonia. W. vanWüllen-Scholten studied the action of soln. of sodium chloride. M. Mugdan found that the chlorides of the alkalies, ammonium, and the alkaline earths accelerate rusting to about the same extent. Bromides, sulphates, and perchlorates are nearly equally active, potassium nitrate somewhat less so, and purified water less still. Iron remains practically unattacked in soln. of potassium (or sodium) chlorate, bromate, iodate, chromate, dichromate, acetate, oxalate, tartrate, ferro- and ferricyanides, cyanide, hydrogen carbonate, borate, hydroxide, and ammonia. The order in which iron is attacked in these soln. is not changed by adding small quantities of acid, or of alkali, or of oxidizing agents such as hydrogen dioxide, potassium ferricyanide, or sodium hypobromite, although the rate of rusting is increased or diminished. Soln. containing a mixture of salts possess properties intermediate between those of soln. of the pure salts; thus, addition of salt to a soln. of sodium hydroxide causes iron immersed in it to rust, although more slowly than in an equally conc. soln. of pure salt. The effect of dil. alkaline soln. was discussed by H. J. Donker and R. A. Dengg, who found that the surface of iron is uniformly attacked, but in more conc. soln. point-corrosion predominates. Alkali hydroxide is more protective than carbonate—*vide supra*. Sulphate soln. attack iron less than chloride soln. Iron is not markedly attacked by neutral soln. containing dichromate, or dichromate and chloride, but it is vigorously attacked if the soln. is not neutralized. The results of J. A. N. Friend and J. H. Brown with barium chloride, and with magnesium chloride and sulphate are summarized in Figs. 381 and 382. V. Zemlyanitzuin and P. Dobrovolsky found that boiling soln. of barium chloride attain a maximum attack after boiling with the metal for 8 to 16 hrs. The attack then decreases gradually owing to the formation of a protective film of hydrated ferric oxide.

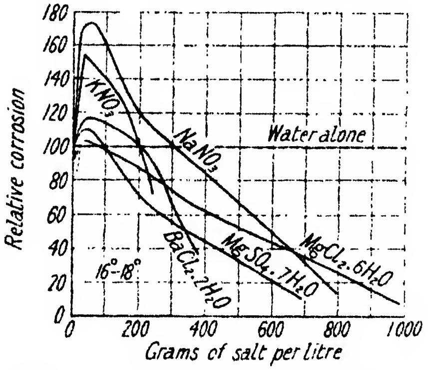


FIG. 381.—The Effect of Aqueous Solutions of Salts on the Corrosion of Iron.

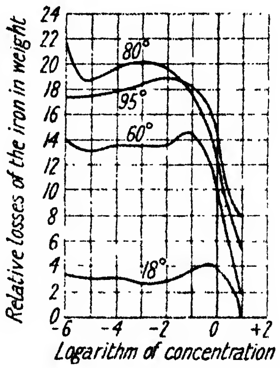


FIG. 382.—The Effect of Solutions of Magnesium Chloride on the Corrosion of Iron at different Temperatures.

The action of magnesium chloride has received much attention owing to its presence in sea-water, which may be regarded as an aq. soln. of sodium and magnesium chlorides. E. Maass and W. Wiederholt, and O. Hauser showed that magnesium salts are strongly corrosive, and in aq. soln. it is largely hydrolyzed to form free hydrochloric acid, particularly if its temp. be raised. E. Heyn and O. Bauer's results with variations of temp. are indicated in Fig. 381, where the concentrations are expressed in mols per litre. The effect with the more dil. soln. reaches a maximum at 80°. The soln. can also act on iron in the absence of air, particularly if the temp. is raised. This was demonstrated by A. Wagner, and R. Pfenninger, and emphasized by J. B. Dodds. E. J. Fox also showed that desert waters containing magnesium chloride have a high H'-ion conc., and are very destructive to steel and iron conveying-pipes. Observations on the corrosive action of *natural waters* were made by F. Auerbach, F. Bamberg, C. O. Bannister and R. Kerr, C. Blacher, H. G. Bowen, G. J. Burrows and C. E. Fawsitt, C. P. Coles, M. J. Falkenberg, A. P. Ford, H. O. Forrest, J. R. Francis, G. W. Fuller, L. W. Haase, R. A. Hadfield, W. M. Hamlet, A. Heinzelmann, T. Hermann, H. M. Howe, G. N. Huntley, I. M. Kolthoff, O. Kröhnke, W. Lulofs, F. Lyon, B. G. McLellan, R. Mallet, A. Mündlein, G. Popp, E. Prinz, W. Reid, J. W. Shipley and I. R. McHaffie, F. N. Speller, F. N. Speller and co-workers, A. Splittgerber, A. T. Stuart, R. Stumper, A. Thiel, F. Tiemann and A. Gärtner, J. Tillmans and co-workers, J. Walker and S. A. Kay, W. G. Whitman and R. P. Russell, R. E. Wilson, W. Windisch, H. Winstanley, and I. H. Woolson; and on the corrosive action of *mine waters*, by R. J. Anderson and G. M. Enos, A. Katz, W. A. Selvig and G. M. Enos, and W. E. Warner. P. Medinger explained the corrosion of gas and water mains in heavy soils, containing *calcium sulphate* as follows: through the ionization of the sulphate, the proportion of calcium ions in soln. becomes so great that the dissociation of the calcium hydrogen carbonate is depressed, and, consequently, the production of H'- and HCO_3''-ions from the free carbonic acid is not so much hindered. The enhanced acidity of a soln. containing free carbonic acid and calcium hydrogen carbonate consequent on the addition of calcium sulphate may be demonstrated by means of litmus.

R. Adie found that iron is attacked more vigorously by **sea-water** in the presence of air than is the case with distilled water. The aeration of sea-water near the surface as it is stirred up by the waves is favourable to corrosion; on the other hand, oxygen was found to be less soluble in sea-water than it is in ordinary water. Again, A. Payen showed that iron is attacked by sea-water in the complete absence of air under conditions where iron can be kept in fresh water an indefinite time without corrosion. The activity of sea-water is consequently due to the salts which it has in soln.—*e.g.* sodium chloride, and magnesium chloride and sulphate. At considerable depths below the surface the supply of air to sea-water is very restricted. From observations by O. Bauer and E. Wetzel, G. D. Bengough and co-workers, J. J. Berzelius, E. Beutel and A. Kutzelnigg, R. Binaghi, J. V. Davies, C. N. Draper, J. A. N. Friend, R. A. Hadfield, H. M. Howe, M. Lidy, R. Mallet, J. T. Milton and W. J. Larke, M. le Naour, D. V. Onslow, J. Percy, M. Portier, J. W. Shipley and I. R. McHaffie, R. Stumper, V. N. Svechnikoff and K. F. Starodoudoff, and H. Wilkinson, on cast iron—guns, cannon-balls, etc.—which had been submerged for 50 and more years in the sea, the iron appears to be slowly converted into ferrous oxide, and partially dissolved, and at the same time the residue becomes soft though retaining its original shape. The carbon appears to form a graphitic mass. Hence, the change is sometimes designated the **graphitization**—or **graphititis**, or *iron cancer*—of cast iron. According to R. Mallet, the sp. gr. of the mass is between 1·3 and 1·8—when that of cast iron ranges from 6·8 to 7·6; and he also quoted the analysis: FeO, 81 per cent.; graphite, 16 per cent.; iron chloride, a trace. In the case cited by J. J. Berzelius, when the mass was first brought to the surface, within half an hour it became too hot to hold in the hand—presumably owing to the oxidation of the graphitic carbon which is almost in a pyrophoric state. F. W. Durkee observed an analogous result by the action of the water of a coal-mine on cast iron. J. W. Shipley and I. R. McHaffie reported cementite and a cementite-phosphide eutectic in the residual skeleton. J. W. Shipley observed a softening of the iron pipes exposed in soils containing calcium sulphate; W. B. Schulte, when exposed to cinders. U. R. Evans noted the breaking down of the cast-iron foundations of a bridge over the Thames.

The graphitization may be produced by other corrosive agents, thus, F. J. Daniell produced a spongy, grey mass, "somewhat resembling plumbago," by the action of dil. hydrochloric acid on cast iron; F. C. Calvert, by the action of dil. hydrochloric or acetic acid for two years; T. Crzeschik, by the action of dil. sulphuric acid; S. Leet, and W. H. Pepys, pyroligneous spirit; T. Thomson, sour paste; R. Mallet, the vapour disengaged by roasting coffee, the action of sherry wine, and of low wines and proof spirit; and M. Freund, by the action of direct electric currents in soln. of sodium chloride or calcium sulphate, although F. Bergius and P. Krassa observed no such action with alternating currents. O. Bauer and E. Wetzel studied the graphitization of cast iron and found that graphitization occurs with iron anodes in tap-water, sea-water, and in 10 per cent. soln. of magnesium chloride or sulphate. R. Mallet also mentioned cases when graphitization was facilitated by the galvanic action caused by the contact of cast iron with a less corrodible metal—*e.g.* copper, or brass. Reports on the corrosive action of sea-water have been also made by T. Andrews, M. Ballay, O. Bauer and E. Wetzel, H. Bauermeister, A. C. Becquerel, B. Bell, G. D. Bengough, R. Binaghi, F. C. Calvert and R. Johnson, E. Cohen, C. P. Coles, P. M. Crosthwaite, P. M. Crosthwaite and G. R. Redgrave, J. V. Davies, E. Davy, W. Denecke, E. Deslongchamps, H. Diegel, S. H. Ellis, U. R. Evans, J. A. N. Friend, R. Girard, J. Grantham, R. A. Hadfield, F. Hanaman, W. J. Hay, T. Holgate, G. Johnstone, W. P. Jorissen, K. Hasegawa and S. Hori, C. J. B. Karsten, F. B. King, G. von Knorre, O. Kröhnke, M. Lidy, A. Liversidge, R. Mallet, T. E. Perks, J. W. Post, H. S. Rawdon, J. Rennie, H. E. Rhoades, H. Rinne, A. Romwalter, A. H. Sabin, F. Schmitz, B. Schultz, E. C. Sherman, J. W. Shipley and I. R. McHaffie, B. Silliman, G. Stauch, T. Steel, F. P. Stowell, R. Stumper, W. Thomson, M. Usener, G. B. Vroom, and H. Wilkinson, etc.—*vide infra* for a comparison of the different varieties of "iron" and steel.

G. Wetzler observed that iron does not rust in aq. soln. of potassium hydroxide, or in aq. ammonia; and A. Payen added that iron remains bright for months when immersed in an aq. soln. of ammonia or of potassium or sodium hydroxide. A soln. of 1 vol. of a sat. soln. of potassium hydroxide and 2000 vols. of water prevents iron from rusting, but the metal is corroded in a 1 : 4000-soln. A soln. of 1 vol. of a sat. soln. of sodium carbonate in 54 vols. of water will prevent rusting, but not so with a 1 : 59-soln. A. Payen also found that a soln. of 1 vol. of a sat. soln. of borax in 6 vols. of water, and 1 vol. of a sat. soln. of lime-water in 3 vols. of water will prevent rusting; but not so with more dil. soln. M. M. Hall also observed that iron does not rust in water containing magnesia or lime. For A. J. Hale and H. S. Foster's observations, *vide supra;* and for the action of alkali hydroxides, *vide supra,* chemical properties of iron. C. H. Cribb and F. W. F. Arnaud observed that very dil. alkaline soln. do not prevent the corrosion of iron. With the conc. of the alkaline soln. expressed as parts of alkali by weight as 100,000 parts of water; and with the corrosion expressed as milligrams of ferric oxide, they found, at room temp., say 16°:

		NaOH				KOH			NH_4OH	
		4	10	20	40	5·6	14·0	28·0	17·0	34·0
Fe_2O_3	16° .	7·0	2·8	0	0	5·8	0	0	5·0	0
	100° .	18·5	19·3	5·8	0	13·7	12·8	0	11·5	0

		$Ca(OH)_2$			$Ba(OH)_2$		
		9·25	18·5	27·75	8·55	21·37	42·74
Fe_2O_3	16° .	7·5	5·0	0	5·2	0	0
	100° .	20·5	3·5	0	14·4	11·3	0

J. D. Pennock and D. A. Morton found that iron does not rust in conc., aq. soln. of ammonia, although freshly rusted iron is attacked. J. A. N. Friend observed no attack by $\frac{1}{30}N$-NH_4OH when kept in sealed tubes for several years. F. J. R. Carulla observed no change in a cast iron still used for ammonia during 18 years; and this was confirmed by J. F. Kempson. Observations were also made by F. Schmitz, W. R. Hodgkinson and N. E. Bellairs, M. Tilgner, C. Matignon and G. Desplantes, and U. R. Evans on the action of aq. soln. of ammonia; by W. Dittmar, W. Venator, G. Zirnite, E. Heyn and O. Bauer, F. Lyon, F. N. Speller and C. R. Texter, J. H. Andrew, M. L. Hamlin and F. M. Turner, H. F. Whittaker, P. D. Merica, and C. E. Stromeyer, on the action of aq. soln. of alkali hydroxides; and by T. Schmelzer by soln. of calcium hydroxide.

The results of C. H. Cribb and F. W. F. Arnaud confirm the observations of A. Payen that dil. soln. of the alkali hydroxides, in ordinary atm. air, do not inhibit the corrosion of iron until a certain limiting conc. of the alkali has been attained. The limiting conc. for alkali hydroxides was found by C. H. Cribb and F. W. F. Arnaud to be respectively 0·10 to 0·20, 0·185 to 0·278, and 0·056 to 0·14 grm. per litre; for sodium and calcium hydroxides, E. Heyn and O. Bauer obtained respectively 10 to 10·0, and 0·18 to 0·89 grm. per litre; and J. A. N. Friend, 1·1 to 2·8 grm. per litre for potassium hydroxide. It must be remembered that in air, the alkali is slowly converted into carbonate, so that permanent protection is attained only when the conc. of the alkali corresponds with the limiting conc. of the carbonate. Using more conc. soln., E. Heyn and O. Bauer found for plates of iron 3×4·5 cm. in area, with the conc. of soln. expressed in grams per litre, and the corrosion as loss of weight in grams:

KOH . .	0·0	2·8	28	168	sat.
Loss . .	0·0685	0·0000	0·0001	0·003	0·0002
NaOH . .	0·0	10	100	sat.	—
Loss . .	0·0653	0·0002	0·0005	0·0002	--
$Ca(OH)_2$ . .	0·0	0·67	sat.	--	--
Loss . .	0·0646	0·0000	0·0000	—	—

U. R. Evans found that soln. of magnesium sulphate at very low concentrations, say 0·001 or 0·01M-$MgSO_4$, produced phenomena not unlike that seen in distilled water, the rust being loose and the upper boundary of the rust-covered area being sinuous. As the conc. of the soln. of magnesium sulphate was gradually increased, the upper boundary of the rust-covered area became straighter and the rust became more clinging; at conc. between 0·15M- and 0·50M-$MgSO_4$, the rust blanket was so adherent that it was not loosened when a jet from a wash-bottle was directed on to the specimen. Conc. soln. of magnesium chloride, calcium sulphate, and calcium hydrocarbonate behaved in the same way; the deposit of iron hydroxide came to within about a mm. of the water-level, the top of this area being often straight and parallel to the water-line. In the intervening space between the deposit of iron hydroxide and the water-line the metallic surface, although free from corrosion, was covered with an adherent white deposit. The rust settling in the vessel was unusually pale, containing calcium or magnesium compounds in addition to iron hydroxide. The explanation of these phenomena is to be found in the limited solubility of magnesium and calcium hydroxides. Electrochemical action commences as soon as the plate is introduced, but the areas which commence to function as cathodes quickly become covered with a deposit of calcium or magnesium hydroxide (or calcium carbonate, in the case of calcium hydrocarbonate soln.). This deposit shields the areas in question from oxygen, stopping the cathodic reaction at the parts shielded, and transferring it to some point still free from deposit; the portions shielded by deposit naturally become anodic. In the course of a few hours the whole of the immersed area has become covered with deposit, and only the narrow strip within the meniscus, which necessarily remains comparatively accessible to oxygen, behaves as cathode, whilst the rest of the immersed area constitutes the anode. Over this large area the soluble iron salts produced by the anodic reaction act on the previously deposited hydroxides of calcium or magnesium, converting them in part into hydroxides of iron, so that the deposit, whitish at first, becomes green and then brown. The rust thus contains variable proportions of magnesium or calcium compounds. Consequently, the action of waters containing calcium or magnesium compounds is slower than that of distilled water, because the access of oxygen to the small cathodic part of the metal is hindered by the white deposit. U. R. Evans also found that zinc sulphate soln. behave like those of magnesium sulphate. J. A. N. Friend and co-workers found that at low temp. magnesium sulphate and chloride retard corrosion at many concentrations; but in some cases there was a marked acceleration. Since these experiments were made on specimens submerged in the soln. where the rate of corrosion is restricted by the conveyance of dissolved oxygen, U. R. Evans repeated the experiments with plates partly immersed in the liquids, and found that for conc. ranging from 0·001M-$MgSO_4$ to 0·5M-$MgSO_4$, the effect of magnesium chloride is always to reduce corrosion below the limit for distilled water:

$MgSO_4$ . .	0M-	0·001M-	0·01M-	0·1M-	0·25M-	0·5M-
Loss . .	0·053	0·034	0·034	0·037	0·033	0·027

The action of solutions of a mixture of salts.—A. Payen[26] observed that with a soln. of equal vols. of sat. soln. of sodium chloride and carbonate and 75 vols. of aerated water, the corrosion of cast iron began in a minute, and with water containing 0·2 per cent. of sodium hydroxide and 0·6 per cent. of sodium chloride, oxidation is confined to small areas around the points at which rusting originates, and it spreads from these patches in vermicular forms. According to J. A. N. Friend and C. W. Marshall, the minimum conc., *C*, of sodium carbonate required to inhibit the corrosion of iron by 0·05N-soln. of various sodium salts runs parallel with the order of the relative strengths, *S*, of the corresponding acids determined by electric conductivity methods; thus:

	Chloride	Iodide	Bromide	Nitrate	Sulphate	Fluoride	Acetate	(Sulphite)
C . .	100	88·9	72·2	53·7	51·85	38·9	8·9	(1·9)
S . .	100	98	98	98	70	10·5	2	(58)

E. Heyn and O. Bauer observed the same critical conc. with mixtures of sodium chloride and carbonate as were obtained with soln. of sodium carbonate alone, although the corrosive action was slightly greater; no limiting conc. was reached. J. A. N. Friend studied the effect with mixtures of potassium chloride and hydroxide, at room temp., and found the following losses of weight in grams, for plates 5×4 cm. in area, with the concentrations of potassium chloride and hydroxide expressed in grams per litre:

KOH	. .	0	2·8	11·2	28	56	168
KCl	0 .	0·0685*	0·0000	0·0000	0·0001	0·0000	0·0001
	5 .	0·0884*	0·0802*	0·0010	0·0008	0·0004	0·0000
	15 .	0·0836*	0·0929*	0·0074*	0·0002	0·0004	0·0000
	50 .	0·0828*	0·0985*	0·0354*	0·0112*	0·0000	0·0001
	150 .	0·0790*	0·0657*	0·0334*	0·0059*	0·0004	0·0003
	300 .	0·0390*	0·0196*	0·0104*	0·0010	0·0004	0·0002

The numbers marked with an asterisk showed that the metal was corroded; the others may be taken to indicate no marked reaction. With no hydroxide present, the attack was uniform, but when the hydroxide was present pitting occurred. In all cases corrosion decreased as the amount of potassium hydroxide increased, becoming zero in the presence of 56 grms. per litre. The results are plotted diagrammatically in Fig. 383. The curve *AB* represents the solubility of potassium chloride in soln. of potassium hydroxide; and *OC*, the minimum conc. of potassium hydroxide required completely to inhibit the corrosion of iron in the presence of the corresponding amounts of potassium chloride. The area *OCA* represents mixtures which attack the iron in spite of the alkalinity of the soln.; and the area *ODBC*, mixtures which prevent the rusting of the iron, The preservation of steel embedded in concrete depends on the complete exclusion of air and moisture, and on the inhibitive nature of the surrounding medium. J. A. N. Friend applied the above results to the preservation of iron in compact **concrete** or **cement,** and showed the need for arranging that the concrete must be so compounded that it is always alkaline enough to inhibit corrosion. This subject was discussed by H. Barker and W. L. Upton, H. Bauerman, L. F. Bellinger, O. Berndt and co-workers, W. J. E. Binnie, B. Blount, P. Breuille, H. P. Brown, H. Buel, C. F. Burgess, W. S. Calcott and co-workers, H. J. M. Creighton, E. A. Cross, E. Donath, H. E. Dünkelberg, W. Dunn, A. P. Ford, W. H. Fox, J. A. N. Friend and co-workers, L. Gadd and C. P. Taylor, R. H. Gaines, H. A. Gardner, F. L. Garrison, M. Gary, M. Girousse, R. Grun, K. A. Goslich, A. Guttmann, M. L. Hamlin and F. M. Turner, A. L. A. Himmelwright, F. W. Hinrichsen, A. A. Knudson, A. S. Langsdorf, M. Lidy, S. Lindeck, K. Lubowsky, H. Luftschitz, F. P. McKibben, C. E. Magnussen and G. H. Smith, A. del Mar and D. C. Woodbury, E. R. Matthews, P. Mecke, W. Michaelis, E. Mörsch, S. Newberry, U. J. Nicholas, E. Noaillon, C. L. Norton, W. Obst, O. T. Olgiati and H. Roberts, J. F. O'Rourke, W. Petry, M. R. Pugh, M. Quedefeld, K. Reinbold, O. Rode, W. Roeder, P. Rohland, E. B. Rose and co-workers, J. W. Schaub, G. F. Shaffer, F. N. Speller, F. W. Taylor and S. E. Thompson, B. H. Thwaite, M. Toch, O. G. Trigg, H. C. Turner, M. C. Tutton, Y. Uchida and M. Hamada, L. Wagoner and F. H. Skinner, W. R. Webster, J. P. Whiskemann, W. G. Whitmann and R. P. Russell, H. F. Whittaker, and B. Zschokke.

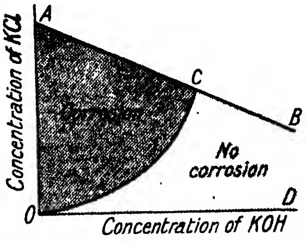


Fig. 383.—The Corrosive Action of Solutions of Potassium Chloride and Hydroxide.

U. R. Evans made analogous observations with respect to the corrosion of mixed soln. of alkali chlorides, nitrates, or sulphates and alkali hydroxide. In the case of a vertical plate immersed in a soln. of alkali chloride, a small addition of alkali will cause the corrosion to be more localized; and there occurs a little corrosion in some pores so constricted that oxygen is excluded and the conditions for anodic attack are set up, while narrow streams of rusting spread downwards from the active pores. The more open pores do not provide the conditions necessary for anodic attack. If more alkali hydroxide is added, the area covered by the corrosion product is reduced, and corrosion will be localized on the sites of a few pores which will be covered by blisters of the membranous hydrated oxide; and, with still higher proportions of the alkali hydroxide, corrosion may be entirely suppressed. At the water-level, with a soln. of alkali chloride alone, the zone just below the water-level is free from attack, but with a mixture of the chloride and hydroxide, intense corrosion may occur at the water-level. The phenomenon—**water-line corrosion**—is thus described by U. R. Evans: At this water-level a dark speck appears on the steel plate. This expands into a dark, triangular flap, floating on the liquid, and attached to the steel; this extends along the water-level, forming a kind of box. The upper side of the box is composed of a tough, dark brownish-red, membranous skin on the water-level, and below, Fig. 384, there is a looser, woolly deposit of hydroxide which is green in the early stages. The iron is not corroded immediately outside the box, but inside, intense corrosion occurs in a short space of time and finally perforation occurs. This corrosion may occur with sulphate, nitrate, or chromate in place of the chloride; and with the liquid agitated or still, hot or

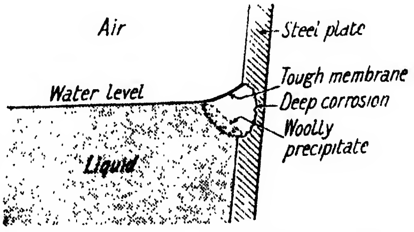


Fig. 384.—Corrosion at Water-level.

cold. The phenomenon is due to the tendency of the protective film to break away at the water-level, and as it springs away from the metal face, and clings to the interface of liquid and air, the conditions for anodic attack are set up, which once started, proceed apace—*vide supra.* The subject was investigated by A. L. McAulay and F. P. Bowden. The water-line or liquid-line corrosion of metals was discussed by G. D. Bengough and co-workers, J. I. Crabtree and G. E. Mathews, U. R. Evans, E. S. Hedges, W. P. Jorissen, E. L. Rhead, W. H. J. Vernon, and K. M. Watson and O. P. Watts; and the submerged corrosion by W. G. Whitman and co-workers.

The passivity induced in iron by contact with soln. of potassium dichromate, etc., has been discussed elsewhere. It is usually attributed to the formation of a thin protective skin of oxide on the surface of the metal. Iron may be kept an indefinitely long time in contact with soln. of potassium dichromate, if not too dilute, without any rusting; and A. S. Cushman suggested that the addition of about 0·36 grm. of the salt per litre should be a suitable protection against boiler corrosion because samples of iron and steel in boiling soln. of this concentration remain free from rust for an indefinitely long time even when air is continually bubbled through the soln. J. A. N. Friend and co-workers discussed the effect of the presence of other salts. For instance, if sodium chloride be present, there will be a state of equilibrium: $2NaCl+H_2O+K_2Cr_2O_7\rightleftharpoons K_2CrO_4+2HCl+Na_2CrO_4$, established, and the free acid will remove the protective film of oxide. Similarly with other foreign salts. If the conc. of the dichromate does not exceed 0·01 grm. per litre, its protective action is slight; and the best results were obtained with 0·1 grm. per litre, except when the conc. of the chlorides is less than about 5 grms. per litre, in which case more dichromate, say 1 grm. per litre, is needed. If potassium chromate be used in place of the dichromate, no free acid is liberated: $2NaCl+K_2CrO_4\rightleftharpoons Na_2CrO_4+2KCl$. J. A. N. Friend and J. H. Brown obtained much better results with this agent, and the presence of a gram of chromate per litre has a marked retarding influence on corrosion. The action of soln. of chromic acid, and potassium dichromate and chlorate was studied by F. Hanaman, M. Mugdan, H. Endo, C. G. Fink and C. M. Decroly, G. W. Heise and A. Clemente, O. P. Watts, A. W. Chapman, F. Numachi, T. G. Thompson, B. E. Roetheli and G. L. Cox, C. V. Thompson, etc. O. Dony-Hérault showed that the corrosion of steel in water can be stopped completely when chromate or chlorate ions are present. F. N. Speller found that ferrous sulphate inhibits the corrosion of iron; and R. E. Hall and W. W. Teague, that ferric salts act as accelerators.

The electrical behaviour of corroding iron was studied by U. R. Evans, and A. L. McAulay and S. H. Bastow. U. R. Evans found that with a mixed soln. of potassium chloride and chromate, the chromate at the cathode plays the same rôle as oxygen. The corrosion at the water-level, Fig. 384, occurs so that inside the box, the metal suffers anodic corrosion, and just outside the box the chromate is reduced, and the yellow soln. disappears. In the cell $Fe|0{\cdot}05M\text{-}KCl|0{\cdot}05M\text{-}KCl, 0{\cdot}025M\text{-}K_2CrO_4|Fe$, the iron electrode not in contact with the chromate is the anode and suffers corrosion, while the other electrode, immersed in the chromate soln., is the cathode and suffers no corrosion. Thus potassium chromate inhibits corrosion at the parts where it can reach, and stimulates corrosion in the parts it cannot reach. A rusting sheet of iron immersed in the soln. of alkali chloride and chromate quickly sprouted fresh rust on the old formations. It was assumed that the chloride diffused through the old rust more quickly than the chromate, and set up the galvanic couple. Hence, concluded U. R. Evans, if chromates are to be used as inhibitors of corrosion, then distribution must be uniform. The action of soln. of borates was studied by F. Hanaman, M. Mugdan, etc. J. A. N. Friend and C. W. Marshall found that borax, on account of its low solubility, is not so convenient an inhibitor of corrosion as sodium carbonate; the conc. of borax required to prevent corrosion by 10 c.c. of a $0{\cdot}01N$-soln. of various sodium salts containing C c.c. of a molar soln. of borax in 10 c.c. of the mixed soln. are as follows. The relative amounts of borax required run parallel with the relative strengths, S, of the acids determined by electrical conductivity methods; thus:

	Chloride	Bromide	Sulphate	Iodide	Nitrate	Fluoride	Acetate	Sulphate	Carbonate
C .	0·36	0·315	0·31	0·33	0·195	0·100	0·070	0·050	0·045
S .	100	97·5	82·5	98	98	17	4	83	?

The action of colloids on rusting.—J. Aston observed that the anodic effect with iron may be obtained by various colloidal hydroxides as well as by gelatin. J. A. N. Friend showed that salts which tend to flocculate the incoherent corrosion product are likely to form a protective coat of a colloid and thus retard corrosion. He suggested that the comparative long life of metal vessels employed in cooking may be ascribed to the colloids in the food. J. A. N. Friend and R. H. Vallance found that the relative corrosion (water 100) produced by soln. with 0·2 per cent. of sucrose is 112·4; and with 0·2 per cent. of the following colloids: gum acacia, 56·9; dextrin, 54·7; potato starch, 54·5; gelatin, 40·9; gum tragacanth, 22·6; egg-albumin, 6·8; and agar-agar, 2·7—*vide supra* for the colloidal theory of corrosion. W. Beck and F. von Hessert discussed the retarding action of agar-agar, starch, silicic acid, and gelatin.

The corrosion and tarnishing of iron exposed to air.—As indicated above, P. A. von Bonsdorff[27] showed that iron remains unaltered in damp air provided no liquid water is deposited on the metal. J. Zumstein mentioned that a polished iron cross fixed on the summit of Monte Rosa in 1820, was found a year later to be entirely free from rust and only a slight bronze-coloured tarnish could be perceived. This can be attributed in part to the low temp., and in part to the purity of the atmosphere at high altitudes. Another famous instance is the iron column at Delhi, described by A. Cunningham, and V. A. Smith, believed to have been erected about A.D. 300. This column is practically free from rust, though it is covered by a bronze-coloured tarnish. R. A. Hadfield attributed the immunity from corrosion at least as much to the purity of the atmosphere as to the composition of the metal. A small portion rusted in a single night when wetted and exposed in England, although a freshly fractured surface suffered no change when exposed four nights to laboratory air. There is also, at the British Museum, an ancient Egyptian hatchet, dating 700 B.C., which is free from rust. W. Rosenhain attributed the apparent immunity of some ancient iron to the corrosion having previously extended down to layers of cinder in the metal, and there stopped; *e.g.* the ancient iron chains which assisted the pilgrims of old to climb Adam's peak, Ceylon, have been worn smooth and round, without perceptible corrosion, but the outer surface is simply a cinder surface which protects the iron below. In London air, a portion of the chain rusted as quickly as any other form of iron. The mechanical protective influence of cinder was discussed by H. M. Howe. J. A. N. Friend and W. E. Thorneycroft found that some specimens of old Roman iron from Richborough and Folkestone were distinctly less corrodible than modern metal. J. Wallace also noticed that iron made in India in the native way does not rust so readily as iron made in Europe.

In dealing with the action of atmospheric air on iron, the surface tarnish appears as a thin adherent film which causes discoloration, and interferes with the bright lustre. It will add to the weight of the metal. The film of oxide producing the tarnish may protect the metal below from further attack, or the tarnish may thicken and flake off to expose a fresh surface of metal to attack. J. A. N. Friend, and W. H. J. Vernon apply the term ***surrosion*** to cases where the metal increases in weight. In corrosion, the metal is eaten away to form a non-adherent product, and when this is removed, the specimen has suffered a loss in weight. G. D. Bengough and U. R. Evans discussed the relation of corrosion to ***erosion***. J. A. N. Friend found that the action of air on iron is indefinitely slow at 100°, for a bright piece of iron-foil showed no perceptible change when kept at this temp. for 5 hrs.; even at 150°, no surface tarnish could be detected by mere inspection, but at higher temp., the surface was tarnished. J. Milbauer observed no change in a piece of polished iron after heating in dry oxygen up to 500°, and 12 atm. press.

The tint of the tarnish produced at higher temp. depends mainly on the time of exposure and temp. With the conditions approximately constant, the tints of the films obtained at different temp. furnish the so-called *tempering colours* used by the old workmen in tempering or annealing steel. Thus, in the case of a steel examined by H. M. Howe, a pale yellow tint was produced at 220°; a straw-yellow at 230°; a golden yellow at 242°; a brown at 255°; a brown and purple at 265°; a purple at 277°; a bright blue at 288°; a full blue at 293°; a dark blue at 316°; and a grey at 350°. The thickness of the films is comparable with the wave-length of light, and they furnish a series of interference tints with the dominant colour altering as the film thickens. The light is reflected from the surface of the metal and also the surface of the film, and as the one train of light-waves merges into the other, the phases may be the same or opposite to one another, and, as shown by L. Nobli, effects analogous to Newton's ring colours may be produced. This subject has been discussed by D. H. Bangham and J. Stafford, F. H. Constable, C. F. Ramann, U. R. Evans, R. C. Gale, G. Jung, K. Inamura, A. Mallock, C. W. Mason, F. Robin, L. Guillet and A. M. Portevin, J. E. Stead, V. Kohlschütter and E. Krähenbühl, C. N. Hinshelwood, M. Kuroda, G. W. Vinal and G. N. Schramm, M. Schmierer, F. A. Fahrenwald, and by G. Tammann and co-workers—*vide supra,* the passivation of iron in air. C. V. Raman studied the reflection of light for various angles of incidence on the oxidized film and concluded that temper colours are produced by the diffraction of light by a granular film of oxide. B. N. Chuckerbutti supported this conclusion. G. Tammann and co-workers, and U. R. Evans support the interference theory of the colours. The colours appear in the correct order during the formation of the film, and by reducing the thickness of the film, the earlier colours are reproduced in the appropriate order. G. Tammann and G. Siebel investigated the rates of change with time of the temper colours of primary cementite, pearlite, pearlitic cementite, and troostite, and found that if the thickness of the equivalent air film, $y\mu\mu$, be plotted against time, t, then, $t=a(e^{by}-1)$, where a is a constant, and b is a coefficient which decreases with increasing temp., T, so that $\log_e b_T = \log_e b_{T_0} - c(T-T_0)$, where c is constant. There are discontinuities with nickel and vanadium steels which are connected with the change of α- to γ-iron. The subject was discussed by J. S. Dunn. T. Turner showed that any colour can be produced by heating the metal long enough at a lower temp. than that corresponding with the particular tint. Thus, the straw-yellow can be obtained at 170° instead of at 220°; and the purple can be obtained at 170° in 12 hrs., at 220° in 1 hr. The subject was also examined by L. Guillet and A. M. Portevin, and C. Barus and V. Strouhal. According to L. Löwenherz, the results vary with the composition of the steel. W. C. Roberts-Austen showed that if steels be heated in vacuo, these colours are not produced, showing that the colours are due to the formation of a film of oxide. S. Stein arrived at a similar conclusion. J. A. N. Friend found that the colours appear even if the air be dried by storage over phosphorus pentoxide for a few months, and concluded that the formation of the colours is a process of direct oxidation of the metal.

G. Tammann and W. Köster, and N. B. Pilling and R. E. Bedworth studied the rate of oxidation of hot metals, and N. B. Pilling and R. E. Bedworth showed that if the vol. occupied by a given amount of the compact oxide is less than the vol. of the metal required to produce that oxide, the film of oxide will be porous and will not protect the metal from further attack. Hence, if M be the mol. wt. of the oxide; m, that of the metal; D, the sp. gr. of the oxide; and d, that of the metal, if Md/mD be less than unity, a porous oxide will be formed, and if greater than unity, a protective oxide will be produced if no cracking occurs. The ratio is less than unity in the case of Li, Na, K, Mg, Ca, Sr, and Ba; and greater than unity in the case of Cu, Zn, Cd, Al, Zr, Th, Sn, Pb, Cr, W, Mn, Fe, Co, and Ni. With iron, the ratio is 2·06. The oxide formed when iron is heated in air is normally slaty-black and consists of two phases, forming a thick outer and a thinner under layer respectively, with an aggregate composition intermediate between FeO and Fe_3O_4. It is prone to form as a hollow, swollen tube around the wire, the surface frequently contorted into grotesque shapes, very often with crests and protuberances of reddish Fe_2O_3, depending somewhat on the temp. of oxidation. When cold, the shape of these suggests that either during oxidation or cooling a liberation of gas occurred, puffing the oxide shell out, and sometimes bursting, leaving small, crater-like mouths. In almost every case the oxide, when cold, was loose and of considerably larger internal dimensions than that of the wire it jacketed; the metal surface was always blue, indicating probably the fracture of the enveloping oxide layer, during cooling, but while still quite hot. This behaviour is apparently closely related to the oxygen conc. of the atm., for Armco iron generally yielded more perfect (*i.e.* smoother surfaced) symmetrical oxides in air than in oxygen, while an extremely perfect coating was formed during an oxidation at a much reduced press., about 10 mm., followed by cooling in vacuo. The rate of oxidation, $dW/dt=k'/H$, where W denotes the weight of oxygen; H, the thickness of the oxide; and t, the time. Since all the oxygen which diffuses through the oxide layer goes to increase its thickness, W is proportional to H, and $dw/dt=k''/W$, so that $W^2=kt$. With electrolytic iron in oxygen, W^2 per sq. cm. per hour is $0{\cdot}17\times10^{-4}$ at 700°, $1{\cdot}00\times10^{-4}$ at 800°, and $6{\cdot}5\times10^{-4}$ at 900°; with Armco iron in oxygen, W^2 is $1{\cdot}95\times10^{-4}$ at 800°, $10{\cdot}1\times10^{-4}$ at 900°, and $43{\cdot}0\times10^{-4}$ at 1000°; and with Armco iron in air, W^2 is $1{\cdot}06\times10^{-4}$ at 800°, $4{\cdot}9\times10^{-4}$ at 900°, and $20{\cdot}5\times10^{-4}$ at 1000°. The nature of the oxidation product is discussed below. The quadratic rule that the quantity of oxygen which combines with the metal is proportional to the square root of the time of exposure is followed by iron in the earlier stages of the oxidation. As soon as the thickness of the oxide increased much, the surface became rough, fissures and local super-oxidized areas developed, and erratic departures from proportionality resulted. Armco iron oxidized at a consistently faster rate, and formed coatings which were, in general, smooth. The oxidation of the Armco then followed the quadratic rule more closely. The oxidation constant, k, for iron at a temp. $T°$ K., is approximately $k=0{\cdot}000028T^{-19{\cdot}3}$, and at 800°, $k=0{\cdot}000100$, and at 900°, 0·00065 grm.^{2} per sq. cm. per hour. G. Tammann and K. Bochoff compared the thickness of films of oxide on iron with the thickness calculated from interference phenomena. The subject was also studied by T. Nishina, F. H. Constable, J. S. Dunn, and Y. Utida and M. Saito. The last-named found for a 2 hours' heating at 1110°, 1000°, 890°, and 770°, that iron wire gained respectively 46·55, 36·03, 14·05, and 5·38 mgrms. of oxygen per sq. cm. According to J. Jahn, with air at:

	Moist air		Dry air	
	199°	200°	198°	297°
Iron . . .	751·1	753·3	747·5	753·9 mgrms.
Gain in weight .	0·0	0·1	0·0	0·3 mgrm.

W. H. J. Vernon found that with copper, the rate of oxidation (tarnish) curve in a humid atmosphere is parabolic; with zinc, linear; and with iron, the attack increases in speed as time goes on—Fig. 385. V. I. Arkharoff studied the X-radiograms of the process of oxidation at high temp.; and A. N. Kossogovsky, the effect of the structure on the scale formation. The heat-tinting of iron-carbon alloys was discussed by L. Guillet and A. M. Portevin, J. Czochralsky, F. Robin, P. Goerens, G. Tammann and G. Siebel, P. Oberhoffer, F. Reiser, T. Turner, L. Löwenherz, and H. Haedicke—*vide supra.*

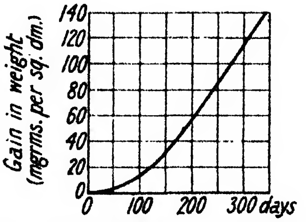


Fig. 385.—The Rate of the Tarnishing of Iron in a Humid Atmosphere.

The composition of the films is discussed in connection with ferrosic oxide. According to J. E. Stead, when iron is heated in air, or oxidizing gases, the surface layers appear to absorb oxygen which passes into solid soln.; and when supersaturated, the oxide falls out of soln. forming separate granules of free oxide; these granules become larger as oxidation proceeds, and eventually join together to form continuous layers. Although there is a fairly sharp line of demarcation between the oxide film and the metal below, the underlying metal is also affected, for the oxidizing gases find the most facile passage into the metal in the boundaries between the crystals, and the gradual changes from solid soln. to free oxide can be traced along the oxidized junctions of the crystals. Fig. 386 shows a longitudinal section through an oxidized steel plate, with a scale of oxide at the top, and steel below. The sample was etched with a cupric reagent, and the white lines indicate the intergranular oxides; and similar remarks apply to the transverse section, Fig. 387, which shows the granular oxides between the crystals. Hence, intergranular brittleness may be developed in the iron. It is also believed that sulphur dioxide, nitrogen, and hydrogen can enter iron and steel along an intergranular path. According to E. H. Hemingway and G. R. Ensminger, after heating 1·01 per cent. carbon steel for 6 hrs. at 1000°, there appeared on the surface delicate pearlitic grains representing a structure stable below the critical point. Independent of this structure was a second system consisting of deeply marked polygonal crystals representing γ-iron boundaries, and also a third system independent of either, which was thought to represent the boundaries of former γ-crystals which had been absorbed by crystalline growth. This outside layer of carbon-free iron was very thin, although with steels of lower carbon-content a layer of greater depth was obtained. This outside layer consisted of ferrite volatilized at the high temp. and redeposited below the temp. at which solid soln. exists. Any iron oxide existing on or in the steel would tend to cause decarburization by breaking down the cementite. G. Tammann and H. Bredemeier considered that the capillary cavities or channels, found in sound metals, probably following the lines where three crystal grains meet, are responsible for the access of oxygen to the interior. The porosity of the metal has been previously discussed. F. H. Constable, J. H. S. Dickenson, G. C. McCormick, W. H. Hatfield, F. Körber, F. Körber and A. Pomp, H. Scott, C. J. Smithells and co-workers, W. Schröder, H. Haedicke, and F. S. Tritton and D. Hanson discussed the formation of films of oxide on iron; E. C. Rollason, intergranular corrosion; and J. Cournot and L. Halm, the effect of polish on the rate of oxidation.

FIG. 386.—Longitudinal Section showing the Intergranular Penetration of Oxygen in Steel (×50).

FIG. 387.—Transverse Section showing the Intergranular Penetration of Oxygen in Steel (×50).

U. R. Evans pointed out that in most cases where iron rusts while it is in contact with a liquid, the rust accumulates outside the pits; but in atmospheric corrosion, where the main surface is dry, water may remain in the pores or pits produced by previous corrosion, and rust will be formed within the pore—*cf.* Fig. 388. The rust occupies a much larger volume than the metal producing it, so that (i) the pore or pit may become plugged with rust and corrosion will cease—Fig. 388; (ii) the liquid will be gradually forced out of the pore or pit by the press. developed;

or (iii) the press. will cause the metal to disintegrate, and corrosion will penetrate further. With pores perpendicular to the surface, the disintegration of the metal is less likely to occur than where the pits run parallel to the surface as in rolled metal, Fig. 389, where the corrosion produces flaking. A. G. E. Matheson discussed the structure of the rolled metal. J. Newman discussed the tendency for rapid corrosion to occur in the "sheltered crevices and nooks" on structural steelwork; and E. F. Law, a failure due to the imperfect welding of a tie-rod which led to the collapse of the roof of a London station. Faulty riveting may produce local corrosion. In all these cases, as U. R. Evans showed, the crannies and nooks may become filled with water, and anodic corrosion by differential aeration currents may be induced.

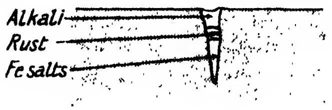


FIG. 388.—Atmospheric Corrosion-plugging.

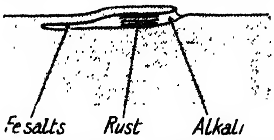
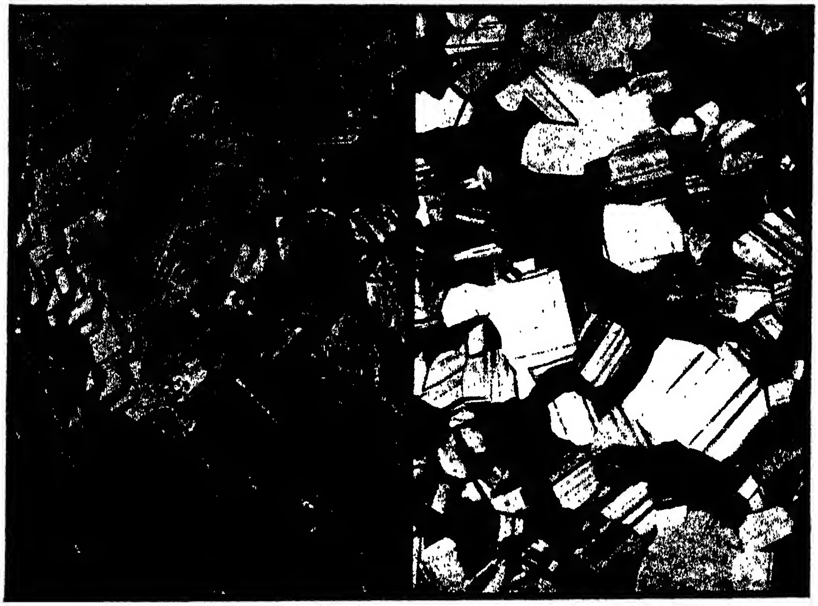


FIG. 389.—Atmospheric Corrosion-flaking.

L. B. Pfeil observed that when iron or carbon steel or alloy steel is oxidized at a red-heat, in air, it does not form a homogeneous deposit, but rather a series of three layers: (i) an outside layer consisting mainly of ferric oxide or a mixture of 68·7 per cent. of ferrosic oxide and 31·3 per cent. of ferric oxide; (ii) a middle layer in a lower state of oxidation containing ferrous and ferric oxides in the proportion approximately 3 : 1; and (iii) an innermost layer, in contact with the unoxidized metal, is still richer in ferrous oxide. The layers, of course, are not uniform in composition; it is probable that they vary in composition through their cross-section, becoming richer in iron on passing inwards. Roughly, the outside layer occupies about 10 per cent. of the total scale thickness; the middle layer, about 50 per cent.; and the innermost layer, about 40 per cent. when the iron has been heated from 3 to 7 days in air at 1000°. When the oxidation is severe, each layer can be separated more or less completely from the other layers, though it is rarely possible to separate the whole of each layer from the other layers and from the core. There may be disturbances: for instance, blistering affects the layer formation, and considerable fluctuations of temp., and the presence of certain impurities may spoil the three-layer deposit. The scale is normally smooth, compact, and free from cracks and fissures in spite of the fact that the oxidation involves an expansion of the order of 100 per cent. Foreign substances on the surface of the iron are not forced away by the formation of the scale, but they remain unmoved and become completely enveloped by the scale. When the oxidation is slow, large crystals of the scale may be formed exhibiting plain crystal faces, so that sometimes the scale surface shows in high relief. H. C. H. Carpenter and C. F. Elam described the formation of crystalline deposits on iron heated in vacuo. They ascribed the scale formation to the occluded, oxidizing gases driven from the iron on heating, and they added that the oxide of iron originally produced is isomorphous with α-iron, and the orientation of the oxide produced on any given crystal of iron is determined by the orientation of the α-iron itself. L. B. Pfeil added that the scale formation can be produced on electrolytic iron, high- and low-carbon steels, alloy steels, and cast iron, provided the partial press. of the oxygen is suited to the other experimental conditions. It is almost immaterial whether the oxygen be supplied as gaseous oxygen at a low pressure, as an oxygen and inert gas mixture, as a reactive gas like CO_2, or as a compound, such as iron oxide, which gives off oxygen owing to dissociation. Variations in the appearance of the scale are mainly dependent on the form of the crystal faces. There is good reason to suppose that a solid soln. series belonging to the cubic system exists at high temp. over the composition range of crystalline scales. Many different forms belong to the cubic system, the commonest developed in magnetite being the cube, the octahedron, and the rhombododecahedron. It is often found that the forms which develop in a substance vary with the conditions (temp., press., etc.) under which the crystals grow. Fig. 390 is from a photograph of the scale crystals by L. B. Pfeil.

L. B. Pfeil showed that any explanation of the scaling of iron must explain the formation of the crystals, and also how it is possible that the outer layers of scale on alloy steels can be free from the alloying element. The two outer layers of scale form a dense, glassy deposit, and the idea that iron is progressively oxidized by the forcing of the already formed scale away from the metal core by the press. exerted by the new scale forming beneath does not explain the facts. If oxygen molecules diffused along porous paths in the glassy scale—*e.g.* through cracks—oxidation would corrode the iron irregularly, and the oxidation at the bottom of a crack or porous place would automatically seal the oxygen path and oxidation there would cease. N. B. Pilling and R. E. Bedworth imply that the iron oxide acts as a carrier for oxygen—the oxygen dissolving in the scale and diffusing through to the core owing to the oxygen gradient, and J. H. Whiteley, that ferric oxide is formed in the scale, and reacts with the iron below to form ferrous oxide. It is probable that there is a continuous series of solid soln. over the major portion of the iron–oxygen system from ferric oxide to ferrous oxide, with a gradually decreasing dissociation pressure on passing from the higher to the lower oxygen-content. Thus, where the scale is in contact with the air the soln. will be enriched in oxygen, but this enriched layer will not be in equilibrium with that beneath, so oxygen will pass inwards until it finally reaches the iron, with which it combines to form ferrous oxide. D. W. Murphy and co-workers said that the nature of the oxidation of iron or steel at elevated temp. which results in scaling, can be predicted from the equilibrium in the systems $Fe–O_2–C$, and $Fe–O_2–H_2$; and D. W. Murphy and W. E. Jominy studied the influence of atm. and temp. on the behaviour of steel in forging furnaces.



FIGS. 390 and 391.—Crystals of Iron Scale (× 10).

L. B. Pfeil rejected the hypothesis that the outside of the scale is that which is formed first at the initiation of the oxidation, and that further oxidation displaces the first-formed scale bodily outwards. He said: At the interface of iron and scale, iron is being continually dissolved in the scale, so that the iron is converted into oxide forming part of the scale deposit. There is thus an outward diffusion of the iron through the scale to the interface of scale and air. The outer part of the scale is thus the last to form, and the middle portion the first to form. No volatile compound is known whose transitory existence would play such a part, and hence it is necessary to assume a counter current diffusion—iron diffusing outwards and oxygen inwards through the scale deposit. It is not of essential importance whether the iron diffuses as iron atoms or in some other form. It is difficult to picture the diffusion of iron combined with oxygen (as ferrous oxide, for example) in a solid soln. of iron and oxygen, and consequently for the sake of simplicity the diffusion of iron atoms has been described. Reference has been made to the soln. of iron in the scale. It is immaterial whether the iron be converted into ferrous oxide first and then dissolved in the scale, or whether the iron dissolves directly in the scale. The essential feature is that scale is normally unsaturated with iron, and that metallic iron will join such scale if the two are heated in contact. In support of his hypothesis, L. B. Pfeil showed (i) that a scale of higher oxygen-content will give oxygen to a scale of lower oxygen-content; (ii) that metallic iron is oxidized by a scale rich in oxygen; and (iii) that iron can pass outwards through the scale to the surface.

Similar results were obtained by I. Kotaira in the oxidation of cupriferous steels. A. Ledebur, L. B. Pfeil, and P. Bardenheuer and K. L. Zeyen discussed the effect of carbon on the results. The subject was studied by U. R. Evans and J. Stockdale, K. Hofmann, O. Lellep, G. C. McCormick, J. H. S. Dickenson, and O. Lutherer and E. R. Weaver. Electromotive forces of relatively large intensity have been observed between the film and the metal, and the subject has been discussed by S. Bidwell, S. P. Thompson, J. Franz, J. M. Gaugain, H. C. F. Jenkin, and C. Barus and V. Strouhal. The effect may be thermoelectric, or galvanic in which the electrolyte is the solid film. The oxidation of cast iron is accompanied by a marked increase in bulk—*vide infra*, the growth of cast iron.

Heat-resisting alloys.—Alloy steels, etc., intended to resist oxidation at high temp. were discussed by numerous observers.

L. Aitchison,[38] N. Armann, R. W. Bailey, H. N. Bassett, A. Bensel, G. R. Brophy, H. C. H. Carpenter, P. Chevenard, J. D. Corfield, J. H. S. Dickenson, J. W. Donaldson, T. G. Elliot and co-workers, K. Endell, F. A. Fahrenwald, H. J. French, E. Schüz, A. Fry, J. Galibourg, C. Grard, H. Gruber, R. A. Hadfield and co-workers, H. H. Harris, W. H. Hatfield, O. Hengstenberg and F. Bornefeld, T. Hoffmann, E. Houdremont and V. Ehmcke, G. H. Howe and G. R. Brophy, C. H. M. Jenkins and co-workers, C. M. Johnson, H. Jüngbluth and H. Müller, J. F. Kayser, F. Körber and A. Pomp, L. Losana, A. McCance, R. S. MacPherran, C. E. MacQuigg, S. A. Main, J. A. Matthews, A. Michel, E. Morgan, F. K. Neath, T. H. Nelson, H. D. Newell, A. L. Norbury and E. Morgan, W. Oertel and A. Schepers, A. E. Perkins, H. D. Phillips, R. J. Piersol, E. P. Poste, W. Rohn, W. Rosenhain and C. H. M. Jenkins, R. J. Sarjant, B. J. Sayles, O. Smalley, S. W. G. Snook, L. W. Spring, L. J. Stanbery, J. Strauss, W. B. Sullivan, R. Sutton, C. Upthegrove and D. W. Murphy, and E. Valenta—*vide* chromium-iron alloys.

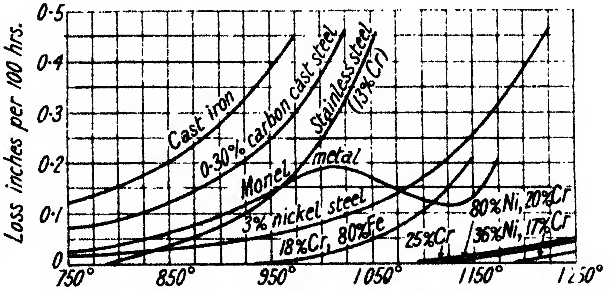


FIG. 392.—The Heat-Resistance of Metals.

F. A. Fahrenwald reported the results indicated in Fig. 392 for the resistance offered by various metals to high temp. oxidation.

The *scaling of iron* similarly refers to the formation of a surface layer of oxide when iron or steel is heated in furnaces; *iron scale* is thus distinct from *rust* in that one is formed at an elevated temp., and the other is formed at ordinary temp. by surface oxidation. The scaling of iron was investigated by H. T. Angus and J. W. Cobb,[29] W. H. Blackburn and J. W. Cobb, J. W. Cobb, J. H. S. Dickenson, J. S. Dunn, W. H. Hatfield, O. Lellep, G. C. McCormick, C. B. Marson and J. W. Cobb, R. Mitsche, J. H. G. Monypenny, R. Stumper, D. W. Murphy and co-workers, A. L. Norbury, J. E. Stead, W. Schröder, and Y. Utida and M. Saito. R. L. Kenyon compared the high temp. oxidation of Armco iron, and mild steel, expressing the results after heating the metal for different periods of time, as the rate of scaling in inches per 1000 hrs. over the entire period of the test:

Time .	1672	3826	6146	7996	10,135	12,295	13,406 hrs.
Armco .	0·0105	0·0099	0·0061	0·00472	0·00453	0·00427	0·00391
Mild Steel	0·0111	0·00693	0·00504	0·00584	0·00790	0·00753	0·00787

The *peeling of malleable cast iron* was studied by F. H. Hurren, W. H. Poole, and J. W. Gardom. According to D. H. Ingall and H. Field, temp. near 950° are most conducive to peeling. The faster the rate of heating to this temp. the greater the tendency to peeling. The peel consists of a layer or layers of ferrite containing granules of free oxide as inclusions. When this layer is once formed, growth will occur with time and suitable temp. conditions. The phenomenon of peeling is a result of oxidation, which commences between 900° and 940°. Once this oxidation has begun, the growth of the oxide layer is a result of a race between the rate of oxidation and the rate of carbon supply from the interior.

The erosion of guns by gases, etc., was discussed by F. Abel and E. Maitland,[30] P. R. Alger, A. E. Bellis, A. Bennington, E. Berl, E. Bravetta, H. C. H. Carpenter, P. Charbonnier, C. Cranz, W. Crozier, E. Demenge, F. A. Fahrenwald, H. Fay, M. Graziani, R. H. Greaves and co-workers, J. Hanny, H. M. Howe, H. G. Howorth, W. J. Huff, H. Hugoniot and H. Sébert, H. J. Jones, W. Klever, A. Lanfroy, H. H. Lester, M. Létang, D. C. McNair, A. Mallock, A. Noble, M. Okochi, F. Osmond, H. Peloux, E. Piantanida, W. C. Roberts-Austen, E. B. D. Secondo, P. Siwy, W. W. de Sveshnikoff, D. K. Tschernoff, T. G. Tulloch, L. Vasseur, P. Vieille, H. E. Wheeler, H. E. Yarnell, and A. G. Zimmermann. J. E. Stead [31] studied the action of blast-furnace gases on iron; U. R. Evans, and H. B. Dixon, the action of the products of combustion of coal gas; J. Parker, the action of town gas; and A. W. Carpenter, L. Losana, A. Dänzer-Ischer, U. R. Evans, A. de Waele, P. Siedler, H. F. Johnstone, F. L. Wolf and L. A. Meisse, O. W. Storey, W. Gumz, and W. H. Hatfield, flue gases, exhaust gases from motors, air in railway tunnels, and the products of combustion of coal. Coal with chlorides (*q.v.*) corroded when coal without chlorides did not. The presence of sulphur dioxide (*q.v.*) is a source of rapid attack.

The corrodibility of different kinds of iron and steel.—*Vide infra* for the various alloys of iron. The general effect of alloys on the corrodibility of iron and steel was discussed by P. Kötzschke and E. Piwowarsky.[32] A. Payen, and J. Newmann observed that grey cast iron corrodes more readily than white cast iron, or bar iron. R. Mallet observed the following results expressed in terms of the corrosion factor:

	Sea-water	Foul sea-water	Foul river-water	Clear river-water
Wrought iron	100·0	118·6	68·8	12·3
Cast iron	63·6	20·5	40·4	9·9
Chilled cast iron . . .	64·4	63·1	51·2	12·9
Cast iron (skin removed) .	77·6	127·8	64·4	23·5

The chilled metals are more susceptible to attack than the metal cast in green-sand, due, he supposed, to the exterior of the chilled casting not being homogeneous; he said that "the voltaic action produced at the surface of chilled cast iron, by want of its homogeneity, increased the corrosion of the metal to a greater extent than its greater density and hardness, and small amounts of uncombined carbon are capable of retarding corrosion, in comparison with other sorts of cast iron." Wrought iron corrodes faster than cast iron except in clear river-water. In clear river-water, wrought iron is nearly as resistant as cast iron, and more so than chilled cast iron. When the outer skin is removed from cast iron, it is more susceptible to corrosion, and it then approximates more closely to wrought iron. L. E. Gruner found that cast irons and spiegeleisen resisted atm. corrosion better than steels, but in sea-water, steels were more resistant. T. Andrews found that cast irons did not resist sea-water so successfully as wrought irons and low carbon steels, although there is little to choose between them and 0·5 per cent. carbon steels. J. Aston and C. F. Burgess found the corrosion factors for the metals exposed to atm. influences: open-hearth iron, 100; Swedish wrought iron, 83; open-hearth steel, 91; Bessemer steel, 65; and medium-grained grey cast iron, 78. E. Heyn and O. Bauer observed for the corrosion factors:

	Distilled water	Tap-water	One per cent. NaCl
Steel . . .	100	100	100
Wrought iron . .	103·7	104·8	103·7
Cast iron . .	97·3	93·2	98·6

Observations on this subject were made by W. Ackermann, D. Adamson, F. Andrews, K. Arndt, J. H. Baker, L. J. Chapman, F. C. Calvert, J. Collins, A. S. Cushman, H. Diegel, G. M. Enos, U. R. Evans, J. Farquharson, J. D. Ford, A. G. Fraser, J. A. N. Friend and C. W. Marshall, W. P. Gerhard, R. Girard, L. E. Gruner, J. T. Haddock, E. Heyn and O. Bauer, H. M. Howe, W. E. Hughes, B. Kosmann, O. Kröhnke, F. Kupelwieser, Langbein-Pfanhauser Werke, R. C. McWane and H. J. Carson, S. Maximowitsch, F. Menne, M. Meyer, H. Otto, W. Palmaer, D. Phillips, H. Pilkington, H. S. Rawdon, E. L. Rhead, W. D. Richardson, M. Rudeloff, M. Schromm, G. Schumann, J. Scott, F. N. Speller, D. M. Strickland, T. N. Thompson, W. Thompson, B. H. Thwaite, M. Uellenhof, W. H. Walker, G. C. and M. C. Whipple, W. G. Whitman and E. L. Chappell, J. H. Woolson, and numerous others.

There are many differences of opinion as to the relative merits of steel, wrought iron, and cast iron in resisting corrosion. H. M. Howe, for example, obtained the opinions of thirty-seven shipbuilding firms as to the relative corrodibility of wrought iron and steel; and of these, seven regarded steel as the more corrodible, eight regarded wrought iron as the more corrodible, and twenty-two were uncertain, or considered that there was no preference. T. Andrews made tests extending over years, and concluded that wrought iron is decidedly the better material. F. N. Speller preferred steel; R. A. Hadfield considered wrought iron better resists the action of sea-water. J. A. N. Friend's observations showed that the superiority of wrought iron, if it exists at all, is comparatively small. H. M. Howe and B. Stoughton came to a similar conclusion, but they found that steel was far less liable to pitting. An analogous conclusion was drawn by A. S. Cushman, J. D. Ford, G. Johnstone, W. Marriott, H. Otto, R. Irvine, W. H. Gibson, A. Schleicher, G. J. Snelus, F. N. Speller, T. N. Thompson, R. H. Gaines, H. Wölbling, W. H. Melaney, F. H. Williams, R. Finkener, etc. K. Arndt found that whilst cast iron rusts uniformly over the surface, the rusting of wrought iron and mild steel is confined to local areas. The difference is due to the adherent character of the protective oxide film on cast iron which is not readily dislodged by rust, whilst the film on wrought iron and steel readily scales off and allows the spongy rust to form. Alterations of wetness and dryness are better resisted by cast iron, and for the same reason. W. Parker found that various steels and wrought irons resisted the action of cold sea-water to the same extent, but steels suffered more than wrought irons when exposed to London air; and steels differed as much amongst themselves in their resistance to corrosion as they differed as a body from the wrought irons. M. Rudeloff also exposed plates of wrought iron, acidic steel, and basic steel to the action of dry air, the air outside exposed to rain, etc., smoke, furnace gases, ditch-water, and sea-water. The results showed as much variation amongst themselves as do steels as a class and wrought irons as a class. A. S. Cushman, and L. J. Chapman said that wrought iron corrodes less than steel. A. G. Frazer found acidic and basic steel plates resisted corrosion in air, river-water, and salt soln. equally well; but in dil. sulphuric acid, basic steel had the advantage. W. G. McMillan came to the same conclusion. Close-grained cast iron is generally superior to steel and wrought iron; and, as emphasized by G. Murdoch, and D. Spataro, provided the metal is free from blow-holes. B. H. Thwaite compiled the available data for cast and wrought iron, and the relative values for corrosion are:

	Foul sea-water	Clear sea-water	Foul river-water	Clear river-water	City and sea-air
Wrought iron	10·450	3·855	7·680	0·655	6·690
Cast iron skin intact	3·50	3·386	2·034	0·604	2·637
Cast iron skin removed	12·275	4·738	3·884	0·584	4·763

Hence, the outer skin formed in the casting acts as a preservative coating. M. Mugdan found that steel behaves like soft iron, whilst cast iron always showed a greater tendency to rusting. S. D. Carothers observed that in sea-air cast iron is less liable to rusting than plain carbon steel, but some varieties of cast iron break down rapidly. Some results by W. H. Hatfield are given in Table LIII—*vide supra* for the action of sea-water on cast iron, etc. R. Girard found that with low concentration of acid, iron and steel behave similarly, but at higher concentrations, polished iron is attacked more quickly than steel. A. Schleicher and G. Schultz found with a rusty and a clean wrought iron plate immersed in water, the latter acts as cathode, and with a clean wrought iron and a cast iron plate, the former acted as cathode.

TABLE LIII.—THE ACTION OF REAGENTS ON DIFFERENT VARIETIES OF IRON AND STEEL.

	Hydrochloric acid		Nitric acid		Sulphuric acid		
	N	Conc.	*N*	Sp. gr. 1·2	*N*	10 per cent.	
Wrought iron	0·1416	0·2217	0·1263	0·6399	0·1452	0·3610	
Mild steel	0·0850	0·1812	0·1154	0·5858	0·1052	0·1032	
Cast iron	0·1340	0·3280	0·1022	0·1300	0·1364	0·1158	
High Si (tantiron)	0·0007	0·0009	0·0003	0·0008	0·0010	0·0006	
Stainless steel	0·0638	0·1799	0·0111	*Nil*	0·0871	0·1126	
	Water	Sea-water	Vinegar	Acetic acid (33 per cent.)	Citric acid (5 per cent.)	Ammonium chloride (5 per cent.)	Magnesium chloride (1 per cent.)
Wrought iron	0·0161	0·0036	0·0100	0·2023	0·1075	0·0084	0·0033
Mild steel	0·0150	0·0047	0·0032	0·1492	0·1458	0·0124	0·0036
Cast iron	0·0226	0·0040	0·1901	0·4819	0·1404	0·0101	0·0032
High Si (tantiron)	0·0002	0·0005	0·0004	0·0003	0·0012	0·0003	0·0004
Stainless steel	*Nil*	*Nil*	*Nil*	0·0232	0·0422	0·0014	0·0018

Many purified metals are more resistant to corrosion than commercial metals. This inertness may be due to the homogeneous nature of the material preventing any but very feeble corrosion currents being set up between different parts, or else a passive state being produced by the formation of a uniform, protective film. L. Losana and G. Reggiani[33] found tempering steel normally increases its resistance to corrosion. B. Lambert and co-workers found that highly purified iron is not corroded in the presence of aerated water under conditions where ordinary iron rusts rapidly. H. E. Armstrong attributed this to passivity. W. E. Hughes observed that electrolytic iron from a chloride bath quickly rusted, owing to the inclusion of traces of chlorides. When iron is deposited from a sulphate bath, it did not rust when wrapped up in filter-paper, and stored in a box. Observations on the apparent inertness of highly purified iron were made by D. J. Demorest, G. P. Fuller, N. S. Kurnakoff and A. N. Aschnasaroff showed that the eutectic with alloys slowly cooled is coarse-grained, and fine-grained if rapidly cooled. The alloys in the former case were readily attacked by some reagents, while the latter resisted attack.

L. Aitchison also found that many metals which formed a solid soln. with iron tend to reduce the attack by dil. acid, and soln. of sodium chloride, but metals which do not form such soln. render the iron more susceptible to attack.

J. A. N. Friend tested the action of aerated water on steels with between 0·05 and 0·32 per cent. **carbon.** There is not a marked difference in the rates of corrosion, and the differences do not always follow the carbon-content. In general, there is a slightly increased corrosion with an increase in the carbon-content of the steel. This agrees with the result of L. Aitchison, who found that steels having between 0·07 and 1·46 per cent. of carbon show very little difference in their resistance to corrosion in a 3 per cent. soln. of sodium chloride. There is a maximum rate of corrosion near the eutectic with about 0·9 per cent. of carbon. G. M. Enos observed that the corrosion of steel by aerated distilled water is not much affected by the carbon-content. The work of H. M. Howe, A. Sang, A. Ledebur, W. D. Richardson, G. Dillner, O. Kröhnke, G. Bardenhauer and K. L. Zeyen, K. Daeves, U. R. Evans and R. T. M. Haines, H. Otto, and W. Parker indicated that the resistance offered by steel to corrosion increases with the proportion of hardening carbon. H. Endo found the losses, expressed in grams per sq. cm., during 5 hrs.' attack, at ordinary temp., with iron containing

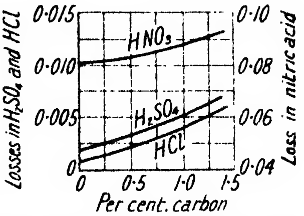


FIG. 393.—The Effect of Carbon on the Corrosion of Iron by Acids.

Carbon		0	0·31	0·52	0·64	0·96	1·16	1·32	1·41 per cent.
Loss	H_2SO_4	0·00197	0·00270	—	0·00338	0·00470	0·00534	0·00702	0·00762
	HCl	0·00092	0·00210	—	0·00328	0·00401	0·00481	0·00568	—
	HNO_3	0·07981	0·08079	0·08303	0·08590	0·08741	0·09135	0·09204	0·09074

This shows that the losses with the three acids vary almost linearly with increasing proportions of carbon. The rate of dissolution of steel is greatly influenced by the state of the carbon, as well as by the condition of the aggregation of the existing phases. P. Bardenhauer and K. L. Zeyen found that cast iron in which the graphite is coarsest is least attacked by *N*-HCl, *N*-H_2SO_4, and *N*-CH_3COOH, but no definite relations were observed with *N*-HNO_3; on the other hand, O. Kötzschke and E. Piwowarsky observed that within the usual limits of graphite, the physical characteristics of the graphite have no effect on the metal in corroding media. L. Aitchison found that the corrosion by 10 per cent. sulphuric acid is a maximum on steel with about 0·9 per cent. of carbon. E. Heyn and O. Bauer observed that the state of the carbon in steel exerts a very great influence upon the rate of dissolution of the metal, at 14°–18°, in 1 per cent. sulphuric acid. H. Endo repeated the work, and his results are summarized by the curves in Fig. 393. Here the losses in weight are in grams per sq. cm. The results with different periods of time are similar with steels with the 0·5 and 0·9 per cent. carbon. Thus, the rate of dissolution decreases up to about 150°, it then increases very rapidly in two stages

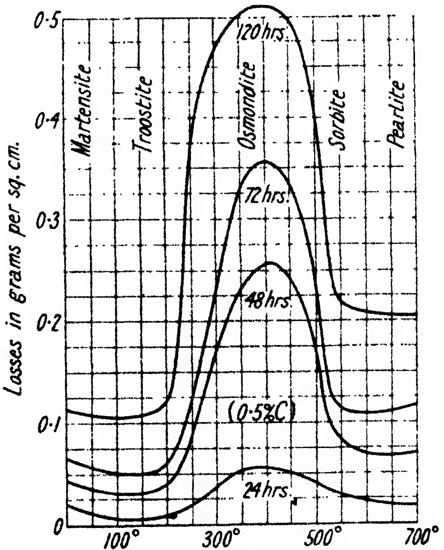


FIG. 394.—The Action of Dilute Sulphuric Acid on Steels Tempered at Different Temperatures.

between 150° and 300°, and between 300° and 400°. After passing the maximum at about 400°, the dissolution decreases rapidly until it becomes nearly constant in the range from 550° to 700°. H. Endo said:

> The decrease of the dissolution up to about 150° is due to the change of the retained austenite into martensite and also to the gradual change of the α-form of martensite to the β-form. From 170°, the carbon dissolving in the martensite begins to set free partly as carbon itself and partly as very fine particles of cementite, the separation taking place most actively at about 250°; hence the rapid increase of the dissolution. The maximum dissolution at about 400° is due to the formation of cementite from the separated carbon and the ground mass of iron, and also to the coagulation of cementite particles to form fine crystals, these changes producing the very fine structure known as osmondite. The decrease of dissolution seen in the range of 400° to 550° may be attributed to the coalescing of the cementite and to the recrystallization of ferrite crystals which result in the reduction of the degree of heterogeneity of the structure, and the further grain-growth of cementite above 550° has no effect on the corrosion.

E. Heyn and O. Bauer's observations were made with a hard steel having 0·95 per cent. of carbon; 0·35, of silicon; 0·17, of manganese; 0·012, of phosphorus; and 0·024, of sulphur. One set of their curves for steels with different proportions of carbon, and tempered at different temp., is shown in Fig. 394. They said:

> The shapes of the curves in Fig. 394 reveal some interesting features. According to the opinions hitherto prevailing, and still held by some, the transition of the martensite of hardened steel into the pearlite of annealed steel is continuous throughout the intermediate stages of tempering. This would lead one to suppose that the curve of solubility in dil. sulphuric acid, instead of showing any sharply defined peaks, would form a line indicating the gradual transition from the solubility of martensite to that of pearlite. The curve, however, runs up to a sharply defined maximum at a temp. of 400°. The simplest and most obvious explanation of this phenomenon is as follows: The transition of the martensite from the unstable phase below 700° into the stable phase of pearlite, due to tempering, does not proceed directly, but indirectly through an intermediate metastable form, to which the name of osmondite has been given. Osmondite is the most soluble of all the forms intermediate between martensite and pearlite. As the tempering temp. gradually increases, the martensite first gradually changes into osmondite, until at 400° the whole mass consists of this alone. In order to prevent confusion in nomenclature, the term troostite has been retained for the designation of the intermediate states between martensite and osmondite, and for the stages intermediate between osmondite and pearlite the term sorbite is used. If the tempering temp. is raised above 400° there again occurs a gradual transition from the readily soluble osmondite to the less easily soluble pearlite. Such transitions from a preliminary condition to a stable final condition, through one or more less stable intermediate conditions, are of not infrequent occurrence in physical and chemical processes. Another remarkable point is the low value for the solubility at a tempering temp. of 100°, which differs little from that of untempered steel. The variation lies, however, within the margin of error for the process, so that whether still another metastable form occurs is not yet proved.

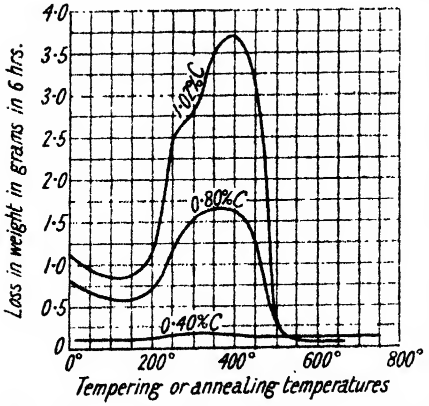


FIG. 395.—The Action of Dilute Sulphuric Acid on Steels Tempered at Different Temperatures.

T. Matsushita and K. Nagasawa's results with 1 per cent. sulphuric acid are shown in Fig. 395. E. Heyn and O. Bauer observed that a definite maximum occurred when the percentage of carbon was only 0·07; with mild steel, there was a minimum on the solubility curve for the quenching temp. 1000° to 1050°, and also two maxima respectively at 850° to 950°, and 1100° to 1250°. The solubility of tempered carbon steel in dil. sulphuric acid rapidly decreases when the tempering temp. lies between 450° and 500°; and from 550° upwards there is no appreciable change of solubility up to the Ac_1-point, indicating that the coagulation of the pearlite is almost complete at 550°. T. Matsushita and K. Nagasawa accordingly classify the temper structures of quenched steel: 100° to 300°—martensite and troostite; 300°—troostite; 300° to 400°—troostite and sorbite; 400°—sorbite (osmondite); 400° to 550°—sorbite and granular pearlite; and 550° to the Ac_1-point—granular pearlite. C. Chappell examined the influence of carbon on the corrodibility of the following steels:

	Carbon	Silicon	Manganese	Sulphur	Phosphorus	Aluminium
No. 1 . .	0·10	0·019	0·091	0·030	0·011	0·02
No. 2 . .	0·24	0·037	0·072	0·028	0·015	—
No. 3 . .	0·30	0·030	0·094	0·021	0·012	—
No. 4 . .	1·55	0·053	0·100	0·020	0·017	0·03
No. 5 . .	0·81	0·048	0·168	0·028	0·016	—
No. 6 . .	0·96	0·018	0·133	0·027	0·014	0·02

The results are indicated in Table LIV. The corrodibility of rolled, normalized, and annealed steels rises to a maximum as the proportion of carbon increases to the sat. point 0·89 per cent. carbon, and it decreases with a higher proportion of carbon. With quenched and tempered steels, there is a continuous increase in corrodibility

TABLE LIV.—THE EFFECT OF CARBON ON THE CORRODIBILITY OF STEEL BY SEA-WATER AT 12°.

Treatment	Steel No.	Carbon per cent.	Loss after 91 days' immersion, per cent.	Loss after 166 days' immersion, per cent.
Annealed at 900° for 20 hrs. and slowly cooled	1	0·10	0·366	0·752
	2	0·24	0·424	0·803
	3	0·30	0·416	0·801
	4	0·55	0·425	0·848
	5	0·81	0·481	0·941
	6	0·96	0·461	0·881
Normalized at 900° and cooled in air . .	1	0·10	0·424	0·786
	2	0·24	0·433	0·812
	3	0·30	0·435	0·827
	4	0·55	0·515	0·974
	5	0·81	0·588	1·088
	6	0·96	0·512	1·042
Rolled . . .	1	0·10	0·399	0·743
	2	0·24	0·385	0·758
	3	0·30	0·375	0·771
	4	0·55	0·478	0·872
	5	0·81	0·508	0·955
	6	0·96	0·456	0·862
Quenched from 800° in water . . .	1	0·10	0·413	0·771
	2	0·24	0·543	0·981
	3	0·30	0·534	0·010
	4	0·55	0·564	1·088
	5	0·81	0·603	1·124
	6	0·96	0·671	1·119
Quenched from 800°; tempered at 400° .	1	0·10	0·337	0·699
	2	0·24	0·384	0·803
	3	0·30	0·477	0·971
	4	0·55	0·560	1·067
	5	0·81	0·568	1·111
	6	0·96	0·591	1·184
Quenched from 800°; tempered at 500° .	1	0·10	0·391	0·754
	2	0·24	0·398	0·757
	3	0·30	0·447	0·806
	4	0·55	0·544	0·903
	5	0·81	0·568	0·930
	6	0·96	0·570	0·956

as the proportion of carbon rises to 0·96 per cent., and no maximum appears. Quenching increases the corrodibility to a maximum; annealing tends to reduce it to a minimum; and normalizing gives intermediate values. In agreement with the results of the action of dil. sulphuric acid, tempering reduces the corrodibility of quenched steels, and the extent of its influence varies with the tempering temp.—*vide supra,* chemical properties, and corrosion of iron. C. Chappell and F. Hodson showed that the corrodibility of steel increases as the percentage of carbon increases; that hardened steels are less liable to corrode than annealed steels. The subject was studied by L. Aitchison, O. Bauer and O. Vogel, C. Chappell, V. Duffek, G. M. Enos, and R. A. Hadfield and J. A. N. Friend. W. Schreck observed that graphite in cast iron increases the rate of dissolution in acids; whilst P. Bardenhauer and K. L. Zeyen, and P. Kötzschke and E. Piwowarsky observed that the mode of graphitic separation and the quantity per cent. area did not affect the corrodibility of cast iron—*vide* local elements. The effect of various alloying elements on the corrodibility of iron was discussed by G. F. Burgess, A. S. Cushman, G. Delbart, V. Duffek, E. Piwowarsky, R. Girard, H. Baumeister, etc.—*vide* the alloys of iron.

M. Rudeloff inquired if rusting affected the mechanical properties of the underlying metal, and found that rusting diminishes the elongation of the metal, and this diminution is relatively the greater the greater the degree of elongation of the metal before rusting. The tensile strength is also diminished, and the degree, as also in the case of the elongation, appears to be proportional to the duration of the rusting. The degree to which the wires could be bent and twisted was most seriously affected by rusting at the commencement. After seven months' exposure to rusting this seemed to have almost entirely ceased to have any influence on these last-mentioned properties. Rusting also rendered the wires distinctly brittle, while the reduction of area had been diminished by as much as 10 per cent. in the worst portion.

The effect of mechanical treatment on the corrosion of iron and steel has been examined by T. Andrews[34] who concluded that the effect of stresses of various kinds—tension, torsion, and flexion—on the corrosion of various kinds of iron and steel is to make the unstrained metal electropositive to the strained metal, so that the unstrained metal was less liable to corrosion than the strained metal. W. H. Walker and C. Dill, and C. Chappell and F. Hodson, came to the same conclusion, but the very opposite conclusion was drawn by C. Hambuechen, T. H. Turner and J. D. Jevons, B. Garre, J. H. Whiteley and A. F. Hallimond, R. A. Hadfield, C. H. Desch, C. F. Burgess, and H. Endo—*vide supra.* G. D. Bengough and co-workers considered that the effect of internal strains is of minor importance in the corrosion of metals in distilled and industrial waters. G. P. Fuller said that the high resistance of electrolytic iron to chemical corrosion is further increased by cold-work. P. Breuil found that the corrosion of cast copper steels is less than with rolled steels, and he attributed the phenomenon to the greater fineness of the rolled steel. Observations were also made by M. F. Cloup, and A. Portevin. According to T. W. Richards and G. E. Behr, if a difference of potential does exist between the strained and unstrained portions of a rod, the effect must be extremely small. J. A. N. Friend said that strained portions of a metal may sometimes act as anode, and at other times as cathode—*vide supra.*

The distribution of corrosion in a manner dependent on the stresses is often ascribed to the change of potential produced by the stress. Thus, W. Spring, and W. H. Walker and C. Dill have shown that an e.m.f. can be produced from a cell of the type: Cold-worked metal | Salt soln. | Annealed metal, and the cold-worked metal is usually the anode or attackable pole. Similarly, an unequally annealed piece may behave in this respect as if it were composed of two different metals. U. R. Evans, indeed, showed that corrosion may follow the highly deformed parts where capillary channels are also laid open—*vide supra.* C. Barus concluded that in rupturing a piece of iron, "as much as one-half of the work done in stretching up to the limit of rupture, may be stored up permanently" in the strained iron.

This energy will be released when the metal is oxidized, and hence, other things being equal, the strained metal will be attacked more readily, the potential of the strained metal increasing with the strain. C. F. Burgess, C. Hambuechen, E. Heyn and O. Bauer, and J. A. N. Friend found this to be the case in acidic media, and the results, summarized in Fig. 396, show that the rate of corrosion in 0·1 per cent. sulphuric acid is roughly proportional to the elongation of the steels with up to 1·35 per cent. of carbon. Incidentally, the steel with the eutectic proportion of carbon was the most readily dissolved. J. A. N. Friend also exposed the same steels in neutral water– *e.g.* in tap-water, artificial sea-water, and with alternate wet and dry exposures– and observed no appreciable difference in the results with the strained and unstrained metals, although some alloy steels showed a difference. G. Tammann observed generally that, other things being equal, metals are less noble after cold-working, that is, they are more readily attacked after being hardened by strain than when in the soft state. If the reverse results are obtained, other disturbing factors may be involved– grain-size, etc.

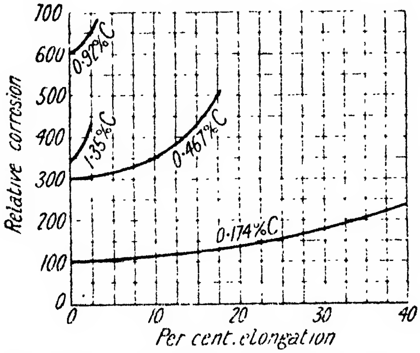


FIG. 396.—The Effect of Strain on the Corrosion of Steel by Dilute Sulphuric Acid.

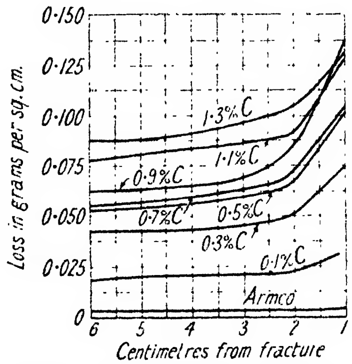


FIG. 397.—The Effect of Tensile Strains on the Corrosion of Iron.

H. Endo found the losses in weight, in grams per sq. cm., during 72 hrs.' action in 1 per cent. sulphuric acid, at 25°, of portions of broken test-bars cut in 1, 2, . . . 6 centimetre-portions from the tensile fracture. The maximum **tensile stress**— kgrms. per sq. cm.– of the carbon alloys, and of Armco iron—free from carbon—were:

Carbon .	0	0·1	0·3	0·5	0·7	0·9	1·1	1·3 per cent.
Stress .	3260	3600	5140	5560	7360	8600	7970	7660

The results showing the effect of tensile strains are plotted in Fig. 397. The amount of corrosion runs parallel with the amount of deformation so that where the stress is greatest, the greatest corrosion occurs, and this with a steel containing 0·9 per cent. of carbon steel. The effect of carbon is shown more clearly in Fig. 398, where the tension refers to the portion nearest the seat of fracture. The results with **torsional strain** are similar, the loss in weight, in 72 hrs. in 1 per cent. sulphuric acid at 25°, increases with the amount of torsion. The maximum loss also occurred with the 0·9 per cent. carbon steel. The effect of carbon is more clearly shown in Fig. 398 where the torsion was obtained by twisting the test-piece through 720°. The most severe attack by the acid occurs where the twist is greatest. In agreement with this, B. Garre observed that the rate of dissolution of iron in dil. sulphuric acid increases linearly with the number of twists to which the metal has been subjected. Twisted rods become softer after being immersed in 1 per cent. sulphuric acid. The annealing of a piece of bent iron decreases its rate of dissolution in acid, but not so much as to make it dissolve at the same rate as the unbent metal.

H. Endo also examined the effect of **compression strains,** and found that the losses, expressed in grams per sq. mm. during 72 hrs.' action of 1 per cent. sulphuric acid at 25°, here increase with the load, but the maximum effect was not obtained with the steel containing 0·9 per cent. of carbon. With **impact strain,** the effect of a number of repeated impacts small enough to cause no permanent deformation is inappreciable.

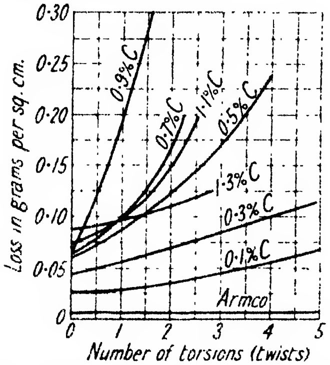


FIG. 398.—The Effect of Torsional Strains on the Corrosion of Iron.

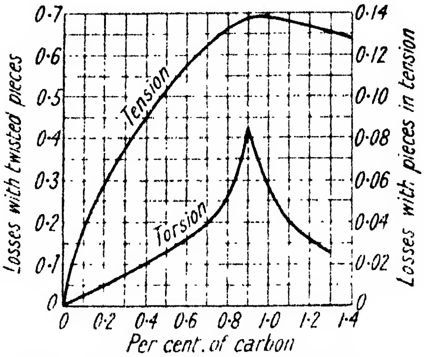


FIG. 399.—The Effect of Carbon on the Corrosion of Steel under Tensile and Torsional Strains.

J. H. Whiteley and A. F. Hallimond found that the products of the reaction of normal and cold-worked iron on nitric acid, with 33·5 grms. of HNO_3 per 100 c.c. at 100°, are very different. Thus, using 0·3 grm. of iron :

		NO	N_2O	N_2	NH_3
Hammering	Normal . . .	96·0	1·0	3·0	1·2 c.c.
	Cold-worked . .	50·0	2·0	5·0	16·7 ,,
Drilling	Normal . . .	75·0	2·0	6·0	5·5 ,,
	Cold-worked . .	55·0	4·0	4·6	13·0 ,,
Wire-drawn	Normal . . .	66·0	3·5	7·0	7·5 ,,
	Cold-worked . .	46·0	2·0	7·0	15·4 ,,

By plotting as ordinate the weight of iron consumed in forming the nitrogen and ammonia in accord with $10Fe+36HNO_3=10Fe(NO_3)_3+3N_2+18H_2O$, and $8Fe+27HNO_3=8Fe(NO_3)_3+3NH_3+9H_2O$, and as abscissæ, the conc. of the acid in grams per 100 c.c., a curve characteristic of the reaction is obtained and it can be termed the *reaction curve.* Wire deformed by twisting or drawing yields progressively advancing reaction curves. The measured differences in the composition of the gases are produced by an amount of energy which, if developed as heat, would not raise the temp. of the material by 1°. The results for twisted and drawn wires are taken to show that cold-working takes place in two stages : (i) the elastically strained crystal units are brought into an interlocked condition ; and (ii) the crystal structure is progressively broken up with the production of the

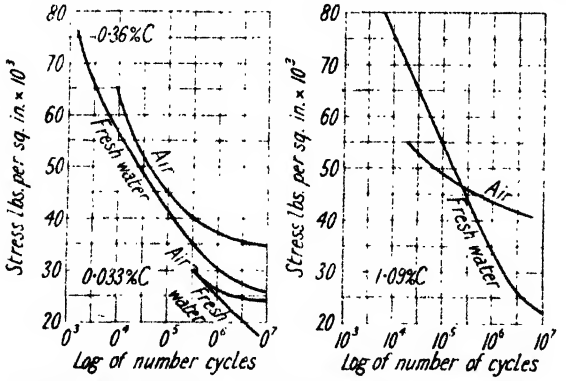


FIG. 400.—The Fatigue and Corrosion-Fatigue Tests of Iron-Carbon Alloys.

so-called amorphous material. The effect of cold-work is removed by annealing at 520°. The energy differences due to differences in grain-size produce no appreciable difference in the reaction curves with nitric acid. J. H. Whiteley and A. F. Hallimond also examined some carbon steels and found similar results. They also inferred that the ferrite component of pearlite is in a partly strained condition.

Observations on the simultaneous effects of stress and corrosion were made by H. Baucke, H. J. Gough and D. G. Sopwith, N. P. Inglis and G. F. Lake, E. Jonson, W. P. Jorissen, A. P. Hague, G. D. Lehmann, and R. R. Moore. D. J. McAdam observed that when metals are simultaneously subjected to corrosion and fatigue, failure may occur at stresses far below the endurance limit—fatigue test—and the effect was designated **corrosion fatigue.** Severe corrosion prior to fatigue, lowers the fatigue resistance much less than a slight corrosion simultaneously with fatigue. The damaging effect of corrosion is greater, the harder the steel. The following represent some of the results of the static and endurance tests obtained when the corrosion was due to a fresh, carbonate water; and with metal ranging from ingot iron with 0·033 per cent. of carbon through 0·11 to 1·09 per cent. carbon steels:

Carbon . .	0·033	0·11	0·24	0·36	0·49	1·09 per cent.
Tensile strength .	43,900	46,400	59,200	79,200	82,900	103,400 lbs. per sq. in.
Elongation . .	45·5	47·5	37·8	31·3	27·8	29·5 per cent. in 2 ins.
Reduction area .	75·0	72·0	59·0	48·7	43·7	50·8 per cent.
Endurance limit .	24,000	25,000	27,000	34,000	34,000	42,000 lbs. per sq. in.
Corrosion fatigue .	20,000	16,000	16,000	25,000	23,000	23,000 ,, ,,

The fatigue tests were conducted with 1450 revs. per minute. The abscissæ of Fig. 400 represent the logarithm of the number of revolutions, and the ordinates, the stresses. H. W. Gillet, B. P. Haigh, A. P. Hague, G. D. Lehmann, A. M. Binnie, F. N. Speller and co-workers, N. P. Inglis and G. F. Lake, and T. S. Fuller also studied corrosion fatigue; and A. M. Binnie, the effect of oxygen on the corrosion fatigue.

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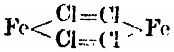
§ 25. The Valency and Atomic Weight of Iron.

According to H. E. Roscoe and A. Harden,[1] J. Dalton's note-books show that, in 1804, he gave 16 (oxygen 7) for the at. wt. of iron; in 1806, he gave 40; in 1807, 50. About this period, on the assumption that the ferric alums are isomorphous with those of aluminium, so that the isomorphism rule is applicable, the atomic weight of iron calculated from the ratio $2Fe : Fe_2O_3$, by J. J. Berzelius (1811) was 54·27; by J. L. Gay Lussac, 56·6; by J. Davy, 55·96; by G. Magnus, 54·25; by W. H. Wollaston, 55·2; and by F. Stromeyer, 55·6. The assumption that the at. wt. of iron is in the vicinity of 56, and not a multiple or submultiple of this number, is in accord with the sp. ht. rule, the isomorphism rule, and the periodic law. The position of iron and the elements of the same family group in the periodic table has been discussed by D. Balareff, E. H. Büchner, G. Oddo, H. Teudt, E. Thilo, and R. Vogel.

Iron is usually either bivalent or tervalent, and A. Laurent and C. Gerhardt distinguished the two forms by using the terms *ferrosum* (Fe=28) and *ferricum* (fe=⅔ of 28) for the eq. of iron in the ferrous and ferric salts respectively, so that the corresponding sulphates were represented $(Fe_2)SO_4$ and $(fe_2)SO_4$, respectively. This was discussed by A. Scheurer-Kestner, A. Wurtz, and M. d'A. Albuquerque.

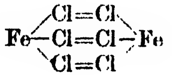
The *bivalency* of iron is not so well established by the vapour density of ferrous chloride, since below 1300° the data agree with the assumption that there is a balanced reaction: $Fe_2Cl_4 \rightleftharpoons 2FeCl_2$; but mol. wt. determinations in bismuth trichloride and in pyridine, according to A. Werner, indicate that the molecule is $FeCl_2$, so that the associated molecules, Fe_2Cl_4, are probably constituted:



$$\mathrm{Fe}{<}\begin{matrix}\mathrm{Cl}=\mathrm{Cl}\\ \mathrm{Cl}=\mathrm{Cl}\end{matrix}{>}\mathrm{Fe}$$

The metal might be octovalent in the tetracarbonyl, $Fe(CO)_4$, and decavalent in the pentacarbonyl, $Fe(CO)_5$, but it is more probable that the iron is here bivalent, and that the bivalent carbonyl radicles are arranged in closed chains—**5**, 39, 27. The bivalency of the iron in ferrous sulphate is confirmed by its isomorphism with the corresponding salts of copper, magnesium, and zinc. The ferrous salts are readily oxidized to ferric salts, where the iron is tervalent. M. Traube assumed that the atom of iron is bivalent. The *tervalency* of the iron in the ferric salts is indicated by the vapour density of ferric chloride which was found by V. Meyer to agree with $FeCl_3$ at temp. between 750° and 1077°; below these temp., the formula was found by H. St. C. Deville and L. Troost to agree with the formula Fe_2Cl_6, so that there is a region where balanced reactions: $Fe_2Cl_6 \rightleftharpoons 2FeCl_3$ obtain. According to P. T. Muller, ferric chloride is unimolecular, $FeCl_3$, in pyridine, alcoholic, or ethereal soln. G. Urbain and A. Debierne found that a soln. of ferric acetylacetonate in benzene has a mol. wt. in agreement with $Fe(C_5H_7O_2)_3$. The tervalency of iron is also confirmed by its replacing aluminium in the alums. Ferrosic oxide is regarded as a ferrous ferrite, $Fe(FeO_2)_2$, where Fe_2O_3 is regarded as an acidic anhydride. W. Küster suggested that the iron in hæmaglobin is bivalent, but W. Manchot said that a tervalent iron atom better explains the facts. The ferrates, M_2FeO_4, are usually taken to illustrate the *sexivalency* of iron, and they are regarded by J. Beckenkamp, G. Grube and H. Gmelin, F. Haber, and W. Pick as salts of the unknown acid anhydride, ferric trioxide, FeO_3. M. Traube also said that there is a doubled atom, or a sexivalent radicle. The compounds FeO_2 and Fe_2O_5 have been discussed by W. Manchot and O. Wilhelms, and L. Moeser and B. Borck—*vide infra.* D. K. Goralewitsch supposed that in the perferrates, M_2FeO_5, the iron atom is *octovalent.* W. C. Bray and M. N. Gorin discussed the possibility of the existence of a *quadrivalent* form of iron.

W. Manchot and co-workers assumed that the iron in Roussin's red and black salts—**8.** 49, 35—is present in a *univalent* state; the same hypothesis had been previously suggested by I. Bellucci and P. de Cesaris. On the other hand, L. Cambi and co-workers, and H. Reihlen and co-workers maintain that the iron atom is here not univalent, but that these salts can be regarded as hyponitrites of tervalent iron. E. Drechsel, S. H. Emmens, and W. G. Brown have tried to make iron *quadrivalent* in ferrosic oxide, and indeed in the other oxides; and W. C. Bray and M. H. Gorin explained some reactions—*e.g.* the oxidation of ferrous salts by hydrogen dioxide, and the reduction of ferric salts by stannous chloride—on the assumption that quadrivalent iron is formed as an intermediate compound. The work of L. Wöhler and co-workers on the equilibrium relations of the oxides with hydrogen is in agreement with the bi- and ter-valency of iron in these oxides. The vapour density of ferric chloride under certain conditions appears to support the quadrivalent hypothesis for the doubled molecule $Cl_3Fe–FeCl_3$; but the doubling of the molecule is attributed by R. F. Weinland and co-workers, and P. Pfeiffer to the effect of the auxiliary valences of the halides:



According to A. Werner, the **co-ordination number** of iron is 6, as in the complex salts $M_3[FeCl_6]$, $M_3[FeCy_6]$, etc., but F. W. Hinrichsen and E. Sachsel added that this hypothesis does not explain the existence of salts of the type $FeCl_3.3CsCl.H_2O$. G. F. Hüttig is in favour of A. Werner's assumption; and H. Lessheim and co-workers added that in Fe^{II}-compounds the co-ordination number is 4 or 6; in Fe^{III}-compounds, 6; and in the Fe^{VI}-compounds, 4. F. Ephraim and E. Rosenberg, and P. Pfeiffer added that in some compounds, $[Fe^{VI}(NH_3)_8][O.CO.C_6H_5]_2$, the co-ordination number is 8; R. F. Weinland and co-workers, and P. Pfeiffer consider that in some complex salts—*e.g.* $M[Fe^{III}(H_2O)_{12}(SO_4)_2]$, and $[Fe^{II}(H_2O)_{12}]$-$[Bi_2Cl_7]_2$- the co-ordination number is 12. F. Hölzl, and P. Pfeiffer studied this subject.

H. Weden discussed the complex salts of iron with various organic compounds. P. Ray investigated the conditions of stability of the co-ordination compounds. E. Hartley, and W. Thomas obtained an optically active *potassium ferric oxalate*, $K_3[Fe(C_2O_4)_3].3H_2O$, etc.; and F. Blau, and A. Werner, optically active complexes of ferrous bromide, iodide and tartrate with *tri-α-dipyridyl ferrous bromide, iodide, and tartrate, e.g.* $[Fe(Dipyr)_3]Br_2.6H_2O$, etc. The subject was discussed by T. M. Lowry.

E. Donath and J. Mayrhofer studied the relation between the affinity and density of the elements; T. Bayley, the **affinity** of the elements Cu, Fe, Co, Ni for oxygen as shown by the colour of the compounds; F. Ephraim, W. Biltz, and A. Werner, the relation between the affinity and the temp. of decomposition of the ammines from which it is inferred that the affinity of ammonia for the central atom is in the order $Ni>Co>Fe>Mn>Cu>Cd>Zn>Mg$; and H. Moissan, and M. Berthelot, the relation between the affinity and heat of formation from which it is inferred that the order is Cr, Mn, Fe, Co, Ni.

A review of the early observations on the at. wt. of iron was made by A. C. Oudemans. T. Thomson made a study of the subject in 1821. In addition to the analyses indicated above, based on determinations of the composition of ferric oxide, some later observations were made on the oxidation of iron, $2Fe : Fe_2O_3$; thus, J. J. Berzelius (1844) obtained 56·05; L. F. Svanberg and E. C. Norlin, 55·83; and E. J. Maumené, 56·00; while other observations were based on the reduction of ferric oxide in hydrogen to give the ratio $Fe_2O_3 : 2Fe$. Thus, H. W. F. Wackenroder obtained 55·97; L. F. Svanberg and E. C. Norlin, 56·09; O. L. Erdmann and R. F. Marchand, 56·03; and L. E. Rivot, 54·25. J. Torrey obtained 55·777 for the at. wt. calculated from the eq. of iron obtained by measuring the volume of hydrogen evolved when the metal is dissolved in an acid. J. B. A. Dumas analyzed ferrous and ferric chlorides, and obtained from the ratio $FeCl_2 : 2Ag$, 56·09; and from the ratio $FeCl_3 : 3Ag$, 56·23. C. Winkler also titrated a soln. of iodine in potassium iodide before and after iron had been dissolved therein. The value of the ratio $I_2 : Fe$ so obtained corresponds with the at. wt., 56·21. O. Hönigschmid and co-workers obtained from the ratio $FeCl_3 : 3Ag$, 55·852, and from the ratio $FeCl_3 : 3AgCl$, 55·854.

The reduction of ferric oxide by hydrogen was examined by T. W. Richards and G. P. Baxter, and found to be affected by several errors which, when eliminated, gave for the ratio $Fe_2O_3 : 2Fe$, an at. wt., 55·887; while G. P. Baxter and C. R. Hoover's observations with the same reaction gave 55·847. The results were discussed by R. Ruer and J. Kuschmann. There is a doubt as to the stability of the ferric oxide between 1050° and 1100°, since 5 grms., previously heated to constant weight in oxygen, lost 0·2 mgrm. when ignited in air. They assumed that the higher weight was due to adsorbed oxygen, whereas the observations of R. B. Sosman and J. C. Hostetter showed that the higher value was more probably correct since the lower value is due to a slight dissociation of ferric oxide into ferrosic oxide and oxygen. This reduces the value 55·847 to 55·840. G. P. Baxter calculated from the ratio $FeBr_2 : 2AgBr$, 55·833; and from the ratio $FeBr_2 : 2Ag$, 55·842. The early calculations give higher values because a different value was taken for the at. wt. of silver. G. P. Baxter, T. Thorvaldson and V. Cobb obtained for $FeBr_2 : 2Ag$, 55·838; and for $FeBr_2 : 2AgBr$, 55·838 using terrestrial iron; and with meteoritic iron, G. P. Baxter and T. Thorvaldson obtained respectively 55·837 and 55·836 by rejecting two results of doubtful value. A. Bilecki discussed the at. wt. of iron. F. W. Clarke calculated for the best representative value for the at. wt. of iron, 55·880; while the International Table for 1931 gave 55·84. G. D. Hindrichs, and M. Gerber discussed some relations of the at. wts.

The **atomic number** of iron is 26. F. Sanford [2] discussed the relation between the at. number, at. charge, and the physical and chemical properties of the element; A. F. Scott, the relation between the at. number and the properties of the ions in the crystal lattice; P. Vinasse, the molecular numbers; and J. D. de Barros, the nuclear numbers. F. W. Aston observed **isotopes** corresponding with at. wts. 56 and 54, the ratio of the two being approximately as 20 : 1 when estimated from the intensities of the lines. The subject was also discussed by W. D. Harkins, and F. H. Lorong. The **atomic disruption** of the atom by bombardment with the α-particles was observed by G. Kirsch, H. Petterson and G. Kirsch, R. Holoubek, G. Stetter, W. Bothe and H. Fränz, A. Wegerich, J. D. Cockcroft and E. T. S. Walton, and H. Pose; but not by E. Rutherford and J. Chadwick, or C. Pawlowsky. R. A. Millikan and G. H. Cameron discussed the possible synthesis of iron by the action of cosmic rays. The **electronic structure,** according to N. Bohr, is (2) for the K-shell; (2, 2, 4) for the L-shell; (2, 2, 4, 3, 3) for the M-shell; (2) for the N-shell; and W. Gerlach suggested that of the 26 electrons there are 2 in the N-shell; 14 in the M-shell; 8 in the L-shell, and 2 in the K-shell. The subject was discussed by N. Akuloff, H. S. Allen, A. E. van Arkel and J. H. de Boer, S. J. Barnett, M. de Broglie, B. Cabrera, A. H. Compton and O. Rognley, K. T. Compton and E. A. Trousdale, P. D. Foote, W. Gerlach, E. H. Hall, W. D. Harkins, A. W. Hull, L. C. Jackson, M. Kimura, H. Lessheim and co-workers, G. A. Lindsay and H. R. Voorhees, J. C. McLennan and co-workers, R. A. Millikan and G. H. Cameron, J. W. Nicholson, C. D. Niven, H. Perlitz, H. Eyring and A. Sherman, G. I. Pokrowsky, P. Ray, W. H. Rothery, R. Samuel and E. Markowicz, H. Shoji, J. D. M. Smith, J. C. Stearns, E. C. Stoner, R. Swinne, F. Wächter, P. Weiss, L. A. Welo, T. D. Yenson, and L. Zehnder. A. T. Williams discussed the relation between the valency and spectral multiplets; P. Vinasse, the relation between the electron arrangements and the fusibility; R. Swinne, the ferromagnetism; D. Jones, the allotropic transformations; J. Beckenkamp, the variable valency; and G. I. Pokrowsky, the synthesis of iron.

J. N. Lockyer, and J. Parry inferred that the evolution of hydrogen from iron when it is heated in vacuo indicates that iron is not an element, but a compound of hydrogen which dissociates under these conditions. The inference is ill-founded.

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§ 26. The Passivity of Iron.

> Ferrum peculiarem monstrat indolem. Lamina polita hujus metalli, mallas egregie obedientis, argenti solutioni immersa per plures hebdomadas nullo visibili modo mutabatur.
>
> T. BERGMAN.

Towards the end of the eighteenth century, T. Bergman,[1] in his essay, *De diversa phlogisti quantitate in metallis*, observed that when a piece of iron is immersed in a soln. of silver in nitric acid, no visible change occurs although the affinity of iron for the acids in general is known to be much stronger than that of silver. Even with regard to nitric acid, other experiments evince the superior affinity of iron, for, as iron precipitates copper from this acid, and copper precipitates silver, we must infer the greater affinity of iron than of silver. In some cases, however, instances of precipitation occurred, which he attributed to the peculiar quality of the varieties of iron which he then employed. Observations similar to those by T. Bergman were made by R. Kirwan in connection with the precipitation of lead by iron; and it is not at all improbable that C. F. Wentzel noticed the peculiar behaviour of iron during his investigation of the neutralization of acids by the metals. In 1790, J. Keir said :

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> I digested a piece of fine silver in pure and pale nitrous [nitric] acid, and while the dissolution was going on and before the saturation was completed I poured a portion of the solution upon pieces of clean and newly scraped iron wire into a wine-glass and observed a sudden and copious precipitation of silver. The precipitate was at first black, then it assumed the appearance of silver, and was five to six times larger in diameter than the piece of iron wire which it enveloped. The action of the acid on the iron continued some little time and then it ceased, the silver redissolved, the liquor became clear, and the iron remained bright and undisturbed in the solution at the bottom of the wine-glass, where it continued during several weeks without suffering any change or effecting any precipitation of the silver.

The liquid had not lost its power of acting on fresh iron, although it had ceased to act on the piece already exposed to it, so that the change was in the iron, and not in the liquid. Once the iron has acquired the state where it no longer precipitates silver, it will not precipitate that metal from other soln. of silver nitrate. The iron is altered in some way " without the least diminution of its metallic splendour, or change of colour. The alteration, however, is only superficial, as may be supposed, for, by scraping off its altered coat, it is again rendered capable of acting on a soln. of silver." The inactive iron was called *altered iron*, and ordinary iron, *fresh iron.* C. F. Schönbein's term **passive iron** has been generally adopted for the inactive iron. J. Keir continued : When the altered iron in a soln. of silver nitrate is touched with a piece of fresh iron, it instantly becomes active ; but in a little while the silver precipitated on both pieces redissolves leaving both pieces of iron in the passive state. The inactive or passive iron does not precipitate copper from a soln. of copper nitrate or sulphate. The iron can be converted into the passive state by being treated with conc. and red fuming nitric acid. The passive iron gradually loses its peculiar property when dried, or when kept in water, but it can be preserved in the passive state by being kept in aqua ammonia. W. Beetz found that the direction of the current in the partitioned cell with copper and dil. sulphuric acid against nitric acid and iron is dependent on whether the iron is active or passive. E. Liebreich said that, unlike active iron, the reaction $Fe \rightarrow Fe^{\cdot\cdot} + 2\ominus$ does not occur, or else it is *nur unmerklich.* E. Becker and H. Hilberg said that the appearance of oxygen at the anode of an electrolytic cell indicates that the iron is entering into the passive state, and the rate of evolution of oxygen indicates whether the metal is wholly or partially passive when measured in terms of Faraday's law. M. le Blanc, indeed, considers iron to be in the passive state when it exhibits chemical polarization in a cell even when the anode liquor contains chlorides, etc., in place of oxidizing agents. F. Tödt said that passive iron gives no current when it is associated in a cell with one of the noble metals ; and R. Kremann and R. Müller considered iron becomes passive when it does not react chemically under conditions where, from its behaviour in the active state, the existence of a driving force for the reaction would be assumed.

J. B. Senderens stated that iron is to be regarded as passive when it remains unattacked in dil. nitric acid, but there are degrees of passivity short of complete inertness. Consequently, for the purposes of a definition, some writers have postulated arbitrary conditions. C. F. Schönbein considered that iron is passive when it is not visibly attacked by acid of sp. gr. 1·35, and no bubbles of gas escape at room temp. An acid of this concentration will itself induce passivity, and accordingly, H. L. Heathcote recommended the use of nitric acid of sp. gr. 1·2, between 15° and 17°, as a test for passivity. An acid of this concentration shows no tendency to passivate iron, and it activates passive iron but very slowly—about 24 hrs. A rod of iron is supposed to be passive when, after immersion in the acid of sp. gr. 1·2, shaking, and then holding motionless, it shows no sign of chemical action on its surface. W. A. Hollis said that iron is passive if it can be placed in fuming nitric acid for 10 seconds, at room temp., without visible attack. W. R. Dunstan and co-workers found that active iron at once begins to deposit copper from a 0·5 per cent. soln. of copper sulphate, but passive iron will remain for hours bright and unaffected. Also, active iron usually shows signs of corrosion in distilled water in 8 to 10 mins., whereas passive iron will remain bright for hours.

F. Flade recommended the electrical potential test of passivating caused by anodic polarization, since passive iron has a lower potential than active iron.

F. Förster distinguished between what he called *chemical and mechanical passivity* according as the reaction is retarded by the inactivity of the metal, or retarded by a protective film on the metal. W. Kistiakowsky said that the iron is *superactive* when it is polarized in alkaline soln. and behaves like platinum charged with hydrogen, $H_2 \rightarrow 2H^{\cdot} + 2\theta$, and the electrode potential is $E_n = -0{\cdot}9$ to $-0{\cdot}5$ volt; *active*, when the surface of the metal is clean, $F_\epsilon \rightarrow Fe^{\cdot\cdot} + 2\ominus$, and $E_n = -0{\cdot}5$ to $-0{\cdot}4$ volt; *subactive*, when there is a film with large pores on the metal, there are local currents, and $E_n = -0{\cdot}4$ to $-0{\cdot}2$ volt; *subpassive*, when there is a film with fine pores on the metal, there are local currents, and $E_n = -0{\cdot}2$ to $+0{\cdot}2$ volt; and passive when the film on the metal is continuous, and $E_n = +0{\cdot}2$ to $+0{\cdot}9$ volt.

The inertness of iron in conc. nitric acid had been noted before J. Keir's observations in 1790, by C. F. Wenzel in 1782, by T. Bergman in 1783, and by R. Kirwan in 1787, yet J. Keir can be regarded as the discoverer of the passivity of iron. The phenomenon, however, must have been waiting for the appropriate "why?" from the time the behaviour of iron in dil. and conc. nitric acids was compared.

H. L. Heathcote observed that the inertness of passive iron is true only so far as the sense of sight is concerned; passive iron is not wholly inactive, but it is the seat of a multitude of changes. E. L. Nichols and W. S. Franklin also showed that the passive metal is not absolutely insoluble in the acid, but the rate of dissolution is extremely slow. If an iron rod be allowed to stand for a considerable time in fuming nitric acid, green crystals of iron nitrate are formed, and, according to H. Gautier and G. Charpy, traces of ammonia and nitrogen peroxide are simultaneously evolved—*vide supra*, the action of nitric acid on iron. C. E. W. Belck, H. Gautier and G. Charpy, H. L. Heathcote, A. J. Maass, E. L. Nichols and W. S. Franklin, E. Ramann, A. Renard, A. Scheurer-Kestner, and L. Varenne also observed that some passivated iron dissolves in the acid. H. Gautier and G. Charpy found that for samples of iron with a given sectional area, the percentage amounts dissolved per 24 hrs. after 2 and 10 days' exposure to nitric acid were:

Sp. gr. of nitric acid		1·28	1·34	1·38	1·48	1·58	
Loss	in 2 days	0·82	0·75	0·29	0·34	5·80	per cent.
	in 10 days	0·59	0·45	0·25	0·33	5·75	,,

Z. C. Mutaftschieff observed with reduced iron after

Time		10	120	300	600	900	1443 mins.
Loss in acid	sp. gr. 1·39	0·00005	0·0015	0·0035	0·0065	0·0090	0·0196
	sp. gr. 1·42	0·00000	0·0014	0·0035	0·0050	0·0093	0·0160

G. Wetzlar first studied the electrochemical properties of passive iron, and said that iron in the passive state occupies a different position in the electrochemical series from what it does in the natural state, and he recognized different degrees of passivity between the active and the inert metal. G. T. Fechner gave for fuming nitric acid the electrochemical series +Pt, An, Fe, Ag, Cu, Bi, Sb—; and for dil. nitric acid, A. de la Rive gave +Ag, Cu, Fe (passive), Fe, Pb, Hg, Sn, Zn—, and with conc. nitric acid, +Fe (passive), Ag, Hg, Pb, Cu, Fe, Zn, Sn—. The electrochemical relations of passive iron to platinum were also discussed by H. Buff, J. F. Daniell, M. Faraday, F. Sanford, and C. F. Schönbein—*vide infra*.

The passivity of iron has been discussed by **E. Baars** and co-workers, **E. Becker** and **H. Hilberg**, **C. Benedicks** and **P. Sederholm**, **G. D. Bengough** and **O. F. Hudson**, **M. Bickermann**, **M. Le Blanc**, **K. Bornemann**, **L. Brunet**, **H. Eggert**, **F. Eisenkolb**, **U. R. Evans**, **F. Flade**, **F. Flade** and **H. Koch**, **F. Förster**, **F. Förster** and **A. Piquet**, **A. Fourgeaud**, **W. Frese**, **H. Freundlich** and co-workers, **A. Günther-Schulze**, **J. A. N. Friend**, **T. Fujihara**, **H. Gerding** and **A. Karssen**, **J. Gillis**, **G. Grube** and co-workers, **F. Haber** and co-workers, **W. A. Hollis**, **W. Hughes**, **N. A. Izgarischeff**, **W. Kistiakowsky**, **V. Kohlschütter** and **H. Schacht**, **P. Krassa**, **B. Lambert**, **S. C. Langdon**, **A. Löb**, **W. Manchot**, **L. McCulloch**, **M. Martens**, **F. J. Micheli**, **E. Müller** and **F. Spitzer**, **H. W. Moseley**, **W. J. Müller**, **G. Patscheke**, **R. Phillips**, **D. Reichinstein**, **E. K. Rideal**, **H. Rohmann**, **W. Rollmann**,

W. Rothmund, A. S. Russell, G. C. Schmidt, E. P. Schoch, G. Senter, S. E. Sheppard, R. Swinne, G. Tammann, T. G. Thompson, F. Tödt, W. H. J. Vernon, E. Yamazaki, etc.

When an iron rod is immersed in nitric acid of sp. gr. 1·35, the metal is vigorously attacked for a few seconds; the rate of evolution of gas then slackens; and finally, to all appearances, ceases. The passivation of iron by conc. nitric acid was observed by W. Beetz, H. Braconnot, H. Buff, H. L. Heathcote, J. F. W. Herschel, J. Keir, R. Kirwan, A. Mousson, E. Ramann, C. F. Schönbein, and L. Varenne; and by fuming nitric acid, by G. T. Fechner, J. Keir, G. S. Ohm, J. M. Ordway, and L. Varenne. According to T. Andrews, the more concentrated the acid, the shorter the period of activity, so that in fuming nitric acid there is virtually no evolution of gas, and the iron does not appear to be attacked any more. G. T. Fechner, and A. de la Rive observed that the passivation is dependent on the concentration of the acid; and, as shown by A. Renard, it is favoured by lowering the temp. Thus, J. F. W. Herschel found that no passivation occurs with boiling acid of sp. gr. 1·399; M. Martens observed no passivation at ordinary temp. with an acid of sp. gr. 1·34; and N. A. E. Millon, that nitric acid with 4 or 4·5 mols. of water passivates the metal at ordinary temp., but not when warmed; H. M. Noad showed that a rod which has been made passive in conc. acid remains passive when transferred to dil. acid of sp. gr. 1·204, although dil. acid gradually destroys the passive state and the metal then dissolves freely in the acid. H. L. Heathcote, and U. R. Evans found that at room temp., the metal is passive in an acid of sp. gr. 1·40, and active in acid of sp. gr. 1·20; S. W. Young and E. M. Hogg found that at room temp. iron can be passivated by an acid of sp. gr. 1·250 or upward but not so at 0°. H. Gautier and G. Charpy observed that the metal is active at 15° in an acid of sp. gr. 1·21, and at 60° in an acid of sp. gr. 1·38; and J. M. Ordway observed that the passive state, *P*, and the active state occur at different temp. with acids of different sp. gr., thus:

1·38		1·42		1·42 (fuming)	
31°	32°	55°	56°	82°	83°
P	*A*	*P*	*A*	*P*	*A*

According to L. Varenne, if the acid has less than 47 per cent. HNO_3, the passive state is not inaugurated. However, even in an acid of that concentration, passivity is induced if the rod be lifted out of the acid and re-immersed; or if the rod be dropped with a shock to the bottom of the containing vessel; or touched with a piece of platinum or gold wire, or a carbon rod; or made the anode of an electric circuit. The curve, Fig. 401, is based on the measurements of S. W. Young and E. M. Hogg; it shows the rate of dissolution of iron in nitric acid of different concentrations when the surface area, the time, and the metal are constant. The decrease in the rate of dissolution in nitric acid of different concentrations takes place in three stages represented in the diagram, Fig. 401, (i) by the curve *AB*, where the speed of the reaction decreases rapidly as the concentration of the acid diminishes; (ii) by the curve *BC*, where the speed of the reaction falls abruptly to a very small value; and (iii) by the curve *CD*, where there is a very slow decrease in the speed of the reaction in the passivating acids. There is thus a fairly definite concentration of acid below which the speed of the reaction increases rapidly, this region is called the *passive break*. The passive break, *BC*, at 0° occurs in an acid containing between 49·78 and 52·09 grms. HNO_3 per 100 c.c.; that is, in an acid of sp. gr. between 1·250 and 1·260. The concentration of the

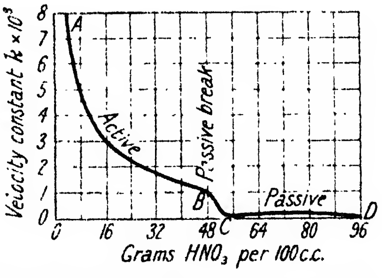

FIG. 401.—The Rate of Dissolution of Iron in Nitric Acid of Different Concentrations at 0°.

acid at which the passive break occurs decreases as the temp. rises from 0° to 10°, and thereafter increases; thus:

		0°	10°	20°	100°
Passive break	Sp. gr.	1·26	1·23	1·25	1·30
	Grms. HNO_3 per 100 c.c.	52·09	45·82	49·78	61·74

T. Andrews, and W. A. Hollis also showed that the passive state can be produced only below a certain temp. which is a characteristic of each metal. Thus, passive iron dipping in nitric acid of sp. gr. 1·42 becomes active at 90°, so that the critical temp. with iron is a little below 100°; with nickel, about 72°; and with cobalt, about 10°. E. S. Hedges found that the temp. at which gas appears when passive iron is heated with 90 to 100 per cent. nitric acid is independent of the concentration of the acid, being between 74·5° and 75·5°. The temp. at which iron goes into soln. is:

Nitric acid	90	95	98	99	100 per cent. HNO_3
Temperature	75·0°	77·5°	83·0°	85·0°	86·5°

Freshly-ignited ferric oxide does not dissolve appreciably until this temp. is reached. This temp. does not correspond with the formation of an allotropic modification of iron. According to W. A. Hollis, the critical temp. depends on whether the iron is heated with the acid, or whether the iron and acid are heated separately before being brought into contact; in the former case, the critical temp. was 94°, and in the latter case 74°, but the actual results are dependent on the degree of purity of the iron. Observations on this subject were made by T. Andrews, T. Bergman, H. G. Byers, M. Corsepius, E. St. Edme, H. L. Heathcote, J. F. W. Herschel, J. P. Joule, J. Keir, R. Kirwan, H. G. Byers and A. F. Morgan, J. M. Ordway, J. B. Senderens, L. Varenne, and G. Wiedemann. W. Heldt said that finely-divided iron does not passivate so readily as compact iron, and T. Andrews found that wrought iron when first dipped in the acid may appear more passive than steel, but after some hours' immersion in the acid it becomes less passive; wrought iron is permanently more passive than tungsten steel; hard steels, with their higher content of combined carbon, are more passive than mild steels. H. M. Noad observed that a preliminary washing of the metal with water renders passivation more difficult. Stirring the acid was found by C. W. Bennett and W. S. Burnham, H. L. Heathcote, E. S. Hedges, W. Kistiakowsky, and P. de Regnon to favour passivation. Z. C. Mutaftschieff found that the stirring of nitric acid of sp. gr. 1·20 for up to 5 hrs. favoured the passivation of iron, but no difference could be detected when the acid was stirred for 5 to 24 hrs.

The presence of nitrous acid or of nitrogen peroxide in the acid was found by W. Beetz, M. le Blanc, R. Escales, P. Günther, W. Heldt, J. F. W. Herschel, A. Klemenc, and A. Voigt to retard the passivation, but if ferrous sulphate be present, the nitrous oxides are absorbed, and the acid then favours passivation. U. R. Evans observed that electrolytic iron is not attacked by nitric acid of sp. gr. 1·40 when solid potassium nitrite or ferric nitrate is present. The admixture of sulphuric acid was found by W. Beetz, M. Boutmy and M. Chateau, and J. F. Daniell to favour passivation. F. Fujihara studied the passivation of iron in dil. alcoholic soln.; and C. Benedicks and P. Sederholm, in soln. of ethyl alcohol, or other organic liquid which reduces the degree of ionization of the nitric acid.

G. S. Ohm, and A. Renard stated that iron is rendered passive when treated with nitrous acid or different nitrogen oxides; and R. Weber passivated iron by contact with fused nitrogen pentoxide at 30°.

S. W. Young and E. M. Hogg consider it probable that when nitric acid is the passivating agent, nitrogen peroxide or trioxide does the actual work because the exposing of iron to either of these agents makes the metal passive, while nitric oxide does not effect this transformation. Colourless, or the so-called water-white, nitric acid does not passivate iron, but the transformation is effected by yellow or red acid. The colour indicates that the acid contains higher nitrogen oxides in soln. The passive break occurs when the conc. of the acid is such that the reaction develops relatively large amounts of nitrogen peroxide. When nitrogen peroxide is bubbled through nitric acid in which iron is normally active, it has the effect of producing passivity; and a similar result is obtained by the addition of nitrites. It is probable that with nitric acid with a conc. lower than that of the passive break, nitrogen peroxide is still being developed because the values for the velocity constant increase with dilution. There is a slow but continuous dissolution of iron in passivating acids no matter how concentrated they are.

Passivity is developed through the agency of oxidizing reactions.—Acids other than nitric acid may passivate iron; thus, W. Beetz, and A. S. Cushman found that *chromic acid* will do the work; R. Phillips, *iodic or chloric acid;* and J. W. Turrentine, *hydrazoic acid.* M. Martens stated that conc. *acetic acid* will passivate iron, but W. Beetz, and W. Rollmann could not confirm this. E. Heyn and O. Bauer showed that soln. of *sodium and ammonium acetates*, 1 grm. per litre, will passivate iron. The statement of M. Martens that alcohol will passivate iron was opposed by W. Beetz, W. Rollmann, and C. F. Schönbein. M. Boutmy and M. Chateau, and N. A. E. Millon found that *arsenious acid* will passivate iron; and W. R. Dunstan and J. R. Hill, that a 1 per cent. soln. of *sodium arsenate* soon passivated iron. The inhibitory action of arsenic films on iron was discussed by E. Heyn and O. Bauer—*vide supra*, the action of sulphuric acid on iron. W. R. Dunstan and J. R. Hill, E. Heyn and O. Bauer, and G. Grube studied the passivation of iron by soln. of *potassium ferrocyanide* and *potassium ferricyanide;* A. Finkelstein, H. L. Heathcote, C. Fredenhagen, and F. Heyn and O. Bauer, by soln. of *potassium cyanide.* Iron becomes more or less passive with conc. *sulphuric acid,* and cast-iron vessels are used for storing 90 to 100 per cent. acid. For concentrations below 80 per cent. H_2SO_4, ordinary cast iron is attacked by the acid, and special ferrosilicon iron is used for containers. The subject was discussed by H. L. Heathcote, J. Meunier, C. E. Fawsitt and A. A. Pain, etc.—*vide infra.* According to Z. C. Mutaftschieff, the prolonged exposure of iron to air reduces its reactivity with nitric acid of sp. gr. 1·39 to 1·42. The potential acquired by iron on exposure to air was discussed by W. Muthmann and F. Frauenberger, and F. Flade; and it is assumed that the iron acquires a film of an oxide by exposure to *air.* The same assumption was made by U. R. Evans, M. Faraday, H. Freundlich and co-workers, F. Haber and F. Goldschmidt, W. Kistiakowsky, R. Mallet, W. Rollmann, G. Tammann, and G. Wetzlar. A. Renard observed that the heating of an iron rod in the flame of a spirit lamp for a few seconds will make the metal passive. The passivation of iron by heating it in air, and the formation of oxide films when iron is heated in air or *oxygen* was discussed by W. Beetz, C. E. W. Belck, M. Boutmy and M. Chateau, H. le Chatelier and B. Bogitch, U. R. Evans and co-workers, M. Faraday, A. Finkelstein, E. Grave, W. Hittorff, M. Martens, H. M. Noad, L. Nobili, E. Ramann, W. Rollmann, C. F. Schönbein, and G. Wetzlar. According to C. A. L. de Bruyn, the inertness of iron covered with a film of oxide is not related to the abrupt change of potential which occurs in the ordinary passivation of iron. The subject was discussed by W. R. Dunstan and J. R. Hill, U. R. Evans, H. L. Heathcote, I. Langmuir, E. K. Rideal, and C. F. Schönbein.

G. Wetzlar, W. R. Dunstan and J. R. Hill, M. Martens, and C. von Hutton observed the resistance of iron to attack by soln. of ammonium or potassium hydroxides. With low concentrations of alkali-lye, A. Thiel and H. Luckmann found that the iron may be attacked in the presence of oxygen. The passivity of iron in soln. of barium hydroxide was studied by W. R. Dunstan and J. R. Hill, and in soln. of calium hydroxide by E. Heyn and O. Bauer. According to C. E. W. Belck, the resistance of iron to soln. containing sufficient alkali hydroxide has not definitely been proved to be due to the passivation of the metal, because W. R. Dunstan and J. R. Hill showed that the apparent passive state is not maintained after the metal has been washed in water, whereas it is so with iron passivated with nitric acid; and M. Mugdan, that with increasing concentration of the alkali-lye, the metal gradually, not abruptly, passes into what appears to be the passive state, and, at the same time, the potential steadily increases to the equilibrium potential of hydrogen. The subject was also discussed by U. R. Evans, J. A. N. Friend, F. Haber and W. Maitland, E. Heyn and O. Bauer, E. Liebreich, W. H. Perkins, E. K. Rideal, and G. W. Whitman and co-workers. F. Haber and F. Goldschmidt showed that iron may resist attack by soln. of alkali-lye, in the presence of carbon dioxide so long as the carbonate and hydrocarbonate can be formed. W. R. Dunstan and J. R. Hill studied the passivation of iron by soln. of *sodium and potassium carbonates*, and by soln. of *borax—vide supra*, the corrosion of iron. G. T. Fechner, and M. Faraday noted that the metal is not attacked by soln. of *alkali sulphide*, although, according to G. S. Ohm, a surface skin of iron sulphide may be formed. Similarly, F. Förster did not consider the resistance of iron to soln. of alkali sulphides to be the same in kind as the phenomenon of passivity. W. R. Dunstan and J. R. Hill, J. A. N. Friend and C. W. Marshall preferred to call these agents *inhibitors* rather than passivifying agents.

O. Dony-Hérault, and W. Beetz showed that soln. of *potassium chlorate, bromate, or iodate* in conc. sulphuric acid passivate iron, but, according to M. Mugdan, soln. of *potassium perchlorate* do not do so. Iron was also found by M. Mugdan to be passive in soln. of alkali chlorates, bromates and iodates. E. Heyn and O. Bauer observed that soln. of potassium chlorate, up to the highest concentrations, perceptibly attack iron, but soln. of potassium bromate and iodate containing 1 grm. per litre, do not do so. W. R. Dunstan and J. R. Hill found that a 1 per cent. soln. of potassium chlorate did not passivate iron, but a 4 per cent. soln. did, whilst 1 per cent. soln. of potassium bromate or iodate were usually effective in passivating iron—as indicated above.

M. Boutmy and M. Chateau, and G. T. Moody observed that iron becomes passive in contact with neutral *hydrogen dioxide*. Thus, clean electrolytic iron can be immersed in a warm dil. soln. of perhydrol without showing any sign of corrosion even though its surface is swept with bubbles of oxygen due to the catalytic decomposition of the hydrogen dioxide. Iron readily dissolves in the presence of acids and hydrogen dioxide. The action of hydrogen dioxide was also studied by W. R. Dunstan and co-workers, and by H. E. Armstrong and R. E. Colgate.

E. Grave attributed the passivity iron acquires when heated in nitrogen to the removal of the activating hydrogen. W. R. Dunstan and J. R. Hill said that passive iron remains passive after it has been heated in nitrogen. G. Tammann discussed the passivity of nitridized iron. A. Renard found that the vapour of nitric acid will passivate iron; and L. Varenne added that compressed nitric oxide acts similarly. According to S. W. Young and E. M. Hogg, nitric oxide does not act at ordinary press., but nitrogen peroxide produces a passivity far greater than that produced by nitric acid when dry gas is allowed to come in contact with the metal—*vide supra*. Iron passivated by dry nitrogen peroxide is more persistently passive than that which is passivated by nitric acid. Mere traces of nitrogen peroxide can render iron passive; for if a little of the gas is allowed to escape into the atmosphere of a room all the iron articles in the room become passive.

E. Ramann observed that iron is passivated by soln. of *ammonium nitrate*; and J. Keir, G. Wetzlar, and B. Lambert, by soln. of *copper nitrate*. G. Wetzlar observed that neutral soln. act more quickly than acidic soln., and J. B. Senderens added that some copper separates from neutral soln. G. Wetzlar also noted that raising the temp. is not favourable to passivity, and B. Lambert, that pressing the iron in an agate mortar before or while in the soln. of the copper salt, activates passive iron. G. Wetzlar reported that iron passivated by a soln. of copper nitrate retains its passivity for weeks, but dipping the passive iron in water makes it active. G. Wetzlar, and M. Martens found that iron is passivated in an alcoholic soln. of copper nitrate. The passivating action of soln. of *copper sulphate* was studied by C. F. Buchholz, G. Wetzlar, J. B. Senderens, and W. Beetz; of a soln. of *copper chloride*, by J. B. Senderens, and of alcoholic soln. of the chloride, by G. Wetzlar, and M. Martens; of aq. soln. of *copper acetate*, by G. Wetzlar, J. B. Senderens, and M. Mugdan; of neutral or ammoniacal soln. of *copper tartrate*, by G. Wetzlar and M. Mugdan. T. Bergman, J. Keir, N. W. Fischer, G. Wetzlar, and W. Beetz observed that iron is passivated by aq. soln. of *silver nitrate;* and E. Ramann, by ammoniacal soln. of that salt. W. Beetz found that silver nitrate is more active than is copper nitrate; and J. Keir, and G. Wetzlar studied the passivation by mixed soln. of copper and silver nitrates. The addition of nitric acid to the aq. soln. of silver nitrate tends to activate the iron. The action was studied by T. Bergman, J. Keir, G. T. Fechner, M. Faraday, W. Heldt, and G. Wetzlar; the action of neutral soln., by G. Wetzlar, W. Beetz, and J. B. Senderens; and the activation by a rise of temp., by J. Keir. G. Wetzlar, and J. B. Senderens observed that the passivity produced by a nitric acid soln. of silver nitrate is retained some weeks on exposure to air. J. B. Senderens studied the passivation of iron in soln. of *silver sulphate;* and J. B. Senderens, and G. Wetzlar, in soln. of *silver acetate.* The passivation of iron by soln. of *mercurous nitrate* was studied by J. Keir, C. F. Schönbein, G. Wetzlar, W. Heldt, and M. Boutmy and M. Chateau; by soln. of *aluminium nitrate*, by E. Ramann; by soln. of *lead nitrate*, by R. Kirwan, J. Keir, and J. B. Senderens; and by soln. of lead acetate, by J. B. Senderens; and by soln. of *ferrous and ferric nitrates*, *cobalt nitrate*, and *nickel nitrate*, by E. Ramann.

M. Boutmy and M. Chateau, J. A. N. Friend, E. Liebreich, G. T. Moody, W. R. Dunstan and co-workers, U. R. Evans, T. P. Hoar and U. R. Evans, R. G. van Name and D. U. Hill, G. W. Heise and A. Clemente, and E. Heyn and O. Bauer discussed the passivation of iron by soln. of chromic acid, *chromates*, and *dichromates;* and M. Boutmy and M. Chateau, M. Mugdan, W. R. Dunstan and J. R. Hill, and E. Heyn and O. Bauer, the passivation of iron by soln. of *potassium permanganate.* Most of the observations on passivity were made with iron containing carbon as an impurity, but R. Lenz showed that purified iron becomes passive under similar conditions, so that the passive state is a property of iron *per se.*

W. Hisinger and J. J. Berzelius, and C. F. Schönbein studied the passivation of iron by anodic polarization. According to E. Ramann, iron readily assumes the passive state when it is used as anode or positive electrode in an aq. soln. of various electrolytes. If the iron be made the anode of an electric circuit, the NO'_3-ions at the surface of the metal passivate the iron. The subject was studied by H. G. Byers, F. Flade and H. Koch, G. Grube, J. L. R. Hayden, H. L. Heathcote, W. Rathert, C. F. Schönbein, and W. Hittorf. M. Faraday found that the dissolution of iron by nitric acid of sp. gr. 1·3 at once ceases if a material like platinum, gold, or carbon is brought in electrical contact with the iron. Here a short-circuited electric cell is set up, and passivity is quickly produced. Contact with zinc under similar conditions has the reverse effect. The effect of zinc in starting activation waves, which, if started in two parts of the passive iron, meet and mutually extinguish one another, was studied by R. S. Lillie.

According to T. Andrews, J. MacLeod-Brown, M. Martens, and P. de Regnon, if an iron rod dipping into nitric acid or other oxidizing agent be in electrical contact with a strip of platinum, it becomes passive, due to the anodic polarization of the iron, for if the two metals be in electric contact, the iron becomes the anode, the strength of the current falls to a very small quantity, and then remains virtually constant for several days. The subject was also studied by H. Buff, M. Faraday, W. Heldt, J. F. W. Herschel, A. J. Maass, L. McCulloch, M. Martens, H. M. Noad, E. Ramann, P. de Regnon, A. Renard, W. Rollmann, and C. F. Schönbein. No passivation was observed by M. Faraday to occur when the iron is in contact with copper; but the effect with silver was observed by M. Faraday, and J. F. W. Herschel; with gold, by J. MacLeod-Brown, E. Ramann, A. Renard, and C. F. Schönbein; and with graphite, by M. Faraday, J. MacLeod-Brown, E. Ramann, P. de Regnon, A. Renard, and J. L. Schönn. The passivation of iron by contact with lead oxide and silver peroxide was noted by M. Boutmy and M. Chateau, H. M. Noad, and C. F. Schönbein. C. F. Schönbein observed that a rod of passive iron may passivate a rod of active iron, if the two rods be placed in electrical contact in the acid. If the surface area of the active rod is relatively greater than that of the passive rod, the phenomenon may be reversed, and the passive rod may become active. J. MacLeod-Brown said that if part of an iron nail is made passive, the remainder of the nail does not assume the passive state. The passivation of active iron by contact with passive iron was studied by U. R. Evans, M. Faraday, G. T. Fechner, H. C. Oersted, E. Ramann, C. F. Schönbein, H. Schröder, G. Wetzlar, and G. Wiedemann.

G. Wiedemann described a number of cases of the passivation of anodic iron in cells with various electrolytes, and various metals—copper, silver, gold, zinc, cadmium, tin, lead, antimony, bismuth, and platinum—by A. Avogadro, W. Beetz, J. G. Brown, M. Corsepius, J. F. Daniell, H. Davy, M. Faraday, N. W. Fischer, F. Flade, W. Hisinger and J. J. Berzelius, A. J. Maass, M. Martens, C. H. Pfaff, A. de la Rive, W. Rollmann, and C. F. Schönbein.

The anodic polarization of iron in soln. of alkali hydroxides was studied by A. J. Allmand and R. H. D. Barklie, H. G. Byers and co-workers, M. Corsepius, C. Fredenhagen, F. Förster and A. Piquet, E. Grave, G. Grube, F. Haber and co-workers, E. S. Hedges, P. Krassa, E. Müller and F. Spitzer, and C. F. Schönbein. The effect in soln. of various salts—*e.g.* sodium chloride was studied by W. J. Müller; sodium chlorate, by H. G. Byers; ammonium sulphate, by E. S. Hedges; sodium sulphate, by H. G. Byers and co-workers, E. S. Hedges, H. W. Moseley, and W. Rathert; potassium sulphate, by A. Finkelstein, and E. P. Schoch and co-workers; copper sulphate, by W. Rathert, and C. F. Schönbein; ferrous sulphate, by C. A. L. de Bruyn; ferric sulphate, by A. Finkelstein; ammonium nitrate, by J. L. R. Hayden: sodium nitrate, by H. G. Byers; potassium nitrate, by H. G. Byers, J. L. R. Hayden, E. P. Schoch and co-workers; alkali carbonates and hydrocarbonates, by H. G. Byers, J. L. R. Hayden, and F. Haber and F. Goldschmidt; mixtures of potassium ferrocyanide and ferricyanide, by G. Grube; potassium cyanide, by A. Brochet and J. Petit, H. G. Byers, A. Finkelstein, E. S. Hedges, and W. Hittorf; potassium phosphate, by H. G. Byers and M. Darrin; potassium permanganate, by H. G. Byers; and potassium dichromate, by H. G. Byers and co-workers. The effect in various acids—*e.g.* hydrochloric acid was studied by H. G. Byers and S. C. Langdon, and E. S. Hedges; in sulphuric acid, by J. Alvares, H. E. Armstrong and R. T. Colgate, H. G. Byers and co-workers, M. Corsepius, U. R. Evans, A. Finkelstein, F. Flade and H. Koch, C. Fredenhagen, E. Grave, E. S. Hedges, H. Koch, W. Rathert, P. de Regnon, G. C. Schmidt and W. Rathert, and C. F. Schönbein; in nitric acid, by T. Andrews, H. G. Byers and co-workers, C. Fredenhagen, E. S. Hedges, W. Hisinger and J. J. Berzelius, M. Martens, H. W. Moseley, W. J. Müller, P. de Regnon, W. Rollmann, and C. F. Schönbein; in phosphoric acid, by H. G. Byers and co-workers, E. S. Hedges, H. W. Moseley, and C. F. Schönbein.

Passive iron was found by A. Finkelstein to behave with respect to oxygen like a reversible gas-electrode, and the cell was studied by F. Flade, C. Fredenhagen, C. M. Gordon and co-workers, G. Grube, M. Mugdan, W. Muthmann and F. Frauenberger, and F. Tödt. The passive iron behaves in this way with no gas other than oxygen. If platinum be replaced by passive iron in the gas-cell, H. Koch found that the intensity of the current is reduced, showing that oxygen is being taken up by the passive iron. O. Scarpa could not decide whether a film of oxide or a film of oxygen was formed on the passive metal. H. C. Byers and S. C. Langdon showed that the potential, E volt, of the cell is dependent on the press. of the oxygen—p lbs. per sq. in. with an iron electrode in $0{\cdot}2N\text{-}H_2SO_4$:

p . .	0	25·8	30·5	34·6	43·9
E . .	1·770	−1·760	−1·751	−1·740	−1·730

The potential of the anodically polarized, passive iron gradually decreased with time. C. A. L. de Bruyn showed that while platinum is not attacked, an electrode of passive iron is attacked by mixed soln. of ferrous and ferric sulphates:

	$FeSO_4$	67·5	48·5	29·0	16·0	1·0 per cent.
	$Fe_2(SO_4)_3$ . .	32·5	51·5	71·0	84·0	99·0 ,,
E	platinum . .	0·632	0·655	0·680	0·699	0·812
	passive iron . .	0·620	0·642	0·665	—	0·745
	ferrosic oxide .	0·619	0·651	—	0·686	0·765

The passivation of iron or anodic polarization of iron in soln. of alkali hydroxide was discussed by F. Förster and co-workers, C. Fredenhagen, H. Freundlich and co-workers, G. Grube and H. Gmelin, F. Haber and co-workers, D. F. Holmboe, P. Krassa, E. Müller and F. Spitzer, and L. Tronsted; and the anodic polarization of iron in fused alkali hydroxide, by C. Liebenoff and L. Strasser, R. Lorenz, C. J. Reed, L. Rolla and R. Salani, and J. F. Sacher. The general results show that the iron behaves as an oxygen, and that the passivation is due to the formation of a film of oxide, or a film of gas electrode.

According to F. Goldmann and E. Rupp, the impact of electrons on non-evacuated surfaces of silver or copper causes them to become passive, so that the bombarded surface is not attacked by iodine vapour, whilst the unprotected parts are quickly covered with a violet film, which is thickest near the boundary. Positive ions or the prolonged action of ultra-violet light produces the same effect. Since passivation does not occur when the surfaces are evacuated or when the evacuated surfaces are subsequently brought into contact with hydrogen, but is pronounced if oxygen is introduced, it is considered to be due to the formation of an oxide film on the exposed part of the metal.

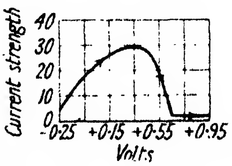

Fig. 402.—The Potential of Iron and the Current Density.

The activation of passive iron.—J. Keir, and H. Buff observed that the activation occurs when the passive metal is left in contact with water—*vide supra.* It is only the moist passive metal that reverts so easily to the active state. The passive metal may be activated if left in contact with nitric acid below the concentration required for passivation, thus, L. Varenne found that iron passivated by nitric acid of sp. gr. 1·42 was depassivated in contact with

Sp. gr. nitric acid .	1·3	1·28	1·26	1·16
Time	264	120	32	12 hrs.

Analogous observations were made by E. St. Edme, H. L. Heathcote, W. Heldt, J. F. W. Herschel, and C. F. Schönbein. U. R. Evans, and H. L. Heathcote, found that iron passivated in conc. nitric acid becomes active on exposure to air; and T. Fujihara, that Armco iron or electrolytic iron, passivated by a 5 per cent. alcoholic soln. of nitric acid, was not attacked by distilled water in an atm. free from carbon dioxide, but in the presence of carbon dioxide, it began to rust in 10 to 20 mins.

H. L. Heathcote obtained the passive metal in a dry state by rapidly spraying, in succession, upon a recently passivated rod of metal, (i) a sat. aq. soln. of potassium dichromate containing 2·8 grms. of potassium hydroxide per 100 c.c.; (ii) a mixture of 100 c.c. of water, 10 c.c. methylated spirit, and 2·5 grms. of potassium hydroxide purified by alcohol; and (iii) absolute alcohol. The dry, passive iron behaved exactly like a metal covered with a film of oxide. The rods were not activated by allowing them to remain several days in the atmosphere of a laboratory; rubbing them well with dry cotton-wool had no effect; and contact with zinc or scratching with glass failed to activate the portions of the passive rod which were not touched. L. Varenne said that passive iron becomes active under a press. of 15 mm. of mercury; and C. E. W. Belck also stated that activated iron becomes passive in vacuo, but H. L. Heathcote did not agree. According to H. L. Heathcote, if a vessel containing iron immersed in nitric acid be evacuated, bubbles of gas form on the surface of the metal and rise to the top of the liquid; but although the mechanical action of these bubbles may sometimes render the iron active, more usually the bubbles cease to form at an early period, and the iron remains quite passive for hours at 15 mm. press. The sudden admission of air sometimes activated the passive iron. He also found that passive iron may be kept in a high vacuum for some hours without change, although spots of activity may develop—possibly because of local action produced by impurities forming local voltaic couples. The general results show that the presence of a gaseous film on the metal is not the cause of the passivity. W. R. Dunstan and J. R. Hill found that at 400°, passive iron remains passive, but at a higher temp., the metal becomes active. According to E. Grave, active iron heated in vacuo is passive in consequence of the removal of occluded hydrogen, but F. Flade and H. Koch found that active iron remains when it has been heated in vacuo to remove as much as possible of the occluded hydrogen. For the presence of occluded gases in iron, *vide supra.*

H. M. Noad, and others have noticed that dil. nitric acid activates passive iron—*vide supra.* A. Meyer, C. F. Schönbein, and others found that the same result is produced by the action of chlorine, bromine, hydrochloric acid, sulphuric acid, and a soln. of potassium nitrate, chloride, etc. Passive iron was found by G. Wetzlar to be activated by various salts—*e.g.* by sodium or ammonium chloride, or by potassium nitrate or sulphate in alkaline soln.; M. Mugdan observed that sodium chloride or sulphate activated passive iron, but not so with potassium nitrate or chlorate. E. P. Schoch and C. P. Randolph found that the anions: halides, sulphates, acetates, perchlorates, nitrates, chromates, chlorates, bromates, iodates, and hydroxides, have a decreasing tendency to activate passive iron. The activation of passive iron by the halides was discussed by A. J. Allmand and R. H. D. Barklie, G. Bodländer, H. G. Byers and co-workers, W. R. Dunstan and J. R. Hill, U. R. Evans, F. Flade and H. Koch, J. A. N. Friend, F. Haber and F. Goldschmidt, J. L. R. Hayden, E. Heyn and O. Bauer, E. Liebreich, A. Smits, and A. Smits and C. A. L. de Bruyn. W. R. Dunstan and J. R. Hill also observed that sulphuric, hydrochloric, formic, acetic, citric, and carbonic acids rapidly activate passive iron. E. St. Edme found that hydrogen converts passive into active iron, but, according to W. Hittorf, and E. Grave, molecular, *i.e.* ordinary, hydrogen does not restore the activity of passive metals. According to W. Beetz, E. Grave, and C. F. Schönbein, however, if the metal be heated in hydrogen—W. R. Dunstan and J. R. Hill said at 240° to 250°—the passive metal is activated. E. Grave, W. Rathert, O. Sackur, G. C. Schmidt, G. C. Schmidt and W. Rathert, and J. Stapenhorst observed that hydrogen *in statu nascendi*, or $H^{\cdot}$-ions, strongly activated the passive metal; and W. Hittorf, J. F. W. Herschel, M. Martens, M. Boutmy and M. Chateau, and M. Bibart observed that the passive metal is activated by treating it with reducing agents—*e.g.*, according to C. F. Schönbein, alcohol and ether make the passive metal active. G. C. Schmidt found that the diffusion of hydrogen through a passivated surface activates the metal. The subject was studied by A. M. Hasebrink, and H. Eggert. In general, the passive state is destroyed by making the metal the cathode of a voltaic couple. M. Faraday, and R. S. Lillie—*vide supra*—observed the activation of the passive metal by contact with zinc.

According to M. Faraday, F. Förster, J. F. W. Herschel, J. Keir, M. Martens, C. F. Schönbein, F. W. Schweigger-Seidel, and G. Wetzlar, passive iron is usually activated when it is in contact with active iron, or when it is in contact with a more electropositive metal like zinc or lead. In J. F. W. Herschel's experiment, an iron rod was divided into two parts by a band of wax about the centre of the rod; and passivity was induced on both ends of the rod. Activity is restored to *one end* by touching that end with a piece of copper while the whole rod was exposed to air; if one end be touched while the whole rod is dipping in the acid, *both ends* become active. In the former case a voltaic couple is formed—the piece of copper is the anode, the end of the rod which is in contact with the copper is the cathode, and the film of acid the electrolyte. The cathode extends only to the wax ring because the electrolyte does not wet the wax. When the rod is wholly immersed, the electrolyte is continuous, and the whole rod acts as cathode and becomes active.

The passive metal can be activated by mechanical treatment—*e.g.* J. F. W. Herschel, J. Keir, F. W. Schweigger-Seidel, J. B. Senderens, C. Tomlinson, L. Varenne, and G. Wetzlar noticed that the active condition may be restored to passive iron by scraping or scratching the metal, or by a mechanical shock, although P. de Regnon was unable to verify this. N. Izgarischeff said that the scratched iron immediately becomes passive if it be returned to the nitric acid; and W. R. Dunstan and J. R. Hill observed that iron passivated by chromic acid, scratched, and then placed in water begins to rust along the scratches. W. Muthmann and F. Frauenberger observed that metals which have become more or less passivated by exposure to air become active when the surface is cleaned mechanically. L. Varenne found that vibratory movements of various kinds activate passive iron. E. S. Hedges observed that iron, previously rendered passive by nitric acid, becomes active when whirled at 3000 revs. per min. after a short period of induction representing the time required for removing the film of oxide which produces the passivity.

W. Hittorf observed that when the circuit of the cell $Fe | NaNO_3, H_2CrO_4 | Pt$ is closed by dipping the iron in the salt soln., the e.m.f. gradually drops from 1·83 to 0·1 volt, the iron becomes quite passive, retaining its metallic lustre, and it is not attacked however long the cell is short-circuited. Passive iron is not really insoluble in nitric acid, for M. Faraday showed that a little passes into soln. during the passage of the current; and C. E. W. Belck observed that the rate of dissolution of the passive iron depends on the conc. of acid, being less in the more dil. acids. H. G. Byers, and H. G. Byers and S. C. Langdon observed that the establishment of anodic passivity in iron is influenced by the condition and previous history of the iron, the nature and concentration of the electrolyte, the stirring of the electrolyte, the temp., the current density, the time of flow of the current, and the concentration of the oxygen dissolved in the electrolyte.

In the electrolysis of sulphate soln., at low current densities, the dominant anion, SO_4'', is alone discharged at the anode to any appreciable extent, but at high current densities, the OH'-ions are also discharged, and oxide or hydroxide, or hydrated oxide begins to accumulate on the anode, and interferes with the dissolution of the iron. It is at this stage that passivity occurs. The electrical passivation of the iron occurs more readily in alkaline soln. since these soln. are favourable to the discharge of OH'-ions; and in soln. of alkali hydroxide alone, a low current density makes the anode passive because the only possible anode product is the sparingly soluble hydroxide. E. P. Schoch and C. P. Randolph found the approximate limiting current densities, in milliamps., to be with N-K_2SO_4, 300; with 0·01N-KOH, 250; with N-K_2SO_4 and with 0·1N-KOH, 10.

According to F. Förster, A. Adler, M. Schlötter, G. C. Schmidt, E. Grave, W. Rathert, and M. le Blanc, passivity is the normal state of purified iron, and the metal is rendered active by contact with some catalyst, say hydrogen (G. C. Schmidt), an alloy of the metal and hydrogen (F. Förster), or $H^{\cdot}$-ions (E. Grave); and this hypothesis is supposed to be supported by B. Lambert and J. C. Thomson's observations—*vide supra*, the corrosion of iron. F. Flade and H. Koch attempted to decide between the hypothesis that (i) purified iron is active and the passivity is connected with the presence of oxygen, and the hypothesis that (ii) purified iron is passive and the activity is connected with the presence of hydrogen. If a specimen of active iron be heated in vacuo, to remove all hydrogen, it still remains active; and if a passive electrode be heated in carbon monoxide to remove oxygen without affecting the hydrogen, a passive electrode remains passive, and an active electrode becomes passive. This last result is attributed to an equilibrium condition between carbon, oxygen, carbon dioxide, and carbon monoxide, and the oxygen formed passivates the active metal. According to W. Rathert, and G. C. Schmidt, the potential at which the passive metal becomes active is not the same as that at which the active metal becomes passive, and that the point of sudden change of potential observed by F. Flade does not represent the boundary potential below which the metal is active and above which it is passive. A metal may be active or passive on both sides of this point, depending on its previous treatment. The potential at which iron becomes passive is dependent in a marked degree on the concentration of the electrolyte in which the anodic polarization is effected, whilst the potential at which passive iron becomes active is not. The appearance of the passivity potential and the activity potential during anodic polarization is dependent on the current density, and consequently on the oxygen concentration on the electrode. These various facts are said to be explained better on the hydrogen than on the oxide theory of passivity. J. Stapenhorst found that iron which has been made passive by chromic acid, becomes active under the influence of hydrogen dissolved in the metal. He believed that this change cannot be explained by the removal of dissolved oxygen or by the destruction of an oxide film. Under suitable conditions, the reverse change may be brought about by the diffusion of nascent oxygen. The potential assumed by a metal in a neutral electrolyte depends on the quantity of oxygen present in the electrolyte soln. If the surface of the metal is renewed by grinding with an emery-wheel, the potential changes from that characteristic of the passive form to the value peculiar to the active form of the metal. Hydrogen and nitrogen tend to preserve the potential of the active form, but otherwise behave as indifferent gases. Oxygen, on the other hand, is not an indifferent gas. Both in the gaseous and dissolved states it exercises a very considerable influence on the electrode potential and conduces to the appearance and maintenance of the passive state. The passivating potential was studied by J. Alvares, C. A. L. de Bruyn, H. G. Byers and co-workers, F. Flade, F. Flade and H. Koch, F. Giordani, C. Fredenhagen, E. Grave, E. Liebreich and W. Wiederholt, W. J. Müller and co-workers, W. Rathert, G. C. Schmidt and W. Rathert, and E. P. Schoch and C. P. Randolph.

According to W. J. Müller and co-workers, in the electrolysis of N-H_2SO_4 sat. with ferrous sulphate, a visible film is formed on the iron anode, and the resistance rises at first slowly, and then rapidly to a maximum. A critical current density at which passivity occurs is attained after a definite time, t; and the mean current density for passivation is directly proportional to $\log t$. H. G. Byers and C. W. Thing found that a current density which is insufficient to cause passivity quickly may do so if a longer time is allowed. They also found iron to be passive at all current densities in a soln. of potassium dichromate and sodium sulphate, and becomes passive in $0{\cdot}2N$-H_2SO_4 at all current densities above 6·0 amps. per sq. dm. H. G. Byers and S. C. Langdon observed that with iron as anode in $0{\cdot}2N$-H_2SO_4, the time required for passivation is much shorter if dissolved oxygen is present at the anode surface. U. Sborgi and G. Cappon found that with iron in an ethyl alcohol soln. of calcium and ammonium nitrates, the metal is passive with high and low current densities; and U. Sborgi and P. Marchetti observed that with an acetone soln. of lithium chloride, iron dissolved as a bivalent metal, and the metal is passive in an acetone soln. of silver nitrate.

C. A. L. de Bruyn found that with a soln. of ferrous sulphate, an iron electrode suddenly becomes passive when the current density reaches 0·4 amp. per sq. cm. This abrupt change was not observed with soln. of ferrous chloride. In an electrolytic cell giving off oxygen from the passive iron electrode, only about 1 per cent. of the current was consumed in the dissolution of iron; the remainder was used in producing oxygen. For active iron, with 0·1 per cent. of carbon, dissolving anodically in a soln. of sodium sulphate, the current efficiency and the current density, in amperes per sq. cm., were:

Current density . . .	0·013	0·020	0·027	0·034
Current efficiency . .	99·9	99·6	99·4	99·1 per cent.

indicating that as long as iron remains active, the current efficiency diminishes slightly as the potential increases. The current efficiency during the anodic dissolution of passive iron, when the current density is 0·0005 amp. per sq. cm., is 1·09 for iron with 0·1 per cent. of carbon; 1·21 per cent. for iron with 0·4 per cent. of carbon; 1·24 per cent. for steel with 1·1 per cent. of carbon; and 4·75 per cent. for cast iron with 3·5 per cent. of carbon. The greater effect with cast iron is attributed to the high carbon-content and coarser structure. Electrolytic iron under similar conditions became active. Passive iron is thus slightly attacked and a comparison of a passive iron anode with a non-corrodible platinum anode in $0{\cdot}1N$-soln. of ferrous and ferric sulphates furnishes the curves, Fig. 403, which show that the potential of passive iron is rather less than that of platinum. G. R. White also showed that iron dissolves anodically in a soln. of sodium nitrate when the current density is low, say, 0·3 amps. per sq. dm., and the current efficiency is 99 to 101 per cent.; but if the current density is raised to 1·7 to 3·3 amps. per sq. dm., the iron becomes passive, and only 0·3 to 1·1 per cent. of the current is then employed in the corrosion of iron. U. R. Evans observed that the relatively small dissolution of iron which occurs when iron is passivated occurs mainly along the water-line, just where any protective skin, which may be formed, breaks down most readily; as a result, a passive electrode through which a current has been flowing some time, may be deeply corroded along the water-line and unchanged over the immersed portion. This attack is not due to contact with the oxygen of the air—Fig. 403—since in the passive state, oxygen bubbles are freely given off all over the immersed portion; when the anode is in the active state, it is often much less attacked near the water-line than it is elsewhere.

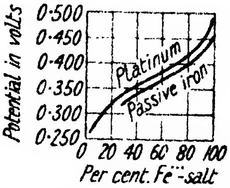

Fig. 403.—The Potentials of Passive Iron and of Platinum.

In general, the corrosion of iron is a result of the electrochemical action caused by the passage of currents between portions of the metal which are at different potentials with respect to the electrolyte in contact with them. Differences of potential with a homogeneous metal may be produced by differential aeration. Two pieces of the same electrolytic iron, similarly ground, were found by A. L. McAulay and S. H. Bastow to give widely different potentials when immersed in an electrolyte. In general, when a piece of iron is placed in an air-free electrolyte, there is a stable potential to which it tends, probably ultimately determined by the hydrogen-ion concentration of the soln. It does not immediately acquire this potential, but after prolonged immersion the stable condition, which proved to be easily reproducible, is attained, and the behaviour of the metal when subjected to experiments using this condition as a starting-point is also reproducible. Mild steel, and cast iron behave similarly, and a difference in composition has but little effect provided that it is not such as to produce air passivity, as in the case of "stainless" steel. Such steel shows completely different behaviour: it resembles a noble metal, is easily polarized by minute currents, and shows no very definite normal potential. The potential which an iron electrode reached after prolonged immersion in an air-free electrolyte was taken as standard. In $0{\cdot}5N$-potassium sulphate this is between 0·75 and 0·80 volt on the sat. calomel scale, the actual value probably depending on the p_H of the soln. When electrodes in the standard state are exposed to air, and then re-immersed in the same electrolyte, they recover the standard state. The film which is responsible for the corrosion current increases in protective power and resistance to destruction with the time of exposure of the iron to air up to about 2 hrs., after which but little further change takes place on further exposure. When this stage is reached, the immersion of the iron in air-free $0{\cdot}5N$-potassium sulphate causes a destruction of the ennobling film in about an hour, and a consequent return of the metal to the standard state in this time. Some film is formed even in the shortest exposures it is possible to give. The destruction of the film is due to action by the electrolyte, it is not destroyed if the electrode is merely left in contact with an inert gas after exposure. More drastic oxidation, such as anodic treatment in alkali-lye, produces a film which takes considerably longer to destroy on exposure to electrolyte than any that are air-formed; eventually, however, the same standard state is achieved in each case. The passage of corrosion currents has no effect on the ennobling film that gives rise to the potential difference which produces them. The potentials are modified temporarily owing to polarization effects, but these effects rapidly disappear when the current is stopped, leaving the film unchanged except for the action of the electrolyte.

A. J. Allmand and R. H. D. Barklie, M. le Blanc, A. Brochet and J. Petit, A. Löb, and R. Ruer compared the corrosion of iron by direct and alternating current. W. J. Shutt and V. J. Stirrup found the time of passivation of iron in $2N$-H_2SO_4 with current densities, D amp. per sq. cm., at 20°, to be:

D . .	0·78	0·911	1·40	2·21	3·23
Time . .	6·01	4·29	2·19	0·86	0·19 secs.

and at 6°:

D . .	0·729	0·923	1·56	2·22	2·57
Time . .	4·44	3·00	0·69	0·32	0·19 secs.

The time of recovery was 0·93 sec. at 20° and 3·21 secs. at 6°.

W. J. Müller studied the time required to produce passivity with an iron anode treated with unit current density in sulphuric acid of different concentrations, and found:

H_2SO_4 . . .	0·06	0·24	0·48	0·94	1·75	3·13	4·88	9·14	13·2
Time (secs.) . .	0·22	0·26	0·60	1·84	2·99	2·99	2·10	1·54	0·92

Increasing the concentration of the acid first decreases the liability to passivity to a minimum with about $3N$-H_2SO_4, and after that the tendency to passivity increases. The effect of high acid concentrations may be attributed to the depression of the solubility, S, of heptahydrated ferrous sulphate in the acidic soln., but the short time needed with low acid concentrations cannot be so explained, but it may be due to the formation of basic salts, in place of hydrated sulphate, as a covering (protective) layer. The activity coeff. for sulphuric acid has a minimum value when the time of passivation is a maximum. The time of passivation is greatly affected by temp., being doubled by a rise of 10°. W. J. Müller found that the time of passivation, t, of iron as anode in soln. of sodium sulphate follows the rule $t=a+b\log(e_m-\epsilon)/(\epsilon-e_s)$, where a and b are constants; e_m denotes the reversible potential of the metal in the pores; e_s, the potential of the coating; and ϵ, the measured potential of the electrode at the time t. The potential-time curves of iron and its alloys were examined by R. May, A. Travers and J. Aubert, W. J. Shutt and V. J. Stirrup, H. G. Byers and co-workers, A. Smits, C. W. Bennett and W. S. Burnham, E. S. Hedges, E. P. Schoch, F. Förster, C. Fredenhagen, E. Heyn and O. Bauer, V. Kohlschütter and H. Stäger, M. Mugdan, U. R. Evans, and W. J. Müller and co-workers.

L. C. Bannister and U. R. Evans used soln. of potassium chromate, and of potassium chloride, and observed that when a metal is covered with a porous film of oxide, it may furnish any value between the potentials of the clean metal and that of the solid oxide. If the oxide film is highly discontinuous, the measured potentials will approach that of the film-free metal—A, Fig. 404; if the pores in the skin of oxide are very small, the measured potential will be higher—B, Fig. 404; and in C, Fig. 404, on the assumption that the elevated potential is due to the high

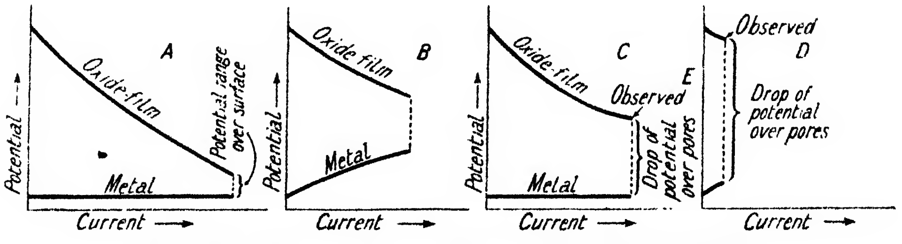

FIG. 404.—Potential Curves of Metals with a Film of Oxide.

resistance imposed by the narrowness of the pores. If, when this stage is attained, the break-down extends from the original weak points, the potential will fall, first rapidly, and then slowly, as the conditions approach the limiting case of *A*, Fig. 404. The shutting off of oxygen by secondary rust will contribute to the fall. Conversely, if repairing conditions prevail, causing the pores to become narrower or less frequent, or rendering the film thicker, the measured potentials will rise. In the limiting case, the pores vanish, and the potential becomes equal to that of the solid oxide—*D*, Fig. 404. It follows, therefore, that a rising potential indicates that weak points in the film are being repaired; and a falling potential, that the break-down is extending; a high final potential indicates that the metal resists attack, a middle value indicates slight rusting; and a low value, profuse rusting. A treatment which increases the resistance of iron to attack, raises the potential; and a treatment which favours corrosion, lowers the potential. The anodic overvoltage was studied by E. Newbery, U. R. Evans, and E. Liebreich and W. Wiederholt. The abrupt change of potential, observed by F. Flade, and others, to occur when iron, as anode in sulphuric acid, becomes passive, was found by W. Rathert to be different from the abrupt change which occurs when the passive metal becomes active. C. F. Holmboe observed that in the anodic passivation of different forms of iron and steel, the rule that the passivation is greater the greater the degree of purity of the iron, is not of general application.

If the potential of an iron anode which has been passivated in a soln. of ferrous sulphate be measured at definite intervals of time, the metal becomes activated; taking time in seconds after the interruption of the current, and referring the potential to a normal calomel electrode:

Time . .	3	12	21	32	40	49	55	64	69	75
Volts . .	0·300	0·265	0·254	0·238	0·220	0·202	0·180	0·130	−0·420	−0·550

The results represented by curve Fig. 405 were obtained with a soln. of 0·473 mol of ferrous sulphate per litre, on an automatic recorder, by C. A. L. de Bruyn. The potential first falls rapidly, *ab*, then slowly, *bc*, and finally, rapidly again, *cd*. The iron is passive until the second rapid decrease occurs. During anodic polarization, hydrogen is displaced by oxygen; when the current is interrupted, the absorbed oxygen is gradually destroyed by the hydrogen diffusing back. The retardation of the activation by the oxygen gradually decreases, and when the concentration of the oxygen is reduced to a low enough value, a rapid change to the active state occurs and the iron then contains hydrogen. The proportion of ferric ions in the soln. is also of importance since they retard the process of activation and favour passivation. The results II, Fig. 405, were obtained with a soln. to which 0·00024 mol per litre of $FeCl_2$ was also added; curve III, with 0·00036 mol $FeCl_2$; and curve IV, with 0·00048 mol $FeCl_2$. This shows that Cl′-ions are powerful catalysts in accelerating the activation which is favoured by a rise of temp.; thus, at 93°, the polarizing current, in milliamps. per sq. cm., is 1·0; at 79°, 0·6; and at 64°, 0·3.

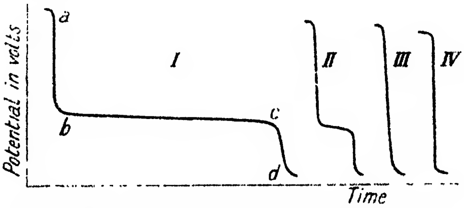

FIG. 405.—The Activation of Passive Iron.

In general, under the conditions necessary for producing the passive state, the anodic potential of iron is reduced. According to J. F. Chittum, in conc. nitric acid soln., the anodic potential of the iron is reduced to a much lower value than is thought to be accounted for by the presence of an insoluble oxide, even by a higher oxide, if any such could be formed under the conditions. In alkaline soln., the anodic potential of iron is reduced to a lower value than can be explained by the presence of an insoluble oxide, and the higher oxide, FeO_2, is soluble in most alkaline soln. Iron, if not disturbed, dissolves very slowly in conc. nitric acid; and in alkaline soln., differential passivity accompanies differential aeration.

The potential of iron in a finely-divided state, as in amalgams $Fe(Hg) \rightarrow Fe^{\cdot\cdot} + 2\oplus$, was shown by W. H. Hampton, and W. J. Sweeney to be 0·441 volt at 25°; and J. C. Warner, and W. J. Sweeney showed that the e.m.f. of a cell $Fe \mid Fe(OH)_2$ sat. soln. $\mid H_2$ is 0·169 volt at 25° with hydrogen at 1 atm. press.; if less than this press., the potential is greater. J. F. Chittum defines passivity as the "tendency of iron to exhibit a potential lower than that of an iron amalgam under the same conditions if the amalgam should behave like sodium amalgam." According to J. F. Chittum, soft iron, and annealed and alloy steels are in equilibrium with $Fe(OH)^{\cdot}$-ions over the range $p_H = 1·0$ to 6·0 when no oxidizing agent is present; and the slope of the curve for the potential with different concentrations of the $H^{\cdot}$-ions is different if chlorides and sulphates are present. Tempered steels are in equilibrium with a higher oxide of iron with values of p_H from 3·0 to 6·0, presumably because the higher oxide is inclosed in surface crevices. In the presence of oxidizing agents, soft iron, and annealed, ordinary and alloy steels are in equilibrium with $Fe(OH)^{\cdot}$-ions over the range $p_H = 1·0$ to 3·0, and in equilibrium with a higher oxide of iron over the range $p_H = 4·0$ to 6·0. With values of p_H exceeding 6·0, the kind of iron oxide with which the metal is in equilibrium is soluble, and as its solubility increases, the tendency for this kind of iron to revert to metallic iron increases to nearly a constant value. This is true only of a higher oxide of iron which is increasingly soluble in alkaline soln. as a ferrate. Consequently, in soln. with p_H exceeding 6·0, the iron behaves as the electrode $Fe + 3H_2O \rightarrow FeO_3'' + 6H^{\cdot} + 4\oplus$. The higher oxide is here assumed to be FeO_2, and it is concluded that a rod of iron behaves as the electrode $Fe + 2H_2O \rightarrow FeO_2 + 4H^{\cdot} + 4\oplus$ except under conditions where the oxide dissolves or is reduced. In the absence of oxidizing agents, or in the presence of reducing agents in soln. with values of p_H between 4·0 and 9·0—the neutral range—the condition unfavourable for the higher oxide electrode is the absence of sufficient oxygen for the catalytic oxidation of the secondary products of corrosion, *e.g.* ferrous ions, should the higher oxide be reduced, or the hydrogen be depolarized if the hydroxyferrous iron electrode is established. This condition may occur when oxygen is absent, or when only a limited supply is present. When the $H^{\cdot}$-ion concentration is greater than corresponds with $p_H = 3·0$, and in the absence of strong oxidizing agents, the higher oxide is unstable, and is largely reduced to the ferrous state. With conditions unfavourable for the existence of the higher oxide, the iron behaves like the electrode $Fe + H_2O \rightarrow Fe(OH)^{\cdot} + H^{\cdot} + 2\oplus$; and the electrode $FeO_2 + 3H^{\cdot} + 2\oplus \rightarrow Fe(OH)^{\cdot} + H_2O$ is present before the iron behaves as a hydroxyferrous ion electrode. The cathode potential of the latter electrode is greater than that of the electrode $FeO_2 + 4H^{\cdot} + 4\oplus \rightarrow Fe + 2H_2O$ until the electrode $Fe + H_2O \rightarrow Fe(OH)^{\cdot} + H^{\cdot} + 2\oplus$ is established; the hydroxyferrous ions are produced except in alkaline soln. where they are catalytically oxidized to the higher oxide through the intermediate formation of a peroxide. When the hydroxyferrous ion electrode is established, it is assumed that there will be both the higher oxide electrode and hydrogen electrode to behave as cathodes.

The iron electrode has its greatest anode potential when it is covered with a film of water, because the lack of polarity in the film prevents the dissolution of the FeO_2 and the presence of FeO_3''-ions; that is, the reaction $FeO_2 + 2OH' = FeO_3' + H_2O$ is suppressed because of the lack of OH'-ions, and the electrode $Fe + H_2O \rightarrow FeO_2 + 4H^{\cdot} + 4\oplus$ has its greatest potential because of the small concentration of the $H^{\cdot}$-ions. The iron electrode has its greatest cathode potential when it is covered with a conc. acid soln. of a strong oxidizing agent. There is then built up a high local concentration of $Fe^{\cdot\cdot\cdot\cdot}$-ions, on account of the solubility of FeO_2 in conc. acid soln., according to the reaction: $FeO_2 + 2H_2O \rightarrow Fe^{\cdot\cdot\cdot\cdot} + 4OH'$, and the stability of the $Fe^{\cdot\cdot\cdot\cdot}$-ions, in the presence of a strong oxidizing agent.

In J. F. Chittum's theory of passivity it is assumed that ordinary iron is passive, and the active iron is the result of a chemical reaction in which iron behaves as a higher oxide electrode, and dissolves in the higher state of oxidation. The time observed by W. J. Müller to be required for the production of the passive state by anode polarization is the time it takes a reversal of the electrode $FeO_2+3H^{\cdot}+2\ominus \rightarrow Fe(OH)^{\cdot}+H_2O$ to raise the concentration of the higher oxide until the iron behaves as the electrode $Fe+2H_2O \rightarrow FeO_2+4H^{\cdot}+4\oplus$.

U. R. Evans pointed out that high $H^{\cdot}$-ion conc. and low current density favour anodic corrosion at a high efficiency, while a low $H^{\cdot}$-ion conc. and high current density favour passivity. Under intermediate conditions it is sometimes possible to produce a condition of **periodic dissolution** in which the iron alternates periodically between the active and passive states—*periodic passivity*, Fig. 406, by A. Smits and C. A. L. de Bruyn. The phenomenon was first mentioned by G. T. Fechner in 1828. Observations were also made by A. Adler, M. Faraday, C. Fredenhagen, H. L. Heathcote, E. S. Hedges, J. F. W. Herschel, J. P. Joule, R. Kremann, W. Kistiakowsky, A. J. Maas, W. Rathert, W. Rollmann, and C. F. Schönbein. J. F. W. Herschel noticed that the current sometimes surges back and forth, and the evolution of gas shows similar pulsations, somewhat resembling those obtained by A. Avogadro with an iron-bismuth couple in conc. nitric acid. A. Smits and C. A. L. de Bruyn pointed out that since the passive state of iron can be removed by bringing the metal in contact with soln. containing halogen ions, it might be possible to set out periodic phenomena which would make their appearance if the halogen ions were added to the electrolyte during anodic polarization. When iron is anodically polarized in a soln. of ferrous sulphate, and a soln. of ferrous chloride is introduced, the catalytic influence of the chlorine ions manifests itself in a fall of potential; if the addition of ferrous chloride is continued, at a given stage, a rapid fall of potential occurs as the iron passes from the passive to the active state. For a given rate of dissolution of iron, determined by the current density, there exists a Cl'-ion conc. at which, at any given moment, the chance of iron remaining passive is just equal to its becoming active. If, at this moment, activation occurs, then whilst the ion anode dissolves extremely slowly when in the passive state, when it becomes active, it passes into soln. at a rate which corresponds with the strength of the current. The influence of Cl'-ions on the anode now changes, for the extent to which the Cl'-ions dissolve in the metal depends on the rate at which the metal ions pass into soln. If this rate be great, fewer Cl'-ions can be dissolved in the metal surface than when the rate of dissolution is small. This changes the state of the active iron. If the iron becomes passive, the soln. of Cl'-ions in the metal again becomes large, and at a definite moment activation occurs. By measuring the potential immediately after the current is interrupted, A. Smits and C. A. L. de Bruyn observed that if the current density is not great enough to cause the iron to become passive, instead of being less negative, the iron becomes more strongly negative, showing that after anodic polarization, iron exhibits a change of potential in the opposite direction to that observed during the passage of the current. Immediately after the anodic polarization of iron, the potential passes through a minimum and then rapidly rises to its original value. The periodic phenomenon was investigated by W. Ostwald, A. Smits and C. A. L. de Bruyn, E. S. Hedges and J. E. Myers, A. Adler, E. S. Hedges, R. S. Lillie, and C. Fredenhagen.

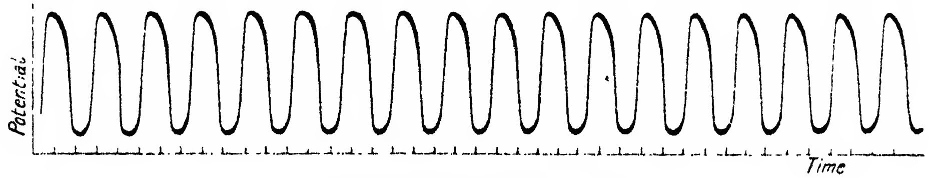

FIG. 406.—Periodic Passivity.

R. S. Lillie showed certain analogies in the activation of passive iron and an irritable and conducting living element like a nerve fibre or a muscle-cell. Thus, when passive iron wire is dipped into nitric acid of a concentration above a certain critical concentration, the activation is only temporary, and is followed immediately by an automatic return of the metal to the passive condition. Activation initiated at any part of such a wire is thus transmitted rapidly along its whole length in a wave-like manner, each region as it becomes active activating the region adjoining, and immediately becoming passive again itself. In order to maintain activity in the living system, constant repetition of stimulation is necessary, and, similarly, chemical activity in a passive wire immersed in nitric acid (sp. gr. 1·42) is an automatically self-limiting process, which can be maintained only by repeated contacts with the activating metal. After a wire has been activated in the usual manner, and has reverted to the passive state, it is found to be impossible to reactivate it until a definite interval of time has elapsed.

G. Wetzlar could not detect any influence by a magnetic field on passive iron, but, according to E. L. Nichols, E. L. Nichols and W. S. Franklin, and T. Andrews, magnetization is also an activating agent, for magnetized steel bars are less passive in warm nitric acid than unmagnetized ones. Thus, T. Andrews found that iron which remained passive in nitric acid of sp. gr. 1·42 up to 90°, became active at 51° when placed in a magnetic field. H. G. Byers and co-workers also observed that the current density required to make iron passive is increased when in a magnetic field. Thus, with 5 per cent. nitric acid, and with hard steels, the current densities in milliamps. per sq. cm. required to make the iron passive without a magnetic field were respectively 382 and 411; with a current for the N-pole, respectively 426 and 466; and with a current for the S-pole, respectively 454 and 503. Hence, soft steel is affected to a greater extent than hard steel; and the positive pole of a magnet is more easily rendered passive than is the negative pole. H. Eggert observed that the anodic behaviour of iron in non-aqueous electrolytes is similar to what it is in aq. electrolytes. Z. C. Mutaftschieff observed that the rate of attack of iron by nitric acid of sp. gr. 1·39 to 1·41 is not affected by the application of magnetic field, but with acid not sufficiently concentrated to effect passivation, the rate is much increased. G. Berndt, T. Gross, R. S. Dean, and U. Sborgi and A. Borgia also studied the effect.

It is probable that most of the metals may be passivated under suitable conditions, for the phenomenon has been recorded with the metals tin, lead, cadmium, zinc, magnesium, silver, copper, tungsten, molybdenum, uranium, platinum, ruthenium, gold, manganese, vanadium, columbium, tantalum, bismuth, chromium, aluminium, iron, cobalt, and nickel. The most satisfactory theory to account for the passivity of iron assumes that it is due to the formation of a superficial film of a product of the action of oxygen on the metal. This, said M. Faraday, fits in with the general observation that the passive state is produced by oxidation processes; that iron coated with oxide is insoluble in acids; and that the passive condition disappears when the metal is polished. In 1836, in reply to a letter from C. F. Schönbein, M. Faraday wrote:

> My strong impression is that the surface of the [passive] iron is oxidized, or that the surface particles are in such relation to the oxygen of the electrolyte as to be equivalent to oxidation; and having thus their affinity for oxygen satisfied and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface and no reiteration of the attraction of the successive particles of iron on the elements of successive particles of the electrolyte.

G. T. Fechner, in 1828, tried and rejected the hypothesis that the passive state is due to the formation of a protective insoluble film; and C. F. Schönbein contested M. Faraday's explanation chiefly on the ground that the passive state persisted in dil. nitric acid which would be expected to dissolve a film of any known oxide if it were formed. M. Faraday, however, pointed out that his explanation had been misunderstood, for he meant *not an actual oxidation but a relation*; a delicate equilibrium of forces where there is association without combination. R. Borchers suggested that passivity is produced by the combination of oxygen atoms with surface iron atoms, but B. Strauss failed to obtain any evidence of the formation of such a layer. E. Ramann assumed that the film is ferrosic oxide which dissolves in dil. but not in the conc. nitric acid; H. L. Heathcote found that the reverse is true of ordinary ferrosic oxide. The nature of the blue film which forms on iron which has been heated to about 290° approximates nFeO.Fe_3O_4, as indicated elsewhere. C. E. W. Belck observed that rods heated 15 mins. in air are passive to nitric acid of sp. gr. 1·2, and to a soln. of copper sulphate. F. Haber and F. Goldschmidt suggested that the film is composed of an oxide $Fe_2O_3.2Fe_3O_4$, which is an electrical conductor. H. L. Heathcote showed that highly polished rods, kept cool during the polishing, always show a dulling of the surface when immersed in conc. nitric acid. The oxide film hypothesis was favoured by H. S. Allen, T. Andrews, W. Beetz, C. W. Bennett and W. S. Burnham, W. R. Dunstan and J. R. Hill, O. Eisenhut, U. R. Evans and co-workers, F. Flade, C. Fredenhagen, H. Freundlich and co-workers, H. Gautier and G. Charpy, F. Goldmann and E. Rupp, C. M. Gordon and F. E. Clark, G. Grube, F. Haber and co-workers, H. L. Heathcote, E. S. Hedges, N. A. Izgarischeff, W. Kistiakowsky, P. Krassa, B. Lambert, E. Liebreich and W. Wiederholt, L. McCulloch, W. Manchot, W. D. Richardson, E. Pietsch and E. Josephy, F. J. Micheli, E. Müller and F. Spitzer, W. Muthmann and F. Frauenberger, H. M. Noad, E. Ramann, E. K. Rideal, W. Rollmann, R. Ruer, E. P. Schoch, L. Tronstad, G. Wetzlar, G. Wiedemann, and H. Wieland and W. Franke.

W. J. Müller and J. G. Königsberger found that the reflecting powers of iron mirrors are always the same when they have been immersed in alkaline soln., both in their natural condition, and when polarized anodically and cathodically. This was taken to prove that the passive state is not due to the formation of a film of oxide; but A. Findlay showed that the argument breaks down because a film of molecular dimensions might suffice to produce passivity, a thickness of the order of the wave-length of light would be required to affect the reflecting power of the metal. H. Freundlich and co-workers have shown that the optical properties of passive iron are not the same as those of active iron. On admitting oxygen to the surfaces of mirrors of pure iron, a sudden change occurs in the phase relations of the two components of elliptically polarized light reflected from the metal. This is attributed to the formation of a film of oxide. The chemical activity of the iron at the same time is reduced so that the iron becomes unaffected by nitric acid of concentrations which have a marked action on iron mirrors if introduced before the admission of oxygen. H. Freundlich and co-workers, F. Förster, E. Liebreich, I. Langmuir, G. Patscheke, L. Tronstad, and H. S. Allen also showed that the surface of passive and active iron have different optical properties, although E. Becker and H. Hilberg could not find much difference. H. S. Allen found that dry active iron exhibits a considerably higher photoelectric activity than the metal which has been passivated by immersion in conc. nitric acid, or by anodic polarization in dil. sulphuric acid. He said that this is in agreement with the assumption that the cause of passivity is to be found in the condition of the gaseous layer at the surfaces of the metal. Analogous results were obtained by W. Frese. H. L. Heathcote said that the assumption that passivity is produced by a protective film of gas does not explain how dry passive iron, rubbed lightly with cotton-wool, can retain its passivity in vacuo. W. J. Müller, W. J. Müller and W. Machu, and W. Machu discussed the effect of a surface film on the potential of a metal. E. Liebreich and W. Wiederholt measured the anodic and cathodic behaviour of iron in 1·0 2N-H_2SO_4 and found discontinuities corresponding with passivity which were explained by the formation of a film of a higher oxide. C. Benedicks and P. Sederholm, and H. Hauschild made observations on surface films. E. Rupp and E. Schmid studied the reflection of electrons from passive iron but could not identify the film which is formed with films of hæmatite or magnetite. J. Gillis, and F. Krüger and E. Nähring examined passive iron by the X-ray method and concluded that films of oxide thicker than 10^{-7} cm. are not present on the surface of the passive metal. This argument is not of much weight when it is remembered, as pointed out by U. R. Evans, that it is highly improbable that films of this order of magnitude would produce the oxide lines in the X-radiograms. The formation of invisible films of oxide on the surface of iron, etc., has been demonstrated by W. H. J. Vernon, H. S. Allen, W. Frese, E. Liebreich, W. Kistiakowsky and I. V. Krotoff, A. L. Bernoulli, T. Fujihara, and F. H. Constable. L. Tronstad added that the film of oxide on passive iron is not totally destroyed on activation, but it becomes porous and spongy; on re-passivation, the holes are refilled with oxide, and the film becomes thicker. The film has an index of refraction of about 3·0, and is about 30 A. thick. The partial destruction of the film on activation is more pronounced on the grains of ferrite than on the grains of cementite. W. Boas and E. Rupp found that iron of passive state yields several electronic beams in addition to those shown by iron in the active state. F. P. Bowden and E. K. Rideal found that the true surface area of metals greatly exceeds the apparent area, especially after abrasion or similar treatment, presumably owing to the opening of innumerable fissures on the surface.

U. R. Evans and co-workers also studied the distribution of the oxide films on such surfaces. U. R. Evans said:

> The ferric oxide film usually present on iron is rapidly destroyed by dil. sulphuric acid owing to the formation of the circuit: Fe | Acid | Oxide; the ferric oxide suffers cathodic reduction to ferrous oxide which is rapidly dissolved by the acid. If the reduction is prevented by the presence of an excess of chromic acid, or by anodic treatment of the specimen as a whole, the film can remain in contact with 0·1M-H_2SO_4 for hours without change. This explains why iron can remain passive in acidic soln. during anodic treatment. The explanation of anodic passivity in acid soln. is as follows. When lead is anodically treated in sulphuric acid, the conversion of the metallic surface into sulphate will protect the metal below, but with an iron anode this will only occur when the liquid has locally become saturated with ferrous sulphate. At that stage, any further current must be expended on the production of oxygen, and although the bubbles stir the liquid, dispelling the saturated layer, the metallic surface may in the meanwhile have been converted into ferric oxide, which will protect the metal so long as the current continues to flow. Indeed, a short interruption of current can also be tolerated without resumption of activity, and this seems to depend on the presence of an oxygen supercharge, which prevents reduction to the rapidly-soluble, lower oxide.

U. R. Evans also observed that:

> The film produced by oxidizing agencies on metals necessarily ceases to thicken as soon as it becomes sufficiently protective to exclude the oxidizing agent. The considerable thickening of the film which occurs on freshly abraded iron proceeds through the production of cracks due to the internal stresses left by the abrasion; only when this cracking of the film has ceased will the thickening come to an end. Since a cracked film produces no passivity, coarsely ground metal requires a longer time to become passive than finely ground metal, and develops a thicker film, especially if substances be present in the solution which are capable of penetrating the smallest cracks (*e.g.* chlorine ions). The films obtained from abraded specimens attain thicknesses of the order 10^{-6} cm., and can be isolated from their bases and studied. In the presence of a regulated amount of penetrating anions, the thickness may come to exceed 4×10^{-6} cm., and the films will then give rise to interference tints. Great thickening is only to be obtained under conditions which render the material less perfectly protective, and there is naturally some danger that the film will break down altogether. Under suitable conditions, however, considerable thickness may be reached. Specimens were prepared showing the complete sequence of interference tints right up to the late second-order colours; although produced at room temp., the sequence of colours is the same as that of the temper colour obtained at high temp. and the tints are, on the whole, brighter.

According to W. Manchot, 3 per cent. ozone in the cold acting on the surface of a metal covered with a thin film of oxide, produces a visible deposit of oxide. This occurs with iron which has been passivated by immersion in nitric acid, or anodically in dil. sulphuric acid, which instantly reacts with the ozone showing that its surface is coated with oxide; but active iron shows no such sensitiveness towards ozone. E. Müller and F. Spitzer found that iron, cobalt, or nickel, when anodically polarized in alkali-lye, becomes coated with the respective oxides, and at the same time becomes passive. They also avoided the presence of the metal by examining the behaviour of platinum electrodes coated with the oxides of the respective metals. These electrodes, on anodic polarization, behaved like passive electrodes of the metals themselves. All this is in agreement with the assumption that the passivity of the metals is produced by a coating of oxide.

F. Haber and F. Goldschmidt showed that iron rendered passive by anodic polarization in alkaline soln. without losing its metallic lustre, becomes coated with a layer of hydroxide on adding halogen ions. F. Haber and W. Maitland found that a very conc. soln. of alkali renders passive iron active and that it acts by dissolving a superficial film of oxide. P. Krassa showed that in boiling conc. alkali soln. polarization of the iron is followed by the anode becoming passive; and the passive state is preceded by the formation of a visible coating on the metal. G. Grube found that in the electrolytic oxidation of ferrocyanides, anodes of iron, nickel, cobalt, copper, lead, and silver in neutral soln. of potassium ferrocyanide and ferricyanide, and anodes of iron, lead, silver, and zinc in alkaline soln. of the same salts, become strongly passive owing to the formation of an insoluble coating on the anode. In some other cases there was no evidence of the formation of an insoluble film, and passivity was ascribed to an oxygen charge retarding the liberation of the cations of the metal. E. S. Hedges concluded that passivity produced by anodic polarization and by chemical means is the result of the formation of a film of oxidized material.

W. Ostwald said that none of the known oxides can produce passivity, and therefore unknown oxides must be unstable because of the ease of the transition from the passive to the active state. According to C. W. Bennett and W. S. Burnham, the various objections which have been made to the oxide-film hypothesis do not apply if it be assumed that an unstable oxide is formed during the passivation of iron, and that this oxide becomes stable when it is absorbed by metallic iron. The surface film of the adsorbed unstable oxide protects the metal from the action of the acid. The increase in the stability of the oxide through adsorption is compared with the effect of sodium hydroxide on a boiling soln. of copper sulphate containing a small amount of manganese sulphate; a precipitate of blue copper hydroxide, $Cu(OH)_2$, is obtained. Cupric hydroxide is probably precipitated if the manganese salt be omitted, but it is decomposed so quickly that cupric oxide, CuO, alone appears as the product of the reaction. The manganese salt, if it be present, is absorbed by the cupric hydroxide which thereby becomes stable under conditions where it would be decomposed if alone. C. W. Bennett and W. S. Burnham said (i) a considerable amount of oxide may be adsorbed without its changing the appearance of the surface. Iron becomes passive when dipped in a soln. of potassium ferrate, and it is assumed that the unstable oxide which produces passivity cannot be higher than FeO_3, and possibly is FeO_2. C. Fredenhagen also noticed that passive iron anode yields a substance which evolves oxygen when chlorides are present. This may be due to the hydrochloric acid formed at the anode reacting with the higher iron oxide to furnish oxygen. Active chromium becomes passive in soln. of chromic acid or sodium chromate, and as in the case of iron in a soln. of potassium ferrate; it might be inferred that the oxide formed on the chromium cannot be higher than CrO_3; but CrO_3 is soluble in the liquid, and therefore C. W. Bennett and W. S. Burnham infer that the unstable oxide is CrO_2, which, on adsorption by the metal, makes the chromium passive. When lead is passivated by making it the anode in an electrolyte of dil. sulphuric acid, the film of lead dioxide, PbO_2, is stable, visible, and unquestioned. U. R. Evans and co-workers showed that the passive film after it has been separated from passive iron, consists of ferric oxide or in part of hydrated ferric oxide with some metal inclusions. W. D. Bancroft, and D. R. Hale found that iron rendered passive by anodic treatment has at first a high potential due to a surcharge of oxygen which may be present as an unstable higher oxide, but A. Smits pointed out that when the iron is allowed to stand, its potential sinks with a marked arrest at about $E_H = 0.54$ volt. Hence, added L. C. Bannister and U. R. Evans, if the original high value is due to a higher oxide, the arrest represents the formation of ferric oxide; the electrode potential is an unsatisfactory test for the oxygen-content of a solid phase; and a higher oxide is not necessary for explaining passivity. W. J. Müller and W. Machu discussed the nature of the films on passive iron. The oxide-film hypothesis of passivity was opposed by G. T. Fechner, C. Fredenhagen, W. Hittorf, F. Krüger and E. Nähring, B. Lambert, M. Martens, W. J. Müller and J. Königsberger, M. Mugdan, W. Muthmann and W. Frauenberger, J. M. Ordway, W. Rathert, and C. F. Schönbein.

In W. Hittorf's so-called *experimentum crucis* to prove that the passivity of chromium is not due to a solid film of oxide, it was shown that chromium becomes passive when made the anode in a soln. of potassium iodide. The experiment is not really decisive, because the hydrogen liberated at the cathode does not reduce the film of chromium oxide which is probably formed on the chromium anode by depolarization of the oxygen present. Adsorption is usually decreased with rise of temp., and the liberated oxide being unstable when freed, is accordingly liable to decomposition. The gradual adsorption of the oxide would give a smooth voltage-current curve free from breaks, since the corresponding e.m.f. would vary continuously from that of metallic iron to that of the adsorbed oxide. The oxide film is not reduced by air, it merely decomposes liberating oxygen, just as many substances liberate oxygen when they are oxidized to higher oxides which decompose readily back to the original oxide. The instability of wet passive iron in air or in vacuo is due to the gradual soln. of the adsorbed oxide in the liquid film; a dried piece of passive iron is comparatively stable, for it can be kept indefinitely. Instead of assuming that the passivity of iron is produced by a film of oxide, others have suggested that a film of oxygen, or a film of a solid soln., or something less definite than the oxide is formed. This view was taken by H. G. Byers and S. C. Langdon, F. Flade, C. Fredenhagen, G. Grube, E. Jordis, I. Langmuir, W. Muthmann and F. Frauenberger, G. Osann, P. de Regnon, E. Pietsch and co-workers, G. M. Schwab and E. Pietsch, I. N. Stransky and Z. C. Mutaftschieff, and G. Tammann.

According to H. O. Forrest and co-workers, the resistance of the stainless chromium steels involves the building up of an insoluble oxide film on the surface of the metal. This film is dense, adherent and not penetrated by the corroding medium, so that it protects the metal from further attack. The rate of attack by oxygenated water during the initial period before the protective film is formed, was found to be of the same order of magnitude with 18·8 per cent. chromium-nickel steel, a 14 per cent. chromium steel, and an ordinary steel. B. Strauss, and R. Borchers attributed also passivation to the union of oxygen with the surface atoms of iron.

E. St. Edme suggested that the film formed during the passivation of iron by nitric acid is iron nitride, not oxide. F. Hanaman discussed the passivity induced by nitridizing the surface of iron by heating it in ammonia gas. A. L. Bernoulli, S. W. Young and E. M. Hogg, A. Mousson, L. Varenne, and C. Fredenhagen said that a surface film of nitrous acid or nitric oxide will make iron passive. W. Beetz, C. F. Schönbein, E. Ramann, and M. Bibart did not agree.

S. W. Young and E. M. Hogg regarded the passive state as the result of a condition of equilibrium between iron and nitrogen peroxide—*vide supra.* When iron is passivated in nitrogen peroxide, a weighable amount of the gas is absorbed by the iron, and on exposure of the passivated iron to moist air, drops of acid liquor are formed on the surface. Iron is capable of absorbing nitrogen peroxide from any soln. in which it is being produced, and the rate of reaction is thereby inhibited. The degree of inhibition will therefore be determined by the concentration of nitrogen peroxide which it is itself capable of maintaining. Since iron passivated by dry nitrogen peroxide is more persistently passive than that which is passivated in nitric acid, it seems probable that the amount of nitrogen peroxide absorbed by iron from even conc. nitric acid is relatively quite small.

C. Fredenhagen said that the passivity produced by anodic polarization in sulphuric acid is different from the passivity produced by immersion in conc. nitric acid, and he suggested that the passivity in the former case is produced by a layer of oxygen gas, and in the latter case, by a layer of nitric oxide. M. Mugdan also attributed the resistance of iron to conc. sulphuric acid to the passivation of the metal; he found that when opposed to the hydrogen electrode, the potential of soft iron in dil. sulphuric acid is 0·2 to 0·3 volt, and in the conc. acid, 0·04 volt; with cast iron the potential is −0·1 volt.

M. P. Appleberg and S. H. Wilkes, and L. McCulloch attributed some cases of passivity to the presence of a sparingly-soluble sulphate film. J. A. N. Friend supposed that the passivity produced by chromic acid is due to the formation of a film of a chromate which is soluble in a soln. of sodium chloride. H. Braconnot, and M. Boutmy and M. Chateau assumed that the passivity in conc. nitric acid is due to the insolubility of iron nitrate in that menstruum, but A. Scheurer-Kestner showed that the extent of saturation of the soln. of iron nitrate in conc. nitric acid, of varying concentration, had no influence on the result. C. Tomlinson, in his work in *catharism*—or the influence of chemically clean surfaces—said that there is no apparent difference between the adhesion of gas on chemically clean surfaces, and the liquid that holds the gas in soln. Conc. nitric acid is a powerful catharizer, and by making the surface of the iron chemically clean enables the acid to adhere to it with force. The formation of a nitrate is prevented because nitrates of iron contain at least 6 eq. of water of crystallization, and this is not present in the stronger acid.

O. Sackur assumed that every electrode contains a certain amount of dissolved hydrogen formed by the interaction of H'-ions in the electrolyte. The H'-ion concentration corresponds with the equilibrium: $M+2H^{\cdot}=H_2+M^{\cdot\cdot}$ for a bivalent metal. The discharged anion—oxygen, halogen, etc.—reacts with and removes the hydrogen. To re-establish equilibrium the reaction proceeds in a direction from left to right, so that the anodic dissolution of the metal is supposed to be a chemical process. Passivity is produced by a slow rate of reaction between the hydrogen and the discharged anion, so that the latter—oxygen, etc.—accumulates on the electrode. Other forms of this hypothesis were suggested by F. Haber and J. Zawadsky, M. le Blanc, E. P. Schoch and co-workers, C. Fredenhagen, H. Kreusler, W. Muthmann and F. Frauenberger, D. Reichinstein, F. Förster, E. Grave, J. Stapenhorst, A. M. Hasebrink, and G. C. Schmidt.

A. Finkelstein attributed the active state to ferrous iron, and the passive state to ferric iron. The inference was based on the change in the electrode potential of iron in mixed ferric and ferrous chloride soln. as the relative proportions of the two salts varied. He regarded ordinary iron as a mixture of ferrous and ferric, whilst ferric iron was considered to be a noble form of the metal produced by a process of oxidation in the passivifying liquid. The ordinary contact e.m.f. measurements place iron near tin in the Volta series, and electrolytic measurements place it near tin in the electrode potential series. This makes ordinary iron appear to be in the ferrous state. According to J. G. Brown, the general chemical properties of iron are more like platinum than tin, and it is more likely that ordinary iron is essentially ferric, and passive, while active iron is ferrous, and the conditions surrounding the surface of ordinary iron are such that when dissolving, it sends ferrous ions into soln. A similar hypothesis was favoured by H. Westling, and W. J. Müller. R. Müller represented the activation of iron as involving the electronic change $Fe\rightleftharpoons Fe^{\cdot\cdot}+2\epsilon$, and the passivation, $Fe\rightleftharpoons Fe^{\cdot\cdot\cdot}+3\epsilon$, so that the change from the active to the passive state is represented by the equation: $Fe^{\cdot\cdot}\rightleftharpoons Fe^{\cdot\cdot\cdot}+\epsilon$. J. B. Senderens, A. Skrabal, J. S. de Benneville, and W. Hittorf seem to have believed that the passive state is produced by the formation of a surface layer of allotropic iron.

There are many references in which the passive state is vaguely attributed to a physical alteration of the surface of the iron. G. Wetzlar attributed the passivation of iron to the assumption of a negative electrical state by the part immersed, while the part not immersed assumes the positive state; J. F. W. Herschel, to a permanent electrical state of the surface of the metal; J. M. Ordway, " to a molecular change induced by momentary electric action set up on first contact of the acid with the metal "; J. F. Daniell, to a change in the relation of the metal to hydrogen and oxygen, possibly as a result of some difference in mechanical structures; J. H. Andrew, to the potential difference between the hydrogenized, amorphous, intercrystalline cement, and the hydrogenized, crystalline phase; and G. C. Schmidt, to the change in the surface tension of the solid metal.

In the electronic theory of A. S. Russell, it is assumed that the orientations of the electrons in the active and passive metal are different. The subject was discussed by I. N. Stransky and Z. C. Mutaftschieff, W. D. Lansing, R. Swinne, U. Sborgi, and A. Smits. M. le Blanc assumed that active iron sends ions into the electrolyte, and that in the case of metals which tend to become passive, these ions combine only very slowly with water: Ion+water⇌Ion hydrate. Accordingly, the concentration of free ions at the electrode becomes so great, and the potential difference between electrode and soln. becomes so large, that the discharge of anions or of oxygen begins. This hypothesis of passivity is based on the observation that even when the ion concentration at the electrode is sufficiently large, polarization occurs both at the anode and cathode in many cases where it was not previously suspected. To explain the facts, a difference between free and hydrated ions is postulated, and it is assumed that the hydration and dehydrations of ions is a relatively slow process.

In the so-called *internal equilibrium theory*, A. Smits assumed that in addition to uncharged atoms and free electrons, iron contains two kinds of ions of different valency—α, or base ions, and β, or noble ions which are in equilibrium. The passive state is assumed when the state of equilibrium is disturbed. During the anodic dissolution of the metal, polarization occurs because the α-ions dissolve more rapidly than equilibrium can be established, and the β-ions collect on the surface of the metal and so make it passive. It also explains why passivity is a surface phenomenon. Ordinary iron always contains hydrogen, and $H^{\cdot}$-ions, like halogen ions, greatly accelerate the change from the passive to the active states, *i.e.* they catalytically accelerate the conversion of α- into β-ions until equilibrium is established. In the anodic soln. of iron, when the current density is such that oxygen is evolved at the anode, all the hydrogen ions, normally present in ordinary iron, are expelled from the surface, and the disturbance of the state of equilibrium between the α- and β-ions reaches a maximum, and the metal becomes passive. The hydrogen soon diffuses from the interior to the surface where it catalytically accelerates the re-establishment of equilibrium, and the metal becomes active again. When iron is immersed in conc. nitric acid, the α-ions dissolve with great rapidity and $H^{\cdot}$-ions are removed from the surface of the metal so that the passive condition is established; with a soln. of ferrous chloride, α-ions dissolve rapidly but passivity is not produced because both the chlorine ions and the halogen ions catalytically accelerate the change from the passive to the active state, and β-ions never accumulate on the surface to produce the passive state. The subject was discussed by H. Gerding and A. Karssen.

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§ 27. Alloys and Intermetallic Compounds of Iron.

> It was recommended by C. Hatchett (1803) that a systematic examination of all alloys of metals should be carried out, proceeding from the most simple binary ones to more complicated ternary or quaternary ones. He can hardly have been aware of the extent of his proposed inquiry. If we operated upon only thirty of the known metals, the number of possible selections of binary alloys would be 435, of ternary alloys, 4060, of quaternary, 27,405, without paying any regard to the varying proportions of the metals, and only regarding the kind of metal. If we varied all the ternary alloys by quantities not less than 1 per cent., the number of these alloys would be 11,445,600.—W. S. Jevons.

J. L. Gay Lussac and L. J. Thenard,[1] and J. H. Hassenfratz obtained an **iron-potassium alloy** in preparing potassium by the action of iron filings on potassium hydroxide, where the vapour of potassium happens to come into contact with the iron in the cooler part of the furnace. The alloy is said to be whiter than iron, malleable, and so soft that it will take an impression from the nail. It is also more fusible than iron ; oxidizes in air ; and effervesces with water and dil. acids. C. Girard and J. Poulain obtained an **iron-sodium alloy** or iron-potassium alloy by exposing molten cast iron to the vapours of the alkali metals at 5 to 6 atm. press. The same alloys were obtained by the action of sodium or potassium chloride or carbonate on heated iron ore, fuel, and flux. E. K. Smith and H. C. Aufderhaar discussed the iron-sodium alloys. F. C. Calvert and R. Johnson obtained what they regarded as **potassium triferride**, KFe_3, by heating a mixture of 12 gram-atoms of iron filings, 16 gram-atoms of potassium tartrate, and wood-charcoal in a crucible. The regulus is hard, but it may be hammered and rolled. It is difficult to file. It readily oxidizes in air, and under water. If the charcoal be omitted from the mixture, F. C. Calvert and R. Johnson said that **potassium diferride,** KFe_2, is formed. These observations all require extending and confirming. P. Oberhoffer discussed the binary alloys with the alkali metals. N. Ageeff and M. Zamotorin studied the diffusion of lithium into iron; and J. E. Hurst, the effect of sodium and potassium on cast iron.

Several reports of the analysis of ancient copper figures show the presence of appreciable quantities of iron. Thus, D. Forbes [2] obtained for a statue of Buddha, probably dating from about 900 B.C., found in the remains of a temple at Sooltangunge, on the Ganges: copper, 91·502 per cent.; iron, 7·591; silver, 0·021; gold, 0·005; traces of manganese and nickel; arsenic, 0·079; sulphur, 0·510; and slag, 0·292— sp. gr. 8·29 at 15°. The statue was probably cast from crude or unrefined copper, and was not an intentional alloy. H. Struve obtained from an ancient ornament of sp. gr. 7·224: copper, 89·7 per cent.; iron, 9·1; and tin, 0·63. R. Budelius, V. A. Skinder, and R. Hunt also described some ancient, ferruginous bronzes from Russia; and W. Flight, an ancient Egyptian, ferruginous bronze. Alloys of iron with more or less copper were examined in a desultory manner from the seventeenth through the eighteenth and nineteenth centuries; and from published work over that period, it is impossible to form a clear idea of the influence of copper on iron and steel. J. E. Stead has collected a number of statements, mainly from different metallurgical textbooks, which emphasize the extreme views held by different writers on the subject. L. Savot (1627) referred to some properties of the **copper-iron alloys**; and G. Jars (1774) mentioned alloys containing about 1 per cent. of copper. T. Bergman made experiments on some alloys of copper and iron with and without arsenic, in an attempt to synthesize nickel. C. J. B. Karsten observed that iron can take up only a very small proportion of copper, and copper, only a very small proportion of iron. M. Faraday and J. Stodart examined some alloys, and their properties were measured by R. A. Hadfield. J. Riley said that when the two metals are melted together, the copper and iron separate from one another on cooling, but a perfect alloy is formed if aluminium be also present. F. L. Garrison found that 5 per cent. of copper will alloy with steel, but he doubted if a perfect alloy could be obtained with 10 per cent. of copper. J. O. Arnold believed that free copper was present in iron containing 1·81 per cent. of copper. H. Schneider patented alloys of cast iron with 5 to 20 per cent. of copper; while D. Mushet found that malleable iron can be alloyed with any proportion of copper until it equals or even exceeds the weight of copper. When steel is alloyed with 5 per cent. of copper, he said that none could be detected on the surface or on the fracture; with 10 per cent. of copper, streaks of copper appear on the fractured surface; and with 33·3 per cent., some of the copper segregates at the bottom of the ingot. The solubility of copper, in iron, decreases as the proportion of carbon in the iron increases. D. Mushet, J. E. Stead, P. Breuil, H. Wedding, and W. Müller also noted that the presence of carbon depresses the solubility of copper in iron. W. von Lipin found that grey Swedish pig-iron could be alloyed with 5 per cent. of copper; iron with 0·13 per cent. of carbon dissolved 3·2 per cent. of copper; and iron with 0·43 per cent. of carbon dissolved less than 2 per cent. of copper. E. J. Ball and A. Wingham prepared alloys of steel with 0·8 to 7·17 per cent. of copper; and J. E. Stead and J. Evans, steel with 0·5 to 1·3 per cent. of copper. V. O. Pfeiffer stated that when mixtures of iron and copper are melted in a magnesia crucible in an electric furnace, there is no depression of the f.p. of either iron or copper. Microscopic examinations of the products indicates that iron and copper are mutually insoluble, and that the supposed alloys are really solidified emulsions; the sp. gr. of the two fused metals being nearly equal, and the viscosity of the iron considerable, separation into two layers takes place, only very slowly. When sufficient time is allowed for the separation, the copper layer is found to be free from iron. In a similar manner, copper and iron-carbon alloys are found to be mutually insoluble, although finely emulsified mixtures are readily obtained. P. Breuil said that castings containing less than 4 per cent. of copper show no segregation no matter what per cent. of carbon is present; steels with 0·103 to 0·173 per cent. of carbon showed no segregation with 32 per cent. of copper; steels with 0·282 to 0·798 per cent. of carbon gave a high segregation with 32 per cent. of copper—the lower part of an ingot contained 24·4 per cent., and the interior 74·8 per cent. A. Riche also obtained a homogeneous alloy with 4·5 per cent. of iron; but if the alloy be kept molten for some time, the iron tends to accumulate in the upper layers. T. W. Hogg observed no signs of the segregation of copper in steel containing 0·05 per cent. of carbon; and W. Müller, no signs of separation with 7·7 per cent. of copper in iron with 0·14 per cent. carbon and 0·09 per cent. of sulphur. J. E. Stead added that some of the conflicting statements on the effect of copper on iron have arisen through overlooking the effect of carbon in preventing the two metals alloying. Pig-iron alloys with only a small quantity of copper, whereas purified iron will alloy with any proportion.

Alloys of the two metals were obtained by direct fusion by J. Percy, J. E. Stead, R. Sahmen, A. Portevin, and E. Martin; F. H. Wigham, F. Dannert, P. Oberhoffer, and J. Riley obtained the alloy by the simultaneous addition of a small proportion of aluminium; C. Gautsch recommended adding 2·5 per cent. of sodium hydrocarbonate when the two metals are being alloyed. D. Mushet obtained alloys by reducing iron-copper pyrites; F. Mahla heated a mixture of cupric and ferric oxides to redness in a stream of hydrogen; H. Wedding and W. Müller reduced the mixed oxides by the aluminothermic process; J. D. Darling added a mixture of cuprous oxide and calcium carbide to molten iron, or a mixture of ferric oxide and calcium carbide to molten copper; E. Sperry added potassium ferrocyanide to molten copper; G. Wetzlar put a strip of iron in an aq. soln. of cupric tartrate and obtained brownish-black copper-iron, but F. Mylius and O. Fromm could not confirm this.

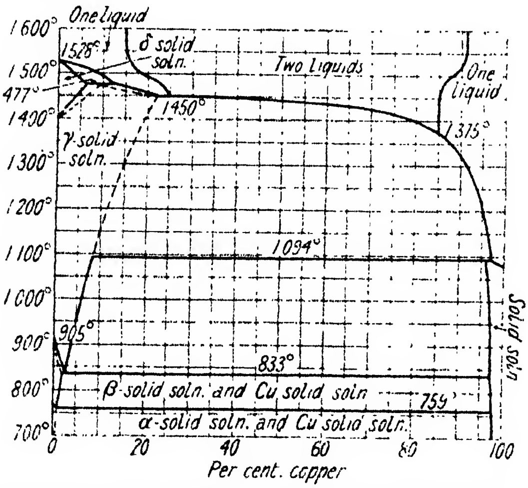


Fig. 407.—Equilibrium Diagram of Copper-Iron Alloys.

P. Siebe observed that iron has no action on electrolytic copper below 1100°, but ordinary "tough pitch" copper with cuprous oxide, is rendered brittle and porous by contact with iron at 750°. This is attributed to the reducing action of hydrogen and carbon monoxide in the iron. F. Sauerwald and E. Jänichen studied the adhesion of the particles of a compressed mixture of powdered iron and copper; and H. E. Diller, and M. I. Zakharova, the diffusion of copper in iron. G. Tammann and W. Oelsen found for the solubility, S per cent., of γ-iron in copper between 850° and 1100°, $\log S = -3792T^{-1} + 3{\cdot}392$; and for $\alpha\beta$-iron in copper between 630° and 850°, $\log S = -4003T^{-1} + 3{\cdot}574$. It was found that

	γ-iron				αβ-iron			
	1070°	980°	885°	852°	852°	770°	680°	630°
S . .	3·68	2·35	1·34	1·04	1·04	0·54	0·22	0·14

and by extrapolation at 200°, $S = 0{\cdot}0000127$, and at 20°, $5{\cdot}9 \times 10^{-11}$. W. Köster represented the solubility of copper in α-iron by Fig. 408. The solid solubility of copper in α-iron at 0° to 600° is 0·4 per cent., and it then increases in accord with log $S=-4125T^{-1}+4{\cdot}32$ to 3·4 per cent. at the eutectoid temp., 810°. P. Siebe, F. Roll, and F. P. Zimmerli studied the action of copper on iron at a high temp. According to R. Sahmen, V. O. Pfeiffer is wrong in his deductions on the nature of the alloys. The equilibrium diagram shows that there are two series of solid soln. with 0 to 3·5 per cent. and 97·3 to 100 per cent. of copper, respectively; and the break in the cooling curve of alloys with 3·5 to 97·3 per cent. of copper shows that the alloy solidifies to a conglomerate of mixed crystals. By gradually adding copper up to 4 per cent., the transition point of γ- to β-iron is lowered from 878° to 715°, and remains constant on further addition of copper. If, however, the solidified alloy is heated for some time at 900° to 1000° and again cooled, the transition takes place at 790°. The change from β- to α-iron has been followed by magnetic observations. It occurs about 790°, and is not influenced by the presence of copper, so that the latter is not miscible in the solid state with α-iron. R. Ruer and C. Fick found that the f.p. curve of the iron–copper system, Fig. 407, shows that three series of solid soln. are formed, one of which is restricted to a very small range of composition at the copper end. R. Ruer and F. Goerens observed that the f.p. curve is not horizontal but extends from 24 per cent. of copper at 1450° to 70 per cent. of copper at 1375°. R. Ruer and C. Fick observed that two liquid phases are formed, and the separation occurs as soon as carbon is added, even when the quantity is only 0·02 per cent. The action of carbon may be merely a deoxidizing one, removing the films of oxide which hinder intermixture of the two emulsified liquids. Copper retains iron in solid soln. up to between 1 and 2 per cent., whilst the iron-rich solid soln. contains about 20 per cent. copper at 1440°, and a much smaller percentage at lower temp. The magnetic change point is lowered to 760° by copper. R. Ruer and F. Goerens added that on solidification, the iron–copper system behaves as if it were a system with three or more substances and, so far as the observations go, does not fit in with the phase rule. The absorption of impurities during the process of melting, in amount sufficient to explain the phenomena, could not be established. It must therefore be assumed that a mol. complex is formed which, on account of its slow velocity of production and decomposition, plays the part of a third substance, but further confirmation of this view was not obtained. C. Benedicks discussed the apparent breaks in the liquidus curve of iron-copper alloys. L. Nowack, G. Masing, S. Kodama, I. Kotaira, A. Müller, and R. Ruer and J. Kuschmann showed that the limited range of miscibility of the two metals in the molten state cannot be explained away by assuming that it is caused by segregation during solidification. The subject was studied by H. Buchholtz and W. Köster, and E. L. Reed. D. Hanson and G. W. Ford found that solid copper dissolves about 4 per cent. of iron at 1100°, and the solubility falls to less than 0·2 per cent. at 750°. A. Müller observed that when an alloy of equal proportions of the two elements is heated at various temp., the structure of the cold product shows that the lower critical temp. for the immiscibility is about 1520°. Carbon reduces the immiscibility because it is soluble in iron only. F. Ostermann observed that the two elements are miscible in all proportions in the liquid state, that in the presence of carbon, there is a range of temp. within which the two metals are immiscible. On adding manganese,

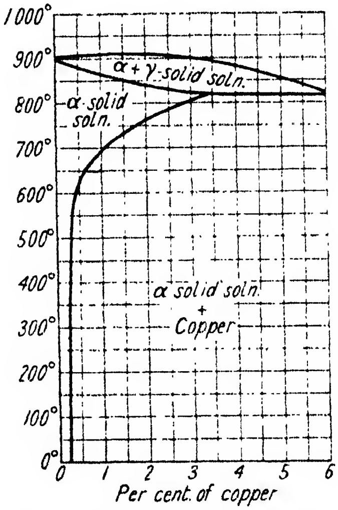


FIG. 408.—The Solubility of Copper in α-Iron.

this range of immiscibility disappears. A. S. Russell observed that where an amalgam of the two metals is exposed to an oxidizing agent, the copper is alone oxidized until the at. proportion becomes Cu : Fe, when both metals are afterwards oxidized at the same rate, in agreement with the assumption that a compound CuFe is formed. A. Müller studied the subject.

According to F. Osmond, as the proportion of copper rises, the arrest A_3 is lowered 40° to 50° in a steel containing 0·847 per cent. of copper; and in a steel with 4·10 per cent. of copper, the arrests A_2 and A_3, coincide at 730° to 720°; whilst A_1 is lowered to 625°–600°. The effect of copper on the allotropes of iron thus resembles that of carbon but to a less degree, and its influence on the recalescence is similar to that of manganese and nickel. The elements may be arranged in two groups: (i) those with at. vols. less than 7·2, the value for iron—*e.g.* C (3·6), B (4·1), Ni (6·7), Mn (6·9), and Cu (7·1); and (ii) those with at. vols. greater than that of iron—*e.g.* Cr (7·7), W (9·6), Si (11·2), As (13·2), P (13·5), and S (15·7). The elements in the first group retard the conversion of β- into α-iron, and that of temper carbon into annealing carbon. Hence, if the rate of cooling is equal, they increase the proportion of β-iron in the cooled metal, and consequently also its hardness; and they are therefore equivalent in effect to a higher or lower degree of tempering. Elements with a higher at. vol. than iron tend to raise, or keep at its normal temp., the conversion of β- into α-iron, and hence they render the reverse change more or less incomplete during heating, and, as a rule, hasten the conversion of temper carbon into annealing carbon. They therefore keep the iron in the α-state at a high temp., and also at a low temp., and their presence in iron would be one cause of softness and malleability, resembling in this respect the operation of annealing, if it were not that their own properties and those of their compounds produce strongly marked secondary effects. P. Breuil also studied the effect of copper on the critical points of steel: (i) With steels having 0·103 to 0·173 per cent. of carbon, no distinct change was observed with the Ar_3 and Ar_2 arrests, when the proportion of copper was below 8 per cent., but above that proportion, there is a long arrest at about 730°; at 740° for steels with 16 per cent. of copper; and at 675° for steels with 32 per cent. of copper. (ii) With steels containing 0·282 to 0·412 per cent. of carbon, the Ar_1-arrest is lowered from 720° to 630° with steels containing 16 per cent. of copper; and with steels containing 0·56 to 0·79 per cent. of carbon, the Ar_1-arrest points all occur between 570° and 600°. A. F. Stogoff and W. S. Messkin found that with copper steels, having 0·7 to 1·2 per cent. carbon and 1 to 5 per cent. of copper, the Ar_1-point is lowered and the temp. interval between the Ar_1- and the Ac_1-points is lowered by increasing the proportion of copper. T. Ishiwara and co-workers studied the ternary system Cu–C–Fe, for alloys with up to 30 per cent. of copper. At 1100° there is an invariant point corresponding with a concentration of 4·3 per cent. C, and 3·3 per cent. Cu at the intersection of the eutectic and monotectic lines. The maximum concentration of the γ-solid soln. is about 3·5 per cent. C and 3·8 per cent. Cu. The eutectoid line starts from the binary iron-copper eutectoid point at 2·3 per cent. Cu and 833° and gradually descends, the copper-content decreasing as the carbon increases. Addition of copper to steel lowers the A_1-transformation point 20° with 2 per cent. Cu; the eutectoid invariant point corresponds with a composition of 0·9 per cent. C, 1·75 per cent. Cu, and 97·35 per cent. Fe at 700°. Saturation of iron with copper to give a uniform solid soln. lowers the A_2-point by about 10°. H. Wedding and W. Müller, H. Buchholtz and W. Köster, A. Carnot and E. Goutal, K. G. Lewis, and M. Hamasumi also made observations on this subject. H. Sawamura, J. W. Donaldson, and F. Roll found that copper decomposes cementite. E. Piwowarsky studied the action of copper in cast iron; C. S. Smith and E. W. Palmer, the precipitation hardness; and G. Masing, the age-hardening of the copper-iron alloys.

According to H. von Jüptner, steel with 3·4 per cent. of copper and dissolved in hydrochloric acid, or an ammonium salt soln. and neutralized hydrogen dioxide, leaves fine, microscopic threads of copper. According to J. E. Stead, the micrographical study of steels containing copper leads to the conclusion that the copper retards the formation of pearlite. The same steels, differing only in copper, under like comparative rapid cooling, when cold, contain more diffused carbide when copper is present than when absent. With very slow cooling, the carbides appear to separate equally well in both the cupreous and normal steels. This peculiarity explains why annealing and slow cooling have the marked softening effect. The growth of the crystalline structure was discussed by R. Kühnel. P. Breuil concluded that the copper steels commercially capable of application are analogous to ordinary steels from the point of view of their micro-structures, but their constituents are finer. The presence of copper increases the quantity of pearlite in the steels, and to some extent it causes the steels to be more highly carburized, and consequently harder. With copper up to 4 per cent., these steels contain no free copper, that element being dissolved in the iron. When the proportion of copper is between 4 per cent. and 8 per cent., saturation occurs ; when over 8 per cent. of copper is present, free copper separates out in fibres in the case of soft or semi-soft steels, and in nodules in harder steels. Liquation is the more noticeable in the ingots in proportion as they contain a high proportion of carbon. When the ingots contain 25 per cent. of copper, liquation is strongly marked, and the ingot is found to consist of two distinct portions, clearly defined. The great hardness of some of these steels after rolling might lead to the supposition that they were martensitic ; but this is not so ; they contain fine-grained pearlite. W. Müller reported that the structure of iron containing copper and sulphide of copper is irregular with respect to the size and joining of the ferrite crystals: the crystals interlock with one another with curved junctions, and this explains the higher tensile strength of iron containing copper as compared with iron containing no copper. The sulphide of copper and the copper itself prevent the formation of pearlite; instead of pearlite, crystals of cementite are formed. The greater hardness of iron containing copper and sulphur is due to this fact. Copper and sulphide of copper distribute themselves mainly between the crystals of ferrite which they envelop, thus affording an explanation of the fact that red-shortness is prevented. In alloys of iron containing 22·2 and 61·7 per cent. of copper, the bulk of the copper is distributed in a similar form surrounding the large crystals of ferrite. In copper containing 7 per cent. of iron it is still possible to discover microscopic traces of copper sulphide, even when the percentage of sulphur is only 0·024. The subject was discussed by J. R. Cain, and W. Herwig.

According to R. Sahmen, the colour of polished surfaces passes continuously from that of iron through various tints to that of copper; and the colour of an alloy with 10 per cent. of iron can scarcely be distinguished from that of copper alone ; an alloy with 20 per cent. of iron has a grey tinge ; and the colour of an alloy with 50 per cent. of iron resembles that of iron but has a pale reddish tinge ; and the colour of an alloy with 70 per cent. of iron cannot be distinguished from that of iron. The fractured surface of an alloy with 85 per cent. of iron is red, because the red crystals of the solid soln. rich in copper are alone fractured, not those rich in iron. Observations on the colour were also made by D. Mushet, J. E. Stead, and P. Breuil. J. H. Carter studied the X-radiograms of the alloys.

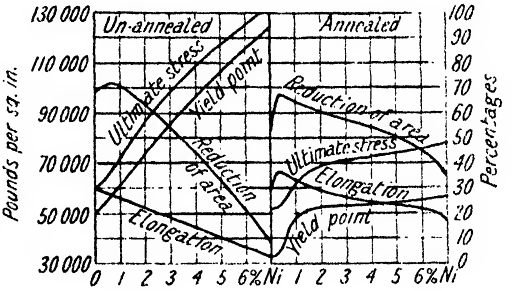
W. Brown said that the addition to iron of up to 1·5 per cent. of copper reduces the sp. vol. of iron 0·0005 c.c. per 1 per cent. of copper, while additions of from 1·5 to 4·0 per cent. have no appreciable effect on the sp. vol. A steel with 0·68 per cent. C ; 0·36, Mn ; and 1·59, Cu, had a sp. gr. 7·8354, a sp. vol. 0·12763, and sp. ht., 0·1180 ; steel with 0·59 per cent. C ; 0·32, Mn ; and 2·50, Cu, had a sp. gr. 7·8366 ; a sp. vol. 0·12761, and sp. ht. 0·1180 ; steel with 0·17 per cent. C ; 1·04, Mn ; and 2·87, Cu, had a sp. gr. 7·8470, a sp. vol. 0·12744, and a sp. ht. 0·1178 ; while steel with 0·04 per cent. C ; 0·16, Mn ; 1·00, Al ; and 3·75 Cu, had a sp. gr. 7·7479, a sp. vol. 0·12907, and a sp. ht. 0·1173. J. O. Arnold made observations on the sp. gr. of the alloy. According to E. Sperry, the addition of 0·75 to 1·0 per cent. of iron hardens copper so that the metal can be sharpened to cut wood. P. Breuil obtained the results shown in Table LV for Brinell's hardness with a steel ball 10 mm. diameter and 3000 kgrms. press. H. Wedding and W. Müller observed that the presence of copper or copper sulphide hinders the formation of pearlite, and promotes the formation of cementite. This helps to explain the greater hardness observed when copper and sulphur are present, but, as C. F. Burgess and J. Aston observed, not in the absence of either copper or sulphur. The subject was discussed by G. A. Roush, A. Kussmann and B. Scharnoff, T. Isihara, G. Tammann, T. Usihara, F. Wever, R. S. Archer, E. K. Smith and H. C. Aufderhaar, K. Taniguchi, C. Pfannenschmidt, W. Buchholtz, and W. Köster; and L. Grenet discussed the hardening of the iron-copper alloys; and M. G. Corson, the ageing of the alloys. R. S. Archer observed no age-hardening with the copper-iron alloys. The viscosity of the alloys was studied by G. Drath and F. Sauerwald.

Table LV.—The Hardness of Iron-Copper Alloys.

Carbon (per cent.)	Copper (per cent.)	Rolled	Reheated	Quenched but not annealed	Quenched and annealed
0·103 to 0·173	0·000	143	124	207	192
	0·490	146	143	311	311
	1·005	146	146	311	277
	2·015	202	174	311	(345)
	3·997	255	183	351	325
0·282 to 0·412	0·000	166	166	460	418
	0·505	202	166	627	460
	1·005	207	196	600	495
	2·025	269	207	817	495
	4·009	302	212	782	782
0·560 to 0·798	0·500	255	228	no mark	555
	0·983	302	223	,,	555
	3·091	418	223	,,	600
	10·500	430	241	,,	782

In 1627, L. Savot mentioned that blacksmiths experience a difficulty in working iron containing copper, so that cupriferous iron cannot be welded; whilst in 1774, G. Jars reported that the general opinion in his time was that *le cuivre est une peste pour le fer,* but that actually small quantities of copper improve the quality of iron, and that even 1 per cent. could be added without destroying the welding power of the metal. C. J. B. Karsten stated that the addition of 1 per cent. of copper sensibly diminished its welding properties; H. H. Campbell, that 0·2 to 0·5 per cent. of copper does not affect the welding properties of wrought iron; A. Ruhfus, that ingot iron which has to be welded should not contain more than 0·3 per cent. of copper, and steel, no more than 0·4 per cent.; while A. L. Colby found that weld steel plates with 0·575 per cent. of copper passed the regulation welding and flanging tests satisfactorily. Hence, J. E. Stead concluded that if much more than 0·4 per cent. of copper is present, the metal will not weld perfectly, but smaller quantities have no detrimental influence. With respect to the effect of copper on the hot working properties of steel, S. Rinman was not very clear whether or not copper produced red-shortness. D. Mushet found that 5 per cent. of copper made steel useless for forging, and the alloy must therefore have been very red-short; C. J. B. Karsten, that 0·5 per cent. did not make malleable iron red-short, but 1 per cent. did; V. Eggertz, that 0·5 per cent. of copper in malleable iron produced only traces of red-shortness, and added that the alloys are good for nothing. M. Faraday and J. Stodart said that the quality of the metal is not improved by adding 2 per cent. of copper. J. R. Bréant added that 2 per cent. of copper makes steel brittle. J. Percy said that copper produced red-shortness; W. Longmaid, that 0·02 to 0·8 per cent. of copper hardened malleable iron without diminishing its toughness; H. H. Campbell, that best steel may contain 0·3 to 0·5 per cent. copper, but with 1 per cent., the metal cracks in rolling; S. Kern, that gun steel may contain 0·27 to 0·36 per cent. copper; A. Willis, that 0·1 per cent. of copper did not produce red-shortness, while 0·3 per cent. caused a slight cracking; M. Choubley, that steel with 0·5 per cent. of carbon and 1 per cent. of copper rolled well; A. Wasum, that steel with 0·23 per cent. carbon was not made red-short by 0·862 per cent. of copper; J. O. Arnold, that steel with 1·81 per cent. of copper rolled well; A. L. Colby, that 0·6 per cent. of copper did not make steel red-short even when the sulphur was as high as 0·08 to 0·10 per cent.; W. von Lipin, that 3 per cent. of copper in steel with 0·13 per cent. of carbon and 0·009 per cent. of sulphur did not produce red-shortness, although with 4·7 per cent. of copper, the metal cracked on hammering; A. Ruhfus, that only when the copper exceeds 0·4 per cent. in ingot iron and 0·5 per cent. in carbon steels does the metal become red-short—provided the sulphur and phosphorus do not exceed 0·05 per cent.; and G. W. Sargent, that if carbon is less than 0·1 per cent. and manganese less than 0·12 per cent., 0·5 per cent. of copper will produce red-shortness. The working properties were also discussed by C. F. Burgess and J. Aston. Hence, J. E. Stead concluded that 0·3 per cent. or even more copper does not produce red-shortness when the sulphur is low.

C. Pfannenschmidt observed that copper augments the bending strength, and the tensile strength of cast iron. C. F. Burgess and J. Aston gave the results summarized in Figs. 409 and 410 for the mechanical properties of the copper-iron alloys. With respect to the influence of copper on the mechanical properties of steel in the cold state, D. Mushet observed that alloys with 50 per cent. of copper possess great strength; steel with 10 per cent. copper is hard and brittle; M. Stengel, that the tenacity of iron is not affected by the presence of more than one-third per cent. of copper; and that the quality of steel is not improved by the addition of copper. M. Krilowsky said that cast iron with 0·25 to 2·0 per cent. of copper is well adapted for casting; it scarcely contracts on solidification; it takes a fine polish, and hardens like steel; its fracture is bright and lamellar, and after slow cooling the fracture is dull and finely granular; it can be readily turned in a lathe; and it is somewhat malleable. The castings as they leave the mould have a continuous, thin layer of copper on the surface. Observations were made by O. von Keil and F. Ebert, F. L. Garrison, A. L. Colby, J. R. Cain, and E. A. and L. T. Richardson. W. Longmaid found that small quantities of copper in malleable iron increased the hardness without decreasing the ductility; F. L. Garrison, that copper in steel sensibly diminishes its tensile strength, but in some cases the metal is improved; E. J. Ball and A. Wingham, that copper increases the tenacity of steel; and H. Schneider, that copper improves the quality of steel. J. O. Arnold found with purified iron, and with steel having 1·81 per cent. of copper and 0·1 per cent. of carbon, the **elastic limit** and tenacity are as follow:



FIGS. 409 and 410.—The Mechanical Properties of Copper-Iron Alloys.

	Elastic limit (tons per sq. in.)	Tensile strength (tons per sq. in.)	Elongation (per cent.)	Reduction of area (per cent.)
Fe	14·39	21·77	47·00	76·50
Cu, 1·81 per cent. .	30·8	34·8	30·5	62·2

H. H. Campbell, for steel with

Cu, 0·10 per cent. . . .	27·4	19·7	27·52	56·30
Cu, 0·35 ,, . . .	26·9	19·6	27·88	59·01

A. L. Colby, for steels with 0·39 and 0·25 per cent. of carbon, and respectively

Cu, 0·553 per cent. . .	17·16	29·25	31·12	51·92
Cu, 0·565 ,, . .	20·64	35·11	24·92	44·67

Observations on cast iron and steel were also made by O. Bauer and A. Sieglerschmidt, H. Buchholtz and co-workers, G. H. Clamer, J. Evans, H. J. French and T. G. Digges, R. Genzmer, R. C. Good, L. Guillet and M. Ballay, D. Hanson and G. W. Ford, J. E. Hurst, F. Johnson, H. B. Kinnear, W. Köster, E. Kothny, F. C. Lea, W. von Lipin, G. Masing, E. Mauer and W. Haufe, W. Mauksch, H. Müller, I. Musatti and G. Calbiani, F. Nehl, Z. Nishiyama, A. L. Norbury, C. Pfannenschmidt, F. Rapatz and H. Pollack, O. Smalley, E. K. Smith and H. C. Aufderhaar, W. H. Spencer and M. M. Walding, J. E. Stead, K. Stobrawa, and A. F. Stogoff and W. S. Messkin. M. Hamasumi found that the addition of up to 1 per cent. of copper increases the strength of cast iron containing 1·87 per cent. of silicon, but proportions between 1 and 4 per cent. had very little influence. A. F. Stogoff and W. S. Messkin found that the hardness, yield-point, and tensile strength of copper steels—with 1 to 5 per cent. Cu and 0·7 to 1·2 per cent. of carbon—increase with increasing proportions of copper with annealed steels, but the elongation, impact strength, and reduction of area reach a maximum with about 3 per cent. of copper. In the case of hardened and tempered copper steels, the tensile strength increases with the copper-content when the structure is hypereutectoidal. Quenched and tempered steels have a high yield-point, and ultimate strength combined with a good elongation and reduction in area. J. E. Stead and J. Evans concluded that between 0·5 and 1·3 per cent. of copper has no deleterious effect on either the hot or cold property of steel; that a large proportion—2 per cent.—makes steel liable to be over-heated; and that on small proportions it raises its tenacity and the elastic limit, but, unlike phosphorus, it does not sensibly make the steel liable to fracture under sudden shock. Like carbon, it reduces the power of steel to extend under stress, but this is not pronounced when the proportion is small. The effect is more marked when large proportions are present. P. Breuil found that the tensile strength of copper steels, as rolled, appears to be greater in proportion as they contain more copper, and the difference is more manifest in proportion as the carbon is lower. Annealing leaves the steels with the same characteristics, but greatly reduces the differences observed in the case of the untreated steels. Quenching restores the differences encountered in the case of cast steels. Copper steels with a tensile strength equal to nickel steels can be obtained. The resistance of copper steels to shock shows that they are no more brittle than nickel steels containing eq. percentages of nickel. The torsion tests give results similar to the tensile strength tests. Copper steels are capable, under torsional stresses, of undergoing a considerable degree of deformation. F. Abbolito studied the resistance to wear.

O. Bauer and H. Sieglerschmidt observed no effect with 0·55 per cent. of copper on the thermal expansion of cast iron, but it reduced the permanent elongation. As indicated above, W. Brown found that copper has very little effect on the sp. ht. of steel with a high proportion of carbon—*vide supra*. J. T. Littleton found for light of wave-length 5893, and alloys with 27·6, 53·4, and 77·6 per cent. of iron, the respective reflecting powers R=52·8, 51·8, and 57·5; the coeff. of absorption k=2·71, 2·96, and 3·41; and the indices of refraction 1·77, 2·24, and 2·62. A. Matthiessen and M. Holzmann observed that the electrical conductivity of copper goes from 93·08 to 34·56 by the addition of 0·48 per cent. of iron, and to 26·95 with 1·06 per cent. of iron; and A. Matthiessen and C. Vogt, that a hard-drawn wire with 0·46 vol. per cent. of iron had a conductivity of 38·852–0·06034θ

$+0{\cdot}0000081280\theta^2$, and between 0° and 100° it falls 13·44 per cent. Observations were made by G. A. Roush, V. O. Pfeiffer, H. Buchholtz and W. Köster, and G. Tammann. The results of C. F. Burgess and J. Aston for the resistance, *R* microhms per cm. cube, are as follow:

Cu .	0·09	0·20	0·42	0·80	1·51	2·01	3·99	5·07	7·05	94·34 per cent.
R .	12·2	12·0	13·6	13·6	14·7	7·0	12·7	12·5	15·8	3·9

P. R. Kosting's results for the sp. resistance, in microhms per cm. cube at 20°, and the temp. coeff. in ohms per ohm per degree, are summarized in Fig. 411. G. Dillner observed that the electrical resistance of iron and steel is augmented by alloying it with copper, but, added M. Fric, the increase extends up to a maximum, expressing the sp. resistance in microhms per sq. cm.:

Copper .	per cent.	0·01	0·05	1·0	2·0	3·0	4·0	10·0
Carbon 0·15	,,	13·81	15·06	16·69	17·46	—	16·71	—
0·35	,,	16·95	17·69	18·78	19·01	—	17·76	—
0·70	,,	20·55	22·03	21·13	—	20·90	—	19·81
1·00	,,	22·58	24·86	24·72	—	24·24	—	—

C. Benedick's rule that the electrical resistance of a steel at ordinary temp. is roughly $R=7{\cdot}6+26{\cdot}8\Sigma C$, where, representing the percentages of the contained elements by their symbols, $\Sigma C=C+(12/28{\cdot}4)Si+(12/63{\cdot}4)Cu+$etc., was found by P. Breuil not to be applicable to copper steels. G. K. Burgess and J. Aston found an increase of 3 to 4 microhms per cm. cube, and R. Ruer and K. Fick, 4·0 microhms for additions of 1 per cent. of copper to iron. W. H. Keesom and co-workers measured the thermoelectric force of the alloys against an alloy of silver and gold; and A. Pepe, against iron and copper. P. R. Kosting studied the thermoelectric force against platinum. A. W. Smith studied the Hall effect. L. C. Bannister and U. R. Evans discussed the electrode potential of these alloys.

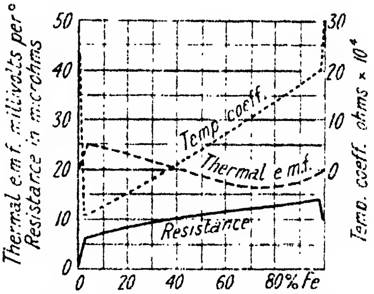


FIG. 411.—The Electrical Resistance of Iron-Copper Alloys.

G. Dillner found that 0·64 per cent. of copper had no effect on the magnetic properties of iron. R. Sahmen observed that an alloy with 98·7 per cent. of copper is magnetizable at room temp., and that the magnetism of alloys with 1 to 10·7 per cent. of copper vanishes at 795°. D. Mushet observed that alloys with 90 per cent. copper are magnetic; and P. Breuil, that steel with 32 per cent. copper is magnetic in the cold; and G. Tammann, that the magnetizability of the alloys rich in copper is possibly conditioned by the presence of crystals of a solid soln. rich in iron; and that the temp. of magnetizability of iron is lowered 27° by 2·5 per cent. of copper. G. Tammann and W. Oelsen measured the sp. magnetization (gauss) of copper-iron alloys containing the following proportions of dissolved and total iron:

	250°	418°	560°	770°	885°	1070°
Dissolved Fe . . .	0·14	0·14	0·14	0·54	1·34	3·68
Gauss 0·502 per cent. Fe .	0·694	0·694	0·713	0·001	0·001	0·002
2·00 ,, ,, .	3·64	3·72	3·72	2·85	1·238	0·019
4·50 ,, ,, .	8·76	8·73	8·82	7·96	6·04	1·18

C. F. Burgess and J. Aston measured the magnetization, or magnetic induction, *B*, of alloys of electrolytic iron and copper—unannealed, annealed at 675° and 1000°, and quenched from 900°—for magnetic fields of intensity *H* gauss, and the results are summarized in Table LVI; while the results for the coercive force ($H_{max.}=200$), and retentivity ($H_{max.}=200$) are summarized in Table LVII. The subject was studied by H. Buchholtz and W. Köster. A. F. Stogoff and W. S. Messkin found that with steels having 0·7 to 1·2 per cent. of carbon and

1 to 5 per cent. of copper, the coercive force, and the product of the coercive force and the remanence are increased more or less proportionally to the copper-content. Observations were also made by E. Gerold, A. Kussmann and co-workers, G. Tammann, A. D. Ross, E. Take, W. Köster, and W. Krings and W. Ostmann, while A. Kussmann and B. Scharnoff observed no relation between the coercive force and hardness.

TABLE LVI.—MAGNETIZATION OF COPPER-IRON ALLOYS.

Copper (per cent.)	$H=10$				$H=100$			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°
0·00	13,100	10,000	13,350	11,800	18,850	18,850	18,200	18,150
0·09	2,900	5,700	7,600	9,200	17,600	18,350	17,400	17,600
0·20	7,700	5,700	10,700	10,300	18,100	18,350	17,650	17,700
0·42	10,150	10,950	11,700	11,500	17,100	18,500	17,700	17,800
0·80	7,700	6,300	10,700	11,000	17,100	18,550	17,550	17,800
0·01	2,900	6,300	5,500	9,200	17,100	18,050	17,450	17,650
1·51	5,600	4,300	3,500	8,200	18,100	18,200	17,250	17,400
2·00	4,500	5,000	5,500	5,600	17,050	18,250	17,100	17,200
3·99	4,500	5,700	4,900	4,100	16,800	18,050	17,050	17,400
5·07	2.900	4,300	3,000	2,950	16,250	17,650	16,700	17,000
6·16	4,500	4,300	2,200	2,400	16,550	17,400	16,200	16,350
7·05	400	3,000	2,400	2,950	14,900	17,200	16,500	16,150
94·34	0	0	0	0	0	0	0	0

TABLE LVII.—COERCIVE FORCE AND RETENTIVITY OF COPPER-IRON ALLOYS.

Copper (per cent.)	Coercive Force				Retentivity			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°
0·00	5·5	6·2	3·1	2·5	12,300	13,800	10,000	8,000
0·09	13·0	8·7	12·1	4·3	12,700	12,000	10,100	8,400
0·20	7·0	9·3	4·0	3·5	11,100	13,300	8,400	8,400
0·42	7·0	6·0	3·7	3·6	9,900	13,300	8,600	9,300
0·80	9·5	9·5	4·1	4·3	11,500	14,900	8,700	9,100
0·01	14·0	9·5	8·8	5·4	11,100	14,500	10,400	8,700
1·51	12·8	10·5	11·3	7·3	11,100	14,300	12,400	12,500
2·00	10·7	10·0	9·0	8·3	10,200	12,800	10,200	9,900
3·99	6·0	9·8	9·3	9·7	9,200	13,200	11,100	11,300
5·07	5·7	10·9	11·5	11·2	8,300	13,200	11,500	11,700
6·16	12·5	10·5	11·8	11·8	9,300	11,600	11,800	12,100
7·05	12·5	13·2	12·5	12·6	7,700	12,500	13,100	11,300
94·34	None	200+	200+	200+	None	500	300	400

According to J. E. Stead, the surface of alloys of 8 to 97·2 per cent. of copper readily tarnished because of the presence of crystallites of iron; and alloys with 0 to 8 per cent. of copper oxidize when melted more rapidly the more copper they contain. C. J. B. Karsten reported that copper is an undesirable element in steel because it makes the metal corrode more rapidly; but later observations have shown that this is not always a valid deduction, since the early cupriferous steels seem to have had sulphur associated with the copper. I. Kotaira found that when a cupriferous steel is oxidized at 1000° for 22 hrs., the surface oxide has only 10 to 20 per cent. of the original copper, and the copper-content of the unoxidized steel increases 5 to 10 per cent. H. Kirscht studied the effect of copper on the oxidation of iron. According to C. Carius and co-workers, the high resistance to rusting of steels with 0·2 to 1·0 per cent. of copper, when exposed to a damp atmosphere, is due to the formation of a tenacious layer of cupric oxide below the iron scale which first forms. This layer is a secondary deposit produced by oxidation of the copper set free when the outer layer of iron oxide is formed. It is possible to arrange conditions to show that the copper liberated is first converted by the ferric ions into cuprous ions, which are immediately reduced so that the steel becomes covered with a film of copper, which then oxidizes to cupric oxide. In the presence of chloride ions the deposited copper is spongy and is rapidly converted into cupric hydroxide, which then accelerates rusting of the iron by the formation of local cells. P. Kötzschke found that 0·3 to 0·4 per cent. of copper decreased the corrosion of cast iron in the atmosphere, and that further additions of copper had no appreciable effect. The resistance to acids was not improved by the addition of up to 0·9 per cent. of copper. F. H. Williams found that soft Bessemer steel containing variable proportions of copper, on exposure to the atmosphere for a month during which the samples were wetted several times daily, the losses by corrosion were:

Copper . . .	0	0·078	0·145	0·263 per cent.
Loss by corrosion .	1·85	0·89	0·75	0·74 ,,

Observations were also made by J. E. Stead and F. H. Wigham, who found the corrosion, during 9 weeks' immersion in a stream of tap-water, for steel with approximately 0·990 C, 0·463 Mn, 0·168 Si, 0·034 S, 0·021 P, and 0·010 and 0·460 copper, to be respectively 12·7 and 10·1 per cent.; steels with 0·430 C, 0·940 Mn, 0·065 Si, 0·030 S, 0·063 P, and 0·250 and 0·480 copper, to be respectively 10·6 and 8·9 per cent.; steels with 0·480 C, 0·933 Mn, 0·070 Si, 0·047 S, 0·084 P, and 0·033 and 0·889 copper, to be respectively 12·0 and 13·5 per cent.; steels with 0·330 C, 1·090 and 0·640 Mn, 0·028 Si, 0·118 and 0·055 S, 0·049 P, and 0·012 and 1·286 Cu, to be respectively 19·0 and 11·5 per cent.; and 0·310 C, 0·676 Mn, 0·084 Si, 0·0475 S, 0·084 P, and 0·012 and 2·000 copper, to be respectively 14·7 and 4·7 per cent. The results with tidal river-water were similar. H. Wedding and W. Müller observed the reduced tendency of copper steels to corrosion or separation of copper sulphide and copper in the form of protective shells around the ferrite grains. D. M. Buck stated that the addition of 0·15 to 0·30 per cent. of copper to mild steel greatly increases its resistance to corrosion in air without interfering with its tenacity or ductility; he also added that the addition of copper helps to neutralize the favourable effect of sulphur on corrosion; S. L. Hoyt also found 0·20 to 0·25 per cent. of copper enhanced the resistance of steel to atm. corrosion; A. S. Cushman said that a small percentage of copper restrains the corroding influence of the acidic atm. of manufacturing towns; but copper is not beneficial under all conditions, for corrosion by immersion in neutral, acidic or alkaline water is either not influenced or influenced detrimentally by copper. He said: if it is desired to make a roof of sheet metal for a building in a smoky atm., and not intended to galvanize or paint it, it would probably be best to select copper steel; but if it is intended to galvanize it or keep it painted with a good paint, pure iron would no doubt give the best results. O. Bauer concluded that in the presence of carbon dioxide and sulphur dioxide, in air, a slight percentage of copper or of nickel seems to have a beneficial influence, but the addition of copper to steel for the purpose of preventing or mitigating corrosion is not generally advisable. J. A. Aupperle and D. M. Strickland, M. Ballay, O. Bauer, O. Bauer and co-workers, F. K. Bell and W. A. Patrick, P. Breuil, C. Carius, H. Cassel and F. Tödt, E. L. Chappell, G. H. Clevenger and B. Ray, W. H. Creutzfeldt, A. S. Cushman and co-workers, K. Daeves, J. A. N. Friend, M. Grison and E. Lepage, R. A. Hadfield, H. Hebberling, W. Herwig, S. L. Hoyt, H. T. Kalmus and K. B. Blake, V. V. Kendall and F. N. Speller, W. Marzahn and A. Pusch, P. B. Mikailoff, F. Nehl, J. V. Neubert, H. S. Rawdon, E. A. and L. T. Richardson, W. D. Richardson, R. T. Rolfe, J. E. Stead, S. S. Steinberg, O. W. Storey, W. H. Walker, and H. Wedding made some observations on this subject. M. Faraday and J. Stodart, and R. Mallet stated that alloys of iron with copper are less corrodible than iron alone. M. Ballay, D. M. Buck, C. Carius, E. Crowe, G. Dillner, H. T. Kalmus and K. B. Blake, W. Müller, J. V. Neubert, C. Pfannenschmidt, E. A. and L. T. Richardson, J. E. Stead and F. H. Wigham, S. S. Steinberg, W. H. Walker, H. Wedding, and F. H. Williams found copper made the alloy more resistant to corrosion: (i) copper increases the resistance of iron and steel to atmospheric corrosion, and its influence is apparent when the copper reaches only 0·03 per cent.; its maximum effect is produced when only 0·05 per cent. is present, and the best amount for commercial steel is about 0·25 per cent. (ii) Steels with 0·05 and with 0·25 per cent. of copper outlast iron containing 0·04 per cent. of copper. (iii) Sulphur in steel accelerates corrosion very markedly, and sulphur oxides in the air accelerate the corrosion of steel, but copper counteracts or retards both these effects. O. Bauer, R. A. Hadfield, and J. A. N. Friend found the differences to be too small to be able to state definitely that there is any improvement; whilst A. S. Cushman said that copper is deleterious. According to F. K. Bell and W. A. Patrick, the rate of dissolution of the alloys in 28·7 per cent. hydrochloric acid decreased below the value for iron alone; the first 0·5 per cent. of copper had the greatest effect since further additions of copper only increased the resistance to attack very slightly. Mere contact with copper wire reduces the rate of dissolution of iron in the acid, whilst platinum and silver are without effect. The results with 57 per cent. sulphuric acid were erratic. It is assumed that the retarding influence of copper is due to the dissolution of some of that metal which is at once re-precipitated in a finely-divided state on the surface of the iron; it is then re-dissolved. The intermittent dissolution and re-precipitation of copper is said to be responsible for the retardation. J. A. N. Friend found that the addition of small quantities of copper to steel exerts a minor influence upon the corrodibility of the metal in neutral corroding media. In tap-water and in salt-water there is nothing to choose between the cupriferous steel and the wrought irons, all of which possess a slight advantage over the steels; in the alternate wet and dry tests the non-cupriferous metals proved slightly superior. In all cases, however, the differences are relatively small, being but slightly greater than the usual eccentricities manifested between different specimens of apparently similar metals. O. Kötzsche and E. Piwowarsky observed that the addition of 0·3 to 0·4 per cent. of copper increases the resistance of grey cast iron to weather by 25 per cent., but up to 0·9 per cent. of copper, the resistance to acid attack is unaltered, and the resistance to salt soln. is reduced. L. Aitchison found that the corrosion of copper steels represented by the loss in weight per 100 sq. cm. when left in the dark in 3 per cent. sodium chloride soln. and 1 per cent. sulphuric acid for 77 days, and 45 hrs. in 10 per cent. sulphuric acid, were:

C	1·18	0·59	0·38	0·30 per cent.
Cu	0·48	1·06	2·52	4·78 ,,
NaCl	1·86	2·13	2·31	2·07
H_2SO_4 1 per cent.	15·1	0·58	9·45	3·22
H_2SO_4 10 ,,	58·3	0·69	0·92	1·02

Y. Utida and M. Saito measured the loss in weight, in grams per sq. cm., suffered when the alloy with about 0·05 per cent. of carbon, is exposed for 24 hrs. to 10 per cent. soln. of the different acids:

Copper	0	0·55	1·06	1·60	2·10	2·88 per cent.
HNO_3	0·9380	0·2410	0·3820	0·4355	0·4875	0·5875
HCl	0·0712	0·0025	0·0027	0·0037	0·0031	0·0026
H_2SO_4	0·0990	0·0220	0·0162	0·0117	0·0098	0·0107

H. Endo's results, during 5 hrs.' action at ordinary temp., are plotted in Fig. 412. In all cases there is a minimum corrosion with alloys containing 1 to 2 per cent. of copper. According to J. E. Stead and F. H. Wigham, steels free from copper dissolved in dil. acids more quickly than those containing copper. C. F. Burgess and J. Aston found that with alloys of electrolytic iron and copper, containing :

Copper	. .	0	0·089	0·422	0·804	1·510	3·990	6·160	7·050 per cent.
Acid corrosion	.	1·300	0·178	0·059	0·104	0·147	0·093	0·143	0·186
Atm. corrosion	.	0·449	0·254	0·268	0·259	0·225	0·171	0·200	0·161

where acid corrosion refers to the loss in grams per sq. dm. when immersed for an hour in 20 per cent. sulphuric acid ; and atm. corrosion refers to the loss in kgrms. per sq. metre per year when exposed for 162 days from July to February. L. Schneider observed that with 10 per cent. sulphuric acid, soft basic steel with 0·01 per cent. of copper had a relative rate of corrosion of 120; pig-iron with 0·12 per cent. copper, 32 ; soft open-hearth steel with 0·14 per cent. copper, 26 ; and soft basic steel with 0·2 per cent. of copper, 19. P. Breuil observed that with dil. sulphuric acid, and different steels, the losses in weight taken as a measure of corrosion were those indicated in Table LVIII. There is a minimum corrosion with the steels with 0·156 to 0·168 per cent. carbon when about 1 per cent. of copper is present, and with steels with 0·336 to 0·400 per cent. carbon, when about 2 per cent. of copper is present. The subject was discussed by P. Bardenhauer and G. Thanheiser, O. Bauer and co-workers, F. K. Bell and W. A. Patrick, C. Carius, C. Carius and E. H. Schulz, J. H. Carter, J. A. N. Friend, V. V. Kendall, V. V. Kendall and E. S. Taylerson, C. Pfannenschmidt, and A. R. Surface ; and O. P. Watts and H. C. Knapp found that the action of sulphuric acid is in some cases accelerated by the presence of silver and copper salts. V. K. Pershke and co-workers studied the action of phosphoric acid.

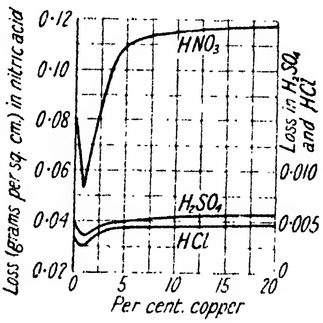


FIG. 412.—Corrosion of Copper Steels by Acids.

TABLE LVIII.—THE CORROSION OF CUPRIFEROUS STEELS.

Composition of steel						Percentage corrosion
C	Mn	Si	P	S	Cu	
0·168	0·100	0·214	0·023	0·013	0·0	5·23
0·158	0·092	0·223	0·016	0·017	0·490	4·40
0·156	0·072	0·209	0·022	0·016	1·005	2·80
0·165	0·108	0·214	0·023	0·017	2·015	3·01
0·156	0·113	0·186	0·029	0·025	3·979	3·34
0·336	0·150	0·316	0·020	0·017	0·0	6·10
0·390	0·139	0·323	0·020	0·018	0·505	3·54
0·400	0·164	0·307	0·022	0·012	1·005	3·21
0·389	0·175	0·242	0·023	0·010	2·025	2·04
0·368	0·139	0·217	0·022	0·011	3·997	2·50

L. B. G. de Morveau [3] prepared a **silver-iron alloy.** He said that when the two metals are fused together, two layers are formed. The lower layer contains 0·31 per cent. of iron, and it is affected by a magnet ; while the upper layer, containing 1·25 per cent. of silver, is very hard, and has a denser texture than iron. C. J. B. Karsten observed that the presence of 0·034 per cent. of silver made the iron red-short ; and diminished its tensile strength very considerably. C. F. Burgess and J. Aston discussed the working qualities of iron-silver alloys. G. Barruel obtained a hard, white alloy, by melting silver with 0·35 per cent. of iron.

C. A. Coulomb said that silver can retain no more than 0·0067 part of iron, and that if 0·003 part is present, the alloy acts on a magnetic needle. W. Longmaid patented iron alloys with minute proportions of silver. M. Faraday and J. Stodart said:

> If steel and silver be kept in fusion together for a length of time, an alloy is obtained, which appears to be very perfect while the metals are in the fluid state, but on solidifying and cooling, globules of pure silver are expressed from the mass, and appear on the surface of the button. If an alloy of this kind be forged into a bar, and then dissected by the action of dil. sulphuric acid, the silver appears, not in combination with the steel, but in threads throughout the mass; so that the whole has the appearance of a bundle of fibres of silver and steel, as if they had been united by welding. The appearance of these silver fibres is very beautiful; they are sometimes one-eighth of an inch in length, and suggest the idea of giving mechanical toughness to steel, where a very perfect edge may not be required. At other times, when silver and steel have been very long in a state of perfect fusion, the sides of the crucible, and frequently the top also, are covered with a fine and beautiful dew of minute globules of silver; this effect can be produced at pleasure. Less than one part of silver in 500 of the steel is present in the buttons. The alloys were later examined by R. A. Hadfield.

G. Tammann and W. Oelsen discussed the solubility of iron in silver and found 0·0004 and 0·0006 per cent. respectively at 1000° and 1600°; and N. Agéeff and M. Zamotorin studied the diffusion of silver in iron. G. J. Petrenko said that the two metals do not alloy at temp. below 1600°; for on cooling the mixtures, there are always two arrests corresponding with the f.p. of iron and silver respectively. M. Faraday and J. Stodart found that hammered steel with 2 per cent. of silver had a sp. gr. of 7·808. C. F. Burgess and J. Aston observed that electrolytic iron with:

Silver . . .	0	0·281	0·492	0·581	0·691 per cent.
Acid corrosion .	1·300	1·021	1·760	1·340	1·170
Atm. corrosion .	0·499	0·317	0·430	0·356	0·450

where the acid corrosion refers to the loss in grams per sq. dm. when the alloy was immersed in 20 per cent. sulphuric acid for 1 hr.; and the atm. corrosion refers to loss in kgrms. per sq. metre per year with alloys exposed to the weather for 162 days from July to February. Iron can be separated from silver by cupellation, by fusion in air, or by fusion with borax and nitre. E. Lüder prepared a series of **silver-iron-copper alloys** and found a miscibility gap extending over most of the diagram, Fig. 413. The alloys separate into two layers of which the upper consists mostly of iron, and the lower of silver and copper with very little iron. Homogeneous liquid alloys of iron and copper are broken up into two layers when silver is added.

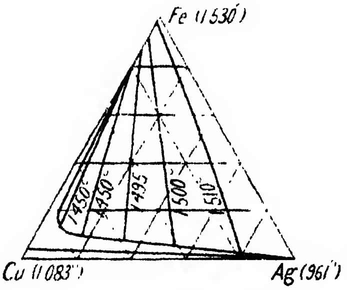


FIG. 413.—The Ternary System: Copper–Silver–Iron.

W. Lewis[4] said that **gold-iron alloys** are readily formed. Gold dissolves twice or thrice its own weight of iron at a temp. far less than that at which the iron melts; so that if molten gold be stirred with an iron rod, it corrodes a part of the iron, and gold adheres to the rod. Hence, J. A. Cramer said that it is not advisable to stir molten gold with an iron rod. Gold is thus an excellent solder for iron. W. Lewis concluded that the colour of gold is made pale by iron, and if there is 3 or 4 times as much iron as gold present, the alloy has a whiteness approaching that of silver. C. Hatchett said that the alloy with equal parts of gold and iron forms a yellowish-grey, hard alloy of sp. gr. 16·885; and M. Faraday and J. Stodart, and C. J. B. Karsten observed that gold and iron can be alloyed in all proportions, and that 8 to 9 per cent. of iron does not diminish the toughness of gold. Richter and Co. obtained white gold-iron alloys; and the subject was discussed by A. H. Hiorns, W. Bersch, and W. T. Brannt. R. A. Hadfield examined some of M. Faraday and J. Stodart's alloys. An alloy with one-sixth of iron is used in jewellery as *grey gold,* and with one-fourth of iron, *blue gold.* E. Isaac and G. Tammann found iron and gold to be miscible in all proportions in the fused state and to form an uninterrupted series of solid soln. on solidification. The break, Fig. 414, extends from 28 to 63 per cent. of gold. At lower temp., partly owing to the change of iron into another form, the break extends from 18 to 85 per cent. of gold. At 1168°, the sat. solid soln. with 28 per cent. of gold, reacts with the fused mass to form a second series of solid soln. At 95 per cent. of gold, the f.p. curve, Fig. 414, shows a minimum at about 1040°. The transition point of iron is not affected by the presence of gold. The alloy with 10 per cent. of gold is harder than iron; and beyond this point the hardness slowly diminishes, and the alloys with more than 70 per cent. of gold are considerably softer than iron. Observations on this subject were made by W. Guertler, L. Nowack, P. Oberhoffer, and W. Wahl. E. Jänecke observed that at 1168° there is a transition point. N. Agéeff and M. Zamotorin studied the diffusion of gold in iron; and H. Sawamura, the effect of gold on the graphitization of cast iron. G. Borelius and co-workers, and M. Faraday and J. Stodart found that hammered steel with 1 per cent. of gold had a sp. gr. 7·870. G. Wertheim measured the elasticity of some gold-iron alloys; A. Matthiessen, and W. Guertler, the electrical conductivity, finding about 1·1 microhms increased resistance per cm. cube for an addition of 1 per cent. of gold. W. Guertler and A. Schulze found that A. Matthiessen's rule to the effect that the absolute increase of the resistance on raising the temp. from 0° to 100° is independent of the increase of resistance brought about by the presence of mixed crystals, and has the same value as that calculated from the increase of resistance of the pure components when raised through the same temp. interval, that is $dW_m/dt = dW/dt$, is not only true over the temp. range 0° to 100°, but also over any other temperature range. It may therefore be also stated in the form that within the range of a given state the differential quotient of the resistance and the temp., dW/dt, increases in a given series of binary alloys proportionally to the vol. conc. of the components. The resistance between 20° and −190° was studied by J. O. Linde. C. G. Knott and J. G. MacGregor measured the thermoelectric force. J. W. Shih found alloys with 10 per cent. of iron to be ferromagnetic, and the magnetic susceptibilities of alloys with smaller proportions of iron to be:

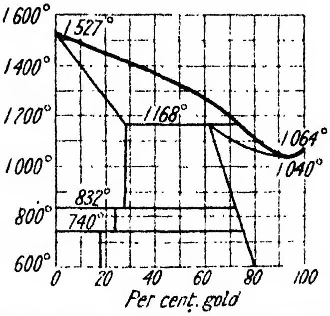


Fig. 414.—Equilibrium Diagram of Iron-Gold Alloys.

Fe	0·07	0·085	0·1	0·5	1·0	2·0	3·5	5·0
$\chi \times 10^6$	−0·041	−0·023	+0·01	0·559	1·52	4·33	12·72	29·76

According to J. L. Gay Lussac and L. J. Thénard,[5] by heating to whiteness a mixture of baryta, strontia, or lime with iron, with or without carbon, no alloy of iron with the alkaline earth metal is formed. W. A. Lampadius, however, heated baryta with iron and charcoal dust, obtained a **barium-iron alloy,** which on exposure to air, formed baryta and iron oxide. E. D. Clarke heated a mixture of barium and iron (2 : 1) in the oxyhydrogen flame, and obtained a brittle alloy the colour of lead. A. Stavenhagen and E. Schuchard obtained the alloys by the thermite process. P. Oberhoffer discussed these binary alloys; and N. Agéeff and M. Zamotorin, the diffusion of barium in iron. J. L. Gay Lussac and L. J. Thénard obtained negative results in the attempt to prepare **strontium-iron alloys** by the method employed for the barium-iron alloys; and they were also unsuccessful in preparing **calcium-iron alloys.** G. Tammann and K. Schaarwächter found that the attack of iron by calcium begins at about 380°, and increases rapidly as the temp. rises. J. J. Berzelius did not succeed in preparing alloys. C. J. B. Karsten stated that iron with 0·1774 per cent. of calcium was deficient in weldability and tenacity, though neither cold-short nor red-short. This iron was produced by adding an excess of limestone to the charge for converting cast iron into malleable iron on the charcoal hearth. According to L. Stockem, calcium dissolves in molten cast iron with great development of heat, but when large quantities are used the metal is rapidly coated with a crust of calcium carbide which prevents further action. Some calcium carbide always remains mechanically entangled in the iron. Ferric oxide reacts vigorously with an excess of metallic calcium; the iron formed is pure and ductile, and does not contain a trace of calcium. O. P. Watts observed no alloying of the two elements fused together in a carbon crucible, but the iron became richer in carbon and silicon—the latter was derived from the silica in the lining of the crucible. C. Quasebart also said that calcium does not alloy with iron whether containing carbon or not. A hollow, iron cylinder filled with calcium was heated at 1400° for 3½ hrs., but no absorption of calcium by the iron was observed. N. Agéeff and M. Zamotorin studied the diffusion of calcium in iron. E. K. Smith and H. C. Aufderhaar observed that up to 0·2 per cent. had no perceptible effect on the shrinkage, strength, or fluidity of cast iron. Calcium has been tried for the deoxidation of iron. O. P. Watts succeeded in removing all the sulphur from iron by means of calcium, but the phosphorus was reduced from 1·96 only to 1·56 per cent. W. Hessenbruch and J. E. Hurst discussed these alloys.

H. Davy[6] prepared an **iron-beryllium alloy** by heating to whiteness a mixture of beryllia, iron, and potassium; and also by bringing slightly moistened beryllia in an atm. of hydrogen, in the circuit of a voltaic battery with an iron wire as cathode. The iron becomes brittle and white, and when dissolved in acids, yields a beryllium and an iron salt. According to F. Stromeyer, if a mixture of beryllia, iron and lampblack is heated to whiteness, an alloy is formed which is whiter and more ductile than iron. When dissolved in acids, it forms a double salt of iron and beryllium. I. Fetchenko-Tchopiwsky studied the cementation of iron with beryllium. G. Oesterheld examined the f.p. of the alloys with up to 21 per cent. beryllium, and the results are summarized in Fig. 415. There is a eutectic point at 1155° and 9·2 per cent. of beryllium. The β–α transformation of iron is lowered by beryllium from 790° to about 647°. There is evidence of the formation of a compound **iron diberyllide,** Be_2Fe; and on polished sections it is darkened by soda-lye. R. H. Harrington also studied the phase diagram; and F. Wever, the effect of beryllium on the range of the γ-phase; the results of F. Wever and A. Müller are summarized by dotted lines in Fig. 415, showing the range of stability of the γ-phase. G. Masing, and W. Kroll found the hardness of some alloys, on Brinell's scale, with a 1000-kgrm. load, a 10-mm. sphere acting for one minute, to be:

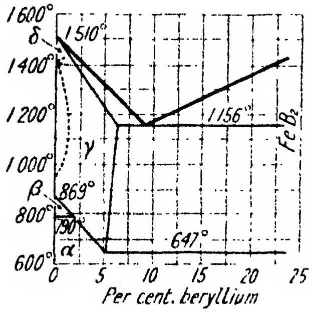


FIG. 415.—Equilibrium Diagram of Iron-Beryllium Alloys.

Beryllium		1·21	2·25	2·97	3·00	3·88 per cent.
Hardness	quenched from 1100°	212	241	221	230	263
	aged at 520°	221	289	353	335	467
	annealed at 950°	212	241	231	252	335

W. R. Whitney found that beryllium improved the mechanical properties and electrical resistance of steel. O. von Auwers observed that the electrical resistance, R ohms per cm. cube:

Beryllium	0·5	1·0	1·5	2·0	3·0	4·0 per cent.
$R\times10^4$	0·193	0·494	0·460	0·475	0·646	0·541

with steel having 1 per cent. each of beryllium and carbon, $R=0{\cdot}0_4248$; 1 per cent. beryllium and 2 per cent. silicon, $0{\cdot}0_4595$. The saturation, value of the magnetization, the remanence, the coercive force, and the maximum permeability of beryllium iron alloys are—Q denotes quenched, and A, annealed :

	Per cent.	0·5	1·0	1·5	2·0	3·0	4·0	1Be, 1C	1Be, 2Si
Saturation	Q .	16,400	16,000	13,000	15,200	8,300	1,120	14,900	10,800
	A .	16,400	12,000	14,200	17,800	10,800	13,300	17,500	15,100
Remanence	Q .	5,400	6,150	4,300	6,000	3,200	4,400	8,800	3,350
	A .	8,500	5,700	5,250	7,800	4,700	7,600	13,200	3,800
Coercive force	Q .	3·05	4·5	6·75	6·75	18·3	10·1	21·3	7·7
	A .	1·6	2·5	2·5	4·75	4·3	23·3	7·1	0·9
Permeability	Q .	16,450	27,650	32,300	40,500	58,500	44,500	187,300	25,800
	A .	13,600	14,230	13,100	37,000	20,200	17,700	93,800	3,420

According to E. D. Clarke,[7] when magnesia moistened with oil is melted along with iron before the oxyhydrogen blowpipe, a brittle, metallic mass is produced supposed to be an impure **iron-magnesium alloy.** F. Stromeyer thought that he had obtained an impure alloy by the method he employed for the beryllium-iron alloy. C. R. Fresenius said that the magnesium in iron is not in an oxidized state. J. J. Berzelius obtained indications of the formation of an alloy of magnesium and iron when a mixture of magnesia, iron filings, and powdered charcoal is heated ; but C. J. B. Karsten never obtained any evidence of the existence of such an alloy ; and J. Parkinson could not prepare magnesium-iron alloys. E. K. Smith and H. C. Aufderhaar, J. E. Hurst, and P. Oberhoffer discussed these alloys. F. C. Lea and L. T. Wills studied the ternary aluminium-magnesium-copper alloys.

The **zinc-iron alloys** are difficult to prepare. Many have assumed that alloys cannot be obtained ; but J. F. Gmelin[8] melted zinc in contact with iron in a closed crucible and noted that the iron became steel-grey in colour, did not become malleable, did not rust, preserved its lustre, etc. G. Tammann and K. Schaarwächter found that the attack of iron by zinc begins at about 420°, and increases rapidly with rise of temp. A. F. Gehlen observed that when cuttings of zinc and iron are heated together, part of the zinc evaporates, and the remainder penetrates the iron making it denser and brittle. C. J. B. Karsten found that in reducing zinciferrous iron ores, the greater part of the zinc volatilized during the operation. The iron *eine bemerkbare Quantitätzink aufnimmt nicht.* C. F. Hollunder found that if a mixture of iron filings and zinc oxide, without charcoal, is heated under a layer of powdered glass, the iron takes up much zinc. P. Berthier, F. C. Calvert and R. Johnson, A. Laurent and C. Holms, A. Erdmann, H. Bablick, W. G. Imhoff, and L. Elsner observed that a vessel of wrought iron or cast iron, in which zinc is continuously melted, becomes corroded by an alloy of zinc and iron ; and P. Berthier, that in galvanizing iron by immersing it in molten zinc, with frequent additions of ammonium chloride, an alloy of zinc and iron is deposited at the bottom of the fused zinc. N. Agéeff and M. Zamotorin, and G. Tammann and H. J. Rocha studied the diffusion of zinc in iron. W. Guertler found that sections of galvanized iron cut obliquely through the outer layers show that the zinc and iron are separated by an intermediate layer of crystals of trizincide, $FeZn_3$. This compound is more electronegative than either iron or zinc, and thus accelerates corrosion if exposed. The zinc layer contains isolated crystals of the monozincide, FeZn, which is also electronegative. Zinc deposited from vapour by the dry process, or from soln. by the electrolytic process, is porous, and also contains minute crystals. C. W. Stillwell and G. L. Clark studied the subject. A. F. W. von Escher investigated the simultaneous deposition of iron and zinc electrolytically—***vide supra.***

A. von Vegesack studied the equilibrium diagram of alloys of iron with up to about 24 per cent. of zinc. This diagram includes the observations of P. T. Arnemann, and S. Wologdine, as well as those of U. Raydt and G. Tammann, who extended the observations over the whole range of the alloys, and prevented the loss of zinc by volatilization, by working at a press. of 110 to 130 atm. The results are summarized in Fig. 416. A. von Vegesack observed that with alloys having between 11 and 24 per cent. of iron, there is a primary separation of crystals which react with the fused mass at 777° to form **iron trizincide,** $FeZn_3$. The crystals of the trizincide separate primarily from alloys with 4 to 11 per cent. of iron, but when the temp. falls to 662°, the compound reacts with the fused mass to form **iron heptazincide,** $FeZn_7$. These two compounds show an inclination to form a solid soln. The heptazincide forms a series of mixed crystals which are saturated when 7·3 per cent. of iron is present. Below 422°, the sat. solid soln. reacts with the fused mass to form another series of solid soln. extending from 0·7 to 7·3 per cent. of iron. U. Raydt and G. Tammann observed the formation of no compound other than those just indicated, but a series of solid soln. of zinc in iron occurs with a saturation point near 80 per cent. iron. A. S. Russell and co-workers, W. M. Peirce, P. Oberhoffer, and S. Wologdine studied the subject. F. Roll found that zinc favoured the decomposition of cementite.

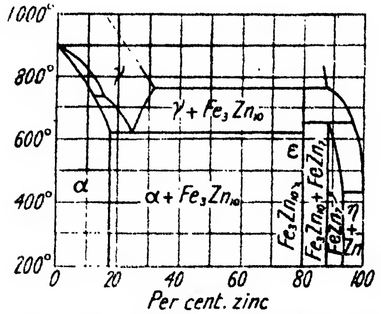


FIG. 416.—Equilibrium Diagram of Zinc-Iron Alloys.

Although only the existence of the trizincide and heptazincide has been established by the thermal process, H. le Chatelier, and S. Wologdine inferred the existence of *iron enneadecazincide*, $FeZn_{19}$; and E. Vigouroux and co-workers, from their study of the e.m.f. of the cell Zn | 0·05*N*-$ZnSO_4$ | $FeZn_x$, the existence of the tri- and hepta-zincides as well as of *iron tritazincide*, Fe_3Zn, and of *iron pentitazincide*, Fe_5Zn. F. C. Calvert and R. Johnson also thought that the crystals obtained in an iron galvanizing bath were those of *iron dodecazincide*, $FeZn_{12}$, but F. Taboury showed that they are identical with the crystals of a solid soln. with 7·3 per cent. of iron, observed by A. von Vegesack. A. S. Russell observed that when an amalgam of zinc and iron is treated with oxidizing agents, zinc is oxidized until definite proportions of the two metals are present when both are oxidized at the same rate, indicating that definite proportions of the two elements are present. The results indicate that compounds with the at. proportions Zn : Fe and Zn : Fe_8 are formed.

A. Osawa and Y. Ogawa obtained Fig. 416 for the equilibrium diagram of the iron-zinc alloys. The X-radiograms of the alloys were determined. Two compounds appear: **iron tritadecazincide,** Fe_3Zn_{10}, is the same as that formerly assumed to be $FeZn_3$. The crystals are cubic with the lattice parameter a=8·93 A., and there are 52 atoms per unit cube. The other compound is iron heptazincide, $FeZn_7$; it furnishes hexagonal crystals with the axial ratio approximating 1·60. The **zinc pentitahenicosizincide,** Fe_5Zn_{21}, alloy; and also the relation between the crystal structure and the atomic properties of the zinc-iron alloys, were studied by A. Westgren.

The observations of C. F. Hollunder, L. Elsner, and P. Berthier showed that the alloys have the general appearance of zinc, but some are whiter; they are also harder and more brittle; in some cases the alloy can be rubbed into crystalline grains by the fingers. A. Westgren, and W. Ekman studied the X-radiograms. A. Osawa and Y. Ogawa noted the similarity of the crystal structure of the zinc–iron system with those of the binary systems of zinc with copper, silver, and gold. The β-phase of the Cu–Zn system corresponds with the α-phase of the Fe–Zn system, and in both the phase forms a body-centred cubic lattice. The γ-phase of the Cu–Zn system corresponds with Fe_3Zn_{10} in the zinc–iron system, and in both, cubic crystals are formed. The ε-phase of the copper–zinc system corresponds with the compound $FeZn_7$, and both have a hexagonal form. The α-phase of the copper–zinc system corresponds with the γ-phase in the iron–zinc system, and both have a face-centred cubic lattice and the latter is stable at a high temp. The cubic lattice of Fe_3Zn_{10} or $FeZn_3$ has a=8·93 A., and has 52 atoms per unit cube. The close-packed, hexagonal lattice of $FeZn_7$ has an axial ratio of about $a : c = 1 : 1·60$, and $a = 2·788$ A. A. J. Bradley discussed this subject. P. T. Arnemann said that the crystals of the solid soln. with up to about 3·3 per cent. iron are harder and more resistant to acids than zinc alone. As the proportion of iron increases, the alloys become harder and more brittle, so that those with 8 to 9 per cent. of iron are extraordinarily brittle and friable. U. Raydt and G. Tammann observed that the alloy with 96 per cent. iron is malleable when cold, but is more brittle than iron, though the alloy with 80 per cent. iron is brittle, and not malleable at ordinary temp. J. E. Hurst, E. K. Smith and H. C. Aufderhaar, and O. Smalley studied the tensile properties of the alloys. K. J. Bayer observed that the alloys are difficult to melt before the blowpipe, and they colour the flame greenish-white. U. Raydt and G. Tammann found that the recurrence of the magnetic permeability occurs :

Fe . .	26·6	43·6	50·0	60·5	67·2	76·0	82·0	87·6	96·0 per cent.
Temp. .	638°–643°	642°	650°	653°	648°	676°	684°	747°	771°

E. Lehmann studied the magnetic properties of the alloys. M. Faraday and J. Stodart, and R. Mallet noted that alloys with copper and zinc are less corrodible than iron. In 1779, W. Keir patented an **iron-copper-zinc alloy** (10 : 100 : 75), and in 1860, J. Aich patented a similar alloy, sometimes called *Aich-metal*. The alloy was recommended as a substitute for copper and brass in shipbuilding and sheathing. It was said to be stronger than copper, and to resist satisfactorily the action of sea-water. H. M. St. John studied these alloys. A related alloy, called *sterro-metal*, contains rather less iron, and a small proportion of tin. Some properties of sterro-metal were described by J. Percy. E. Sorel called an alloy of iron, copper, and zinc (10 : 10 : 80) *unoxidizable cast iron*, or *white brass*. It was said to have the appearance of zinc; the hardness of copper; to be more tenacious than cast iron; and to be susceptible of turning, filing, and tapping. H. N. Warren said that **magnesium-zinc-iron alloys** are used in pyrotechny; and that they are produced by the electrolysis of sodium and magnesium chlorides in the presence of ferrous chloride and zinc, and also by the action of an alloy of sodium and zinc on a mixture of sodium and magnesium chlorides, and then on ferrous chloride.

E. Isaac and G. Tammann examined the **iron-cadmium alloys,** and concluded that cadmium is insoluble in fused iron, and when iron is brought in contact with fused cadmium, it is either insoluble, or forms a compound insoluble in fused cadmium. The temp. of volatilization of cadmium, 770°, limits the range of temp. possible under ordinary press. G. Tammann and W. Oelsen found that cadmium at 400° and 700° dissolves respectively 0·0003 and 0·0002 per cent. of iron. Observations were also made by G. Tammann and K. Kollmann, W. H. Spencer and M. M. Walding, and P. Oberhoffer. N. Agéeff and M. Zamotorin studied the diffusion of cadmium in iron. C. F. Burgess and J. Aston found that an alloy with 5 per cent. of added cadmium forged, welded, and machined easily. A. S. Russell observed no evidence of the presence of a compound of cadmium and iron when an amalgam containing the two metals is treated with oxidizing agents. The cadmium is first removed, then the iron.

It is difficult to form **mercury-iron alloys** or **iron-amalgams** directly from the elements. J. Nicklès [9] said that iron does not take up mercury; P. Casamajor considered that it does. According to T. W. Richards and R. N. Garrod-Thomas, the solubility of iron in mercury is about 0·00135 per cent.: that is, about a milligram of iron in 100 grms. of mercury. E. Palmaer observed 0·00007 per cent. between 20° and 200°; G. Tammann and co-workers gave $1·1 \times 10^{-17}$ grm. per 100 grms. of mercury at 18°; and N. M. Irvin and A. S. Russell, $< \times 10^{-5}$ grm. per 100 grms. of mercury. N. M. Chuiko said that the iron amalgams are colloidal soln.

V. Colvin said that steel can be directly amalgamated by direct contact with mercury and by magnetizing soft steel filings, and dissolving the filings in mercury, a magnetic iron-amalgam is formed. E. H. Amagat observed that at a press. of 4000 atm., mercury will pass through cast iron, 8 cm. thick, and appear like "fine rain," the mercury passes through the intramolecular pores; L. P. Cailletet and co-workers also observed that at a high temp., and a relatively low press., mercury can pass through steel; and P. W. Bridgman observed that surfaces of steel, broken under mercury, are readily amalgamated, but not if the broken surface has had the slightest contact with air. He said:

> When the amalgamation is once started, the rapidity with which it spreads through the metal is greatly increased by hydrostatic press. The spread of mercury through the mass of the steel and the subsequent destruction of the hollow cylinders is produced by two causes, both of which must act together. One is the natural chemical affinity between mercury and steel, shown by the ready amalgamation of freshly broken surfaces. But the amalgamation is never started by the action of press. alone. In all those cases in which amalgamation occurs, there is in addition to the chemical affinity a strain of such a nature as to distend the pores of the metal. This allows the entrance of mercury into the pores so that amalgamation may begin, and also facilitates its further growth, which is most rapid in the direction in which the pores are most distended. In all cases in which rupture occurs the strain is of such a type as to distend the metal, and, on the other hand, in all those cases in which amalgamation is not produced by press., the strain is such as to compress the metal, closing up the pores.

H. Davy showed that an iron-amalgam is produced by the action of an amalgam of an alkali metal on iron; but E. Ramann observed that dry sodium-amalgam does not react when it is heated with powdered iron. L. P. Cailletet observed that iron may be superficially amalgamated by contact with sodium-amalgam and water. V. Colvin, R. Böttger, E. Ramann, J. Schumann, W. Kettembeil, P. Oberhoffer, and P. Casamajor obtained the amalgam in a somewhat similar manner. The last-named observed that:

> If the sodium-amalgam has sodium enough in it to make it pasty, it will cover iron with a silvery coat. This coat may be rubbed off, leaving the oxidized surface unaltered. If brought in contact with water, or, still better, with a soln. of ammonium chloride, the sodium-amalgam is decomposed and the mercury will sink into the iron. If the sodium-amalgam is liquid it will adhere in little drops all over the surface of a piece of iron shaken up in it; by the action of water, of acids, or of ammonium chloride, the droplets will spread on the iron, which will become amalgamated. The coat of mercury left on iron by the various agencies I have mentioned is not a superficial layer, for the mercury sinks into the metal, modifying its physical and chemical properties. In the case of pure soft iron it is difficult to notice any decrease of tenacity after amalgamation. With hard-tempered steel, however, the increased brittleness is very marked. In the case both of iron and steel a fresh fracture shows that mercury has penetrated deeply into the metal.

V. Colvin also obtained iron-amalgam by the action of an amalgam of the alkaline earths on iron. L. P. Cailletet, and P. Casamajor also found that ammonium-amalgam will give up its mercury to iron when rubbed up with it very persistently. Even then there are in every piece of iron certain spots where the mercury will not adhere. The intervention of acidulated water, by decomposing ammonium-amalgam with great energy, facilitates the amalgamation of iron in these difficult portions. P. Casamajor also observed that to amalgamate iron with zinc-amalgam, mercury should be placed in a vessel and covered with dil. sulphuric or hydrochloric acid. If, now, a piece of iron is agitated, in contact with the mercury and the acid, no combination will take place; but if pieces of zinc are placed in the mercury, in a few minutes iron placed in the above conditions will become coated with mercury. If after a while the power of the mercury seems to decline, more zinc must be added. The zinc is only attacked when iron, or some other metal more electronegative than zinc, is brought in contact with the zinc-amalgam and the acid, so that the expense in zinc is very slight.

According to C. Klauer, when sodium-amalgam is immersed in a sat. soln. of ferrous sulphate, a silvery, tenacious mass of iron-amalgam is formed, the separate globules of which readily follow the magnet, and when exposed to air become covered with flakes of hydrated ferric oxide. C. F. Schönbein observed that the amalgam is formed by rubbing a conc. soln. of ferrous chloride with 1 per cent. sodium-amalgam, and washing the product with water. H. Moissan employed a somewhat similar process. A. Aiken triturated zinc-amalgam with an aq. soln. of ferrous chloride, and kneaded the heated product to ensure the union of the 2 elements—A. A. Damour added that the amalgam cannot be obtained in this way. R. Böttger prepared iron-amalgam by rubbing together in a porcelain mortar, a mixture of mercuric chloride and finely divided iron (2 : 1), then add 2 parts of cold water, and when the mass begins to get hot, adding a few drops of mercury. H. Reinsch added iron to a soln. of copper sulphate mixed with a little hydrochloric acid; brushed off the copper deposit, and dipped the metal in a soln. of mercuric chloride acidified with hydrochloric acid. H. A. von Vogel recommended mixing together iron filings and alum (1 : 2); adding two or three parts of mercury and half a pint of water; triturating for an hour at a gentle heat; and finally washing the product with water.

According to J. P. Joule, the electrolysis of a soln. of ferrous sulphate with a mercury cathode, and an iron wire as anode, furnishes iron-amalgam. Using a Daniell's cell, the iron wire gradually dissolved, and an equal portion was taken up by the mercury, which in so doing lost its fluidity, and at length formed a mass of greyish-white crystals with a metallic lustre. The time required is about a day. J. F. W. Herschel previously obtained the iron-amalgam. The amalgam was also prepared by the electrolysis of a soln. of a ferrous salt with a mercury cathode, by J. Schumann, R. E. Myers, T. M. Drown and A. G. McKenna, L. P. Cailletet, P. Casamajor, and A. Zamboni.

E. Palmaer said that X-radiograms of iron-amalgam show that particles of iron are suspended in mercury; and the subject was discussed by R. Brill and W. Haag. According to J. P. Joule, the amalgam with 100 of mercury and 0·143 of iron was quite liquid; with 1·39 of iron it was also liquid; with 2·97, semi-fluid; with 11·8, soft, and of sp. gr. 12·19; with 18·3, solid and greyish-white; with 47·5, solid with a metallic lustre; with 127·6, solid, friable, and of sp. gr. 10·11. According to J. Schumann, E. Ramann, and J. P. Joule, if the amalgam be allowed to stand for some time, or if it be shaken violently, or rapidly stirred, it is decomposed, and the iron floats as a black powder on the liberated mercury; if the soft amalgam be compressed, some black powder also separates out. If amalgamated and ordinary iron are placed in acid and connected by a wire, the amalgamated metal is attacked, and the unamalgamated metal acts as cathode, and, added J. P. Joule, the amalgamation of iron produces a contrary effect to the amalgamation of zinc. Amalgamated iron is positive towards iron, and negative towards copper. H. Reinsch said that when used in a galvanic battery, it gives a stronger and more uniform current than ordinary iron. C. Hockin and H. A. Taylor observed that the e.m.f. of amalgamated iron to amalgamated zinc in a conc. soln. of zinc sulphate, is about 0·486 volt; with a solid iron-amalgam, 0·407; and with mercury containing only a trace of iron, 1·258 volts. According to J. P. Joule, R. Böttger, C. Klauer, C. P. Steinmetz, and A. Zamboni, the iron in the amalgam retains its magnetic qualities, for the amalgam is attracted by a magnet, and it can be permanently magnetized. H. Nagaoka observed that the magnetization increases proportionally with the iron content; the coercive force is high, being 240 gauss with an amalgam with 1·78 per cent. of iron, and 370 gauss with 2·3 per cent. of iron. G. Tammann and W. Oelsen found for amalgams with 0·062 per cent. of iron, the sp. magnetization 0·280 gauss. L. Stjepanek studied the electromagnetic induction. J. Férée observed that iron-amalgam is stable if kept away from contact with air, but in dry air it forms ferrous oxide and mercury; and A. Zamboni said that the dry amalgam is stable in dry air, but it forms a black powder in moist air. C. Klauer, R. Böttger, and H. Reinsch observed that the amalgam in air acquires a yellow film of ferric oxide. M. Krouchkoll said that iron-amalgam is more stable than aluminium-amalgam. J. P. Joule said that when heated to the b.p. of mercury, the liberated iron oxidizes, throwing off red sparks, and leaving a hard lump of oxide. R. Böttger obtained finely powdered iron by distilling the amalgam out of contact with air. M. Faraday and J. Stodart, and R. Mallet noted that alloys with mercury are less corrodible than iron. J. P. Joule observed that if the amalgam be left under water for a few days, it becomes covered with rust, and C. F. Schönbein added that if the amalgam be shaken in air with dil. sulphuric acid, ferrous sulphate and hydrogen dioxide are formed. A. S. Russell and co-workers studied the order of removal of metals from amalgams by oxidizing agents and found Zn, Mn, Cu, Cr, Fe, Mo, Co, Hg, Ni, and W. M. Rabinovich and P. B. Zywotinsky found that iron is dispersed in mercury, above the solubility limits to form colloidal soln. An electromagnet removes no iron from a soln. with 0·0018 to 0·0035 gram-atom per gram-atom of mercury, hence it is inferred that these soln. are colloidal. P. Casamajor added that in dil. sulphuric acid, the amalgam loses only two-thirds of its contained iron. H. A. von Vogel added that if the amalgam be triturated with argentite or silver glance, the mercury is transferred to the silver. A. S. Russell and H. A. M. Lyons studied the **zinc-iron-mercury system.**

The **boron-iron alloys** have been discussed from the point of view of the borides **5.** 32, 4. L. Troost and P. Hautefeuille[10] prepared an alloy with 11 per cent. of boron and found that it could be forged; while an alloy with 23 per cent. of boron was brittle and could not be forged. H. N. Warren obtained alloys by reducing ferrous borate with charcoal; and W. R. Hulbert obtained them by the thermite process. A. Binet du Jassonneix, S. Curie, W. Guertler, L. Guillet, H. W. Gillett and E. L. Mack, T. Miyaguchi, H. Moissan, P. Oberhoffer, N. Parravano and C. Mazzetti, J. W. Richards, and J. M. Weeren also prepared these alloys; and they were discussed by A. Campion, I. Fetchenko-Tchopiwsky, E. Lievenie, J. Ohly, and N. Parravano and C. Mazzetti; and T. P. Campbell and H. Fay studied the cementation of iron by boron.

G. Tammann and K. Schaarwächter said that the attack of iron by boron begins at about 440° and increases rapidly with rise of temp. J. Laissus, and N. Agéeff and M. Zamotorin discussed the diffusion of boron in iron. N. Tschieschewsky and A. Herdt's equilibrium diagram is indicated **5.** 32, 4; and that of G. Hannesen is shown in Fig. 417. This diagram also includes the effect of boron on the critical temp. from the f.p. down to 500°. The transformation of γ- to β-iron decreases from about 895° for pure iron down to 710° for alloys with over 0·8 per cent. of boron. During the solidification of the molten alloy, δ-iron crystallizes out first, until the soln. contains 1·38 per cent. boron, and γ-iron then separates until the soln. has 4 per cent. boron. After that, the pentitadiboride separates out. The eutectic, boron-pearlite, has a f.p. of 1164°. The δ-iron changes into γ-iron at 1414°. The regions of solid soln. of $\beta+\gamma$-iron and of $\alpha+\gamma$-iron are indicated in the diagram. F. Osmond observed that the presence of boron lowered the γ-transformation temp. R. Walter stated that a small proportion of boron promotes the graphitization of cast iron; H. A. Schwartz, that a large proportion inhibits graphitization; and F. Roll, that boron partly preserves and partly decomposes cementite.

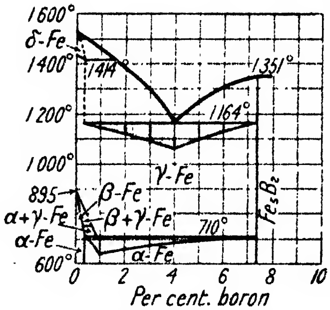


FIG. 417.—Equilibrium Diagram of the Iron-Boron Alloys.

The eutectic system has Fe–C at 1150°, Fe–B at 1165°, Fe_3C–Fe_2B at 1155°, and Fe–Fe_3C–Fe_2B at 1100°. The system at the end of the crystallization of the molten alloy has zones of solid soln. and iron hemiboride. Measurements were also made of the hardness of the alloys. F. Wever studied the effect of boron on the domain of the γ-phase—*vide* **5.** 32, 4, and G. Hägg, the X-radiograms of the hemiboride.

H. Moissan and G. Charpy found that an alloy with 0·58 per cent. of boron and 0·17 per cent. of carbon can be rolled; and is readily worked at a dull red-heat, but crumbles under the hammer if too strongly heated. A. Campion did not observe the excessive brittleness and hardness reported by N. Tschieschewsky and A. Herdt. R. Wasmuht, and N. Tschieschewsky discussed the hardening of steel by boron. L. Guillet observed that boron steels with 0·215 to 0·844 per cent. boron have (i) a solid soln. of ferroboron with a small proportion of boron; (ii) pearlite; and (iii) a substance which was regarded as iron borocarbide. This third constituent produces the brittleness of boron steels; this brittleness disappears on tempering owing to the borocarbide passing into soln. The general effect of boron is to increase the tensile strength, especially after tempering; but a maximum effect is obtained with 0·8 per cent. of boron with low-carbon steels. Observations were also made by P. Blum, the Elektrochemische Werke Bitterfeld, J. E. Hurst, E. Kothny, J. V. McCrae and R. L. Dowdell, T. Miyaguchi and I. D. K. Kaisha, J. Ohly, J. Scott, M. Vasvari, F. C. Weber, and by P. Marsich, and E. K. Smith and H. C. Aufderhaar. A. M. Portevin said that the resistance to shear, and, in particular, the elastic limit on shearing, increase rapidly with the percentage of boron in steel with 0·25 per cent. of carbon. G. Hannesen found that rapidly cooled alloys have the martensitic structure, and the alloys as well as the boride are ferromagnetic. The quenched alloys are softer than those which are slowly cooled. Alloys with primary pentitaboride are hard, and scratch corundum. G. Hägg, and S. B. Hendricks and P. R. Kosting studied the X-radiograms of iron borides. R. Wasmuht, and W. R. Whitney found that boron improves the mechanical properties and electrical resistance of steel. The effect of boron on the electric at. resistance, and the magnetic properties were likewise observed by T. D. Yensen, and the results are summarized in Fig. 419. With increasing proportions of boron, the electrical resistance, the hysteresis loss, the coercive force, and the retentivity all decrease slightly until the amount of added boron becomes appreciable, when all these qualities increase; but even then, boron has a deteriorating effect on the magnetic properties of iron. C. Matignon tested the acid-resisting properties of the ferroborons. E. D. Gleason studied the **iron-carbon-boron-copper alloys.**

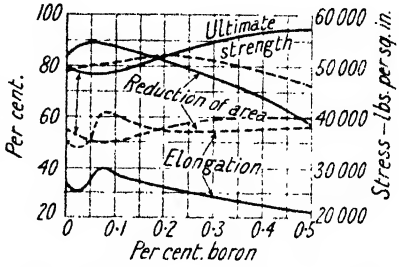


FIG. 418.—The Mechanical Properties of Boron Steels.

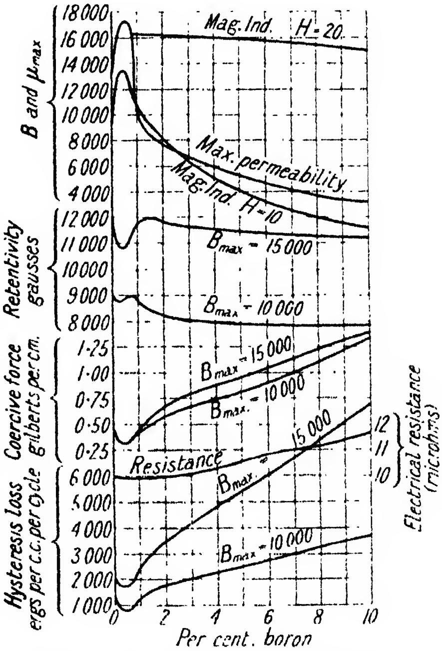


FIG. 419.—Electrical and Magnetic Properties of Boron-Iron Alloys.

H. Davy[11] prepared an **iron-aluminium alloy** by the same method as that which he employed for the alloy of iron and beryllium; and H. St. C. Deville, by passing the vapour of aluminium chloride over iron at a high temp.; G. Tammann and K. Schaarwächter observed that the attack of iron by aluminium begins at about 660° and increases rapidly with rise of temp., as well as by the direct alloying of the two elements; and W. R. Hulbert obtained them by the thermite process. Alloys were also prepared by F. R. Michel, P. Oberhoffer, E. T. Richards, J. Escard, J. W. Richards, W. Guertler, J. Czochralsky, W. Venator, J. Ohly, A. Wahlberg, S. Kern, O. I. Vher and co-workers, J. M. Weeren, and F. C. Calvert and R. Johnson. M. Faraday and J. Stodart obtained alloys which when forged into bars and the surface polished and treated with dil. sulphuric acid, exhibited the damasked surface peculiar to *wootz* or *Indian steel;* but neither C. J. B. Karsten, nor T. H. Henry could find any aluminium in wootz. C. F. Burgess and J. Aston found that alloys with about 2 per cent. aluminium forge and machine easily.

J. Cournot discussed the cementation of iron with aluminium; R. Kremann and co-workers, and R. Irmann, the solubility of aluminium in iron; and A. Hauttmann, G. Grube, N. Agéeff and M. Zamotorin, and N. Agéeff and O. I. Vher, the rate of diffusion of aluminium in iron. F. C. Calvert and R. Johnson obtained what they regarded as *iron tetritaluminide*, Fe_4Al, by heating for 2 hrs. at a white-heat a mixture of 3 mols. of aluminium chloride, 40 gram-atoms of iron, and 8 mols. of lime; *iron tritadialuminide*, Fe_3Al_2, occurs in silver-white beads in the slag from the previous operation; and F. Wöhler obtained *iron dialuminide*, $FeAl_2$, by melting together a mixture of aluminium ferrous chloride, and sodium potassium chloride (10 : 5 : 20). W. C. Roberts-Austen, and L. Guillet made a partial study of the equilibrium diagram; and A. G. C. Gwyer showed that the f.p. curve of iron falls rapidly in passing from 100 to 50 per cent. iron, and at this point there is a distinct break after which the f.p. curve falls slowly from 50 to 30 per cent. of iron, and then rapidly to the f.p. of aluminium. There are two series of solid soln. respectively with 40 to 48 per cent. and 66 to 100 per cent. of iron. The end-member of the first series is thought to be **iron trialuminide,** $FeAl_3$. Alloys with 60 to 65 per cent. of iron show eutectic breaks in the cooling curve at 1087°, and the breaks occur at a higher temp. with from 50 to 57 per cent. of aluminium. Alloys with 52 to 65 per cent. of iron have a eutectic of the same structure, but the latter differs from the eutectic with 50 per cent. iron. The curve *ef*, Fig. 420, represents the lowering of the temp. at which the magnetic permeability disappears on the heating curve as the proportion of aluminium is increased. N. Kurnakoff and co-workers found that in the interval between 32·1 and 39·5 at. per cent. of iron, iron trialuminide, $FeAl_3$ (or possibly Fe_2Al_6), crystallizes from the fused mass, but below 1100°, this compound decomposes into the α- and γ-solid soln. of aluminium in iron. Between 24·2 and 34 at. per cent. of iron, a stable δ-phase is formed having properties different from those of the adjoining phases. This phase shows a minimum electrical conductivity and temp. coeff., and a maximum hardness. It is also very

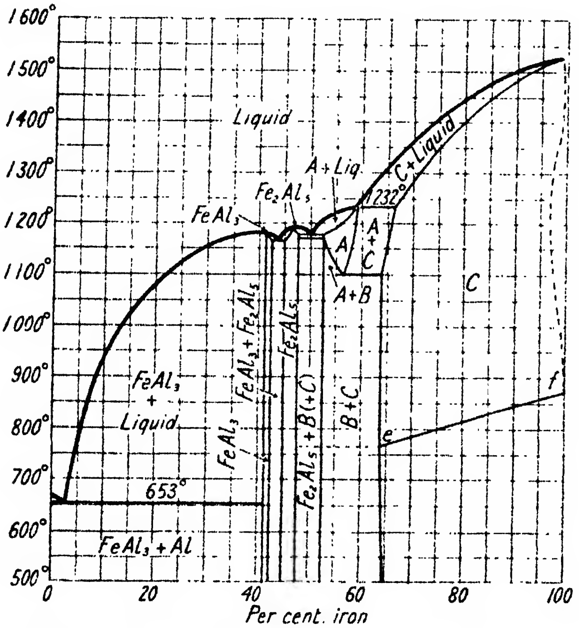


Fig. 420.—Equilibrium Diagrams of Fe-Al Alloys.

brittle. It is considered to be a chemical individual of variable composition. A. G. C. Gwyer and H. W. L. Phillips' study of the system is summarized in Fig. 420. Alloys with 0 to 40 per cent. of iron form a eutectiferous series, the eutectic alloy contains 1·89 per cent. of iron, and freezes at 653°. The liquidus rises to a slight maximum with 40·6 to 41·1 per cent. of iron, and above this range, the alloys are homogeneous. This establishes the existence of iron trialuminide, $FeAl_3$, not N. Kurnakoff and co-workers' Fe_2Al_3. There is a second maximum with about 45·3 per cent. of iron, where over a small range the alloys are homogeneous, and probably contain **iron hemipentaluminide,** Fe_2Al_5, which forms a eutectiferous series with a limited solid solubility with $FeAl_3$. The trialuminide before etching is Chinese white, and the hemipentaluminide is pale lavender; both are attacked by soda-lye; the trialuminide is alone attacked by hydrofluoric acid. All the alloys with 40 to 50 per cent. of iron are brittle, and spontaneously disintegrate in a few days. The liquidus gradually slopes from the Fe_2Al_5 maximum at 45·19 per cent. to a minimum at 49·5 per cent., and beyond that point rises steeply to 58 per cent. where a break occurs. The alloys in the range form a eutectiferous series with appreciable solid solubility. The constituents are Fe_2Al_5, and a solid soln. *A*, which is unstable and breaks up below the solidus. The eutectic line is at 1165°, and *A* breaks up at 1158°, into Fe_2Al_5 and the solid soln. *B*. At 1232° there is a peritectic reaction resulting in the formation of another compound with 59 per cent. of iron. The magnetic transformation occurs at *ef*, Fig. 420. G. Tammann and W. Salge studied the residues left after treating the alloy with an acidified soln. of ammonium persulphate. W. Biltz and C. Haase gave 3·896 for the sp. gr. of Al_3Fe at 25°/4, 35·2 for the mol. vol.; and 25 Cals. for the heat of formation. The subject was studied by L. Grenet, V. N. Svechnikoff, and F. Wever and A. Müller, whose results for the range of stability of the γ-phase are summarized by the dotted line in Fig. 420. F. Roll found that aluminium partly preserves and partly decomposes cementite—*vide* cast iron. O. von Keil and O. Jungwirth also investigated the influence of aluminium on the iron and iron–carbide system. The eutectic composition of the iron–carbon system is reduced by 0·16 per cent. carbon by the addition of 1 per cent. of aluminium; and the pearlitic transformation is slightly reduced by the addition of up to 3·5 per cent. of aluminium, but, as the proportion of aluminium is increased from 3·5 to 8 per cent., it is raised again; and with more than 8 per cent. of aluminium, the intensity of this transformation is very small; and the γ-field ceases to exist with hypoeutectic alloys having less than 5 per cent. of aluminium; the finely-granular distribution of graphite, which corresponds with metastable freezing and spontaneous decomposition, is rendered more prominent; with 5 to 9·5 per cent. of aluminium, the edges of the primary, solid soln. crystals have a decreasing tendency to decompose, and these zones become more readily soluble in acids; and with over 9·6 per cent. of aluminium, the solid soln. becomes stable and readily soluble in acids. The addition of 2·3 per cent. of aluminium to iron with a high proportion of carbon results in the complete separation of the carbon as graphite; with 11 per cent. of aluminium, the graphite completely disappears; and with 18 per cent. of aluminium, the graphite is again completely precipitated. E. Söhnchen and E. Piwowarsky found that aluminium raised the eutectoid temp. and reduced the solubility of carbon in iron. The subject was discussed by J. W. Donaldson, W. L. Fink and K. R. van Horn, and E. L. Reed.

The use of aluminium as a deoxidizing and solidifying agent in the manufacture of steel ingots is so general that its employment is regarded as almost indispensable. E. Adamson, H. M. Boylston, J. E. Carlin, G. F. Comstock, W. F. Darch, W. Eilender and H. Diergarten, C. af Geijerstam, L. Grabau, G. Guzzoni, R. A. Hadfield, C. H. Herty and co-workers, K. Hilgenstock, H. O. Hofman, W. J. Keep, O. von Keil and F. Ebert, J. W. Langley, F. W. Lürmann, J. V. McCrae and R. L. Dodwell, P. Marsich, G. Melland, J. R. Miller, N. Petinot, E. Piwowarsky, M. C. Smith, A. Spiral, S. Sirovich, K. Styffe, T. Swinden,

T. Turner, U. le Verrier, and M. H. Wickhorst studied the effect; and T. D. Yensen and W. A. Gatward thus summarize the action: When aluminium is added to molten iron, it will reduce iron oxide to metallic iron. Furthermore, it will reduce CO or CO_2 gases to free carbon and thus degasify, quiet the bath, and prevent blowholes during solidification and cooling. If the iron is sufficiently liquid, the Al_2O_3 formed will pass to the surface; if it is not, the Al_2O_3 will become entangled in the iron, increase the viscosity, and cause the iron to be more or less unsound. When added in sufficient quantities, 2 to 5 per cent., aluminium will cause carbon to be completely precipitated as graphite and thus transform, for example, white cast iron into grey iron. If 10 to 20 per cent. aluminium is added, however, the carbon may all be in the combined form Fe_3C. As the heat of combustion liberated by the oxidation of aluminium is much greater than that absorbed by the reduction of iron oxides, clearly illustrated by the use of thermite in welding iron, the addition of aluminium to oxidized iron or steel causes a rise in the temp. of the bath. This fact, and not any appreciable lowering of the melting-point, is the cause of the higher fluidity noticed when a small percentage of aluminium is added to the bath. Aluminium is a more powerful deoxidizer than silicon for it does not commence to combine with iron until all oxides present are reduced. F. Osmond showed that aluminium dissolves in iron with the absorption of heat, although an evolution of heat usually attends the phenomenon. This is attributed to the heat liberated by the decomposition of oxides of iron by the aluminium. G. Masing and O. Dahl discussed the expression of the alloys and the formation of warts during the cooling of the alloy owing to the liberation of occluded gases; and W. E. Remmers, the effect of aluminium on the growth of cast iron. For the cementation of these steels, *vide supra.*

A. Westgren and co-workers, K. Schäfer, W. L. Bragg, and A. J. Bradley and A. H. Jay discussed X-radiograms of the iron aluminides. Z. Nishiyama studied the X-radiograms of these alloys, and found for the *a* lattice parameter; the sp. gr.; and the elastic modulus, *E* kgrms. per sq. cm., at 23·0° to 23·2°:

Al . .	2	4	6	8	10	14 per cent.
a . .	2·874	2·884	2·886	—	2·897	2·904 A.
Sp. gr. .	7·6932	7·4619	7·2196	7·0418	6·8848	6·6443
$E\times10^{-6}$.	2·113	2·165	2·090	2·106	1·929	1·826

The microstructure of the alloys was studied by R. A. Hadfield, A. G. C. Gwyer, L. Guillet, and T. D. Yensen and W. A. Gatward; and with the smaller proportions of aluminium, they consist of solid soln. of the constituent elements. J. E. Johnson, F. Wever and A. Müller, A. Borsig, W. J. Keep, and T. W. Hogg studied the action of aluminium in causing the separation of graphite from the carbide in cast iron. E. Piwowarsky found that grey cast iron is appreciably softened by less than 0·10 per cent. of aluminium; and G. Melland and H. W. Waldron, that with rapidly cooled cast iron, with about 0·24 per cent. of silicon, up to 0·25 per cent. of aluminium is needed before any influence on the graphite separation can be detected; with 0·50 per cent. of aluminium, most of the carbon occurs in the graphitic state, and larger proportions of aluminium seem to cause a reversion to combined carbon—possibly owing to the formation of a complex carbide. With slowly cooled samples, the presence of the element is more marked and is more sensitive to varying conditions—*e.g.* casting temp., proportion of silicon, etc. At least 0·9 per cent. of carbon is retained in the whole series whether slowly or rapidly cooled. In general, aluminium decreases the solubility of carbon in iron, and, like silicon, it has a softening influence. A. B. Everest obtained rather different results with iron-carbon alloys free from silicon. Soft, machinable grey irons are produced by adding up to 8 per cent. of aluminium. Aluminium acts less powerfully than silicon as a softener since 2 to 3 per cent. of aluminium are needed to produce an iron comparable with one containing 1 per cent. of silicon. The maximum percentage of carbon graphitized is

61 in the presence of 4 per cent. of aluminium, against 70 per cent. in the presence of 3 per cent. of silicon. The graphite formed with aluminium is finer than in the case of silicon. With aluminium between 8 and 18 per cent., the alloys are hard and brittle, and the carbon is all combined; with between 18 and 25 per cent. of aluminium, the alloys are soft, and graphite is precipitated. Alloys with over 25 per cent. aluminium are not stable in the atmosphere.

L. Guillet observed that the presence of aluminium prevents the pearlite from assuming its ordinary forms; it is in a manner contorted, and it forms little nodules which are more easily coloured by picric acid, and the more closely resemble troostite as the proportion of aluminium increases. With a high proportion of aluminium it is even possible to have free cementite formed in a hypo-eutectoidal steel. The effect of quenching is to transform only the nodules of the pre-existing pearlite giving place to martensite, generally encircled round its edges by troostite. The iron-aluminium soln. is incapable of dissolving carbon. So long as the amount of aluminium is below 3 per cent., the quenching has no effect, but with higher proportions of aluminium, while quenching has no effect on the tensile strength, the elastic limit, or the resistance to shock, whilst the elongation and reduction in area are reduced. Annealing develops the nodular structure of the special form of pearlite without changing the microstructure in any other way; and during the operation all aluminium steels are softened. The presence of aluminium delays case-hardening, and when the proportion of aluminium attains 7 per cent., case-hardening becomes impracticable, and only nodules of cementite are found. H. Sawamura gave the constitutional diagram of aluminium and cast iron alloys. The effect of aluminium on the graphitization of cast iron is indicated above.

F. Wever and A. Müller found the sp. gr. of alloys with 8·64, 13·60, and 21·24 at. per cent. of aluminium to be respectively 7·38, 7·10, and 6·78, values rather lower than those calculated by the mixture rule. T. W. Hogg observed that the sp. gr. of an alloy with 9·62 per cent. aluminium is 6·99 when the calculated value is 6·54 to 6·65—assuming the sp. gr. of steel is 7·80 or 7·88, and that of aluminium 2·60 or 2·70. An alloy with 20 per cent. of aluminium has a sp. gr. 6·31 when the calculated value is 5·59 to 5·69. Hence, the observed sp. gr. are higher than the calculated values. G. Melland and H. W. Waldron gave for the sp. gr. of cast iron at 20°:

Al . .	0	0·024	0·527	1·78	4·24	8·31	11·80 per cent.
Sp. gr. .	7·64	7·58	7·12	7·11	6·88	6·53	6·69

Z. Nishiyama's values are indicated above. W. Brown obtained the following values for the sp. gr. and sp. vol.:

C	Si	Cr	Al	Sp. gr.	Sp. vol.	Sp. ht.
0·67	2·25	--	0·50	7·5930	0·13170	0·1158
0·24	0·18	--	2·25	7·5132	0·13310	0·1165
0·22	--	1·5	4·50	7·1582	0·13970	0·1195

The results show that up to 4·5 per cent. aluminium increases the sp. vol. by 0·0025 per 1 per cent. aluminium. The subject was discussed by B. Simmersbach, and J. O. Arnold. R. A. Hadfield, and G. Tammann and V. Caglioti measured the hardness of some of these alloys. Representing the percentage proportions of C : Al in the alloys, R. A. Hadfield's data for the sp. gr. are:

C : Al . .	0·20 : 0·61	0·17 : 0·72	0·21 : 1·60	0·24 : 2·29	0·26 : 9·14
Sp. gr. . .	7·781	7·755	7·624	7·554	6·672

E. Gumlich represented the sp. gr., D, of the alloys with p per cent. of aluminium by $D = 7·865 - 0·1166p$. C. Benedicks and N. and G. Ericson studied the sp. vol.; and L. Losana, the viscosity of the molten metal; and A. Kussmann and B. Scharnoff, the hardness. E. Söhnchen and E. Piwowarsky found that additions of aluminium up to 1 per cent. halve the hardness of iron-carbon alloys; from 1 to 8 per cent. has little effect, and further additions of aluminium increase the hardness to its original value with 11 per cent. aluminium. The subject was studied by K. Taniguchi, and O. Meyer and R. Hobrock; and the corrosion fatigue, by P. Brenner.

W. Brown found that the presence of up to 2 per cent. of aluminium has little effect on the sp. ht. F. Wüst and co-workers gave for the mean sp. ht. of aluminium steel between 0° and 1000°, $102\cdot39\theta^{-1}+0\cdot21870+0\cdot0000024\theta$; and for the true sp. ht., $0\cdot21870+0\cdot0000048\theta$. The mechanical properties of the alloys were studied by W. W. Christie, C. A. Edwards, F. L. Garrison, R. C. Good, L. Guillet and co-workers, R. A. Hadfield, W. J. Keep, E. Kothny, W. Kroenig, I. Musatti and G. Calbiani, A. L. Norbury, P. Ostberg, S. A. Pogodin, A. M. Portevin, A. Schulze, A. E. M. Smith, E. K. Smith and H. C. Aufderhaar, and K. Styffe, who found that up to 5 per cent. aluminium has very little effect; but with more than 5 per cent. of aluminium, the alloys are stronger in tension, but they become brittle. R. A. Hadfield observed that if 0·2 per cent. of carbon is present, the limits of forgeability are between 5·6 and 9·14 per cent. aluminium, while L. Guillet found the limits to be 7·18 and 9·25 per cent. for alloys with 0·8 per cent. carbon. T. D. Yensen and W. A. Gatward observed that with alloys prepared in vacuo, the tensile strength increases in direct proportion to the aluminium-content up to at least 6 per cent., the ultimate strength of the latter being 60 kgrms. per sq. mm. in the unannealed state, and 50 kgrms. per sq. mm. in the annealed state. The corresponding figures for purified iron are 34 kgrms. and 25 kgrms. per sq. mm. The toughness is only slightly affected by the aluminium-content. A selection from the results for iron with no more than 0·02 per cent. of carbon is summarized in Table LIX. The alloys, annealed at 1000°, were cooled at the rate of 30° per hour. M. Wählert found for alloys of iron with:

TABLE LIX.—MECHANICAL PROPERTIES OF SOME AL-FE ALLOYS.

	Al (per cent.)	Yield-point (lbs. per sq. in.)	Ultimate strength (lbs. per sq. in.)	Elongation (per cent.)		Reduction area (per cent.)
				Before necking	Ultimate	
Unannealed	0·00	50,700	54,700	4·0	26·0	84·3
	0·02	40,200	46,400	5·0	28·0	93·4
	0·80	86,300	86,500	—	25·0	86·9
	2·67	47,700	59,700	13·0	36·0	81·6
	4·55	81,800	84,400	2·5	23·0	81·6
	6·24	77,700	86,000	5·0	28·0	74·7
Annealed at 1000°	0·00	17,600	34,900	33	60	93·5
	0·02	13,900	34,470	32	60	91·6
	0·80	21,700	40,100	26	56	91·5
	2·67	30,100	49,400	28	49	89·0
	4·55	41,900	60,200	22	49	83·8
	6·24	53,400	69,800	11	27	55·5

Al	100	98·0	96·0 per cent.
Brinell's hardness . .	30	34	40
Tensile strength . .	10·8	11·7	12·8 kgrms. per sq. mm.
Elongation	38·5	30·0	24·2 per cent.

G. Melland and H. W. Waldron found the crushing load in tons per sq. in. to be for iron with aluminium:

Al	0	0·25	0·389	0·722	1·250	2·375	3·82
Crushing load .	101·2	42·5	50·63	45·3	45·18	51·0	50·10

Z. Nishiyama's values for the elastic constants are indicated above. Observations were made by H. Bohner, and R. L. Templin and D. A. Paul. R. A. Hadfield observed that at liquid air temp., −182°, the tenacity increases, and the ductility decreases. E. E. McCollough studied the thermal expansion of some alloys; and A. Schulze found that the values of the coeff. of thermal expansion $\times 10^6$ were as follow:

Aluminium	0·52	2·17	5·66	10·52 per cent.
20°–100°	11·60	11·74	11·96	12·20 $\times 10^{-6}$
100°–300°	13·19	13·21	13·42	13·70 $\times 10^{-6}$
300°–500°	14·42	14·50	14·88	15·12 $\times 10^{-6}$

W. F. Barrett and co-workers found that as the proportion of aluminium increased up to 5·50 per cent., the electrical resistance increased from 10·9 to 70·0 microhms. Observations were made by S. A. Pogodin, and G. Tammann, and V. Caglioti. J. H. Partridge found that aluminium raises the electrical resistance of cast iron. T. D. Yensen and W. A. Gatward's results for the electrical resistance, given in Table LX, show that this property increases about 12 microhms for each per cent. of aluminium added. When the aluminium-content exceeds 3 per cent., the rate of increase falls off more gradually. N. Kurnakoff and co-workers observed the singular points indicated in Fig. 421 for the electrical conductivity and the temp. coeff. of the conductivity of these alloys; A. Schulze, the electrical resistance. G. Tammann and E. Sotter found that the potential of the iron-aluminium alloys in 0·1N-H_2SO_4 slowly falls with time when cathodically polarized, and rises when anodically polarized. A film of oxide is formed as passivity develops. A. M. Portevin observed that with steel containing approximately 0·13 per cent. of aluminium, with different percentages of carbon, the electrical resistance, R microhms per cm. cube at 20°–23°, is:

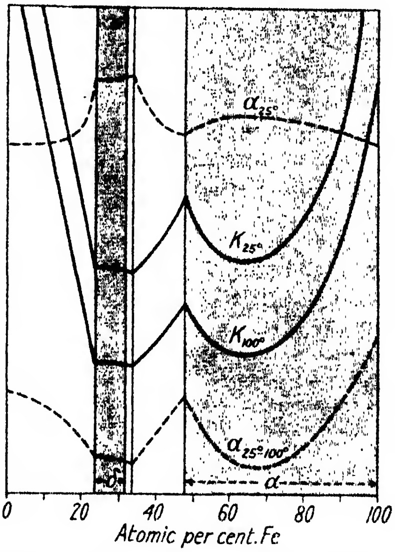


Fig. 421.—The Electrical Conductivity and Temperature Coefficient of the Conductivity for Iron-Aluminium Alloys.

Al		0·51	1·08	2·04	3·05	5·08	7·18 per cent.
R	Normal . .	17·1	26·3	35·9	50·7	63·6	76·6
	Hardened .	17·5	27·2	35·5	51·4	65·4	77·3

and for steels with approximately 0·75 per cent. of carbon:

Al		1·05	2·09	2·89	4·65	9·15	14·90 per cent.
R	Normal . .	30·3	47·4	53·0	65·6	92·6	87·8
	Hardened .	41·8	57·2	60·9	76·5	100·6	99·6

W. F. Barrett and co-workers gave 11·1 microhms per cm. cube for the increase in the resistance of iron produced by 1 per cent. of aluminium; A. M. Portevin gave 11·7 microhms; T. D. Yensen and W. A. Gatward, and E. Gumlich, 12·0 microhms. C. Benedicks' formula for the conductivity—*vide supra*, Fe-Cu alloys—is not generally applicable. Observations were also made by E. Gumlich, and M. Kuroda. E. L. Dupuy and A. M. Portevin measured the thermoelectric force of aluminium steels against copper over a range of temp. from −80° to 100°. The results expressed in millivolts with steel annealed at 1000°, and quenched from 1000°, are as follow:

C		0·17	0·13	0·08	0·81	0·66	0·67	0·86	per cent.
Al		2·04	3·04	7·18	4·65	7·00	9·15	14·90	,,
Annealed	−80°	−7·50	−11·50	−16·60	−10·00	−11·30	−15·10	−8·60	
	100°	−12·65	—	—	−14·65	−16·05	—	−13·15	
Hardened	−80°	−8·10	−11·70	−16·80	−13·60	−15·60	−14·60	−12·80	
	100°	−11·50	−10·05	—	−16·30	—	—	−14·05	

Observations were made by E. Sedström. J. H. J. Daggar stated that the addition of above 5 per cent. of aluminium rapidly destroys the magnetic properties of iron. The magnetic qualities of the alloys were examined by M. E. Thompson and co-workers, S. W. Richardson and L. Lownds, S. W. Richardson, R. L. Wills, W. M. Hicks, T. D. Yensen and W. A. Gatward, J. H. Partridge, E. Gerold, C. Eickmeyer, W. F. Barrett and co-workers, L. Guillet, A. Schweitzer, E. Gumlich, and G. Dillner and A. F. Enström. T. D. Yensen and W. A. Gatward found that aluminium, like silicon, has a beneficial effect when added in small quantities. The results for alloys with no more than 0·02 per cent. of carbon are summarized in Table LIX. The best alloys obtained, contained about 0·40 per cent. of aluminium, annealed at 1100°, and cooled at the rate of about 30° per hour, had a maximum permeability above 35,000. The hysteresis losses, for $B_{\text{max.}}=10,000$ and 15,000, are 450 and 1000 ergs per c.c. per cycle, respectively. For higher aluminium-contents the magnetic quality decreases gradually, so that the alloy containing 3·5 per cent. aluminium has a maximum permeability of 20,000 and hysteresis losses for the given densities of 1000 and 2200 ergs, respectively. This loss is only one-half that of the 3·5 per cent. commercial silicon steel. A. Kussmann and B. Scharnoff observed no relation between the coercive force and hardness. E. Gumlich studied the magnetic saturation of iron-aluminium alloys; and A. Schulze the magnetostricture in different magnetic fields. Observations were also made on the effect of the magnetic intensity, and magnetic concentration on the magnetostricture.

G. Tammann and G. Siebel found that the introduction of aluminium results in a marked reduction in the rate of oxidation of iron. J. E. Stead stated that the presence of aluminium increases the liability of steel to corrosion. G. Tammann and E. Sotter discussed the passivity of the alloys. A. Hauttmann observed that the increases in weight, in grms. per sq. m. per hour, due to oxidation which occurs when the iron-aluminium alloys are heated for 48 hrs. in air, are:

Al	0	1·84	3·72	9·44	22·34	38·32	per cent.
Oxidation	45·7	36·2	31·5	0·57	0·29	0·14	

F. C. Calvert and R. Johnson observed that dil. sulphuric acid will extract the iron from the alloys and leave the aluminium; and F. Wöhler, that soda-lye extracts the aluminium and leaves the iron. The alloys are soluble in hydrochloric acid. C. F. Burgess and J. Aston observed that the corrosion of alloys of electrolytic iron with 0, 0·067, and 1·333 per cent. of aluminium is represented by a loss of respectively 1·300, 0·628, and 0·760 grms. per sq. dm. when immersed for an hour in 20 per cent. sulphuric acid; or by loss of respectively 0·499, 0·513, and 0·390 kgrm. per sq. metre per year when exposed to the weather for 162 days from July to February. S. Satoh studied the nitridizing of these steels by heating them in ammonia at 560° to 580°; and O. Bauer, and A. von Zeerleder, the effect of aluminium on the resistance of steel to dil. sulphuric acid. H. Gruber found that with alloys 60×13×12 mm. after an hour's exposure to hydrogen sulphide:

	Al : Fe	700°	800°	900°
Gain in weight	0 : 100	0·76	5·51	10·0
	5 : 95	1·37	4·89	12·8
	10 : 90	0·33	2·38	19·1
	15 : 85	0·05	0·15	25·0

The study of light aluminium alloys for aeronautical and other work involved observations on alloys containing preponderating proportions of aluminium.

TABLE LX.—MAGNETIC AND ELECTRICAL PROPERTIES OF FE-AL ALLOYS.

	Al (per cent.)	Permeability (max.)	Density (gausses)	Permeability		Hysteresis loss (ergs) (c.c. per cycle)		Retentivity (gausses)		Coercive force (per cm.)		Sp. elect. resistance (micr-ohms) (at 20°)
				B = 10,000	B = 15,000	B = 10,000	B = 15,000	B = 10,000	B = 15,000	B = 10,000	B = 15,000	
Unannealed	0·00	1,500	6,000	1,162	605	5340	10,100	5080	6,560	1·7	2·1	9·7
	0·02	2,260	5,200	1,885	1,035	—	—	—	—	—	—	—
	0·80	1,620	6,500	1,250	577	5890	10,630	6580	6,980	2·1	2·4	19·4
	2·67	2,400	4,820	764	394	5080	8,970	4770	4,870	1·9	2·1	40·2
	4·55	763	4,200	477	220	9600	16,000	4500	4,700	3·2	3·5	59·0
	6·24	600	3,200	333	160	—	—	—	—	—	—	—
Annealed at 90°	0·00	17,800	9,000	17,750	8,290	954	2,060	9080	14,200	0·33	0·40	9·7
	0·02	24,300	12,160	22,250	12,500	986	2,240	9360	14,600	0·32	0·43	10·2
	0·80	14,000	8,000	12,500	3,950	878	2,458	8600	12,750	0·35	0·47	19·2
	2·67	12,300	8,000	11,750	1,250	1195	2,680	8600	11,700	0·40	0·60	39·9
	4·55	14,600	7,200	12,560	590	1304	3,440	9600	11,900	0·42	0·57	57·3
	5·72	11,500	6,000	7,700	273	1290	3,150	8600	10,200	0·41	0·45	68·7
Annealed at 1000°	0·00	17,500	7,000	16,650	7,500	890	2,100	8835	13,000	0·30	0·41	9·7
	0·02	20,800	6,200	18,150	7,500	699	1,780	9195	13,000	0·23	0·35	10·2
	0·80	20,900	7,000	17,230	3,950	700	1,590	8920	11,800	0·23	0·25	19·2
	2·67	19,700	7,500	16,150	2,000	763	1,790	8800	11,400	0·23	0·26	39·7
	4·55	19,800	6,000	11,750	483	985	2,530	8800	11,300	0·27	0·50	57·9
	6·24	16,050	3,200	7,400	259	922	2,830	8200	9,100	0·27	0·31	70·4

R. J. Anderson said that no binary alloy of aluminium and iron is employed commercially. C. A. Edwards studied the mechanical properties of the binary alloys with up to 5 per cent. of iron; and H. Schirmeister, alloys with up to 12·5 per cent. of iron. S. A. Pogodin, O. L. Kowalke, C. A. Edwards, W. Rosenhain, J. Ohly, F. C. Lea, N. A. Ziegler, M. Ballay, E. T. Richards, A. V. Farr, S. F. Herman and F. T. Sisco, V. Fuss, K. Yamaguchi and I. Nakamura, and L. J. Wills also studied the properties of some ternary **aluminium-copper-iron alloys**; V. Fuss, of some ternary **aluminium-magnesium-iron alloys**, and of some **aluminium-zinc-iron alloys**; C. A. Edwards, L. J. Wills, some quaternary Al–Cu–Fe–Mg and Al–Cu–Fe–Zn alloys.

W. Kroll[12] studied some **gallium-iron alloys.** According to E. Isaac and G. Tammann, **thallium-iron alloys** were not obtained because the b.p. of thallium, 1515°, is below the m.p. of iron. J. G. Gahn[13] heated to whiteness a mixture of ceric and ferric oxides, and charcoal, and obtained a green, porous, brittle, magnetic mass, which appeared to be metallic when filed. Observations were made by P. Oberhoffer.

H. C. Kremers and R. G. Stevens found that the **lanthanum-iron alloy** (85 : 15) is hard, but is not pyrophoric when scratched with a file. A 30 per cent. alloy is much harder, and shows no increase in pyrophoric qualities. The alloy is resistant to tarnishing in air. N. Agéeff and M. Zamotorin studied the diffusion of cerium in iron. The **cerium-iron alloys** were investigated by R. Vogel, H. Suchanek, L. W. Spring, A. Trillat, and A. Hirsch. Starting from 95·6 per cent. cerium, free from neodymium and praseodymium, but with lanthanum and traces of iron, melting at 775°, R. Vogel found that the f.p. falls to a eutectic at 635° and 5 per cent. of iron. The rising branch of the curve shows the existence of **iron hemiceride,** $CeFe_2$, which changes at 773° into **iron pentitadiceride,** Fe_5Ce_2—or, according to F. Clotofsky, into **iron ceride,** CeFe. L. Guillet studied the hemiceride. The second break in the curve is at 1085°, where this ceride breaks up into solid soln. rich in iron, and liquid. The solid soln. contains up to 15 per cent. of cerium at 1085°, diminishing on cooling to about 11 per cent. cerium at 850° and lower temp. It undergoes two polymorphic changes due to those of iron at 840° and 795°. The latter is recognized by the appearance of magnetic properties on cooling. The change in the saturation of the solid soln. at these transition points is too small to be observed; the two cerides do not form solid soln. The reactions in the solid state take place slowly, and there is a difficulty in obtaining equilibrium. The hemiceride is magnetic at ordinary temp. but becomes non-magnetic at 116°. It is uncertain how far the second compound is magnetic since the alloys contain the magnetic solid soln. which becomes non-magnetic at 795°. The hardness is a maximum at 60 per cent. cerium. F. Clotofsky found that the curve showing the variation of the potential difference with composition with a soln. of 0·3N-cerium chloride and 0·2N-ferrous chloride has breaks corresponding with the existence of iron ceride, CeFe, and with **iron hexitaceride,** $CeFe_6$, but the composition of the latter is not certain. H. Beck said that at 800°, molten cerium takes up considerable amounts of iron ultimately forming what he regarded as **iron decitaceride,** $CeFe_{10}$. A. B. Schiotz obtained alloys approximating Ce_2Fe_3 by the electrolysis of soln. of ferrous and cerous salts. R. Vogel found that the sat. solid soln. of cerium and iron is more resistant to oxidation than pure iron; the compounds are readily oxidized. The pyrophoric properties of the alloys reach a maximum with 70 per cent. of cerium, and depend on the presence of one or other of the compounds. Pyrophoric cerium alloys usually consist of a hard compound embedded in a softer, readily oxidizable ground mass. The pyrophoric alloys obtained by alloying mischmetall with about 30 per cent. of iron were patented by A. von Welsbach; and the subject was discussed by H. Kellermann— **5.** 38, 10. P. Martin studied Kerr's effect. The mechanical properties of alloys with cast iron were examined by R. Moldenke, E. Kothny, E. K. Smith and H. C. Aufderhaar, J. E. Hurst, etc.; and the magnetic properties by G. Rassat. H. W. Gillett and E. L. Mack thus summarize the effects of cerium:

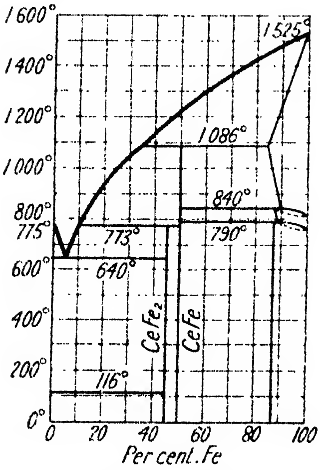


FIG. 422.—Equilibrium Diagram of the Ce-Fe Alloys.

> Cerium is readily oxidizable and, like uranium, is difficult to introduce into steel without segregation and loss. Cerium can combine with sulphur and act like manganese in preventing the formation of iron sulphide. Some sulphur may be eliminated by the use of cerium, but cerium steels retain some of the sulphur compounds or some oxidation products of cerium as inclusions and are prone to excessive dirtiness. Up to amounts which can be introduced without too much difficulty, the effect of cerium on the critical points, the propensity for hardening and the mechanical properties seems to be very small. Tests on certain steels are generally vitiated as far as showing the alloying action of cerium by the multitude of non-metallic inclusions present. Cerium is probably present in steel, at least in part, as carbide. A steel containing 0·25 per cent. cerium gives a strong acetylene-like odour on exposure of a fresh fracture. After giving various tests in detail and analyzing the results, they conclude that cerium appears to have no true alloying effect in steel and does no good. Since it gives rise to inclusion, it probably does harm. There is a possibility that it might be used as a scavenger to eliminate or control sulphur if means could be found to eliminate the accompanying inclusions.

The **iron-silicon alloys,** and *ferrosilicon* were discussed in connection with the iron silicides—**6.** 40, 13. G. Tammann and K. Schaarwächter [14] found the attack of iron by silicon begins at about 1000°. R. Walter observed that when soft iron together with silicon or a high percentage ferrosilicon is heated to 1250°, a vigorous reaction occurs, the temp. rises above 1800°, and the mass melts. The early samples of siliceous iron contained up to about 6 per cent. of silicon; and the siliceous cast iron known as *glazed pig,* or *burnt pig,* formerly rejected as useless, may now be manufactured deliberately. J. Percy, and C. J. B. Karsten obtained highly siliceous iron by heating iron and silica in the presence of carbon; the silica is not reduced if carbon be absent. Alloys were made by E. Riley in 1872; and by A. Pourcel in 1878. T. E. Holgate gave a number of analyses showing that the proportion of carbon decreases as the silicon-content increases; and in 1862, H. Caron had observed that silicon transforms combined carbon into the graphitic state. G. J. Snelus, in 1871, and C. Wood also, in 1885, observed silicon converted combined carbon into free carbon and so transformed white cast iron into grey cast iron. The alloys were discussed by J. Ohly, W. Schut and J. D. Jansen, J. Arnott, G. Kothny, H. D. Hibbard, R. P. Hudson, H. Buchholtz, H. Koppenberg, C. Wallmann, K. von Kerpely, J. Silberstein, H. Jungbluth, M. Debar, C. A. Heise, W. Guertler, R. Walter, F. Peters, A. T. Lowzow, J. Escard, J. W. Richards, J. Härden, E. Piwowarsky, R. Namais, E. Donath and M. Hailsig, P. Girod, A. Ledebur, G. P. Scholl, J. Ohly, B. L. Vanzetti, W. Pick and W. Conrad, F. M. Becket, H. C. H. Carpenter, M. G. Corson, P. H. Brace, W. G. Merten, H. Delomenie, and E. Lievenie. Some of the trade-names of the corrosion-resisting iron-silicon alloys are: *duriron, tantiron, corrosiron, thermisilid, elianite, ironac,* and *métillure*. They carry from 13·5 to 16·9 per cent. of silicon, 81 to 85·5 per cent. of iron, 0·2 to 1·25 per cent. carbon, 0·06 to 0·78 per cent. of phosphorus, 0·01 to 0·15 per cent. of sulphur. Métillure has 0·25 per cent. of aluminium, and elianite, 2·23 per cent. of nickel. T. D. Yensen found that carbon is more effective as a deoxidizer than silicon, and that 2 to 3 per cent. of silicon is about as effective as 0·3 per cent. of carbon. Silicon can dissolve in iron in all proportions, but only 4 to 5 per cent. of carbon dissolves in the absence of special impurities or metalloids. The control of the proportion of silicon in pig-iron was discussed by W. H. Morris; and J. W. Thomas showed the variations in the proportions of silicon in pig-iron as the iron flows from the blast-furnace. The deoxidizing powers of silicon were discussed by C. H. Herty and G. R. Fitterer. The behaviour of silicon in cast iron, etc., was studied by I. L. Bell, C. F. Joseph and A. L. Boegehold, O. von Keil and F. Ebert, G. Jüngst, P. Oberhoffer, M. H. Wickhorst, A. Smith, J. M. Weeren, J. S. Kennedy, P. Girod, W. Venator, and B. Neumann. T. Turner, and W. J. Keep and E. Orton observed that white cast-iron which gives porous and brittle castings yields a metal free from honeycombing, and possesses greater strength when it is associated with a little silicon. With up to 2 per cent. silicon, the iron becomes grey, and possesses a maximum strength. With more silicon, the iron remains grey, but becomes weaker, and closer grained. C. F. King observed that in pig-iron the carbon liberated on cooling is proportional to the proportion of silicon, and he also estimated the rate of elimination of the metalloids in the Bessemer process. F. Gautier said that some of the alleged ill-effects of silicon, by C. J. B. Karsten, etc., may be due to the presence of silica, which, as H. von Jüptner emphasized, may accumulate between the crystal grains, and lower the tenacity of the metal. R. A. Hadfield also favoured this view, for he observed that the presence of up to 2 per cent. silicon imparted a remarkable ductility and toughness in the bending and tenacity tests. L. Guillet said that the only silicon steels capable of being rolled are those with less than 5 per cent. silicon and 0·20 per cent. carbon, and with 2 per cent. silicon and 0·80 per cent. carbon. According to R. A. Hadfield, a specimen with 0·24 per cent. silicon did not forge well since it cracked while being hammered; but samples with 0·79 to 5·53 per cent. of silicon forged at a yellow-heat. Samples with higher proportions of silicon are red-short and crumble at a low red-heat even when there is only 0·25 per cent. of carbon; with a higher proportion of carbon, the metal becomes red-short with a lower proportion of silicon. The red-shortness is not removed by further additions of silicon, or of manganese. The fractures with 2·18 per cent. silicon are silky, and with higher proportions they are coarsely crystalline. T. D. Yensen found that the limit of forgeability of iron-silicon alloys lies between 7 and 8 per cent. silicon. A critical range occurs between 2·55 and 2·60 per cent.

silicon in which the alloys are very brittle, being in some cases unforgeable. According to R. A. Hadfield, neither annealing nor water-quenching has any effect on the structure of cast or forged silicon steel. There is a striking change in the fracture on exceeding 2·5 per cent. silicon. The crystals become large, have a glazed appearance, and cleave after the manner of speigeleisen. As this crystalline structure becomes more marked, the metal becomes very brittle, approaching silicon cast iron, and is non-malleable. The presence of silicon in steel is fatal to welding. C. F. Burgess and J. Aston discussed the working qualities of the silicon-iron alloys.

F. Osmond found that silicon combines with iron with the evolution of heat, but the resulting compound is decomposed by an excess, and it can exist only if sufficient silicon be present. A. Fry, N. Agéeff and M. Zamotorin, M. Dubowicky, and L. Guillet discussed the diffusion of silicon in solid iron; and W. F. Holbrook and co-workers, in liquid iron. The equilibrium diagrams of the iron–silicon system, and of the iron–carbon–silicon system were discussed in connection with the iron silicides **6.** 40, 13. There is not yet general agreement in all parts of the equilibrium diagram—particularly below 15 per cent. silicon. B. Stoughton and E. S. Greiner's summary is indicated in Fig. 423. The curve of magnetic transformation, *FKG*, occurs at 760° with an alloy having 1·76 per cent. Si, drops to 450° as the silicon increases to 17·04 per cent., and remains at 450° with alloys having up to 25 per cent., it is perceptible with alloys having 27·30 per cent. but not with alloys having a higher proportion of silicon. The curve *FKG* thus represents the effect of silicon on the A_2-transformation of iron. N. B. Pilling observed a sharp line of demarcation between brittle and ductile alloys—probably the dotted line, Fig. 423; and B. Stoughton and E. S. Greiner observed confirmatory evidence on the temp.—electrical resistance curve. Alloys with less than 33 per cent. of silicon undergo a complex series of transformations on cooling; the line *AB* is supposed to represent the peritectic formation of Fe_3Si at 1255°, because T. Murakami observed no evidence of heat corresponding with *CD* in alloys with less than 18 per cent. of silicon, and because on extrapolating N. B. Pilling's results, the curve *AB* connects with the peritectic reaction at *B*. It may be that the curve *AB* connects with *CD* at *C* instead of the peritectic reaction at *B*. T. Murakami regards the magnetic transformation *FK*, and *KG* as changes of phase, and the line *HI* represents a transformation of Fe_3Si_2. The lines separating the γ- from the α-phase have been traced by F. Wever and P. Giani, R. Frilley, H. Esser and P. Oberhoffer, M. Bamberger and co-workers, and A. Sanfourche. Fig. 423 is based on the assumption that four silicides are formed. M. G. Corson considered that his photomicrographs demonstrate the existence of **iron tritasilicide,** Fe_3Si, formed by a peritectic reaction between the melt and the solidus at *B*; then a peritectic reaction sets in at 1020°, the line *DE*, between Fe_3Si and FeSi, to form **iron tritadisilicide,** Fe_3Si_2, thus $Fe_3Si + 3FeSi \rightleftharpoons 2Fe_3Si_2$. The ditritasilicide is decomposed at temp. exceeding *DE*, and the tritasilicide is decomposed when heated to *BN*.

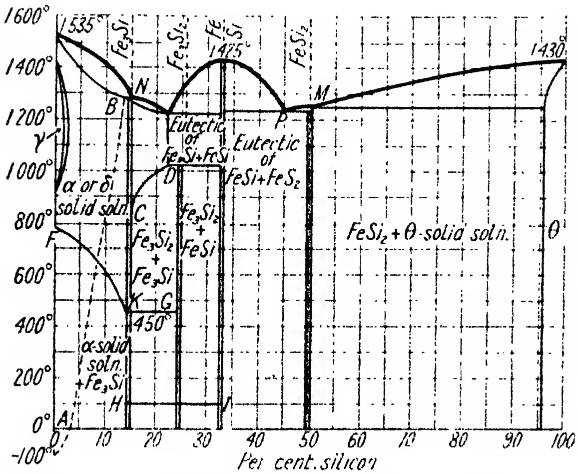


Fig. 423.—Equilibrium Diagram of the System: Iron–Silicon.

There is a maximum in the m.p. curve corresponding with **iron monosilicide,** FeSi, and a hidden maximum in its m.p. curve corresponding with **iron silicide,** $FeSi_2$. F. Wever and H. Möller found that the monosilicide has 4 mols. in a unit cell, and $a=4{\cdot}467$ A. Whilst there is a doubt, the probabilities are in favour of the existence of Fe_3Si, Fe_3Si_2, and $FeSi_2$. Alloys with over 33·3 per cent. of silicon are comparatively simple; there is a eutectic at 45 per cent. silicon, and the disilicide at *M*. There is only 5° difference of temp. between the eutectic at *P* and the m.p. of the disilicide at *M*. The θ-phase is a solid soln. of the disilicide in silicon. According to J. L. Haughton and M. L. Becker, the liquidus and solidus curves of the α-solid soln. lie close together and fall at 35 per cent. silicon to 1198°; the eutectic temp. with the ϵ-phase—FeSi. The maximum of the liquidus curve in the ϵ-region is at 1410°, and falls at 51 per cent. silicon to the eutectic with the ζ-phase at 1213°. The ζ-phase is thought to be **iron hemipentasilicide,** Fe_2Si_5, which forms a eutectic with 59 per cent. of silicon at 1208°. Iron is but slightly soluble in silicon, but the solubility of silicon in iron at the eutectic point is 18·5 per cent. and it falls to 15 per cent. at about 800°. In agreement with T. Murakami, the arrest on the cooling curve, at about 1030°, is attributed to the formation of iron tritadisilicide, Fe_3Si_2. There is another arrest at 950°, which has not yet been interpreted. Silicon lowers the $\beta\alpha$-transformation until it meets the boundary of the η-phase at 490° and 14·5 per cent. of silicon, after which the curve is horizontal up to 25 per cent. silicon. The magnetic transformation at 82° is due to a change in the η-phase. R. T. Haslam and L. E. Carlsmith, and A. Fry studied the diffusion of silicon in iron—*vide* cementation—and A. Sanfourche, the cementation of iron with silicon by means of silicon tetrafluoride. F. Wüst and O. Petersen, and G. Charpy and A. Cornu-Thénard showed that the solubility of carbon in iron decreases as the proportion of silicon increases. The solubility of carbon in iron was discussed by W. Gontermann, K. Honda and T. Murakami, D. Hanson, H. Voss, F. Roll, A. Merz, T. F. Pearson, A. L. Norbury, J. H. Andrew, M. L. Becker, H. Moissan, F. Poboril, and J. E. Stead. F. Wüst and O. Petersen found that the presence of silicon causes the ledeburite point to occur with a lower proportion of carbon, or at a higher temp.; and, as indicated above, it renders the formation of cementite more difficult, and favours the production of graphite. M. L. Becker found that as the silicon increases up to 4 per cent., the solubility of carbon at any constant temp., between 940° and 1100°, decreases, whilst the effect of temp. in raising the solubility becomes less marked. Below 940°, probably in the neighbourhood of 920°, the solubility drops to zero. The effect of silicon on the Ar_4-arrest was also discussed **6.** 40, 13, and in connection with the equilibrium diagram of the carbon-iron alloys. F. Osmond, W. Gontermann, T. D. Yensen, L. Grenet, T. Naske, K. Honda and T. Murakami, and G. Charpy and A. Cornu-Thénard showed that the effect of silicon is to raise the temp. of the A_3-arrest, and to diminish its intensity; whilst R. Ruer and R. Klesper, A. Sanfourche, F. Wever and P. Giani, G. Phragmen, and D. Hanson have shown that the A_4-arrest occurs at decreasing temp. and gradually disappears. This, coupled with the fact that A. Westgren and G. Phragmen found that the space-lattice of δ- and α-iron are the same, led P. Oberhoffer, D. Hanson, and T. D. Yensen to suggest that with silicon above, say, 1·5 to 2·5 per cent., the A_3- and A_4-arrests merge into one another, and γ-iron is no longer present in the system. F. Wever and H. Möller studied the X-radiograms of the monosilicide. F. Wever and P. Giani also found that the $\alpha\rightarrow\gamma$ transition temp. is raised and the $\gamma\rightarrow\delta$ transition temp. is lowered by increasing proportions of silicon, and no transition occurs when more than 1·8 per cent. of silicon is present. The subject was studied by J. H. Andrew, R. S. Archer, A. Carnot and E. Goutal, G. de Chalmot, W. Claus and R. Hensel, W. Haufe, A. Hayes and co-workers, K. Honda and T. Murakami, A. Jouve, A. Kriz and E. Poboril, P. Lebeau, A. L. Norbury and E. Morgan, P. Oberhoffer and C. Kreutzer, G. Phragmen, N. B. Pilling and G. P. Halliwell, C. Schols, H. A. Schwartz and co-workers, H. Scott, E. Vigouroux, and F. Wever. F. Körber described the "etching colours" of the iron-silicon alloys.

H. A. Schwartz and A. N. Hird observed that in the freezing of the eutectic for the ternary system, the silicon will be rejected to the liquid and will be found – possibly as a silicocementite—in the eutectic cementite if the cooling is slow enough for equilibrium conditions. G. Charpy and A. Cornu-Thénard thus summarized their observations on this subject. The A_3-point rapidly decreases as the proportion of silicon increases. The A_2-point falls gradually in the temp. scale when the percentage of silicon rises; it loses little by little its intensity, but still persists when 7 per cent. of silicon is present. In this case, the A_2-point is the only anomaly appearing on the thermal diagram of alloys containing a low proportion of carbon even when the rate of variation in temp. is sufficiently accelerated. The effect of silicon on the eutectic temp. of the pearlite precipitation was examined by F. Wüst and O. Petersen, A. P. Hague and T. Turner, and W. Gontermann. D. Hanson also studied this subject. E. Söhnchen and E. Piwowarsky observed that silicon reduces the solubility of carbon in iron, and 5·7 per cent. of silicon raises the eutectoid temp. to 940°. F. Wever and P. Giani, E. Gumlich, and K. Honda and T. Murakami studied the effect of silicon on the temp. of the β- to α-magnetic change. W. Guertler and G. Tammann found that with the following atomic proportions of silicon, the Ar_2-point was but little affected:

Silicon . .	0·06	10·40	20·00	29·10	38·60	47·50 at.
Ar_2-arrest . .	760°	750°	745°	735°	720°	720° per cent.

According to G. Charpy and A. Cornu-Thénard, the individuality of the A_2-point is more clearly indicated by the fact that it is possible, at will, to retain in or eliminate from its vicinity the *A_1-point*, by bringing into play the precipitation of graphite. The temp. at which the A_1-point occurs rises with increasing proportions of silicon, reaches and finally passes the A_2-point, and at the same time it becomes fainter. After reaching a given proportion of silicon and a given rate of variation of temp., the A_1-point completely disappears, and all the carbon in the metal is then graphite. The effect of silicon on the critical temp. of iron was discussed by E. Gumlich, W. E. Ruder, A. P. Hague and T. Turner, F. Osmond, J. O. Arnold, G. Charpy and A. Cornu-Thénard, R. Ruer and R. Klesper, B. Kjerrman, F. L. Meacham, T. Baker, P. Debye, H. Faxen, L. M. Brillouin, I. Waller, F. Wever and P. Giani, H. Esser and P. Oberhoffer, P. Oberhoffer and H. Heger, E. H. Schulz and F. Bonsmann, A. Sanfourche, F. Wüst and O. Petersen, T. D. Yensen, W. Gontermann, and K. Honda and T. Murakami—*vide* **6**. 40, 13.

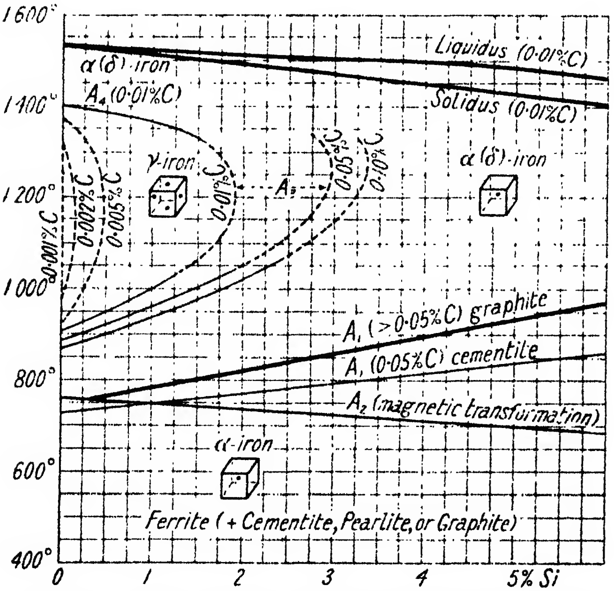


FIG. 424.—The Constitutional Diagram of Alloys of Iron with Small Proportions of Silicon.

The results of C. Kreutzer with the X-radiograms are summarized in Fig. 424. With up to 2·2 per cent. of silicon, α-iron changes into δ-iron through γ-iron; with 2·2 to 2·5 per cent. of silicon there is a region where α- and γ-iron can co-exist, but above 2·5 per cent. of silicon, the α-phase changes directly into the δ-phase. Accordingly, T. D. Yensen represented the constitution of the low-silicon alloys of iron, with 0·001 to 0·1 per cent. of silicon, by Fig. 424. The dotted lines have not been established experimentally. The A_3-arrest increases rapidly with a decrease of carbon, below 0·05 per cent., when the proportion of silicon is constant, and this leads to the conclusion that the A_3- and A_4-transformations depend on the carbon-content in such a way that the lower the carbon, the less the proportion of silicon needed to eliminate these points. Hence, the 1·5 to 2·5 per cent. of silicon reported to be needed to efface the A_3-arrest is really dependent on the proportion of carbon, and with no carbon no silicon would be required to obliterate the A_3-arrest provided oxygen and other interstitial impurities can be kept out. A. Westgren and G. Phragmen observed that the γ to δ-transformation is a reversion of the α to γ-transformation, and P. Oberhoffer, and G. Phragmen found that with 2·5 per cent. silicon steel, the α- and δ-ranges form one common domain; and E. C. Bain made a similar observation with respect to chromium steel.

The silicon is presumably present as silicide in molten cast iron; and during solidification when the eutectic breaks up into solid cementite and austenite, the silicide was thought by W. Gontermann to divide itself between the cementite and austenite. J. E. Stead observed that in low silicon irons, the austenite retains the silicon in solid soln. as silicide, but as the proportion of silicon in the iron increases, some unites with the carbide to form iron carbosilicide—silicocementite, possibly $Fe_3(Si,C)$. Indeed, he observed that two different cementites crystallize from high silicon irons—one, comparatively free from silicon, becomes red on heat-tinting, and the other, comparatively rich in silicon, remains white during the heat-tinting. The highly silicified cementite is unstable, and J. E. Stead considered that it is responsible for the graphitic condition of cast irons. The carbon in the iron carbide may be precipitated at high temp. by the diffusion of the silicide from the austenite. In the cooling of solid, high silicon irons, the austenite, remaining after the separation of the primary graphite, deposits more cementite associated with more or less silicide, and the silicocementite will be less likely to persist the higher the proportion of silicon in the iron. At the temp. of the pearlitic change, there is still present the solid soln. of cementite containing much silicide. As the solid soln. is resolved into pearlite, and if the proportion of silicon is high, the whole of the pearlitic carbide dissociates into a ferritic matrix with the silicon in solid soln. as silicide. The cooling curve of grey cast iron with a trace of combined carbon; graphite, 3·30 per cent.; manganese, 0·676; silicon, 4·321; sulphur, 0·025; and phosphorus, 1·660, has an arrest at 1118°, the primary f.p., and freezing is extended to 1030° as the iron carbide, containing the bulk of the silicon, dissociates; the arrest at 943° is due to the freezing of the iron-phosphorus-carbon eutectic; the arrest at 850° is due to the formation of pearlite, and the arrest at 690° is probably due to the formation of pearlite in the eutectic of iron and phosphorus, and it points to the conclusion that silicon is not a constituent of the austenite of the ternary eutectic. P. Bardenheuer and M. Künkele, and P. Oberhoffer and C. Kreutzer studied the effect of silicon on the arrests. D. Hanson studied the effects of 0·4 and 1·9 per cent. of silicon on annealed and quenched iron-carbon alloys. T. F. Pearson also examined the effect of silicon in hastening the graphitization of carbon-iron alloys—*vide supra*, cast iron. K. Schichtel and E. Piwowarsky found that the solubility of carbon in liquid iron is lowered by the presence of silicon, and the effect on the carbon solubility curve is shown in Fig. 425. The effect on the proportion of carbon in the eutectic, and on the eutectic temp. is shown in Fig. 426. Observations

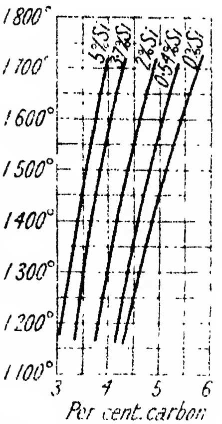


FIG. 425.—The Effect of Silicon on the Solubility of Carbon in Iron.

were also made by F. E. Bachman, W. Gontermann, A. L. Norbury, K. Honda and T. Murakami, B. S. Summers, and F. Wüst and O. Petersen. The reduction per unit of silicon, up to 3 per cent., is smaller the higher the proportion of silicon, and with over 3 per cent. of silicon, the reduction is proportional to the content of silicon, but increases from 0·28 to 0·40 unit of carbon per unit of silicon as the temp. rises from 1200° to 1700°. The addition of 1·2 to 6 per cent. of silicon to hypoeutectic alloys of carbon and iron causes graphite to separate in a very finely divided form, but with hypereutectic alloys, the graphite separates in needles—*vide supra*, graphitization. With ternary, iron-carbon-phosphorus alloys, the addition of 1·2 to 2·8 per cent. of silicon displaces the porphyritic line, *CE*, towards the iron end of the diagram, and as the proportion of silicon increases, the solidification range becomes smaller and smaller, and the proportion of molten metal which solidifies in primary crystals is larger. Hence, with composition almost up to the eutectic, the graphite separates completely from the primary crystals, in a finely dispersed form. P. Oberhoffer found that the range of existence of the γ-phase becomes smaller as the proportion of silicon increases, and disappears with alloys having over 5 per cent. silicon. D. G. Anderson concluded that with 1·1 per cent. of silicon, the combined carbon in cast iron rose sharply as the total carbon dropped below 3·4 per cent., and the strength rose sharply as it dropped to about 2·9 per cent.; with higher proportions of silicon, the combined carbon rose as the total carbon fell below 2·5 per cent.; with 2 per cent. of silicon, the maximum strength corresponded with about 1·9 per cent. of carbon; and with 2·2 per cent. of silicon, with about 1·95 per cent. of carbon. G. Tammann and W. Salge studied the residues left after treatment with an acidified soln. of ammonium persulphate. L. Guillet said that the constitution of silicon steels is virtually independent of the percentage of carbon, so that the lines separating the different zones are nearly parallel to the carbon axis. The subject was investigated by A. B. Albro, H. Birnbaum, M. G. Corson, L. Grenet, J. L. Haughton and M. L. Becker, B. Kjerrman, A. Kriz and F. Poboril, E. Lissner, A. Merz and F. Fleischer, N. B. Pilling, T. Sato, and T. D. Yensen. B. Stoughton and E. S. Greiner, and H. Sawamura gave Fig. 427 for the constitution of silicon cast iron. Field I contains cementite, silicoferrite, and temper carbon; while field II contains silicoferrite and temper carbon. The solid soln. Fe–C–Si was not observed. H. Scott found that silicon has a marked effect on the temp. of transformation of martensite to troostite. O. von Keil and F. Kotyza studied the effect of silicon on the solidification of iron-carbon alloys.

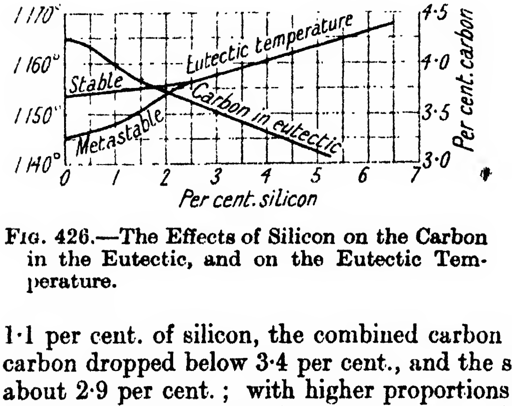


FIG. 426.—The Effects of Silicon on the Carbon in the Eutectic, and on the Eutectic Temperature.

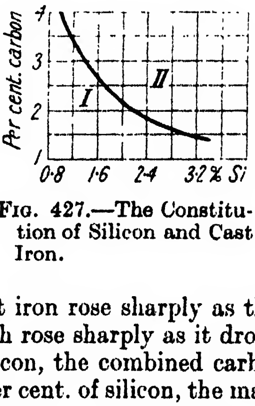


FIG. 427.—The Constitution of Silicon and Cast Iron.

P. Oberhoffer and W. Oertel examined the re-crystallization of a 4 per cent. silicon steel showing the grain-size as a function of the annealing temp. W. H. Hatfield, and E. Piwowarsky discussed the influence of the size of casting, the rate of cooling, and the casting temp. on the properties of a silicified cast iron; and V. N. Krivobok, the re-crystallization of the cold-worked alloy. E. Adamson, A. E. Allison, O. Bauer and K. Sipp, S. J. E. Dangerfield and co-workers, D. Hanson, F. C. Nix and E. Schmid, R. T. Rolfe, H. Sawamura, and A. Stadeler studied the action of silicon on malleable cast irons, etc. The deoxidizing action of silicon was discussed by E. Adamson, H. M. Boylston, G. K. Burgess and G. W. Quick, J. E. Carlin, A. L. Feild, C. H. Herty and co-workers, H. M. Howe, O. von Keil and F. Kotyza, F. W. Lürmann, E. G. Mahin and F. J. Mootz, E. Oughterbridge, N. Petinot, E. Piwowarsky, W. E. Remmers, H. Schenck, A. E. M. Smith, T. Swinden, E. Thews, and others—*vide supra*. For the cementation of these steels, *vide supra*. The effect of phosphorus and silicon was studied by W. Hummitzsch and F. Sauerwald, O. von Keiland, R. Mitsche, and B. Kjerrman.

T. D. Yensen, H. Möller, and Z. Nishiyama studied the X-radiograms of these alloys, and obtained for the lattice parameter, *a*; the sp. gr. at 15·1°; and the elastic modulus, *E* kgrms. per sq. cm.:

Si . . .	0	1	2	4	6	8 per cent.
a . . .	2·869	2·868	2·866	2·864	2·858	2·847 A.
Sp. gr. . .	7·8610	7·7933	7·7344	7·5677	7·5053	7·4258
$E \times 10^{-6}$.	2·157	2·164	2·194	2·175	2·205	2·103

H. Möller, E. R. Jette and E. S. Greiner, and F. Wever and H. Möller studied the crystal lattice of FeSi. F. C. Nix, and A. T. Lowzow studied the microstructure and the texture of the alloys; F. Körber, the etching colours; and T. A. Wilson, the orientation of the crystals.

The sp. gr. of the iron-silicon alloys was previously discussed. W. Brown gave for a steel with 0·028 C and 0·07 Si, the sp. gr. and sp. vol. respectively 7·8771 and 0·12695; with 0·020 C and 2·50 Si, respectively 7·6934 and 0·12998; and with 0·26 C and 5·50 Si, 7·5100 and 0·13315, so that an increase up to 5·5 per cent. silicon increases the sp. vol. by 0·0011 c.c. per 1 per cent. silicon. P. Paglianti said that the sp. gr. decreases 0·058 per 1 per cent. increase of silicon. J. Rothe, and B. Simmersbach made observations on this subject. E. Gumlich represented the relation between the sp. gr., *D*, and the per cent., *p* contents, by $D=7·874-0·0622p$. According to W. J. Keep, and R. A. Hadfield, high percentages of silicon in the cast or forged metal cause a considerable increase in shrinkage or contraction. P. Paglianti observed that the Brinell's hardness increases about 3·5 units for even 0·1 per cent. rise in the proportion of silicon. F. Robin studied the acoustic properties and found that the metal becomes aphonic when 1 per cent. silicon has been added. In addition to the observations of R. A. Hadfield on the mechanical properties of the iron-silicon alloys, mentioned in connection with the iron silicides, observations were also reported by L. Guillet. T. Turner measured the sp. gr. of silicon-iron-carbon alloys, and the results are indicated below. Observations were also made by A. Abraham, J. O. Arnold, C. Bedel, R. A. Hadfield, E. Heyn, K. von Kerpely, A. T. Lowzow, A. L. Norbury and E. Morgan, J. Rothe, E. H. Schulz and F. Bonsmann, A. Schulze, M. von Schwarz, and A. Wahlberg. C. Benedicks' results are summarized in Fig. 186. M. von Schwarz gave for the iron-silicon alloys, at 18°:

Silicon .	0·2	2·0	15·0	29·3	40·2	51·8	65·9	79·4	93·4	100 per cent.
Sp. gr. .	7·883	7·784	7·032	6·198	5·378	4·406	3·367	2·787	2·363	2·309

E. Widawsky and F. Sauerwald found that the introduction of 1 per cent. of silicon raises the sp. vol. of the iron-carbon alloys 0·0010 c.c. per gram. The subject was studied by C. Benedicks and N. and C. Ericson, and W. Denecke. O. Hengstenburg found:

Silicon . .	25	33·4	50·1	61·5	95·0 per cent.
Sp. vol. . .	0·155	0·165	0·213	0·254	0·419

T. Turner measured the hardness of the iron-silicon-carbon alloys and he found, on the sclerometer scale:

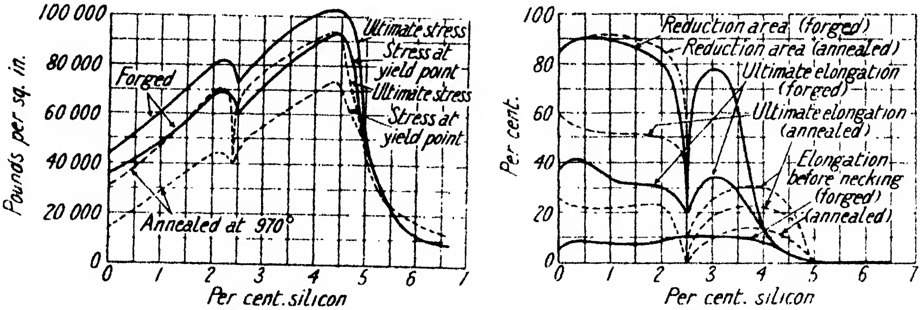
Silicon .	0·19	0·45	0·96	1·96	2·51	3·92	4·74	7·83	9·80 per cent.
Graphite .	0·38	0·10	0·24	1·62	1·19	1·81	1·66	1·48	1·12 ,,
Comb. C .	1·00	1·90	1·85	0·56	0·68	0·20	0·37	0·38	0·69 ,,
Hardness .	72	52	42	22	22	27	32	42	57
Sp. gr. .	7·719	7·670	7·630	7·350	7·388	7·218	7·170	7·138	6·924

Observations on the hardness were also made by A. Ledebur, R. A. Hadfield, A. Wahlberg, G. Tammann and V. Caglioti, K. Taniguchi, and H. O'Neil. E. Söhnchen and E. Piwowarsky found that the hardness of iron-carbon alloys is almost halved by the addition of 1 per cent. of silicon, but further additions reduce the hardness more slowly. According to T. D. Yensen, if N denotes Brinell's hardness of alloys with [Si] per cent. of silicon, $[\mathrm{Si}]=0{\cdot}092(N-86)\ 0{\cdot}777$ at 20°. A. Krüger discussed the age-hardening of silicon steels; H. O'Neil the effect of annealing on cold-worked single crystals of the alloys. The elastic limit, and tensile strength are expressed in kilograms per sq. mm.; and the elongation, and reduction in area in percentages. Observations were also made by A. Abraham, T. Baker, G. A. Bisset, P. Blum, F. Bonsmann, G. Charpy and A. Cornu-Thénard, L. M. Clark, H. I. Coe, A. L. Colby, S. J. E. Dangerfield and co-workers, F. Delaroziere, E. Diepschlag and F. Eggert, P. Eyermann, I. Fetchenko-Tchopiwsky, J. E. Fletcher, F. L. Garrison, H. W. Gillett, N. G. Girshovich and E. K. Vidin, R. C. Good, W. Haufe, R. H. Holbrock, G. R. Johnson, J. A. Jones, A. Jouve, K. von Kerpely, P. Kleiber, F. Körber and A. Pomp, H. Koppenberg, E. Lemaire, J. V. McCrae and R. L. Dowdell, T. Meierling and W. Denecke, J. Meiser, A. L. Norbury, F. Rapatz and H. Pollack, W. E. Ruder, F. Sauerwald, E. H. Schulz and H. Buchholtz, E. H. Schulz and co-workers, E. K. Smith and H. C. Aufderhaar, K. Tamaru, A. le Thomas, T. Turner, A. Wahlberg and E. Heyn, C. Wallmann, and R. Wasmuht; while P. Paglianti's results for soft iron are summarized in Table LXI. T. D. Yensen's results with silicon-iron alloys containing only 0·01 per cent. of carbon, melted in vacuo, are shown in Figs. 428 and 429. There is in all cases a critical point with about 2·60 per cent. of silicon, when the alloys are comparatively brittle. The maximum tensile strength, 10,500 lbs. per sq. in., occurs with a silicon-content of 4·5 per cent. W. Giesen observed that silicon steel of pearlitic structure with up to 6 per cent. of silicon has an exceedingly low tensile strength, elastic limit, elongation, and hardness—only the breaking strength and brittleness increase with the silicon-content. Silicon steels with 6 to 8 per cent. of silicon and with a pearlitic and graphitic structure, and silicon steels with over 8 per cent. of silicon with a graphitic structure have no useful industrial applications, but the non-graphitic steels have a limited application. In the case of iron, the toughness increases until the silicon has attained 4·5 per cent., and any excess beyond that decreases the toughness. With over 4·5 per cent. of silicon, the hardness increases rapidly, and the metal has a tendency to fracture. Every increase of the elastic limit and tensile strength decreases the elongation; and with 4·5 per cent. of silicon, the

TABLE LXI.—MECHANICAL PROPERTIES OF SILICON-IRON ALLOYS.

Silicon (per cent.)	Elastic limit (kgrms. per sq. mm.)	Tensile strength (kgrms. per sq. mm.)	Elongation (per cent.)	Reduction of area (per cent.)
0·001	11·53	25·38	61	80·9
0·010	11·28	24·53	53	81·5
0·090	10·05	24·88	64	94·8
0·230	10·48	24·95	60	84·7
0·400	18·28	29·53	55	91·0
0·673	18·66	31·80	45	88·2
0·822	18·42	31·74	50	91·6
1·710	25·07	38·14	50	90·6
2·730	35·01	47·66	19	15·5
3·40	40·13	54·49	21	28·7
4.44	51·26	64·38	24	25·1
4·90	33·53	33·53	0	0
6·57	9·13	9·13	0	0

elongation and reduction of area fall to zero. Z. Nishiyama's values for the elastic constant are indicated above. J. J. Porter discussed the effect of silicon on the fluidity of the molten alloy.



FIGS. 428 and 429.—Mechanical Properties of Silicon-Iron Alloys Melted in Vacuo—Forged and Annealed at 970°.

G. Charpy and A. Cornu-Thénard found that the dilation curves of iron-silicon alloys show that the addition of silicon to iron does not appreciably affect the coeff. of expansion between 0° and 700°; while with 3·9 per cent. of silicon, the metal shows no dilational anomaly. A. Schulze's values for the coeff. of thermal expansion $\times 10^6$ are as follow:

Silicon	0·08	1·03	2·40	8·37 per cent.
20°–100°	12·51	12·29	12·03	$11·31 \times 10^{-6}$
100°–300°	13·64	13·41	13·32	$12·73 \times 10^{-6}$
300°–500°	15·01	15·00	14·76	$14·19 \times 10^{-6}$

A. L. Norbury and E. Morgan studied the effect of silicon on the growth of cast iron. W. Brown observed that the sp. ht. of the alloys with 0·028 C and 0·07 Si is 0·1134; with 0·20 C and 2·50 Si, 0·1200; and with 0·26 C and 5·50 Si, 0·1194. This shows that an increase of up to 2 per cent. of silicon raises the sp. ht. 0·003 per 1 per cent. Si, and that further additions have very little effect. Observations were made by M. Padoa, and G. Tammann and V. Caglioti.

In addition to the observations on the electrical resistance indicated in connection with the iron silicides, A. Schulze, and E. Kolben made some measurements; J. H. Partridge observed that silicon raises the electrical resistance of iron; and T. D. Yensen found for the resistance at 20°, R microhms:

Si . .	0·001	0·010	0·068	0·148	0·472	1·74	3·55	4·92 per cent.
R . .	9·83	9·89	10·75	11·8	16·2	31·2	51·5	66·5

so that the sp. resistance increases about 13 microhms for the first per cent. of silicon added; and about 11 microhms for each additional per cent. added. H. le Chatelier, and E. Gumlich found an increase in the resistance of 14·0 microhms per cm. cube for 1 per cent. of silicon; W. F. Barrett gave 10·3; C. F. Burgess and J. Aston, 12·0; P. Paglianti, and T. D. Yensen, 13·0; and A. L. Norbury, 13·5 for the best representative value. According to T. D. Yensen, if R microhms per cm. cube be the resistance at 22°, and [Si] the percentage of silicon in the alloy, $[\mathrm{Si}]=0·0544(R-9·6)$ if R be 16·05 or less, and in other cases $[\mathrm{Si}]=0·35+0·09(R-12·16)$. E. L. Dupuy and A. M. Portevin found the thermoelectric force of silicon steel against copper, expressed in millivolts, to be:

		Annealed		Hardened	
		−80°	100	−80°	100°
0·2 Carbon	0·41 . .	+2·10	−0·30	+1·10	−0·90
	0·93 . .	−2·90	−6·10	−1·30	−5·00
	1·06 . .	−4·80	−8·28	−5·00	−8·40
	5·12 . .	−6·80	−10·80	−6·90	−10·40
0·8 Carbon	1·16 . .	−3·40	−6·00	—	—
	5·54 . .	−8·20	−12·00	−8·90	−10·79

Observations were made by E. Sedström. T. C. Mackay found the increment in the Hall effect to be proportional to the percentage of contained silicon up to 5 per cent. A. W. Smith studied the effect of temp. on the Hall effect. T. D. Yensen gave for purified iron, and iron with 4 per cent. of silicon: initial permeability, 700 and 440 respectively; maximum permeability, 26,000 and 15,500; saturation value, 22,600 and 25,000; hysteresis loss (ergs per c.c. per cycle for B=10,000), 600 and 500; retentivity, 8600 and 5200; coercive force, 0·20 and 0·15 gilberts per cm.; electrical resistance, 10 and 55 microhms at 20°; and sp. gr., 7·9 and 7·6.

The magnetic properties of the silicon-iron alloys were discussed in connection with the iron silicides. Observations were also made by E. Kolben, R. Pohl, A. Jouve, F. E. Raven, K. Daeves, H. Scott, W. F. Barrett, F. C. Caldwell, J. H. Hruska, M. Otto, J. C. Stearns, T. D. Yensen, W. E. Ruder, J. D. Ball and W. E. Ruder, T. Spooner, W. A. Wood, R. Cazaud, E. Peterson, H. D. Hibbard, H. de Nolly and M. Veyret, M. Fallot, M. A. Hunter and J. W. Bacon, E. Gerold, M. von Moos and co-workers, S. R. Williams, C. H. Willis, H. F. Parshall, P. Reusch, H. Nathusius, F. Goltze, J. H. Partridge, O. von Auwers, C. F. Burgess and J. Aston, G. J. Sizoo, P. Paglianti, R. Becker and H. F. W. Freundlich, C. Bedel, etc. The results of T. D. Yensen are summarized in Fig. 430, where the magnetic permeability is expressed in terms of $\mu=B/H$; the flux density and retentivity in gausses; the coercive force in gilberts per cm.; and the hysteresis loss in ergs per c.c. per cycle. The best alloys contained 0·15 and 3·40 per cent. of silicon, and were annealed at 1100°. The maximum permeability for both alloys is over 50,000, and the hysteresis loss for $B_{\max.}$, 10,000 and 15,000, is about 300 and 1000 ergs per c.c. per cycle respectively. This hysteresis loss is respectively one-eighth and one-third of the corresponding loss for silicon steel. E. Gumlich found that alloys with p per cent. silicon—for values of p up to 5 per cent.—the saturation value $4\pi I_{\max.}=21,600-480p$. A. Schulze studied the magnetostriction, and also the effect of the intensity and concentration of magnetization; T. Spooner studied the effect of temp. on the induction; E. P. T. Tyndall, the Barkhausen effect; L. Néel, the Curie point; O. von Auwers, the influence of grain-size on the magnetic properties; and J. D. Bell, the magnetic reluctivity, that is, the inverse of the metallic permeability, $\mu-1$, of silicon steel.

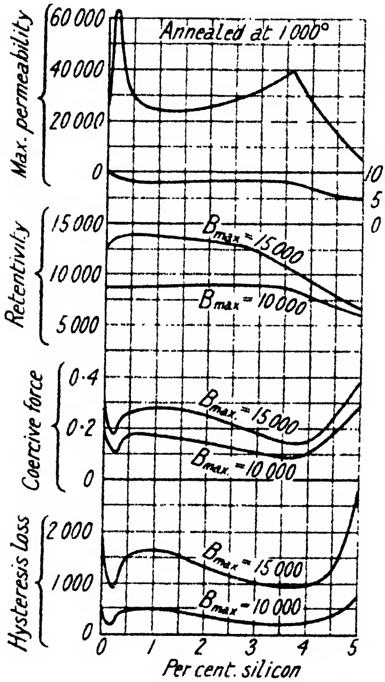


FIG. 430.—Magnetic Properties of the Iron-Silicon Alloys.

E. Martin studied the absorption of hydrogen and nitrogen by silicon steels and found that there is a small rise in the solubility of the gases in molten iron for small quantities of silicon, but with higher proportions the solubility is less than it is for purified iron. With nitrogen in α-iron, however, the solubility of nitrogen is greater than it is for iron alone. L. B. Pfeil observed that a three-layer scale—*vide supra*—is formed when silicon steel is heated in air for some hours at 1000°; no silicon appears in the two outer layers, but all is concentrated in the innermost layer where it occurs about three times more concentrated than in the original steel. Probably some ferrous silicate was formed in the inner layer. In 1838, R. Mallet found that iron rich in silicon is not readily attacked by acids; a protective skin of silica may be found. T. Turner found that pig-iron containing 18 per cent. of silicon was not appreciably rusted after a few years' exposure to the air of the laboratory. J. A. N. Friend and C. W. Marshall observed that if allowance be made for the tendency of silicon in cast iron to throw out carbon as graphite, the presence of 1·24 to 2·28 per cent. of silicon exerts no appreciable influence on the corrodibility of the metal either in neutral or acidic media. On the other hand, the presence of 0·12 to 0·13 per cent. of silicon in mild steel enhances its resistance to atmospheric corrosion, and to sea-water. Observations were also made by F. Ulzer and E. Baderle, M. von Schwarz, and by C. F. Burgess and J. Aston, who found that with iron alloyed with silicon:

Silicon . . .	0	0·233	1·190	1·897	2·826
Acid corrosion . .	1·300	1·630	1·190	1·800	1·270
Atm. corrosion . .	0·499	0·509	0·307	0·606	0·635

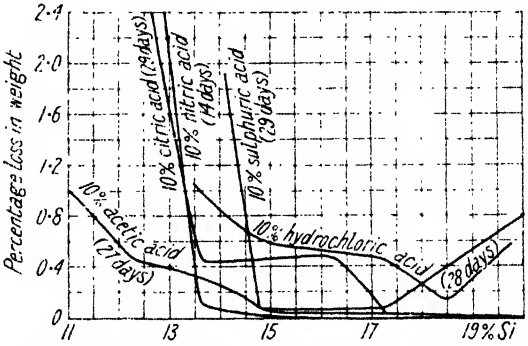


FIG. 431.—The Action of Acids on the Iron-Silicon Alloys.

where the acid corrosion refers to the loss in grams per sq. dm. when immersed for an hour in 20 per cent. sulphuric acid; and the atm. corrosion refers to the loss in kgrms. per sq. metre per year when exposed 162 days from July to February. H. Fromm studied the scaling of silicon steels. P. Askenasy noted the resistance of silicized iron to steam at 1000°. P. Kötzschke found that 1·5 to 3·0 per cent. of silicon in cast iron does not influence the rate of corrosion in hydrochloric acid; in conc. alkali-lye, silicon in cast iron is strongly attacked. O. L. Kowalke said that 16 to 20 per cent. of silicon gives the maximum resistance to corrosion by sulphuric, hydrochloric, nitric, acetic, and citric acids, and his results are summarized in Fig. 431. The resistance of silicon-iron alloys to acids was discussed by A. Jouve, J. Hoffmann, S. J. Tungay, P. Bres, A. Mangin, W. Schreck, P. Kötzschke, P. Kötzschke and E. Piwowarsky, H. G. Haase, H. Endo, W. Denecke, M. G. Corson, E. Piwowarsky, G. Krebs, E. Leuenberger, M. Spanner and M. Goltermann, T. F. Banigan, C. Matignon, E. Becker, and J. W. Hinchley. E. H. Schulz and F. Bonsmann found that the resistance of silicon steels to acids and acidified water is small, but it can be improved by the addition of 0·3 per cent. of copper. According to W. D. Richardson, and W. H. Hatfield, cast iron containing silicon is less readily attacked by nitric acid, and more readily attacked by hydrochloric acid than is the case with iron of a higher degree of purity. A. Jouve observed that iron with 20 per cent. of silicon is not readily attacked by acids. Thus, with 20 per cent. nitric acid, the alloy lost 0·6 per cent. in 12 hrs., and 0·9 per cent. in 48 hrs. With 12 and 24 hrs.' exposure to conc. nitric acid, the losses were respectively 0·0215 and 0·0142 per cent.; nitric acid (1 : 1), 0·0243 and 0·0168 per cent.; conc. sulphuric acid 0·1174 and *nil* per cent.; sulphuric acid (1 : 1), 0·0975 and *nil* per cent.; tartaric acid, *nil* per cent.; acetic acid, 0·0958 and 0·460 per cent.; and oxalic acid, 0·0676 and *nil* per cent. Hydrofluoric acid was the only satisfactory solvent. Y. Utida and M. Saito measured the gain in weight in grams per sq. cm. when alloys with about 0·05 per cent. carbon are heated for an hour at 1100°; and also the loss in weight in grams per sq. cm., when the alloys are immersed in 10 per cent. acids for 24 hrs. They found:

Silicon	0	1·33	4·16	7·00	9·88	13·02 per cent.
At 1100° in air	0·0212	0·0405	0·0025	0·0019	0·0012	0·0009
HNO_3	0·9380	0·6830	0·4775	0·4485	0·2818	0·1897
HCl	0·0712	0·1115	0·1038	0·0648	0·0397	0·0274
H_2SO_4	0·0990	0·1762	0·1256	0·1041	0·0513	0·0167

H. Endo measured the losses in weight in grams per sq. cm. during 5 hrs.' action, at ordinary temp., of alloys with 0·45 to 0·55 per cent. of carbon, and different proportions of silicon. E. H. Schulz and W. Jenge represented by Fig. 433 the loss in grams from a silicon-iron alloy 20 mm. diameter by 125 mm. length in 5 per cent. boiling hydrochloric acid. The corrosion of these alloys was studied by H. H. Abram, P. Askenasy, J. A. Aupperle, T. F. Banigan, W. C. Carnel, M. G. Corson, H. E. Diller, G. M. Enos, J. Escard, F. Espenhahn, A. B. Everest and co-workers, H. G. Haase, R. A. Hadfield, W. H. Hatfield, F. Körber O. L. Kowalke, W. Mason, C. Matignon, B. Neumann, W. Oertel and K. Würth, W. E. Pratt and J. A. Parsons, W. D. Richardson, P. D. Schenck, E. H. Schulz and W. Jenge, G. Tammann, J. G. Thompson, and R. Walter. A. M. Portevin and A. Sanfourche studied the action of phosphoric acid. F. Körber studied the etching films produced by an alkaline picrate soln. P. Kötzschke and E. Piwowarsky observed that the percentage of silicon should be kept as low as possible (below 1·5 per cent.) for grey cast iron to have the best resistance to corrosion by acids and salt soln.—*vide supra*. T. F. Banigan examined the action of sulphuric acid on iron. M. Wunder and B. Jeanneret studied the action of phosphoric acid on ferrosilicon; and W. Hummitzsch and F. Sauerwald studied the ternary system: iron-phosphorus-silicon. J. G. Thompson and co-workers studied the action of soln. of urea and of ammonium carbonate; W. G. Imhoff, the action of molten zinc; and J. A. Hedvall and F. Ilander, the action of calcium oxide.

The average composition of the iron-silicon alloy *tantiron* is said to contain:

Silicon	Total Carbon	Manganese	Phosphorus	Sulphur
14 to 15	0·20 to 0·60	0·20 to 0·35	0·16 to 0·20	0·05 per cent.

to have a tensile strength about 25 per cent. less than cast iron; an impact test of 8 to 10 ft. lbs. for ¾-in. bars; not to rust except at the skin; and to be but little affected by sulphuric, nitric, or acetic acids—conc. or dil., cold or hot. L. Leprovost studied the corrodibility of the **iron-copper-silicon alloys** and found that the 78 : 8 : 16 alloy resists nitric and organic acids very well, but is rapidly attacked by hydrochloric acid. P. Lebeau observed that a silicide, or iron is soluble in silicide of copper, and crystallizes out on cooling.

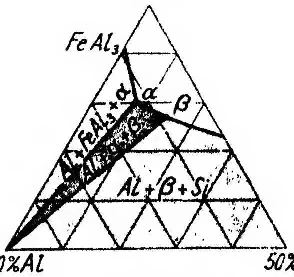


FIG. 432.—Phase Relations at 560° in the System: Fe–Al–Si.

A. G. C. Gwyer and H. W. L. Phillips studied the constituents of the **aluminium-silicon-iron alloys** cast at room temp., and they observed the existence of aluminium silicide, and iron trialuminide, as well as of various solid soln., 0 to 100 per cent. silicon, and 0 to 100 per cent. aluminium. H. Endo observed a 3 to 4 per cent. change in vol. during the melting or freezing of *silumin*, an alloy of iron, aluminium, and silicon (0·5 : 87·5 : 12). H. C. H. Carpenter and C. C. Smith, D. Hanson, E. H. Dix, P. D. Merica and co-workers, V. Fuss, W. L. Fink and K. R. van Horn, E. H. Dix and A. C. Heath, A. G. C. Gwyer and H. W. L. Phillips, and W. Rosenhain and co-workers also studied the iron-aluminium-silicon alloys. The phases include α and β solid soln. of iron and silicon. The X-radiograms indicate that the α-phase is a solid soln.

of silicon in $FeAl_3$, whilst the β-phase is a ternary soln. with an excess of aluminium. E. H. Dix and A. C. Heath's diagram of the phase relations at 560° is shown in Fig. 432. The nitridization of these alloys was studied by T. Oertenblad; and W. Hummitzsch and F. Sauerwald, and F. Sauerwald and co-workers studied the **iron-phosphorus-silicon alloys** and found Fe–Fe_2Si–FeSi is an independent ternary system; Fe_2P and FeSi is quasi-binary; and Fe_3P–FeSi is not quasi-binary. There is a ternary eutectic with 6·35 per cent. Si, 7·45 per cent. P, and 86·20 per cent. Fe, at 1018°.

The **iron-titanium alloys,** and the preparation of *ferrotitanium* were discussed in connection with titanium—**7.** 41, 3 and 6. C. J. B. Karsten[15] observed that traces of titanium occur in many varieties of cast iron; and E. Riley found that some titanium is also present in some cast irons. M. Faraday and J. Stodart did not succeed in alloying titanium with steel, by intensely heating a mixture of steel filings, rutile, and a little charcoal. J. Percy did not succeed any better. Some of M. Faraday and J. Stodart's alloys were examined by R. A. Hadfield. R. Mushet obtained a titaniferous steel or iron by heating titaniferous iron sands, like the New Zealand titaniferous sand, with iron or steel and some carbonaceous matters. R. Mushet obtained a number of patents for the application of titanium to the manufacture of iron or steel; and its manufacture was studied by A. J. Rossi, P. Girod, E. Bahisen, C. Grandjean, G. H. Stanley, J. B. Nau, W. Heym, P. Oberhoffer, J. Chállansonnet, G. T. Holloway, W. Venator, E. von Maltitz, E. H. Rothert, O. Simmersbach, L. O. Kellogg, R. W. Stimson and W. Borchers, F. C. Weber, J. Ohly, G. P. Scholl, W. and H. Mathesius, S. S. Steinberg and F. S. Kusakin, F. Peters, C. T. Starke, J. Escard, J. W. Richards, W. Guertler, F. M. Becket, S. Heuland, H. C. Sicard, B. Osann, A. Haenig, and J. W. Thomas. A. Stavenhagen and E. Schuchard, and W. R. Hulbert obtained the alloys by the thermite process. The use of titanium in steel for the removal of nitrogen was discussed by R. W. Raymond, J. B. Nau, H. Braune, and E. von Maltitz; it has also been employed as a deoxidizing agent—a subject discussed by P. H. Dudley, C. V. Slocum, G. B. Waterhouse, H. Schiemann, G. Vivanti, H. M. Boylston, B. Stoughton, M. H. Wickhorst, E. F. Lake, J. E. Hurst, E. Piwowarsky, J. Hörhager, G. F. Comstock, W. A. Janssen, W. Huppertz, O. J. Steinhart, A. Carnot and E. Goutal, L. Jordan, C. H. Gale, F. A. J. Fitzgerald, G. K. Burgess and G. W. Quick, etc. It has also been employed for preventing the segregation of steel. The alloys have also been recommended for making rails more durable, but, according to E. von Maltitz, H. Otto, and A. Pjaessezky, the evidence in favour of the use of titanium for this purpose is by no means satisfactory.

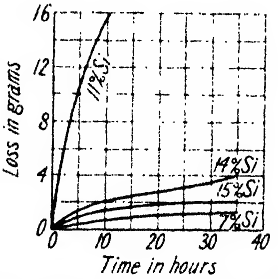


FIG. 433.—The Action of Hydrochloric Acid on Iron-Silicon Alloys.

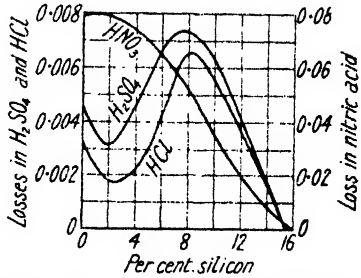


FIG. 434.—The Corrosion of Silicon Steels by Acids.

J. Laissus, and N. Agéeff and M. Zamotorin discussed the diffusion of titanium in iron. The equilibrium diagram of the iron–titanium system was partially explored by J. Lamort, and it was discussed in connection with the iron titanide, Fe_3Ti. A. Carnot and E. Goutal made observations on the subject. R. Vogel studied a portion of the system: Fe–Ti–C. Portions of the binary systems Fe–Ti, and Fe–C are known, and the system Fe_3Ti–C has been partially explored by K. Tamaru. If it forms a eutectic equivalent to Fe_3C+Fe_3Ti, the equilibrium diagram of the ternary system may approach Fig. 435. The three curves, E_1O, E_2O, and E_3O, are eutectic curves, in which the three surfaces, AE_2OE_1, E_1OE_3C, and E_2OE_3B, represent the beginning of the crystallization; and the point of intersection, O, is the ternary eutectic. The eutectic plane, CNB, passes through these points forming the fields with a binary solid soln., FN, and cementite, FNC; the binary solid soln., QN, and iron tritatitanide, QNB; and the ternary solid soln. $AQNF$. As crystallization proceeds, the three-phase triangular fields, f_1a_1C, f_2a_2C, and NOC, appear. K. Tamaru found that in the ternary alloys of iron and carbon with less than 4 per cent. of titanium, all the titanium is retained in solid soln. in the ferrite. Titanium decreases the amount of carbon in the iron-carbon eutectic, and also the solubility of carbon at high temp. E. L. Reed, and A. Michel and P. Bénazet studied the effect of titanium on the transformation points of steel.

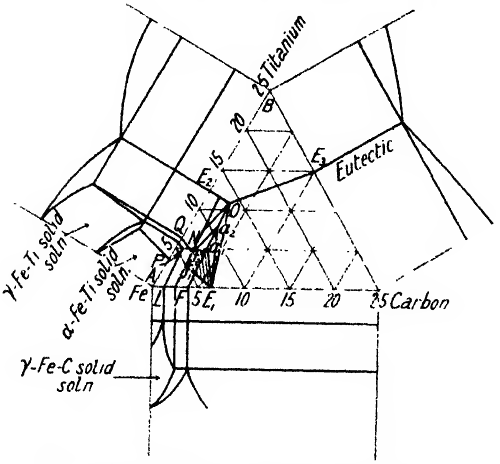


FIG. 435.—Portion of the Ternary System: Fe–C–Ti.

A. M. Portevin observed that titanium raised the temp. of the martensite and pearlite transformation of steel with 0·6 per cent. of carbon—1 per cent. of titanium raises it about 50°, while a higher proportion of titanium produces a less rapid change. Thus, with 0·6 per cent. carbon steels, the transformation points are:

Ti . .	0·32	0·64	0·72	2·57	4·63	8·71 per cent.
Ac_1 . .	755°	800°	810°	812°	825°	828°
Ar_2 . .	716°	765°	765°	765°	765°	768°

With steel having 0·1 per cent. carbon, the beginning of the transformation is lowered by titanium, while the austenite and pearlite transformation remains constant at 690°. Thus, with 0·1 per cent. carbon steels, the transformation points are:

Ti . . .	0·42	0·88	1·40	2·57 per cent.
Ar_3 . . .	860°	850°	830°	830°
Ar_2 . . .	780°	780°	780°	780°
Ar_1 . . .	690°	690°	690°	690°

J. Lamort found that the magnetic transformation falls linearly from 780° to 690° as the proportion of titanium rises to 21 per cent. The subject was studied by A. Michel and P. Bénazet, who found that titanium lowers the A_4-arrest, and raises the A_3-arrest, making the γ-field of the system bounded by a closed curve extending outwards to about 1·5 per cent. of titanium. R. Vogel said that increasing the titanium-content, with slow cooling, reduces the temp. of the transformation of carbon; the effect is most marked with 1 per cent. carbon and 6 per cent. titanium. It consists in the formation of an osmonditic structure characterized by a great susceptibility to attack by acids. The almost complete absence of the carbon transformation is due to the sluggishness of the pearlite transformation caused by the titanium. Part of the titanium appears to form titanoferrite, a part is probably associated with the iron carbides, and part appears as titanium carbide. W. A. Janssen, and J. Lamort also observed that some titanium nitride may be present. C. V. Slocum said that if 5 to 8 per cent. of carbon is present in ferrotitanium, most occurs as graphite, and about 0·12 to 0·18 per cent. is there as combined carbon. E. Piwowarsky found that in cast iron containing 1 per cent. of silicon, the addition of up to 0·5 per cent. of titanium lowered the proportion of combined carbon, but with higher silicon—1·7 and 2·6 per cent.—the influence of titanium was indefinite. For the cementation of these steels, *vide supra.*

J. Lamort found that Brinell's hardness increases from 96 to 500 on the addition of 21·5 per cent. titanium—*vide infra.* W. Giesen found that steel with up to 12 per cent. titanium behaves like ordinary steel with respect to the hardness, tensile strength, and brittleness. The tensile strength of the metal is considerably increased by the addition of titanium, especially in the case of cast irons. The titanium also hinders the formation of air-bubbles, and thus furnishes better and more compact castings. L. Guillet added that steels with up to 10 per cent. titanium are pearlitic. The mechanical properties are not much affected by titanium; though the tensile strength may be slightly increased and the elongation diminished. The elastic limit and resistance to shock are not changed. A. M. Portevin found that the tensile strength and elastic limit on shearing increase slowly as the proportion of titanium increases, as shown in Table LXII. The last five results in this table are due to G. B. Waterhouse. Observations were also made by L. Guillet, H. W. Gillett and E. L. Mack, J. Ohly, R. Moldenke, A. L. Colby, E. K. Smith and H. C. Aufderhaar, J. H. Küster and C. Pfannenschmidt, R. Wasmuth, I. Musatti and G. Calbiani, E. Kothny, W. Kroll, R. C. Good, W. E. Remmers, J. W. Donaldson, J. Arend and M. Loebe, A. E. M. Smith, C. H Gale, B. Stoughton, J. E. Johnson, M. H. Wickhorst, F. Bertrand, J. E. Hurst, B. Feise, E. von Maltitz, L. Treuheit, W. Venator, H. Mathesius, G. F. Comstock, H. Otto, A. Pjaessezky, P. Blum, J. V. McCrae and R. L. Dowdell, K. Taniguchi, and H. Fleck.

A. M. Portevin found the electrical resistance, *R* microhms per cm. cube, at 18° of steels with 0·1 and 0·6 per cent. carbon:

TABLE LXII.—MECHANICAL PROPERTIES OF TITANIUM STEELS.

Composition		Elastic limit (kgrms. per sq. mm.)	Tensile strength (kgrms. per sq. mm.)	Elongation (per cent.)	Reduction of area (per cent.)	Brinell's hardness
C (per cent.)	Ti (per cent.)					
0·12	0·41	33·9	40·7	20	—	99
0·14	1·40	36·1	48·2	19	—	101
0·14	2·57	34·6	45·2	17·5	—	90
0·70	0·64	52·6	94·1	9	—	207
0·62	1·72	53·3	87·7	10	—	212
0·61	2·57	58·8	90·4	10·5	—	212
0·64	4·63	57·8	89·8	9·5	—	212
0·65	8·71	52·5	117·5	8·5	—	248
0·10	0·00	27·0	39·3	30·2	61·0	102
0·10	0·025	27·1	41·9	28·7	56·4	112
0·11	0·050	27·1	40·9	31·6	63·6	110
0·12	0·075	27·0	42·9	29·7	64·3	113
0·15	0·100	28·2	44·1	30·6	60·0	115

0·1 C	Ti . . .	0·42	0·88	1·40	2·57 per cent.
	R Normal . .	13·1	13·8	15·1	16·1
	R Hardened .	13·6	14·3	15·5	17·0

0·6 C	Ti	0·32	0·64	0·72	2·57	4·63	8·71 per cent.
	R Normal . .	19·8	21·0	21·4	22·2	25·1	28·7
	R Hardened .	29·3	30·3	31·0	31·5	34·3	37·9

According to K. P. Applegate, the addition of less than 1 per cent. of titanium improves the magnetic permeability a little, and reduces the loss by hysteresis. J. Lamort found that the remanence of iron alloys increases slowly as the proportion of titanium rises to 14 per cent., and thereafter rapidly; the magnetization falls rapidly as the titanium rises above 14 per cent.; an alloy with 23 per cent. titanium is practically unmagnetizable. M. A. Hunter and J. W. Bacon, and A. Michel and P. Bénazet studied the magnetic properties of the titanium steels.

N. Tschieschewsky and N. Blinoff, and S. Satoh studied the nitridization of these steels by heating them in ammonia at 560° to 580°, and M. Wunder and B. Jeanneret, the action of phosphoric acid. H. Endo represented the losses in weight, in grams per sq. cm., of some titanium steels in different acids for 5 hrs. at ordinary temp. by Fig. 436, the proportion of carbon was 0·42 to 0·46, and the proportions of titanium were:

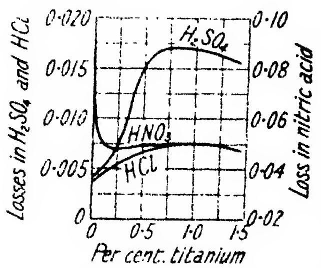


FIG. 436.—The Corrosion of Titanium Steels by Acids.

Titanium	.	0·089	0·178	0·388	0·446	0·592	0·902	1·100	1·338 %
Loss	H_2SO_4 .	0·00539	0·00490	0·01352	0·01427	0·01660	0·01683	0·01599	0·01577
	HCl .	—	0·00541	0·00565	0·00545	0·00712	0·00754	0·00781	0·00735
	HNO_3 .	0·04553	0·05152	0·04593	0·04507	0·05102	0·05222	—	0·04834

E. Wedekind,[16] and T. E. Allibone and C. Sykes prepared a **zirconium-iron alloy,** or ferrozirconium, by fusing a mixture of the two elements in vacuo. Alloys were also prepared by J. L. Brown and H. S. Cooper, J. B. Grenagle, H. L. Coles and J. R. Withrow, E. K. Smith and H. C. Aufderhaar, F. M. Becket, R. H. McKee, H. C. Sicard, J. W. Marden and M. N. Rich, H. W. Gillett and E. L. Mack, C. M. Johnson, H. E. Potts, H. Fleck, E. Kothny, R. C. Good, W. Stimson and W. Borchers, H. C. Meyer, J. Garçon, L. Bradford, W. Guertler, E. M. Becket, L. Persoz, P. Guy, A. L. Feild, R. Tull, F. B. Riggan and H. C. Aufderhaar, and G. K. Burgess and R. W. Woodward—see **7.** 42, 6. J. Laissus discussed the diffusion of zirconium in iron. R. Vogel and W. Tonn studied the equilibrium diagram, and their results are summarized in Fig. 437. There is formed **iron tritadizirconide,** Fe_3Zr_2, melting at 1640°. The effects on the transformation points are indicated in the diagram. About 0·7 per cent. of zirconium dissolves in γ-iron.

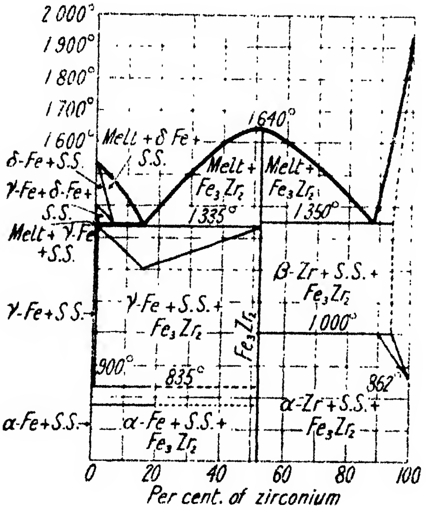


FIG. 437.—Equilibrium Diagram of the Fe–Zr System.

Zirconium, like titanium, is regarded as a possibly useful scavenger for iron and steels. F. M. Becket, and A. L. Feild found that it combines with and eliminates sulphur; and it may reduce the nitrogen-content of steel. Zirconium is also said to counteract the brittleness by the impact test due to the presence of phosphorus. The subject was also studied by J. V. McCrae and R. L. Dowdell, J. E. Hurst, and C. T. Evans, who attributed the good effects of zirconium rather to its scavenging action than to its work as an alloying element. Thus, F. M. Becket found:

	0·70 C; 0·15 Zr		0·70 C; no Zr	
Drawing temperature	375°	412°	375°	412°
Elongation (per cent.)	8·3	12·7	5·2	7·5
Reduction of area (per cent.)	23·3	45·8	6·6	22·9
Yield-point (lbs. per sq. in.)	185,962	172,620	128,125	180,180
Ultimate strength (lbs. per sq. in.)	227,203	198,828	197,800	207,144
Izod impact test	7·5	14·8	7·5	10·5
Brinell's hardness	414	407	433	418

T. E. Allibone and C. Sykes found that iron retains in soln. about 0·3 per cent. zirconium at ordinary temp. The eutectic alloy contains 15 per cent. zirconium. Beyond this, up to 30 per cent. zirconium, the second constituent appears in constantly increasing amount, but then it has not yet been identified. The m.p. of the eutectic is near that of iron. The hardness—*vide infra*—of the alloys constantly increases from 1 to 30 per cent., and there is a steeper rise from 0 to 1 per cent. This indicates the presence of a solid soln. at low percentages. The second constituent is not so brittle as the nickel alloy of the same composition. The Brinell hardness of the alloy is 290, or five times that of iron. Alloys with 0 to 6 per cent. of zirconium were forged hot, the optimum forging temp. increases with increasing proportions of zirconium; the forging of samples with over 8 per cent. of zirconium was not successful. The samples were normalized at 970° until the hardness was constant. The 5 per cent. alloy had a tensile strength 50 per cent. greater than that of iron, and a ductility 10 per cent. less. The observed tensile strengths, in tons per sq. in., were:

Zirconium		0	0·3	0·6	1·05	1·48	3·38	5·20
Brinell's hardness	forged	105	123	——	146	160	181	206
	cast	57	71	135	140	148	160	183
Tensile strength		19·20	21·9	20·3	25·3	25·2	31·1	30·5
Ductility		26·0	38·0	26·0	21·0	22·0	16·0	0·1 per cent.

The effect of zirconium is to lower the Ar_3 transition points of iron from 900°, but the Ar_2-arrest is not affected. Zirconium shows no analogy with silicon. H. W. Gillett and E. L. Mack thus summarize the effect of zirconium:

> Zirconium should be classed with its chemical sister, titanium, as a possibly useful scavenger rather than an alloying element. Much work on zirconium in steels of the high silicon-nickel type failed to show any trace of true alloying behaviour due to zirconium; or, at least, that it has any greater effect than so much silicon. F. M. Becket, and A. L. Feild have produced far more definite evidence as to the scavenging value of zirconium in plain carbon steels than exists in the case of titanium. They show clearly that zirconium combines with sulphur, and may also eliminate some sulphur. This action is quite analogous to that of manganese and of cerium. It is said that steels treated with zirconium are unusually free from dispersed slag particles. Rather good evidence is also adduced to show that zirconium combines with nitrogen and it may decrease the total nitrogen content of the steel. In some way not yet understood, zirconium appears to reduce the brittleness, on impact test, due to high phosphorus-content. The mechanical properties of heat-treated carbon steels with small amounts of zirconium are changed but slightly and the average effect is that to be expected from increased cleanliness of the steel, *i.e.* slight improvement in both strength and ductility, rather than an increased hardness and strength concomitant with lowered ductility, as would be expected from a true alloying element. C. T. Evans states that while, for the production of a certain chromium-tungsten cutlery steel, he prefers to add silico-zirconium, the zirconium of which is practically eliminated before the steel freezes, he can at times get just as good results without zirconium, and only uses it because he finds that the properties aimed for are more readily obtained by the use of zirconium as a scavenger. No data have yet been presented to show that zirconium has any alloying effect, either alone, or when present in combination with the common alloying elements.

W. Zieler studied the deoxidizing and desulphurizing action of zirconium in steel, and noted that inclusions of zirconium sulphide do not make steel brittle. F. R. Palmer found that 0·4 per cent. of zirconium sulphide added to a high chromium steel improves its machining and grinding properties; there was a slight loss of toughness and tensile qualities, but the product was suited for corrosion-resisting parts. The zirconium sulphide helped to prevent air-hardening in low-carbon grades of stainless steel, and raised the temp. necessary for hardening. A. M. Portevin and A. Sanfourche, and M. Wunder and B. Jeanneret studied the action of phosphoric acid. C. Sykes measured the electric resistance, and magnetic induction of some iron-zirconium alloys.

F. Roll[17] showed that with the **germanium-iron alloys,** the germanium partly preserves and partly decomposes cementite. C. A. Edwards and A. Preece found that the solubility of tin in solid iron increases with increasing temp. up to 760°, and then becomes less as the temp. is further raised to the m.p. of iron. Their equilibrium curves are summarized in Fig. 438, with the effect of tin on the γ-phase of iron observed by F. Wever and W. Reinecken. C. O. Bannister and W. D. Jones studied the diffusion of tin into iron.

G. Tammann and K. Schaarwächter found that the attack of iron by tin begins at about 215°, and increases with rise of temp. C. J. B. Karsten said that the alloying of 1 per cent. of tin with iron does not make the latter red-short, the metal can be worked while white-hot, but at that temp. it always gives off white vapours; he also added that 0·19 per cent. of tin lowers considerably the tensile strength of iron. T. Bergman prepared **iron-tin alloys** with iron ; tin as 1 : 22, and as 2 : 1. Alloys were made by W. Guertler. S. Stevanovic found that in a series of alloys the crystals near Fe_4Sn_5 in composition are hexagonal and those near $FeSn_2$ are tetragonal. J. L. Lassaigne observed that in the distillation of mercury, in cast-iron retorts, from mirrors silvered with tin-amalgam, an alloy of iron and tin is formed approximating **iron tritastannide,** Fe_3Sn; and it occurred in tetragonal needles. It can be freed from the excess of tin by boiling it with hydrochloric, or by treating it with nitric acid. The compound, thus purified, forms shining, square needles of sp. gr. 8·733. The compound is brittle, and when the powder is projected in the flame of a candle, it burns with the emission of sparks and a white smoke. It does not rust in air when it is moistened with water; it is not attacked by nitric acid—conc. or dil., hot or cold—it dissolves slowly in boiling hydrochloric acid, and rapidly and completely in aqua regia. This compound was prepared by W. P. Headden. L. J. Spencer described some probably tetragonal crystals of Fe_3Sn obtained at the bottom of some baths of molten tin. J. Percy also commented on the rust-resisting properties of an alloy with 9 per cent. of tin. C. A. Edwards and A. Preece found that **iron hemistannide,** Fe_2Sn, is stable between 760° and 900°, but can react with tin at 800° to produce the monostannide. H. St. C. Deville and H. Caron said that **iron stannide,** FeSn, crystallizes from a soln. of iron in an excess of tin; it was also prepared by W. P. Headden. C. A. Edwards and A. Preece found that the monostannide is stable at all temp. below 800°, and reacts with tin below 496° to form the distannide. C. Nöllner said that some tin from the East Indies, when digested with hydrochloric acid, left a residue consisting of small crystals of **iron distannide,** $FeSn_2$, of sp. gr. 7·446. C. A. Edwards and A. Preece observed that the distannide exists below 496°, and when heated above that temp. forms the monostannide and a liquid rich in tin. W. P. Headden also obtained this compound. P. Berthier, and W. P. Headden, reported *iron tetritastannide,* Fe_4Sn, and *iron tritatetrastannide,* Fe_3Sn_4; C. F. Rammelsberg, *iron pentastannide,* $FeSn_5$, and *iron hexastannide,* $FeSn_6$; and W. P. Headden, *iron hemitristannide,* Fe_2Sn_3; *iron pentitahexastannide,* Fe_5Sn_6; and *iron tetritapentastannide,* Fe_4Sn_5; and *iron ennitastannide,* Fe_9Sn. The proof of the chemical individuality of all these products is wanting. E. Isaac and G. Tammann found that tin and iron are only partially miscible in the fused state; at 1140°, with from 50 to 89 per cent. of tin, two layers are present. Tin is soluble to the extent of about 19 per cent. in crystallized γ-iron; at 1140°, the layer rich in iron decomposes into a solid soln. and a fused mass, and, at 893°, the solid soln. reacts with the fused mass to form what may be **iron tritastannide,** Fe_3Sn. These changes appear as breaks in the cooling curve. At 780° there is a third break which is thought to represent a polymorphous transition; there is a fourth break at 496°.

From 89 to 100 per cent. tin, the f.p. curve falls rapidly. F. Wever and W. Reinecken observed no gap in the miscibility of the molten metals, and they found that the sat. solid soln. contains 18 per cent. of tin; C. A. Edwards and A. Preece observed a miscibility-gap, but obtained no evidence of the formation of the tritastannide; R. Ruer and J. Kuschmann showed that the two metals have a limited miscibility which is not explained away by assuming that the separation into two layers is caused by segregation during solidification. This combines with the liquid phase at 1132° to form the compound Fe_3Sn if the alloy contains between 18 per cent. and 48 per cent. of tin. Below 890°, this compound decomposes into $FeSn_2$ and mixed crystals, or, if the alloy contains more than 41·3 per cent. of tin, combined with tin to form the same compound. The compound $FeSn_2$ undergoes polymorphic transformations at 780°, 755°, and 490°. Tin does not affect the temperature of the magnetic $(\alpha \rightarrow \beta)$ transformation of iron. The $\alpha \rightarrow \gamma$ transition point, however, is raised 40° by 1 per cent. of tin, and the $\gamma \rightarrow \delta$ transition point depressed 140°. With a conc. greater than about 1·9 per cent. of tin, iron does not pass through the γ-phase at all in cooling. C. A. Edwards and A. Preece studied the constitution of the iron-tin alloys, and they showed that the thermal transformations at about 760° and 800°, which F. Wever and W. Reinecken attributed to polymorphic changes occurring in the distannide, are more probably due to the decomposition and formation of the hemistannide and monostannide. G. Tammann and W. Salze studied the residue left after treatment of the alloy with an acidified soln. of ammonium persulphate. E. F. Kohman and N. H. Sanborn discussed the formation of a tin-iron alloy in the production of tin-plate. J. W. Donaldson, and F. Roll observed that tin with cementite produces grey cast iron.

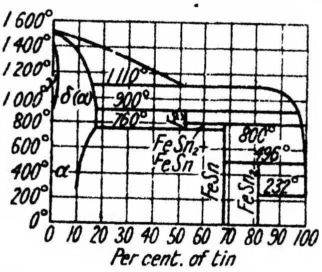


FIG. 438.—Equilibrium Diagram of the Fe-Sn Alloys.

TABLE LXIII.—MAGNETIZATION OF IRON-TIN ALLOYS.

Tin (per cent.)	$H=10$				$H=100$			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°
S	9,500	10,000	10,850	8,400	17,450	18,000	17,200	—
El	13,100	10,000	13,350	11,800	18,850	18,850	18,200	18,150
0·29	2,150	8,650	9,400	9,000	18,250	18,250	17,600	17,900
0·34	3.900	6,400	9,400	11,000	18,600	18,350	17,700	17,900
0·69	5,800	7,600	11,300	13,750	18,100	18,650	18,200	18,400
0·72	9,400	11,700	11,300	14,150	19,250	19,200	18,500	18,700
1·57	8,700	11,700	14,000	14,350	18,050	18,400	18,300	17,600
2·06	12,900	12,400	13,350	13,750	17,250	17,950	17,400	17,500

W. F. Ehret and A. F. Westgren found that the FeSn lattice is hexagonal with $a=5{\cdot}292$ A., and $c=4{\cdot}440$ A., and unit cell has three FeSn mols. The Fe_2Sn-cell has two mols. per unit cell. The cell is hexagonal with $a=5{\cdot}449$ A., and $c=4{\cdot}353$ A. The unit cell of $FeSn_2$ is hexagonal; it contains 12 atoms, and has $a=5{\cdot}317$ A., and $c=9{\cdot}236$ A. J. E. Hurst, W. H. Spencer and M. M. Walding, C. F. Burgess and J. Aston, E. K. Smith and H. C. Aufderhaar, P. Blum, and W. Keller described some working qualities of the tin-iron alloys. A. L. Norbury studied the effect of tin on the hardness of iron. K. Taniguchi also studied the hardness of these alloys. A. Ledebur observed the tensile strength, T tons per sq. in., and the percentage elongation of ingot iron and crucible steel to be:

	Ingot iron					Crucible steel			
Tin	0	0·10	0·19	0·25	0·63	0·23	0·50	0·68	per cent.
T .	20·9	26·2	24·6	25·1	29·7	45·9	45·9	46·9	
Elon.	31·3	28·7	18·0	26·8	19·7	15·5	16·5	3·5	

Alloys with as little as 2·5 per cent. of iron are magnetic ; and the temp. at which iron loses its magnetic properties is practically unaffected by the presence of tin. C. F. Burgess and J. Aston measured the magnetization, or magnetic induction, *B*, of alloys of iron and tin—unannealed, annealed at 675° and 1000°, and quenched at 900°— for magnetic fields of intensity *H* gauss, and the results are summarized in Table LXIII ; while the results for the coercive force ($H_{\text{max.}}=200$), and retentivity ($H_{\text{max.}}=200$) are summarized in Table LXIV. " S " refers to Swedish iron, and " El " to electrolytic iron.

TABLE LXIV.—COERCIVE FORCE AND RETENTIVITY OF IRON-TIN ALLOYS.

Tin (per cent.)	Coercive force				Retentivity			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°
S	5·5	4·8	3·9	5·0	11,400	12,700	9,000	8,500
El	5·5	6·2	5·1	2·5	12,300	13,800	10,000	8,000
0·29	23·5	7·5	5·3	5·0	12,100	11,700	9,100	8,700
0·34	12·3	8·9	5·5	3·6	12,300	12,700	9,400	8,600
0·69	7·5	7·7	4·3	3·7	8,000	12,300	10,400	12,100
0·72	7·0	5·7	3·9	2·9	11,000	13,200	8,700	8,900
1·57	6·0	4·0	4·0	3·3	10,000	13,100	11,900	10,800
2·06	3·0	4·3	3·5	2·5	8,100	11,300	9,300	8,600

F. Wever observed that with increasing proportions of tin, the $\alpha\rightarrow\gamma$ transition temp. is raised and the $\gamma\rightarrow\delta$ transition temp. is lowered. F. Wever and W. Reinecken found that iron takes up 18 per cent. of tin in solid soln. The γ-iron region is reduced by and disappears with 1·9 per cent. of tin. Iron tritastannide decomposes at 890°, producing iron distannide, $FeSn_2$, which separates along *h* to *q* ; the distannide undergoes allotropic transformations at 780°, 755°, and 490°. The liquidus is horizontal with between 48 and 75 per cent. of tin. The compound Fe_3Sn decomposes at 890°. A. S. Russell exposed a mixed tin and iron amalgam to the action of an oxidizing agent, and found no sign of the formation of a compound ; as soon as the tin is nearly all oxidized, the oxidation of the iron begins. F. Wever showed that with over 2 per cent. of tin, the γ-transformation of iron disappears, and the A_3 and A_4 points of iron meet, and with more than that proportion of tin, the α- and δ-iron areas are continuous—*cf.* chromium-iron alloys. P. Goerens and K. Elligen found that tin acts on pig-iron similarly to antimony (*q.v.*). M. Faraday and J. Stodart said that steel is not improved by alloying it with tin. L. Guillet observed that tin dissolves in molten iron, and when 5 to 7 per cent. has been added, a stannide is formed which is found in the shape of needles usually in well-defined clusters. The carbon remains in the pearlitic stage. Tin makes steel brittle and unworkable when the proportion exceeds 1·5 per cent. L. Guillet, and M. Hamasumi noticed the hardening effect of tin on iron. E. H. Saniter observed an alloy with 0·35 per cent. of tin gave off a white fume when rolled ; it rolled fairly well, but did not draw to wire satisfactorily. Alloys were also described by C. F. Burgess and J. Aston, B. Eyferth, H. J. French and T. G. Digges, P. G. J. Gueterbock and G. N. Nicklin, G. Jones, W. Longmaid, E. Mauer and W. Haufe, L. Mayer, P. Oberhoffer, J. Percy, S. Rinman, H. de Sénarmont, J. E. Stead, and M. Stirling. The use of imperfectly de-tinned sheet-iron in the manufacture of steel may introduce a small proportion of tin. A. Ledebur showed that 0·1 per cent. of tin in low-carbon steel raised the breaking-point 1·4 tons per sq. in., and reduced the elongation 0·8 per cent. J. E. Stead found that sensible quantities of tin raised the yield-point and maximum stress, and also increased the hardness of steel when hot. The presence of tin should be low because it tends to make the metal difficult to roll, and hard and stiff when in the heated state. J. H. Whiteley and A. Braithwaite also showed that the presence of small proportions of tin—even 0·06 per cent.—in medium carbon steel is liable to impair its ductility; the harmful effect increases with the carbon-content, but in mild steel, 0·06 per cent. had no detrimental effect. The degree of brittleness produced by tin is influenced by the heat-treatment. E. Griffiths and F. H. Schofield studied the thermal and electrical conductivities of some aluminium bronzes containing iron; and L. Néel, the Curie points. M. Faraday and J. Stodart, and R. Mallet noted that alloys with tin are less corrodible than iron. C. F. Burgess and J. Aston found that alloys of tin and electrolytic iron lost, in grams per sq. dm., when immersed in 20 per cent. sulphuric acid for an hour; and in kgrms. per sq. metre per year when exposed to the weather for 162 days from February to July:

Tin		0	0·288	0·342	0·686	1·568 per cent.
Loss	Acid	1·300	0·284	0·350	0·386	1·030
	Atm.	0·499	0·337	0·190	0·239	0·283

A. S. Russell and H. A. M. Lyons studied the system **mercury-tin-iron alloys**; and H. Brintzinger and F. Rodis, the action of chromous chloride on some **tin-iron-bismuth alloys**.

L. B. G. de Morveau[18] stated that the **lead-iron alloys** are formed with difficulty when the two are fused together, they form two alloys one above the other, the lower one containing very little iron, and the upper one very little lead. E. Biewend thought that he had obtained a hard, brittle, lustrous, steel-grey alloy with 3·24 per cent. of lead by reducing a slag containing iron and lead in a crucible lined with charcoal. S. Rinman, and F. L. Sonnenschein also obtained what they regarded as ferriferous lead. E. Isaac and G. Tammann, J. Percy, P. Oberhoffer, and C. J. B. Karsten were unable to prepare iron-lead alloys because the two elements are not miscible either in the solid or molten state, and no compounds are formed. E. K. Smith and H. C. Aufderhaar, J. E. Hurst, and W. H. Spencer and M. M. Walding discussed these alloys. A. S. Russell observed that when an amalgam of the two metals is oxidized, the lead is first removed, and then the iron; there is no sign of a compound. G. Tammann and W. Oelsen found that at 400° and 1600°, lead dissolves respectively 0·0003 and 0·0002 per cent. of iron. F. Roll showed that the presence of lead promotes the formation of graphite in cast iron. N. Agéef and M. Zamotorin studied the diffusion of lead in iron. L. Guillet, and W. Guertler and F. Menzel found that the immiscibility of the iron-lead and copper-lead in the binary systems persists to a large degree in the **copper-lead-iron alloys.** The cooled mixtures show two or three layers, the three consisting essentially of the three metals, each showing inclusions of the other two; where two layers are formed, one is iron containing inclusions of copper and lead, the other consists of copper crystals in a ground of lead, although in the liquid state the copper is completely miscible with the iron. C. E. Eggenschwiler studied the **copper-tin-lead-iron alloys.** C. F. Burgess and J. Aston found that the working properties of an alloy with lead were poor; they also observed that alloys with 0 and 0·061 per cent. of lead lost 1·300 grms. per sq. dm. in each case when immersed for an hour in 20 per cent. sulphuric acid; and respectively 0·499 and and 0·273 kgrm. per sq. metre per year when exposed to the weather for 162 days from July to February.

The preparation of the **iron-vanadium alloys,** or *ferro-vanadium*, was discussed in connection with vanadium—**9.** 54, 3. For the occurrence of vanadium in iron, ***vide*** **9.** 54, 2. In 1896, M. K. Hélouis[19] first made systematic tests on the use of **vanadium steels**; this was followed, in 1900, by F. Werner, and J. O. Arnold, who obtained the alloys by adding ferro-vanadium to the molten steel just before it was teemed from the clay crucible. The preparation of vanadium-iron alloys was also described by B. de Alzugaray, L. J. Barton, F. M. Becket, W. F. Bleecker and W. L. Morrison, R. Cazaud, A. P. Child, A. Cone, A. S. Cushman, J. Escard, H. Fleek, H. J. French, P. Froger, N. J. Gebert, G. Gin, P. Girod, W. Guertler, A. Haenig, A. Heinzel, W. Heym, G. T. Holloway, E. Houdremont and co-workers, R. M. Keeney, H. B. Knowlton, W. L. Morrison, P. Müller, K. Nishida, P. Oberhoffer, W. Oertel and co-workers, J. Ohly, F. Peters, N. Petinot, E. Pohl, F. Rapatz, J. W. Richards, B. D. Saklatwalla, R. Scherer, E. Schilling, G. P. Scholl, J. K. Smith, S. S. Steinberg and P. S. Kusakin, O. J. Steinhart, G. and E. Stig, G. Surr, and W. Venator. W. R. Hulbert obtained them by the thermite process. J. E. Stead observed that ordinary pig-iron may contain up to 0·262 per cent. of vanadium; L. Blum also observed it in blast-furnace slags. J. Laissus, and N. Agéeff and M. Zamotorin dicussed the diffusion of vanadium in iron. R. Vogel and G. Tammann prepared alloys by the aluminothermite process in a crucible lined with fused magnesia. When an ordinary crucible was employed, up to 7 per cent. of silicon was dissolved from the walls. The f.p. curve falls from 1750°, the m.p. of vanadium, to a minimum with 31·5 per cent. of vanadium and then rises to the m.p. of iron, 1525°. Except at the minimum, the crystallization intervals are considerable, and, as the alloys are homogeneous throughout, the metals form a complete series of mixed crystals. The behaviour of the alloys containing silicon is considerably more complicated; the minimum of the f.p. curve is lower, and at 1380° there is a break in miscibility from 55 to 90 per cent. of vanadium. In the alloys containing 20 to 52 per cent. of vanadium, there is a transition between 1100° and 1250°, the nature of which has not been elucidated. The vanadium steels, except those very rich in iron, are hard and fairly brittle, but can be filed and hammered. The presence of silicon greatly increases the hardness and brittleness. Pure vanadium-iron alloys are acted on by nitric acid, but those containing silicon, only by hot aqua regia. The results of M. Oya are summarized in Fig. 439; they agree with those of R. Vogel and G. Tammann. M. Oya also found that the alloys form a complete series of solid soln., that the A_4-point is rapidly lowered by vanadium, but that the A_2-point rises rapidly to form a loop at 2·5 per cent. vanadium. The A_2-point rises at first gradually, attains a maximum with 15 per cent. vanadium, falls slowly to 20 per cent., and is rapidly lowered to room temp. with 35 per cent. J. A. M. van Liempt discussed the solid soln. of the two elements. E. Maurer and co-workers observed that with 2·5 per cent. of vanadium, the γ-transformation of iron disappears, and the A_3- and A_4-points of iron meet, so that with over that proportion of vanadium, α- and δ-iron are identical—*cf.* chromium-iron alloys. F. Roll observed that vanadium stabilizes the cementite in cast iron. V. N. Svechnikoff studied the γ-phase.

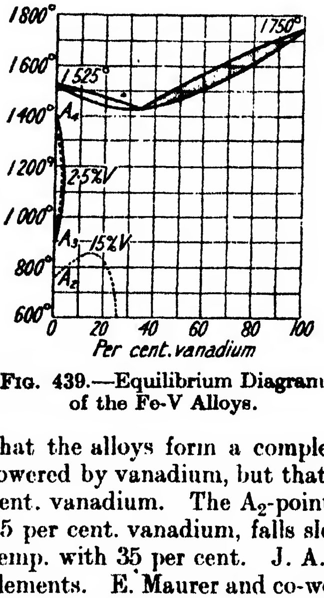


FIG. 439.—Equilibrium Diagram of the Fe-V Alloys.

G. L. Norris observed that the presence of vanadium in cast iron increased the transverse strength and tensile strength, and lengthened the life of locomotive cylinders. J. K. Smith said that the beneficial effects of vanadium on steel are (i) the result of its acting as a unique scavenger in removing both oxides and nitrides, forming fluid and readily separable products, so that the metal is directly toughened. W. H. Hatfield does not agree with this for cast iron. J. K. Smith also attributed the favourable effects of vanadium (ii) to the passage under normal conditions of a proportion of vanadium into solid soln. with the ferrite, so that the ferrite is then more resistant to wear and to the formation of slip-bands, and it opposes the ready passage of carbides through it, so that vanadium steel has a tendency to be sorbitic in character; and (iii) the direct strengthening of the steel owing to the formation of complex carbides. F. M. Becket, and C. F. Burgess and J. Aston discussed the working qualities of the iron-vanadium alloys; and Z. Nishiyama, the X-radiograms. F. L. Coonan, and R. Moldenke made some observations on the influence of vanadium on cast iron; and W. H. Hatfield concluded that additions of vanadium have a definite influence on the physical properties of cast iron, in that it helps the carbon to persist in the combined state, by making it more stable. The combined carbon does not differ physically from the normal carbide of cast iron. P. Pütz said that a small addition—0·2 per cent.—of vanadium suffices to raise the Ar_1-point nearly 10°, but further additions do not raise this point any higher; and the $Ar_{3\text{-}2}$ point is raised proportionally with the increase in the percentage of vanadium. A. M. Portevin observed that with steels having 0·2 per cent. of carbon, the breaks in the heating and cooling curves are as follow:

Vanadium.	0·60	0·75	1·04	1·54	2·98	5·37	7·39	10·27 per cent.
Heating .	810°	810°	795°	800°	840°	812°	860°	--
Cooling .	905°	985°	920°	945°	950°	960°	—	—
	810°	810°	805°	800°	830°	815°	840°	820°
	730°	730°	690°	—	--	—	590°	570°

whereas with a steel with 0·8 per cent. carbon the results were more definite, being:

Vanadium.	0·25	0·60	0·80	1·15	1·58	2·89	4·99	7·85 per cent.
Heating .	800°	800°	800°	798°	785°	790°	782°	780°
Cooling .	740°	738°	740°	740°	732°	730°	720°	700°

P. Nicolardot said that the V_3C_2 or the V_2C carbide is formed in steel, and this forms with the cementite a complex iron vanadium carbide. P. Pütz supposed that the vanadium carbide present in the vanadium steels is $V_{2n}C_{3n}$. J. O. Arnold and A. A. Read stated that with steels containing as little as 0·71 per cent. of vanadium, vanadium replaces iron in the carbide to form a mechanical mixture of $11Fe_3C+V_4C_3$; and as the proportion of vanadium increases, more is found with the carbide, until with 2·32 per cent. of vanadium, the carbide of the steel is $2Fe_3C+V_4C_3$; and with higher proportions of vanadium—say, 5·84 per cent.—practically all the iron of the carbide is replaced by vanadium. L. Guillet found that the higher the proportion of carbon, the more is the vanadium required to avoid the presence of pearlite. The pearlite steels are hardened by quenching a proportion as the vanadium-content rises. Steels containing carbide and pearlite are less affected. Steels with carbide are slightly softened; the carbide is never all dissolved, whatever be the temp. of quenching. As a rule, annealing softens the vanadium steels. In the pearlitic steels containing much carbide, the carbide is precipitated as graphite, and in that case the steels become extremely brittle. Case-hardening in a pearlitic steel may result in the production of much carbide.

M. Oya's observations on the ternary system involving low-vanadium steels showed that the solubility of carbon in the γ-phase, markedly decreases on the addition of vanadium, and hence the existing range of the γ-phase in this system is very narrow. In the region of the γ-phase there exist three proeutectoid surfaces in which the α-phase, Fe_3C and V_4C_3 begin to separate, respectively. The A_1-point, that is, the eutectoid temperature, in the Fe–Fe_3C system is raised 15° by the addition of 0·5 per cent. vanadium and remains constant on further increasing the vanadium. The binary eutectoid reaction ($\gamma \rightarrow \alpha + V_4C_3$) takes place in the temp. range from 745° to about 1330°. A non-variant reaction, $V_4C_3+\gamma \rightleftarrows Fe_3C+\alpha$, takes place in the neighbourhood of the composition of about 0·5 per cent. vanadium and 0·9 per cent. carbon. The subject was studied by E. L. Reed, R. Vogel and E. Martin, F. Wever and W. Jellinghaus, and H. Hougardy. C. H. Mathewson and co-workers investigated the Fe–V–O_2 system.

Observations on the subject were made by P. Blum, J. Challansonnet, E. T. Clarage, J. W. Donaldson, E. O. Fitch, W. Giesen, L. Guillet, A. Haenig, R. Maréchal, E. Martin, G. L. Norris, N. Petinot, A. M. Portevin, K. Ruf,

M. Sauvageot, and D. Zuege. J. O. Arnold said that vanadium forms a true steel, 100 per cent. pearlite, when 4·8 per cent. of vanadium is present, and 0·83 per cent. of carbon. Vanadium pearlite has $72Fe+V_4C_3$. H. Scott observed that vanadium had no marked effect on the transformation temp. of martensite to troostite. J. Challansonnet found that vanadium hindered the graphitization of steel—*vide* nickel-vanadium steels. E. Piwowarsky, A. Campion, J. W. Donaldson, H. Sawamura, and J. E. Hurst studied the effect of vanadium in cast iron.

A. Osawa and S. Oya represented the relation between the lattice parameter, a A., and the percentage of vanadium, [V], in iron-vanadium alloys by $a=2·852+0·000614[V]+0·0000131[V]^2$. Z. Nishiyama found the lattice parameter, a; the sp. gr.; and the elastic modulus, E kgrms. per sq. cm., at 15·1° to 15·3°, to be:

V . . .	0·1	2	3	4	6	7	8 per cent.
a . . .	2·857	2·860	—	2·866	2·868	—	2·871 A.
Sp. gr. . .	7·8548	7·8602	7·7999	7·7905	7·7617	7·7206	—
$E\times10^{-6}$ . .	2·162	2·127	2·151	2·142	2·130	2·093	—

Observations were also made by F. Wever and W. Jellinghaus, who found:

Vanadium.	0	13·4	28·6	38·4	47·8	63·6	79·8	100 per cent.
$a\times10^8$ cm.	2·860	2·865	2·875	2·88	2·89	2·925	2·955	3·04

K. Ruf measured the sp. gr. of iron-vanadium alloys. W. H. Hatfield gave for alloys with combined carbon 2·9 per cent., 0·66 Si, 0·28 Mn, 0·03 S, 0·08 P, and

Vanadium		0	0·138	0·22	0·45	0·65 per cent.
Hardness	Brinell's . . .	387	418	430	418	430
	Scleroscopic . .	48	48	48	47	48

G. W. Quick and L. Jordan recommend these steels for the balls in Brinell's test for hardness. G. Tammann and V. Caglioti studied the recovery of the hardness after cold-work. L. Guillet observed that the pearlitic steels have a tensile strength and an elastic limit which rise rapidly with the percentage of vanadium; the elongation and reduction of area slowly decrease, while still preserving relatively high values; the brittleness does not increase; but the hardness increases rapidly. The tensile strength and elastic limit of steels containing pearlite and carbide are lower as the proportion of vanadium is lower, and, in consequence, of the carbide, are higher. The elongation and reduction of area increase, but the resistance to shock decreases rapidly. The mechanical properties of steels containing carbide vary but little with their composition. The tensile strengths and elastic limits are low; the elongations and reduction of area are high, but the products are brittle. These results were discussed by G. Auchy, M. Ballay, J. Baxeres, P. Blum, H. M. Boylston, A. L. Colby, E. F. Cone, E. O. Fitch, H. Fleek, R. C. Good, R. Hohage and A. Grützner, W. A. Johnson, W. Kahlbaum and co-workers, O. von Keil and F. Ebert, M. Kinkead, A. B. Kinzel and C. O. Burgess, E. Kothny, R. W. Moffatt, I. Musatti and G. Calbiani, A. L. Norbury, W. Oertel and F. Pölzguter, P. Prömper and E. Pohl, A. Rys, E. B. Saklatwalla and co-workers, E. K. Smith and H. C. Aufderhaar, H. P. Smith, J. K. Smith, B. E. D. Stafford, J. Strauss and G. L. Norris, K. Taniguchi, J. L. Uhler, M. Vasvari, and F. Werner. Z. Nishiyama's results for the elastic modulus are indicated above. J. O. Arnold and A. A. Read obtained the results indicated in Table LXV. C. L. Clark and A. E. White measured the influence of temp. on the tensile strength. E. Piwowarsky said that vanadium increases the resistance of iron to shock. According to F. Robin, the resistance of the vanadium steels to crushing is very high so long as the formation of double carbide does not occur. The resistance to crushing of carbon-vanadium steels, like their hardness, is sharply accentuated by slight additions of vanadium. Near 1000°, the crushing strength of a steel with 0·8 per cent. of carbon and 0·2 to 1·5 per cent. of vanadium is rather low. E. Piwowarsky observed that the addition of silicon increases the amount of combined carbon, and this influence is greater when the silicon is low.

R. W. Moffatt found that vanadium steel castings have a greater resistance to impact than straight carbon steel castings; they are also tougher and more ductile.

TABLE LXV.—MECHANICAL TESTS ON VANADIUM STEELS.

Percentage Composition				Yield-point (tons per sq. in.)	Maximum stress in tons per sq. in.	Elongation (per cent.)	Reduction of area (per cent.)	Alternating stress (alternations endured)
C	Si	Mn	V					
0·60	0·05	0·06	0·71	12·0	35·9	22·0	41·4	119
0·63	0·09	0·07	2·32	14·0	35·0	24·5	52·0	191
0·93	0·21	0·11	5·84	17·0	33·4	25·0	53·2	135
1·07	0·32	0·12	10·30	15·0	33·7	23·0	31·5	119
1·10	0·47	0·12	13·45	18·0	37·0	10·0	9·7	15

K. Ruf measured the thermal expansion between 0° and 250° and found that alloys with over 6 per cent. of vanadium show no marked anomaly in the thermal expansion at higher temp. K. Ruf measured the sp. resistance for the thermoelectric force against platinum. Observations were also made by E. T. Clarage, E. F. Lake, P. Pütz, A. McWilliam and E. J. Barnes, J. K. Smith, H. R. Sankey and J. K. Smith, M. K. Hélouis, W. Giesen, A. M. Portevin, R. Hohage and A. Grützner, E. Maurer, A. Campion, and R. Moldenke. G. Tammann and V. Caglioti discussed the recovery of resistance after cold-work. A. M. Portevin found that the addition of 1 per cent. vanadium raised the electrical resistance of iron 6·7 microhms per cm. cube; and with steels containing 0·1 to about 0·2 per cent. of carbon—normal and hardened by quenching from 1000° to 20°—had the following values for the electrical resistance, R microhms per c.c.:

Vanadium	0·60	0·75	1·04	1·54	2·98	5·37	7·39 per cent.
R Normal	14·0	15·1	16·2	18·8	30·1	31·7	38·6
R Hardened	15·7	19·9	21·7	21·9	31·8	31·6	38·4

and with steels having about 0·8 per cent. carbon:

Vanadium	0·25	0·80	1·15	2·89	4·99	7·85	10·25 per cent.
R Normal	21·4	22·4	19·3	22·5	20·9	37·5	107·2
R Hardened	38·2	42·6	31·5	31·8	27·6	37·5	107·0

G. Mars stated that from the general behaviour of vanadium steels, the presence of vanadium confers no special advantages in the use for permanent magnets, and is not likely to have a stronger remanence than normal steel. J. Challansonnet found vanadium lowered the Curie point. F. Wever and W. Jellinghaus obtained the two magnetization curves for alloys with 29·5 per cent. V, and 33·5 per cent. V (Fig. 440, dotted). J. J. Lonsdale observed that the coercive force of vanadium steel is increased when it has been heated above its critical temp., and when it has been annealed and quenched. The permeability is lower than that of other steels containing the same amount of carbon, but the hysteresis and coercive force are greater.

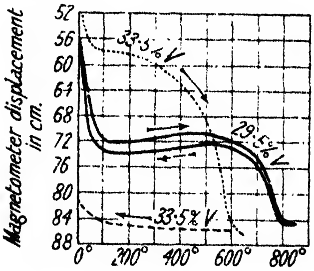


FIG. 440.—Magnetization Curves of Iron-Vanadium Alloys.

L. Kirschfeld measured the hydrogen absorbed by the ferrovanadium alloys. Alloy I had 9·1 per cent. of vanadium and 0·07 per cent. of carbon; II had 22·0 per cent. of vanadium and 0·56 per cent. of carbon; III had 70·9 per cent. of vanadium. Values for Fe, iron, and V, vanadium, are also indicated in the isothermal and isobaric (about 760 mm.) curves, Figs. 441 and 442. The absorption increases as the proportion of vanadium increases, but is always less than the value calculated by the mixture rule. The isobars for 9 and 22 per cent. of vanadium show minima at 700° to 800°, but with 71 per cent. of vanadium, the minimum disappears, and the isobar approximates to that for vanadium alone. The isotherms of the alloys assume the parabolic form at a higher temp. According to G. Tammann and G. Siebel, the thickness of the air-films, $y\mu\mu$, is represented by $t=a(e^{by}-1)$, where a and b are constants, t represents the time. There is a discontinuity in the curves connected with the transformation of α- into γ-iron. Some of L. Kirschfeld and A. Sieverts' results are shown in Fig. 443. L. B. Pfeil observed that when vanadium steel is heated at about 1000° for many hours in air, the three-layer scale which is formed—*vide supra*—has a concentration of vanadium in the innermost layer, and only small amounts occur in the middle and outer layers. G. Tammann and G. Siebel studied the oxidation or temper colours of vanadium steels. Vanadium steels ought to be more acid-resistant than ordinary steels because vanadium carbide is not readily attacked by acids. L. Aitchison found that the corrosion of vanadium steels represented by the loss in weight per 100 sq. cms. after exposure in the dark to 3 per cent. sodium chloride soln. and 1 per cent. sulphuric acid for 77 days, and 10 per cent. sulphuric acid for 45 days, was as follows:

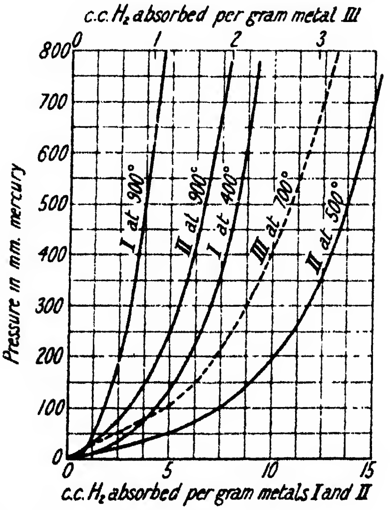


FIG. 441.—The Effect of Pressure on the Absorption of Hydrogen-Temperature Constant.

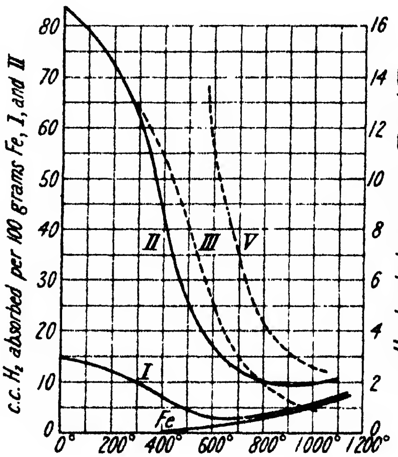


FIG. 442.—The Effect of Temperature on the Absorption of Hydrogen-Pressure Constant.

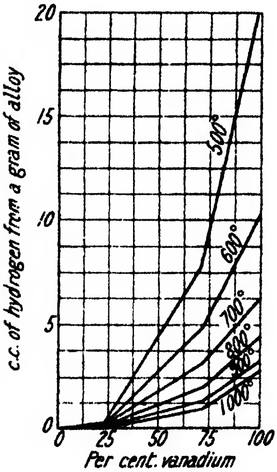


FIG. 443.—The Adsorption of Hydrogen by Iron-Vanadium Alloys.

C	0·60	0·63	0·93	1·07	1·10 per cent.
V	0·71	2·32	5·84	10·30	13·45 ,,
NaCl	1·73	1·74	1·87	1·66	1·49
H_2SO_4 { 1 per cent.	5·82	4·73	4·48	5·56	3·63
H_2SO_4 { 10 ,,	8·05	12·42	20·25	17·40	16·18

H. Endo's results, summarized in Fig. 444, show the losses in grams per sq. cm., during 5 hrs.' action, at ordinary temp., with alloys containing 0·54 to 0·66 per cent. of carbon, and

Vanadium		1·04	4·33	6·67	8·97	13·72	22·01	22·01	27·56 %
Loss	H_2SO_4	0·01411	0·01778	0·01609	—	0·01056	0·00686	0·00438	0·00336
	HCl	0·01599	0·01682	0·01436	—	0·00879	0·00434	0·00308	0·00192
	HNO_3	0·08600	0·09624	0·06950	0·06728	0·01889	0·00177	0·00025	0·00005

A. B. Kinzel, and L. Guillet studied the action of nitrogen; and M. Wunder and B. Janneret, the action of phosphoric acid; and H. J. French, the action of hydrogen sulphide and other corrosive agents; and N. Tschieschewsky and N. Blinoff, the action of nitrogen. The general uses of vanadium steels were discussed by E. F. Lake, P. Girod, P. Breuil, J. A. Mathews, O. M. Becker, H. R. Sankey and J. K. Smith, M. Dierfeld, H. Fleek, G. G. Blackwell, E. Lievenie, and J. Ohly; and ferrovanadium as a catalyst, by I. E. Adaduroff and G. K. Boreskoff. E. Piwowarsky, and J. Challansonnet studied the **titanium-vanadium-iron alloys.**

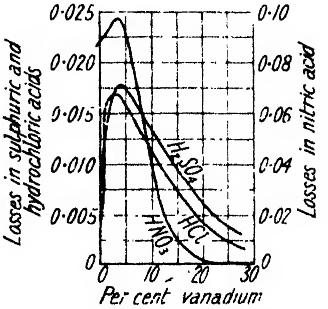


FIG. 444.—The Corrosion of Vanadium Steels by Acids.

J. G. Gahn and J. J. Berzelius[20] obtained a **tantalum-iron alloy** by heating a mixture of tantalic oxide and iron filings in a charcoal crucible. The product is hard, and scratches glass. Hydrochloric acid slowly extracts the iron, leaving the tantalum behind. Alloys were described by W. Heym, G. T. Holloway, W. Guertler, H. J. French and T. G. Digges, and F. C. Kelley. J. Laissus discussed the diffusion of tantalum in iron. A. M. Portevin found that the tantalum steels are pearlitic; and that the effect of tantalum on the shearing tests is small. The values for resistance to shear, tensile strength, etc., in Table LXVI are expressed in kilograms per sq. mm. L. Guillet obtained the results indicated in Table LXVII. The alloys were described by O. J. Steinhart, and P. Breuil. A. M. Portevin observed that the

TABLE LXVI.—THE MECHANICAL PROPERTIES OF TANTALUM STEELS.

Percentage composition				Resistance to shear	Elastic limit shearing (kgrms.)	Contraction on shearing (per cent.)	Tensile strength (kgrms.)	Elastic limit (kgrms.)	Reduction of area (per cent.)
C	Si	Mn	Ta						
0·120	0·120	0·190	0·09	21·1	8·4	21	41·5	29·8	67·4
1·700	0·190	0·150	0·15	21·5	9·2	18	42·6	30·4	68·8
0·180	0·240	0·220	0·60	21·5	10·0	19	45·3	31·1	67·4
0·160	0·160	0·230	1·05	23·2	10·0	20	47·8	31·5	62·3

TABLE LXVII.—THE MECHANICAL PROPERTIES OF TANTALUM STEELS.

Percentage composition		State	Elastic limit (kgrms. per sq. mm.)	Tensile strength (kgrms. per sq. mm.)	Elongation (per cent.)	Reduction of area per cent.)	Brinell's hardness
C	Ta						
0·12	0·09	Normal	29·8	41·5	53·0	67·4	107
		Hardened	46·2	65 0	14·5	71·0	159
0·17	0·15	Normal	30·4	42·6	31·0	68·8	107
		Hardened	45·7	62·1	15·0	73·1	153
0·18	0·60	Normal	31·1	45·3	28·0	67·4	112
		Hardened	46·6	65·8	13·0	74·9	155
0·16	1·05	Normal	31·5	47·8	28·0	62·3	116
		Hardened	49·1	70·0	10·0	55·8	169

electrical resistance of steel is very little affected by the addition of up to 1·05 per cent. of tantalum. M. Faraday and J. Stodart,[21] G. T. Holloway, and R. Mallet noted that **columbium-iron alloys** are less corrodible than iron.

M. Faraday and J. Stodart,[22] in their experiments on the alloys formed by different metals with iron, prepared some **chromium-iron alloys.** They found that an alloy with about 2·9 per cent. of chromium was as malleable as iron, and exhibited a damasked surface. Some of these alloys were examined by R. A. Hadfield. W. Sowerby said that in the southern part of India, the celebrated hog-spears and knives made by Anachelan of Salem, Madras, were manufactured from the chrome iron-stone found in the district. J. E. Stead observed that ordinary steel, and iron may contain up to 0·120 per cent. of chromium. The work, *Sur les alliages du chrôme avec le fer et avec l'acier*, was taken up by P. Berthier, who stated that the two metals could be alloyed in all proportions; that the alloys were very hard, brittle, and crystalline; and that they were a greyer and brighter white, less fusible, less magnetic, and less easily attacked by acids than iron alone. E. Frémy also prepared an alloy by heating a mixture of chromic oxide and iron in a blast-furnace, and said that the alloy frequently crystallizes in long needles, and that it resembles cast iron but scratches the hardest bodies, even hardened steel. R. Mushet used a similar mode of preparation. J. Percy also reported the alloys to be formed by heating a mixture of hæmatite and chromic oxide, in a charcoal-lined crucible, filled up with charcoal powder, and heated to whiteness for a couple of hours. Patents were obtained by J. Bauer in 1865–1869, A. Parkes in 1870; and H. Biermann wrote on the subject in 1873; and, according to A. Brustlein, chrome steel was manufactured at Unieux, Loire, in 1877. The *ferrochromium* of J. Bauer was obtained by heating a mixture of powdered chromite, and charcoal or anthracite along with a flux containing calcium or sodium fluoride, lime, and borax, in a plumbago crucible at a high temp. S. Kern also prepared it by melting chromite and charcoal in a plumbago crucible; and E. Héroult, by heating chrome ore with fluxes in an electric furnace. W. Borchers recommended the following process:

> In preparing ferrochromium, the ore is first mixed with the following substances: charcoal, 12 to 15 per cent.; resin or pulverized pitch, 6 to 7 per cent.; glass scrap, 5 per cent.; and quartz sand, 10 to 12 per cent. An intimate mixture is desirable, and can be best secured by piling the ingredients in a heap, each forming a separate layer, and then removing in vertical sections to form a new heap. After repeating this process several times the mass will have a uniform appearance. The ore is then fused in a graphite, or strong clay crucible, the bottom of which is covered with a thin layer of fine glass and coarse charcoal. The cover of the crucible is sealed with clay; only a small opening should be left for the escape of gases. The ore can be reduced by a crucible furnace with good draught, but to melt the metal a gas regenerative furnace will be required. Where a Siemens furnace for crucible steel is at hand this may be employed to advantage for smelting ferrochromium.

W. R. Hulbert obtained the alloys by the thermite process. The preparation of ferrochromium was described by W. B. Ballantine, F. M. Becket, H. Behrens and A. R. van Linge, C. Benedicks, W. Borchers and R. W. Stimson, H. Brearley, A. Brustlein, T. H. Burnham, R. Calberla, H. C. H. Carpenter, F. Cirkel, A. W. Clement, J. Escard, G. Gin, P. Girod, M. A. Grossmann, W. B. Hamilton and T. A. Evans, J. Hébert, W. Heym, E. Houdremont, F. Hütte, R. M. Keeney, R. S. Kerns, Firma Krupp, S. Meunier, H. H. Meyer, P. Monnartz, P. Oberhoffer, F. R. Palmer, D. St. Pierre du Bose, H. D. Phillips, V. S. Polansky, J. W. Richards, W. R. Saltrick, G. P. Scholl, E. J. Shackleford and W. B. D. Penniman, H. C. Sicard, F. T. Sisco, J. K. Smith, S. S. Steinberg and P. S. Kusakin, O. J. Steinhart, G. Surr, C. Tama, W. Venator, R. Waddell, H. Wedding, and R. S. Wile; G. Fuseya and K. Sasaki studied the electro-deposition of chromium-iron alloys. F. P. Zimmerli compiled a bibliography on chromium steels.

N. Agéeff and M. Zamotorin, J. Laissus, W. van Drunen, and F. C. Kelley studied the diffusion of chromium in iron. G. Grube and W. von Fleischbein showed that when a rod of iron is surrounded with powdered chromium and heated in hydrogen, the chromium-content of the surface layer of the iron and the depth of penetration of the chromium increase with rising temp. and increasing duration of heating. Thus,

	24 hrs.	72 hrs.	96 hrs.		
Surface layer .	5·3	28·4	43·3	47·4	52·9 per cent.
Penetration .	0·3	1·7	—	—	—

the composition is then constant for a depth of about 0·3 mm., and probably represents the solubility of chromium in iron at the several temps. The chromium-content of a rod does not diminish uniformly with increasing depth, and the diffusion coeff. is therefore different at different depths. The diffusion layer consists of mixed crystals of iron and chromium arranged radially. J. Laissus studied the cementation of iron by chromium.

According to R. A. Hadfield, unlike aluminium or silicon, chromium does not confer soundness on steel. When the proportion of carbon is high, as in pig-irons, sound ingots free from honeycombs may be obtained, but an alloy with 1·35 per cent. of chromium and 0·28 per cent. of carbon "rose" badly in the moulds. Aluminium does not act so powerfully with low-carbon chromium steels as it does with carbon steels. Alloys with more than 11·13 per cent. of chromium,. and 1·27 per cent. of carbon were not forgeable, but with less chromium the steels could be forged. If less carbon was present, probably steels with higher proportions of chromium would be forgeable. Chromium is not favourable to welding, for, as A. Brustlein also showed, a comparatively small proportion of chromium interferes with the welding. It may be possible to fuse chromium and attach it to steel or to wrought iron, but the ordinary process of welding two bars together is not possible. F. Reiser said that an alloy with 0·2 per cent. of chromium is unsuited for puddling. C. F. Burgess and J. Aston discussed the working qualities of the alloys.

In the study of the thermal diagram, W. Treitschke and G. Tammann observed that the f.p. curve consists of a number of irregular bends, and they suggested that the results can be explained by assuming that a compound is formed which is completely miscible in the solid state with its components. P. Monnartz supposed that the compound formed is **iron dichromide,** $FeCr_2$, and that it shows as a maximum on the f.p. curve with 66 per cent. of chromium. K. Bornemann discussed the subject; and E. Jänecke stated that the conclusions of W. Treitschke and G. Tammann are wrong because of the presence of aluminium in their alloys. He said that there is a single eutectic which can form mixed crystals with either component. The eutectic is at 1320°, and 75 per cent. of chromium; and the limit over which the mixed crystals can form, is 55 to 85 per cent. of chromium. K. Fischbeck represented the iron–chromium system as having two eutectics—Fig. 445—and a maximum corresponding with **iron hemichromide,** Fe_2Cr. These different conclusions all show that there is something yet to learn about this system.

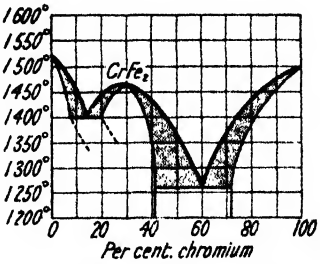


FIG. 445.—Equilibrium Curves of the Iron-Chromium Alloys.

E. Pakulla, A. von Vegesack, and T. Murakami inclined to the hypothesis that the two metals form solid soln. in all proportions; and that the apparent eutectics are due to the lack of diffusion during solidification which results in solid soln. differing in concentration. Thus, a dark etching portion showed a marked diminution in quantity on annealing at 1100° for 2 hrs., and it was inferred that a prolonged annealing would render the structure homogeneous. A. von Vegesack said that chromium and iron form a continuous series of solid soln. The m.p. of iron is depressed to a minimum of 1490° by the addition of up to 28 per cent. of chromium, and it then rises to over 1700°, the m.p. of chromium. The lower values for the m.p. of chromium are due to the presence of carbon. A. Westgren and co-workers also found that the lattice dimensions vary continuously with composition in agreement with the observation that *a*-iron and chromium have the same type of lattice. P. Oberhoffer and H. Esser represent the equilibrium curves by Fig. 446. T. Murakami showed that the A_2- and A_3-transformation points are lowered by chromium, and E. Pakulla and P. Oberhoffer obtained similar results. A. B. Kinzel found that the chromium-iron austenite loop runs from 0 to 12·2 per cent. of chromium; its upper boundary runs from 1400° to 900°, and its lower boundary from 900° and 0 per cent. of chromium to 900° with 12 per cent. of chromium.

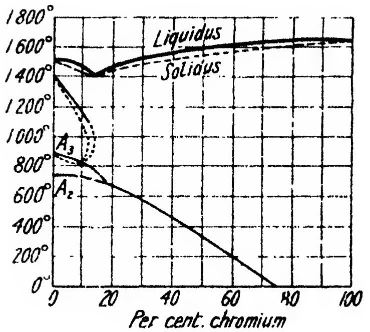


Fig. 446.—Equilibrium Diagram of the Iron-Chromium Alloys.

The equilibrium diagrams for the chromium and iron carbides have been previously indicated—**5**. 39, 19, Fig. 29, and **5**. 39, 20, Fig. 31. The diagram for the ternary system: Fe–Cr–C, has not been completed; only a few limited areas have been partially explored. P. Goerens and A. Stadeler found that the solidification temp. of iron remains practically constant at about 1130° when chromium is present to the extent of 10·4 per cent., but with higher proportions of chromium, the solidification temp. rises rapidly, attaining 1535° with 62 per cent. of chromium. With up to 21 per cent. of chromium, the carbide inversion remained at about 700° to 715°, and with higher proportions it could not be observed. The following is a selection from the results:

C . .	4·0	4·2	4·4	4·7	5·7	5·9	7·0	7·4	9·2 per cent.
Cr . .	0·0	1·2	2·7	5·0	13·7	20·5	33·4	43·2	62·0 ,,
F.p. . .	1130°	1126°	1128°	1128°	1145°	1161°	1270°	1370°	1535°
A_1-arrest .	711°	709°	710°	713°	715°	710°	*nil*	*nil*	*nil*

E. D. Campbell and J. F. Ross, H. Nienhaus, F. Adcock, F. Wever and W. Jellinghaus, E. Friemann and F. Sauerwald, T. Murakami, T. F. Russell, N. H. Aall, J. H. Andrew and H. A. Dickie, T. Kase, F. Wever and W. Jellinghaus, and P. Oberhoffer and K. Daeves made observations on the effect of chromium on the eutectic and eutectoid points of the carbon–iron system. A. B. Kinzel said that the austenite loop in the iron–chromium system ends with 12·37 per cent. of chromium. J. H. G. Monypenny measured the solubility curves of cementite; with the higher proportions of chromium, the cementite network does not dissolve until the pearlite carbide is dissolved; and the carbide dissolves rapidly above 1050° to 1100°. The cementite and carbide appear to dissolve simultaneously with the 1·36 and 2·8 per cent. chromium steels, indicating a possible difference in the two carbides. C. R. Austin found that for alloys having a chromium-iron ratio from 1 : 20 to 1 : 5, the addition of chromium up to 15 per cent. has relatively little effect on the amount of carbon in the eutectic, while with 20 per cent. of chromium, the eutectic has a little less than 4 per cent. carbon. There is no definite break on the curves other than the eutectic until the amount of chromium reaches 20 per cent., when there is a break with about 1·3 per cent. carbon. There is evidence of a maximum on the carbon side of the eutectic. With alloys having 30 to 50 per cent. chromium, the addition of carbon up to about 2·5 per cent. lowers the f.p. of the alloys linearly with increasing carbon; and the amount of carbon in the eutectics is nearly the same in all these cases. K. Fischbeck represented the data as a quaternary system involving the four phases Fe, Cr, Fe_3C, and Cr_5C_2. With steel, F. Osmond observed that chromium lowers the beginning of the A_3-transformation, and raises the end of the A_1-transformation, while the action of chromium on the A_2-transformation is not noticeable. S. Curie found that the transformations occur at a higher temp. with chromium steels than with ordinary steels. H. C. H. Carpenter obtained the following results for the change-points of the carbide with chromium steels:

Carbon	Chromium	Cooled from	Change-point
0·54	1·12	918°	729°
		1127°	728°
		1250°	709°
0·27	3·24	910°	738°
		1127°	736°
		1250°	721°
1·09	9·55	900°	776°
		1230°	750°

Hence, it was concluded that chromium tended to raise the carbide change-point, so that if 700° be taken as the change-point for carbon steels, the change-points rose respectively to 729°, 738°, and 776° on cooling from about 900° as the proportion of chromium was increased. Again, although when cooling from progressively higher temp., the change-point was lowered only a little, indicating that chromium tended to raise the carbide change-point, the temp. from which the steel was cooled had no great influence on that point. C. A. Edwards and co-workers found for the carbide transformation on heating, Ac_1, and cooling Ar_1:

Cr		1·96	4·20	6·18	8·08	10·39	12·08 per cent.
C 0·35 per cent.	Ac_1 .	797°	817°	833°	835°	835°	830°
	Ar_1 .	743°	764°	768°	774°	764°	762°
Cr		2·09	3·92	5·07	6·16	8·12	10·41 per cent.
C 1·0 per cent.	Ac_1 .	790°	795°	805°	825°	829°	836°
	Ar_1 .	748°	757°	767°	785°	794°	800°

H. Moore observed that the position of the Ac_1-transformation is progressively raised by additions of chromium from 746° with a steel containing 0·25 per cent. of chromium, to 821° when 6·417 per cent. of chromium is present. With steels having about 3 per cent. of chromium another critical point occurs below the Ac_1-point, and magnetic observations show that it is the Ac_2-point. The occurrence of the Ac_2 point below Ac_1 is taken to support the hypothesis that the carbide formed is insoluble in β-iron. A. McWilliam and E. J. Barnes observed the critical temp. shown in Table LXVIII with steels containing 2 per cent. of chromium.

TABLE LXVIII.—THE CRITICAL TEMPERATURES OF 2 PER CENT. CHROMIUM STEELS.

Carbon (per cent.)	Heating			Cooling		
	Ac_1	Ac_2	Ac_3	Ar_3	Ar_2	Ar_1
0·20	765°	791°	822°	785°	765°	732°
0·25	759°	789°	810°		758°	731°
0·32	753°		785°		748°	733°
0·50	759°		778°		721°	
0·65		783°			718°	
0·85		777°			714°	

A. B. Kinzel stated that the A_4-arrest is gradually lowered from 1400° to 1250° with the addition of 10 per cent. chromium, and with 12·25 per cent. chromium, the A_4- and A_3-arrests coincide; the A_3-arrest is not changed. With 12·37 per cent. of chromium, the transformation could not be observed, and the austenitic loop ends at this point. A. B. Kinzel also found that the addition of up to 4 per cent. of chromium gradually lowers the A_4-transformation from 1400° to 1250°; and with higher proportions of chromium, the lowering is more abrupt, so that with 12·25 per cent., the A_4- and A_3-arrests coincide. The A_3-arrest is not affected.

Fig. 447 represents a portion of the standard iron-carbon diagram—*vide* Fig. 31, **5**. 39, 20—which changes very little with a small proportion of chromium. The area A_4BM represents a region of mixed austenite and δ-iron; and the area A_3SP, a region of mixed austenite and α-iron—the term δ-iron is used to indicate material that has been heated above the A_4-arrest, in contrast to α-iron, *i.e.* a material which has been transformed from austenite by cooling through the transformation temp. at the proper rate. Both δ-iron and α-iron crystallize in a body-centred cubic lattice, and the $\gamma\rightarrow\delta$-transformation is a reversion of the $\alpha\rightarrow\gamma$-transformation, and P. Oberhoffer found that in the re-crystallization of the iron-silicon alloys, the A_2- and A_3-arrests approach one another with increasing percentages of silicon, and coincide with 2·5 per cent. silicon. This was confirmed by P. Oberhoffer and C. Kreutzer. A. Westgren and G. Phragmen's X-radiograms confirm this. E. C. Bain inferred that a similar phenomenon occurs with the iron-chromium alloys, and this was confirmed by A. Westgren and co-workers. In the complete absence of carbon, the γ-change disappears completely when enough alloying element is present. Since A. Westgren and G. Phragmen have shown that chromium crystallizes only in one single type of lattice, it follows that the γ-range should be limited to alloys rich in iron, and E. C. Bain showed that this occurs when about 14 per cent. of chromium is present; P. Oberhoffer and C. Kreutzer gave 12·62 per cent. of chromium with 0·01 per cent. of carbon; and F. Stäblein, 18 per cent. of chromium with 0·03 per cent. of carbon. As chromium is added to the iron, there is a slight rise in the A_3-point, and a sharp drop in the A_4-point until, with about 14 per cent. of chromium the two points meet, and beyond that there is no transformation to γ-iron. Hence, when carbonless iron-chromium alloys containing over 14 per cent. of chromium are heated to a high temp., the α-iron remains as such. When carbon is present, M. A. Grossmann showed that the conditions are very different. The results can be represented on a ternary diagram, Fig. 447. A. von Vegesack also observed that the transformation point of γ- to α-iron is lowered by the addition of chromium, and cannot be observed when over 15 per cent. of chromium is present. P. Oberhoffer and H. Esser gave 14·77 per cent. as the limit at which γ-Fe can be no longer observed. This agrees with C. Kreutzer's observations of the X-radiograms. The effect of chromium on the $\alpha\rightarrow\gamma$- and the $\gamma\rightarrow\delta$-transformations could not be observed because of the volatilization of the chromium; but the α-phase passes directly into the δ-phase when over 15 per cent. of chromium is present. J. A. Jones, J. P. Gill, A. Michel and P. Benazet, L. R. Austin, L. J. Barton, E. Jänecke, T. Murakami and Y. Fujii, E. L. Reed, W. Haufe, J. E. Johnson, A. Merz, E. Maurer and co-workers, V. N. Krivobok and M. A. Grossmann, H. F. Moore, and P. Oberhoffer and C. Kreutzer, discussed the range of the Ac_1-arrest; H. Moore, the A_2-arrest; and V. N. Svechnikoff, the γ-phase.

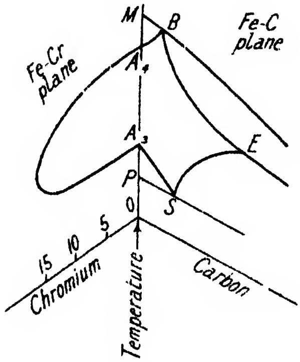


FIG. 447.—Portion of Equilibrium Diagram for Iron-Carbon-Chromium Alloys.

F. Osmond concluded that chromium exists in steel in at least three states—separately or simultaneously: (i) as dissolved chromium; (ii) as a complex compound of chromium, iron, and carbon in the form of isolated globules; and (iii) as a solid soln. with the ternary complex. The triple complex is very hard, and when incorporated with a more malleable matrix, it naturally communicates to it a certain degree of hardness. The chromium and iron carbides have been previously discussed. H. Behrens and A. R. van Linge reported that a non-magnetic crystalline complex **iron chromium carbide,** $Cr_2Fe_7C_3$, is obtained as a residue by treating ferrochromium with 13·3 per cent. chromium and 5·5 per cent. carbon with acid; while a 50 per cent. carbon chromium alloy with acid yields Cr_3FeC_2. A. Carnot and E. Goutal obtained residues corresponding with $Fe_3C.3Cr_3C_2$, and $3Fe_3C.Cr_3C_2$ from two chromium steels; P. Williams obtained $3Fe_3C.2Cr_3C_2$ by heating a mixture of chromic oxide, iron and petroleum coke in an electric furnace; while J. O. Arnold and A. A. Read concluded that the carbides in chromium steel—with carbon 0·64 to 0·85 per cent., and chromium 0·65 to 23·7 per cent.—varied with the composition. Thus, the residues, remaining after the acid treatment of alloys with nearly 0·85 per cent. carbon, corresponded with the mol. ratios $Fe_3C : Cr_3C_2 : Cr_4C$:

C .	0·64	0·84	0·835	0·85	0·88	0·85	0·85	per cent.
Cr .	0·65	0·99	4·97	10·15	15·02	19·46	23·70	,,
Ratios	20 : 1 : 0	12 : 1 : 0	4 : 1 : 1	1 : 1 : 1	2 : 0 : 1	2 : 0 : 1	2 : 0 : 1	

and T. Murakami inferred that the α-carbide is $(Fe_3C)_{18}Cr_4C$; the β-carbide is $(Fe_3C)_9Cr_4C$; and the γ-carbide is $(Fe_3C)Cr_4C$. He supposes that the lowering or suppression of the carbide change in low-chromium steels is caused by dissolved chromium. Above the Ac_1-point, the carbide Cr_4C dissolves in austenite, and by heating it to a suitable temp., it dissociates: $2Cr_4C \rightleftharpoons Cr_3C_2 + 5Cr$. High temp. favour the constituents on the right. During cooling, re-combination to form Cr_4C proceeds only slowly, and therefore, in alloys containing Cr_4C, the carbide change is lowered by the normal cooling from a high temp., by the retarding action of the dissolved chromium. The hardness of chromium steel is attributed to the solid soln. of the carbide Cr_3C_2 in a soln. of chromium in iron. The subject was discussed by P. Oberhoffer, and F. Rapatz. H. C. Boynton found that the pearlite in a 1 per cent. chromium steel is seven times harder than that of ordinary steel, but the ferrite was about the same in both cases, and it was hence assumed that at least 1 per cent. of the chromium is in the form of carbide. C. A. Edwards and co-workers assumed that in the ternary system, there is a region I, containing $Fe_3C + (Fe_3C)Cr_3C_2 + Fe$, and that as the proportion of chromium increases, the mols. of Fe_3C will be all used up in forming the double carbide, $Fe_3C.Cr_3C_2$, that is, FeCrC; and there appears region II, containing the double carbide, some unknown chromium carbide, say, Cr_5C_2, along with a solid soln. of iron and chromium with steels containing still less carbon; and there remains a region III, with chromium carbide along with a solid soln. of chromium and iron. T. F. Russell's experiments also indicate that FeCrC is the only double carbide formed; and he concludes tentatively, from measurements of the electrical resistance, that when chromium is added to a plain carbon steel, the chromium first associates itself with the iron carbide until the mol. ratio of chromium to carbon is 4·3, corresponding with FeCrC, and probably only a small proportion of chromium goes with the ferrite to form a solid soln.—*chromoferrite*. With further additions of chromium, the bulk goes into solid soln. with the iron, and raises the electrical resistance. This agrees with the observations of C. A. Edwards and A. L. Norbury. Even when the ratio Cr : C exceeds 4·3 : 1, some of the chromium is associated with the carbide, as indicated by observations of J. O. Arnold and A. A. Read, etc., to form another carbide with a higher proportion of chromium, but T. F. Russell considers that this chromium is either carried down mechanically, or else is in solid soln. with the carbide. M. A. Grossmann found that the carbon in a high chromium iron is not distributed uniformly after heat-treatment. The subject was studied by A. Carnot and E. Goutal, T. Meierling and W. Denecke, W. E. Remmers, F. Sauerwald and co-workers, E. L. Henderson, O. Smalley, E. Valenta, and H. Wentrup and W. Stenger. F. Roll showed that chromium stabilizes the cementite in cast iron, and the subject was investigated by J. W. Donaldson, T. F. Jennings, H. Sawamura, and T. Isihara.

K. Daeves found that the solubility falls off rapidly at first as the chromium-content increases, then more slowly, the general form of the curve being hyperbolic. Points on the curve were determined by observing what chromium-content was necessary, with a given carbon-content, to cause the appearance of a eutectic in the structure of the metal. To make the hard alloys workable, for the preparation of polished surfaces, it was necessary to heat for several hours at 800°, just below the Ac_1-point, by which treatment the solid soln. was broken up and the metal softened. Etching was accomplished by electrolysis in ammonium persulphate soln. In eutectoid alloys, the cementite is practically unattacked by hot sodium picrate soln. Cold alkaline potassium ferricyanide turns the hard constituent of the eutectic brown to yellow, leaving the mixed crystals untouched. The solubility curve explains many of the known properties of chromium steels. The melting-point of steel and the arrest points are little affected by chromium up to 10 per cent. About a dozen complex carbides have been reported, and in no particular case has its existence as a chemical individual been established, although the existence of FeCrC is highly probable. H. Brearley added that after numerous and fruitless attempts he had learned to distrust evidence based on the chemical analysis of residues employed to establish the existence of compounds which can be distinguished microscopically in steel. By means of X-radiograms, A. Westgren and co-workers found that the Cr_3C_2 carbide crystallizes in the rhombic system, and the elementary parallelopiped has 20 atoms, and the dimensions $a_1=2{\cdot}8121$ A., $a_2=5{\cdot}52$ A., and $a_3=11{\cdot}46$ A. The carbide usually given as Cr_5C_2 is considered to be Cr_7C_3. It is trigonal, and the elementary prism contains 80 atoms, and it has the dimensions—edge of base, 13·98 A., and height, 4·523. Another carbide, Cr_4C, *chromium tetritacarbide*, has a face-centred cubic lattice with 120 atoms, and side, $a=10{\cdot}638$ A.

L. Guillet found that quenching acts upon chromium steels in the same manner as it does on carbon steels, but with a far greater intensity, for the increase in tensile strength and elastic limit are much greater than with ordinary steels containing the same proportion of carbon. The martensitic steels are but little altered by quenching; while those richest in chromium are slightly softened. The troostite steels are hardened by quenching. Steels containing carbides are slightly softened by quenching from 850° without undergoing any alteration in their structure; quenching from 1200° has the effect of partially dissolving the double carbide and of producing γ-iron, while the hardness and brittleness are reduced. Annealing slightly softens all chromium steels. With steels containing carbide, annealing produces an increase in the grain-size, while in steels containing much chromium, an eutectoid carbide appears to be formed. The subject was studied by T. Murakami and co-workers, E. C. Bain, E. Houdremont, A. M. Portevin, K. Daeves, and D. Uno. J. H. G. Monypenny emphasized that the change with increasing amounts of chromium are all continuous, and there are no abrupt changes which can be represented sharply by boundary curves. L. Guillet found certain steels are austenitic when quenched from high temp., and J. H. G. Monypenny found that high carbon chromium steels, when quenched from a sufficiently high temp., are almost wholly austenitic. The proportion of carbon required varies with the proportion of chromium, being lower as the latter is higher. The region between the lines, Fig. 447, represents a mixture of the two. If the austenitic steel be tempered at 450°, the apparent drop in hardness is due to the presence of some martensite in the untempered sample; at 450°, there is an incipient decomposition of the austenite; at 600°, the hardness is a maximum, and the structure is martensite with a network of troostite; at 700°, the martensite is broken down, and the hardness drops considerably; while at 750°–800°, the carbide balls up. The austenite can be transformed into martensite by press. By slow cooling, it can be shown that the martensite is a transition product between austenite and pearlite, and it is obtained by a slower rate of cooling than is needed for austenite. The sequence of changes from austenite is martensite→troostite→carbide. W. Giesen said that steels low in chromium are pearlitic; and with medium chromium, martensitic; and that high-chromium steels, etched with picric acid, contain white globules of a carbide—*vide supra*. Observations on the microstructure were also made by C. A. Edwards and co-workers, W. Aichholzer, and E. Maurer and H. Nienhaus. T. F. Russell found that with alloys with up to nearly 12 per cent. of chromium and 1 per cent. of carbon, the steels were all pearlitic when cooled about 40 minutes, and all the steels recalesced between 700° and 770°. L. Guillet's pearlitic steels can be made martensitic by the air-cooling of small pieces. P. Oberhoffer also considers that the martensite area should be taken away from the diagram; and A. M. Portevin demonstrated what he considered to be the instability of the martensite zone. H. Scott found that chromium in certain proportions raised the temp. of the transformation of martensite to troostite. E. C. Bain showed that alloys containing more than about 25 per cent. of chromium are without transformation, the α-iron and δ-iron solid soln. being continuous and identical; and any carbon in excess of 0·40 per cent. is required to produce an appreciable amount of austenite at any temp. Alloys with over 10 per cent. of chromium furnish δ-iron in a form sufficiently stable to be quenched unchanged at room temp.; it is formed at a decreasing temp. with increasing chromium-content, and at room temp., it is then ordinary ferrite and is permanently stable. In the absence of appreciable quantities of carbon, chromium, in excess of about 14 per cent., does not dissolve in γ-iron, so that γ-iron is not produced in alloys containing more than this amount of chromium. Carbon increases the solubility of chromium in γ-iron, and renders it a stable constituent in alloys with over about 14 per cent. chromium. Alloys of iron with less than 10 per cent. of chromium behave like low-carbon steels, producing a material on quenching which is structurally martensitic, with rather lower carbon-content than would be found in a steel with the same structure. Both chromium and carbon render austenite more sluggish and reluctant to change into α-iron or martensite on cooling; and about 12 per cent. of chromium is required to preserve any appreciable austenite at room temp. after quenching in water, even when the carbon is as high as 0·3 per cent. W. Giesen reported that pearlitic chromium steels with 0 to 8 per cent. chromium and 0·5 per cent. carbon, or 0 to 5 per cent. chromium and 0·95 per cent. carbon, differ very slightly from ordinary carbon steels with a corresponding amount of carbon. The elastic limit, breaking strength, and elongation are similar; the hardness increases with the proportion of chromium, and is independent of the carbon-content, whilst the brittleness is less than in carbon steels with the same carbon-content. Chromium steels with 8 to 18 per cent. of chromium and 0·3 per cent. of carbon, or steels with 5 to 12 per cent. of chromium and 0·95 per cent. of carbon of martensitic or troostitic structure have a high tensile strength, elastic limit, and breaking strength in comparison with pearlitic chromium steels, whilst their ductility is low, the hardness is very high, and the brittleness medium. If the proportion of chromium exceeds 25 per cent. when 0·3 per cent. of carbon is present, and over 22 per cent. with 0·95 per cent. of carbon, the elastic limit sinks considerably, whereas the brittleness increases in the same proportion and attains a high value. The ductility and breaking strength are then medium. The tensile strength with a troostitic structure is much less than when the structure is martensitic. Chromium steels with martensitic or troostitic structure are very hard, and have a high elastic limit and tensile strength, with low elongation and contraction. Annealing makes pearlitic chromium steels milder, as is also the case when the martensitic steel is hardened—small quantities of γ-iron being formed in each case. A double carbide, chromium steel has a white appearance after heating to 1250°, and when quenched from this temp. the carbide structure disappears provided the proportion of chromium is high enough. Chromium steels with the double carbide structure are very liable to fracture; those of pearlitic structure are said to be best adapted for commercial use. J. O. Arnold said that chromium does not form a true steel with 100 per cent. pearlite. X-radiograms show that for each of the chromium carbides substitution of iron for chromium may to some extent take place. In the cubic form the chromium may be replaced by iron up to about 25 per cent.: in the trigonal carbide the iron-content may rise to 55 per cent., but in the rhombic carbide only a few per cent. of chromium can be replaced by iron. No definite double carbide, the presence of which would necessitate the presence of both iron and chromium atoms, is found. The solubility of the carbide in austenite is reduced as the chromium is increased, and the cementite line consists of two distinct portions corresponding to the solubility of different types of carbide. With 3 per cent. chromium, for example, the lower portion of the curve represents the solubility of the trigonal carbide, and the higher temp. region the solubility of cementite. With 15 per cent. of chromium the lower temp. portion gives the solubility in the γ-phase of the cubic carbide, and at higher temp. of the trigonal one.

According to A. Westgren and co-workers, A. von Vegesack's observations show that it is probable that along the trigonal carbide and γ-metal eutectic, and along the trigonal carbide and α-metal eutectic, the temp. rises continuously with an increasing percentage of chromium. This means that the points representing the liquid in equilibrium with the cubic and trigonal carbides and α-metal, or with trigonal carbide and α- and γ-metals, are both situated outside the respective triangles of the ternary system. The liquidus surface of cementite falls with an increasing percentage of chromium. The point of intersection of the liquidus surfaces of cementite, trigonal carbide, and γ-metal form a minimum point in the homogeneity range of the liquid phase. The evidence indicates that with a fairly low content of chromium, cementite is stable towards graphite so that the liquidus surface of cementite should intersect that of graphite. If the liquidus surface of cementite sinks with an increasing proportion of chromium, then that of graphite must necessarily decline still more rapidly. This indicates that chromium carbide mols. are present in the liquid phase. All three chromium carbides may separate from austenite on annealing. The homogeneity range of austenite is limited by four surfaces, three of which correspond with carbides, and one with the α-phase. E. C. Bain, and B. Kalling and G. Pagels have shown that the stability of austenite towards the α-phase rises with the carbon-content. It is remarkable that the cubic carbide can be in equilibrium with austenite at these low temp. The chromium-content of the metal phase, being in equilibrium with both trigonal and cubic carbides, is reduced to less than half its value at the moment of solidification. The maximum iron-content of the cubic carbide, however, seems to increase. As the chromium-content is raised the area of the γ-iron phase is gradually reduced and finally disappears: the eutectic occurs at a lower carbon-content than in iron-carbon alloys, for example, at about 3·7 per cent. with 15 per cent. of chromium.

In annealed chromium steels containing only 1 or 2 per cent. of chromium, the only carbide found is cementite, the iron of which is partially replaced by chromium. The difference of distribution of the carbide in such steels appears to be due not to any definite difference of composition, but to something of the nature of segregation. The carbide in stainless steel is the cubic carbide sat. with iron. In a steel, used for dies, containing about 1 per cent. of nickel, 11 per cent. of chromium, and 2 per cent. of carbon, the trigonal carbide occurs, rather more than half of the chromium of which is replaced by iron. K. Hilgenstock discussed the desulphurizing action of chromium on steel; R. J. Anderson, O. Bauer and K. Sipp, F. B. Coyle, A. B. Everest, C. D. Foulke, D. Hanson, J. R. Houston, A. Labo, E. Piwowarsky and co-workers, H. J. Schuth, E. K. Smith and H. C. Aufderhaar, L. Thiery, and M. Waehlert, the action of chromium on cast iron, etc.; and H. Styri, the heat-treatment of chromium steels.

P. Schoenmaker, and K. Honda and T. Murakami discussed the structure of chromium steels; W. Riede, and A. Phillips and R. W. Baker, the effect of chromium on the grain-growth; and G. D. Preston, A. E. van Arkel and W. G. Burgers, A. Westgren, and Z. Nishiyama, the X-radiograms. The lattice parameter, a; the sp. gr.; and the elastic modulus, E kgrms. per sq. cm., at 15·1° to 20·5°, are:

Cr . .	1·85	3·49	5·34	7·22	8·04	11·67	13·23 per cent.
a . .	2·865	2·869	2·869	2·871	2·872	2·871	2·873 A.
Sp. gr. .	7·8346	7·7980	7·7722	7·7474	7·7614	7·7419	7·7261
$E \times 10^{-6}$.	2·137	2·163	2·187	2·216	2·162	2·212	2·253

A. Westgren showed that the lattice dimensions of iron-chromium alloys vary continuously with the composition:

Chromium .	0	8·3	19·3	32·1	51·6	72·6	80·3	100·0 per cent.
a . . .	2·861	2·863	2·866	2·868	2·871	2·874	2·876	2·878 A.

Analogous observations were made with the cubic and trigonal carbides in which part of the chromium was replaced by iron. E. C. Bain discussed the X-radiograms; and R. Blix, the X-radiograms of ferro-chromium associated with nitrogen. According to R. A. Hadfield, the sp. gr. of chromium steels is as follows:

C .	0·07	0·14	0·77	0·77	1·27	2·12	4·00	5·00	6·00	6·47 per cent.
Cr .	0·22	0·57	3·51	5·19	11·13	16·74	8·30	28·00	44·00	66·00 ,,
Sp. gr.	7·777	7·759	7·740	7·712	7·675	7·595	7·597	6·954	6·814	7·000

F. Stäblein said that the sp. gr. of iron-chromium alloys decreases by 0·0033 for every 1 per cent. of chromium. J. H. G. Monypenny gave for a steel—0·3 C; 12·6 Cr—annealed at 950°, 7·731, which became 7·738 on tempering at 700°; for samples fully hardened and tempered: mild steel, 7·869; 0·3 C, 10·6 Cr, 7·751; 0·3 C, 12·6 Cr, 7·738; 0·08 C, 12·3 Cr, 7·779; 0·08 C, 15·4 Cr, 7·722; and 0·1 C and 20·4 Cr, 7·683. C. Benedicks and co-workers also measured the sp. vol. of stainless steels. The subject was discussed by J. O. Arnold, B. Simmersbach, H. A. Dickie, and J. H. Andrew and co-workers.

K. Ruf measured the sp. gr. of alloys of iron and chromium. W. Brown found the sp. gr. and sp. vol. of steels with 0·90 per cent. of carbon and 2·00 per cent. chromium are respectively 7·7611 and 0·12885; with 0·43 per cent. of carbon and 3·25 per cent. of chromium, respectively 7·7653 and 0·12878; and with 1·09 per cent. carbon and 9·50 per cent. chromium, respectively 7·7032 and 0·12982; so that with up to 3·3 per cent. of chromium, the sp. vol. can be represented by 0·1269 +0·00034 Cr, where Cr denotes the percentage of chromium, and higher proportions – up to 9·5 per cent.—have no further effect on the sp. vol. H. Rowsing and J. Sissener noted the changes in vol. which occur during the heat-treatment of chromium steels.

According to R. A. Hadfield, annealed steels or unannealed steels with 0·39 per cent. of carbon and up to 3 per cent. of chromium, are easily filed; with increasing proportions of chromium, the samples become harder and annealing makes very little difference to this property. With over 9·18 per cent. of chromium and 0·71 per cent. of carbon, the steel is very hard and can scarcely be touched with a file. The relative hardness of steels by the sclerometer test was found to be:

C . . .	0·16	0·12	0·27	0·39	0·77	0·86	0·71 per cent.
Si . . .	0·07	0·08	0·12	0·14	0·50	0·31	0·36 ,,
Mn . . .	0·18	0·18	0·21	0·25	0·61	0·29	0·25 ,,
Cr . . .	0·29	0·84	1·18	2·54	5·19	6·89	9·18 ,,
Hardness . .	22	21	24	24	55	38	43

when that of lead is 1; copper, 8; the softest iron, 15; and very hard white iron, 72. M. Brustlein, and J. B. J. D. Boussingault also stated that chromium steel with a very low proportion of carbon does not harden when water-quenched; and G. Rolland observed that chromium does not take the place of carbon in hardening steel. G. Tammann and V. Caglioti studied the recovery of hardness after cold-work. R. A. Hadfield's results are taken to show that chromium in its effect on iron, in the absence of carbon cannot be regarded as a hardening agent; but if not less than 0·35 per cent. of carbon be present, quick cooling is followed by a considerable hardening; and this under conditions where in the absence of carbon the alloy would not have been hardened. He also showed that if sufficient carbon be present, chromium makes the steel self-hardening. W. Giesen found that the hardness of steels with 0·5 per cent. of carbon and 0 to 8 per cent. of chromium, or 0·95 per cent. carbon and 0 to 5 per cent. chromium, increases with the chromium-content, and is entirely independent of the carbon-content; steels with 8 to 18 per cent. of chromium, and 0·3 per cent. of carbon, or 5 to 12 per cent. of chromium, and 0·95 per cent. of carbon, are extremely hard. Chromium steels with the martensitic or troostitic structure are exceedingly hard. The hardness of chromium steels was discussed by E. C. Bain, A. Campion, H. A. Dickie, J. W. Donaldson, C. A. Edwards and co-workers, V. Fedoroff and N. Trofimoff, L. Grenet, L. Guillet, M. Hamasumi, D. Hanson, H. Jüngbluth, T. Kase, A. Kussmann and B. Scharnoff, J. H. G. Monypenny, T. Murakami and Y. Fujii, H. O'Neill, E. Piwowarsky, A. M. Portevin, H. Redenz, M. Rudolph, L. R. Seidell and G. J. Horvitz, K. Taniguchi, and O. Smalley. W. H. Hatfield's results are indicated in Table LXIX. C. R. Austin measured the effect of annealing at different temp. with steels containing approximately 0·35 per cent. of carbon, and found Brinell's hardness to be:

Cr	. . .	1·95	4·02	6·18	8·08	10·39	12·08 per cent.
Temp.	805° . .	205	180	200	175	185	185
	850° . .	195	137	160	174	190	190
	960° . .	146	163	170	177	200	192
	Oil . .	645	512	286	255	248	270

where the samples in the last line were quenched in oil from 960°. Similarly, with samples of steel containing nearly 1·0 per cent. of carbon:

Cr	. . .	2·09	3·92	5·07	6·16	8·12	10·42 per cent.
Temp.	805° . .	207	255	210	223	223	153
	850° . .	202	225	202	210	207	143
	960° . .	269	321	228	202	196	140
	Oil . .	418	350	340	350	241	2455

where the last two samples in the last line were quenched in oil from 1200°–1300°, the others, from 960°. Steels with the martensitic structure are hard, the hardness is scarcely affected by tempering at 500°, and the martensitic structure persists, tempering at 500° to 600° softens the steel corresponding with the breaking up of the martensitic structure and the appearance of carbide. This is more pronounced by tempering at 700°–750° when the carbide granules are larger. Annealing at higher temp. results in an increase in the hardness corresponding with the re-solution of the carbides. C. A. Edwards and co-workers studied the relation between Brinell's hardness and the velocity of cooling from the initial temp. indicated in the diagram; and the hardness of the steels cooled from different initial temp. in air—*vide* Table LXIX for some data on the hardness of these steels.

F. Robin studied the acoustic properties of chromium steels; and D. S. Muzzey, the longitudinal vibrations of magnetized cylinders. The mechanical properties of chromium steels were measured by W. Aichholzer, J. H. Andrew, C. O. Burgess, A. L. Colby, J. H. Critchett, H. J. French, H. J. French and H. K. Herschmann, J. P. Gill, E. Greulich, L. Guillet and co-workers, R. A. Hadfield, R. Hall, G. A. Hankins and co-workers, E. L. Henderson, V. O. Homerberg and I. N. Zavarine, E. Houdremont and co-workers, A. Hultgren, J. A. Jones, E. Kothny, F. C. McGrail, P. G. McVetty and N. L. Mochel, A. McWilliam and E. J. Barnes, P. Marsich, N. N. Menshih, F. W. Meyer, K. H. Müller and E. Piwowarsky, I. Obinata, W. Oertel and K. Würth, C. W. Pfannenschmidt, F. Rapatz, H. Redenz, M. Schmidt and O. Jungwirth, B. Stoughton and W. E. Harvey, and E. C. Wright and P. F. Mumma. F. L. Coonan, and L. Guillet said that with pearlitic steels, the tensile strength and elastic limit are higher, the higher the proportion of chromium, without, however, differing greatly from those of ordinary steels with the same proportion of carbon. The brittleness is increased a little. The martensitic steels are said to have the same qualities as nickel and manganese steels, but have less brittleness. The mixed martensitic and carbide steels also resemble the manganese steels; while the double carbide steels have a somewhat low tensile strength and elastic limit, and they have high contractions and medium elongations. Z. Nishiyama's measurements of the elastic modulus are indicated above. The observations of C. R. Austin are summarized in Table LXIX. The tensile strength of steel with 1·96 per cent. of chromium, not tempered, was 44·0, and after tempering an hour at 610°, it was 74·4, and the elongation 11·0 per cent. The tensile strength of the 4·02 per cent. chromium steel, not tempered, was 78·0, and after tempering an hour at 610°, 56·3, and the elongation was 18·7 per cent. The tensile strengths and percentage elongations of the steel, tempered at 500° and 650°, with 6·18 per cent. of chromium, were respectively 60·4 and 17·2; with 8·08 per cent. Cr, 59·2 and 18·0; with 10·39 per cent. Cr, 56·4 and 17·2; and with 12·08 per cent. Cr, 60·1 and 18·7. Again, the tensile strength of the steel with 2·09 per cent. Cr, tempered at 500° and 650°, was 85·7; the tensile strength and elongation of the steel with 3·92 per cent. of chromium, tempered an hour at 500° and 650°, were respectively 81·0 and 11·0; and likewise for the steel with 5·07 per cent. of chromium, respectively 75·8 and 12·5. The tensile strength of the steel with 6·16 per cent. of chromium, tempered an hour at 500° and 650°, was 49·0, and when tempered an hour at 650°, 59·0. The test-pieces broke in the shoulder in the cases where the elongations are not stated. The mechanical properties were discussed by H. H. Abram, L. Aitchison, P. A. E. Armstrong, C. R. Austin, H. W. Baker and A. H. Gibson, P. Blum, C. B. Callomon, F. B. Coyle, H. C. Cross, H. A. Dickie, J. W. Donaldson, P. Eyermann, H. J. French, G. Gabriel, F. L. Garrison, N. J. Gebert, J. P. Gill, R. C. Good, W. Guertler, A. Hultgren, W. H. Hatfield, W. Haufe, J. E. Hurst, T. F. Jennings, J. A. Jones, W. Kahlbaum and co-workers, B. Kjerrman, J. H. Küster and C. Pfannenschmidt, C. B. Lord, T. D. Lynch and co-workers, R. S. MacPherran, P. G. McVetty and N. L. Mochel, Y. Matsunaga, T. Matushita, J. H. G. Monypenny, H. Moore, R. R. Moore, I. Musatti and G. Calbiani, J. B. Nealey, A. L. Norbury, O. K. Parmiter, A. R. Page and J. H. Partridge, A. Phillips and R. W. Baker, F. Rapatz and H. Pollack, W. Riede, A. Rys, K. Sasakawa, A. Schulze, F. W. Shipley, E. K. Smith and H. C. Aufderhaar, T. Swinden and P. H. Johnson, and W. Zieler. J. H. G. Monypenny obtained the results indicated in Table LXX for the effects of tempering and annealing on steel-1 with 0·07 per

TABLE LXIX.—THE MECHANICAL PROPERTIES OF CHROMIUM STEELS.

Percentage composition				Annealed 805°			Annealed 850°			Annealed 960°		
Cr	C	Si	Mn	Yield point (tons per sq. in.)	Tensile strength (tons per sq. in.)	Elongation (per cent.)	Yield point (tons per sq. in.)	Tensile strength (tons per sq. in.)	Elongation (per cent.)	Yield point (tons per sq. in.)	Tensile strength (tons per sq. in.)	Elongation (per cent.)
1·96	0·33	0·05	0·13	—	46·8	26·6	25	45·2	26·15	18	34·8	23·4
4·02	0·30	0·15	0·17	(26)	32·0	28·8	15	32·1	35·1	19	38·8	25·8
6·18	0·37	0·32	0·23	38	43·9	25·0	16	36·6	34·2	21	40·2	25·0
8·08	0·43	0·43	0·25	36	40·8	29·7	21	39·4	32·0	20	43·8	23·4
10·39	0·37	0·50	0·19	18	41·2	31·2	20	42·7	27·3	24	42·6	25·8
12·08	0·38	0·58	0·24	22	44·0	32·8	21	42·4	29·7	20	43·6	23·4
2·09	1·00	0·17	0·29	26	44·8	26·5	29	45·3	31·2	30	60·5	9·35
3·92	1·09	0·27	0·18	25	56·4	20·3	24	52·2	19·5	42	58·9	3·1
5·07	1·07	0·19	0·21	26	47·2	25·8	24	43·5	30·5	26	52·7	18·7
6·16	0·97	0·31	0·14	27	49·6	32·6	24	47·1	26·5	24	44·4	26·5
8·12	1·02	0·37	0·10	34	53·2	18·0	24	47·1	23·4	24	43·4	25·0
10·42	1·14	0·46	0·07	21	34·8	34·4	16	33·3	32·0	18	32·3	28·9

cent. C, 0·08 Si, 0·12 Mn, 0·57 Ni, and 11·7 Cr. The results correspond with the effects on the hardness indicated above.

TABLE LXX.—THE EFFECT OF ANNEALING TEMPERATURES ON THE MECHANICAL PROPERTIES OF CHROMIUM STEELS.

	Treatment	Yield-point (tons per sq. in.)	Maximum stress (tons per sq. in)	Elongation (per cent.)	Reduction area (per cent.)	Brinell's hardness	Izod impact (ft.-lbs.)
I	O.H. 930°	—	73·2	13·5	41·9	340	28
	W.H. 200°	—	73·0	12·0	38·0	340	34
	W.H. 300°	—	72·4	12·5	36·4	332	38
	W.H. 400°	-	72·3	15·5	51·0	332	38
	W.H. 500°	58·8	72·4	18·0	52·2	340	36
	W.H. 600°	38·0	49·1	22·0	62·4	241	65
	W.H. 700°	30·6	40·4	26·5	65·8	196	79
	W.H. 750°	27·9	36·4	31·0	68·8	179	87
	W.H. 800°	33·6	53·6	13·5	44·6	255	40
II	W.H. 650°	38·0	61·9	7·0	13·4	302	7
	W.H. 700°	40·8	59·7	10·0	18·3	385	8
	W.H. 750°	33·6	58·9	10·0	18·3	281	8
III	A.H. 950°; W.H. 700°	26·0	36·8	34·0	62·6	—	69
	A.H. 1000°; W.H. 700°	32·0	44·2	23·0	53·4	—	55
	O.H. 1000°; W.H. 700°	34·0	45·4	24·0	60·4	—	75

The symbols O.H. and W.H. refer respectively to oil- and water-hardening. The results show that up to 500°, the tensile strength is not affected by tempering, but the ductility (elongation and reduction in area) and toughness (impact test) are improved; between 500° and 600°, the tensile strength falls rapidly, while the ductility and toughness increase in value; at 600° to 750°, these results are more accentuated; between 750° and 800°, corresponding with the dissolution of the carbides, the steel shows evidence of hardening. By increasing the proportion of carbon, the tensile strength gradually rises, while the ductility and toughness become less; when the proportion rises to 0·3 per cent., the steel becomes hypereutectoidal, and gives high values for Brinell's hardness. These steels cannot be softened by tempering below a tensile strength of 50 to 55 tons per sq. in. With still higher proportions of carbon, the materials contain large proportions of free carbide. The series for steel-II refer to a high-carbon chromium steel: 1·42 C, 0·12 Si, 0·35 Mn, 0·44 Ni, and 13·1 Cr. The results for a high-chromium steel-III refer to a steel with 0·17 C, 0·26 Si, 0·18 Mn, and 15·9 Cr. As the proportion of chromium increases, a higher quenching temp. is needed to harden the steel, and eventually the possible increase in hardness obtainable by quenching from at least 1200° is very small. The tensile strength obtainable after hardening and tempering is rather lower than with lower-chromium steels, at the same time the ratio of yield-point to maximum stress is also lower.

J. H. G. Monypenny found the modulus of elasticity—*i.e.* Young's modulus—in tension, expressed in lbs. per sq. in., for a steel with 0·09 C, and 12·0 Cr, was $0{\cdot}0_4296$; and for a steel with C 0·23 and Cr 12·8, $0{\cdot}0_4306$. H. H. Abram obtained values ranging from $0{\cdot}0_4296$ to $0{\cdot}0_4323$ for a series of stainless steels with 0·10 to 0·43 C, and 12·37 to 14·7 Cr. The former also gave $0{\cdot}0_4125$ for the modulus of elasticity in shear for a steel with 0·25 C, and 12·5 Cr. C. L. Clark and A. E. White studied the effect of temp. on the tensile properties of chromium steel. For the effect of hydrogen, see that element.

The fatigue, that is, the failure of the steel under alternations of tension and compression over a long period of time, has been examined by F. H. Moore and J. B. Kommers, D. J. McAdam, H. J. Gough and co-workers, etc. The fatigue range for a chromium steel with a tensile strength of 43·5 tons per sq. in., was ±21 tons per sq. in. for a hundred million cycles of stress; and it behaves with respect to fatigue like other ferrous metals. D. J. McAdam made corrosion-fatigue and fatigue tests of stainless steel, as well as some static, mechanical tests. The endurance tests were made with cycles running 1450 revs. per min.—*vide* the corrosion of iron. The corrosion was effected by fresh carbonate water, and by salt-water, river-water with about one-third the saline contents of sea-water. The results were:

Chromium	11·54	12·20	13·35	15·09	per cent.
Nickel	0·08	0·18	0·08	0·15	,,
Silicon	0·09	0·23	0·22	0·10	,,
Carbon	0·33	0·08	0·13	0·09	,,
Copper.	0·84	0·13	0·45	0·01	,,
Tensile strength . . .	97,600	61,500	91,200	102,700	lbs. per sq. in.
Elongation	27·7	41·0	25·3	27·7	per cent. in 2 ins.
Reduction of area . . .	59·5	67·5	63·5	59·0	,,
Fatigue	52,000	39,000	59,000	—	lbs. per sq. in.
Corrosion-fatigue Fresh . .	35,000	30,000	40,000	33,000	,, ,,
Corrosion-fatigue Salt . .	—	—	13,000	—	,, ,,

J. H. S. Dickenson showed that at temp. exceeding 500°, ordinary steels and alloy steels of various types stretch by plastic flow, and finally break with much smaller loads than the values for the tensile strength obtained at the same temp. Hence, a steel with, say, a tensile strength of 20 tons per sq. in. at 650°, would stretch continuously and finally break at a far less load if given sufficient time. For a 0·30 per cent. carbon steel, and a 0·26 C, 14·68 Cr steel, he found that the maximum stress in tons per sq. in., and the percentage reduction of area, at different temp., are as follow:

		14°	100°	400°	500°	600°	700°	800°	1000°
Tenacity	0·3 C .	43·2	40·4	40·8	27·6	20·8	12·6	7·2	4·0
	14·68 Cr .	54·0	49·9	44·4	38·0	27·6	17·4	8·8	6·1
Reduction	0·3 C .	64·8	59·2	67·8	79·4	86·1	92·8	99·0	99·8
	14·68 Cr .	57·0	54·6	52·2	64·4	70·7	84·1	91·4	91·4

The periods required for the same materials to break down at different temp. while under a load of 8·5 tons per sq. in:, were:

	500°–550°	550°–600°	600°–650°	700°	775°
0·3 C . . .	3400 hrs.	956 hrs.	28 hrs.	3 mins.	6 secs.
14·68 Cr . . .	10,000 hrs.	1728 hrs.	79 hrs.	3 mins.	6 secs.

W. H. Hatfield also made some observations on this subject. With ordinary carbon steels, there is a range of brittleness, called *blue brittleness*—*vide supra*, tensile strength—roughly between 300° and 500°. It is indicated by means of the notched-bar impact test. F. Robin observed that variations in the resistance of pearlitic chromium steels to crushing are similar to those of martensitic steels generally (*q.v.*). The resistance increases rapidly in liquid air, and it diminishes thereafter at rising temp., but not uniformly. Above 500°, the resistance diminishes more rapidly, and attains a high value at 1100°. The high-speed tool steels—*vide infra*—are the only steels at these temp. which show an even higher resistance. According to J. H. G. Monypenny, various nickel alloy steels show a maximum brittleness about 600°, and a minimum about 700°; beyond that temp., the bars bend but do not break. The chromium steels have fairly uniform impact values with rise of temp., and show no range of blue brittleness. The effect of the initial temp. on the physical properties of the alloy was discussed by J. H. Andrew and co-workers, and C. L. Clark and A. E. White; and the effect of annealing, by C. B. Callomon—*vide* the physical properties of iron.

According to J. H. G. Monypenny, stainless steel is rather more difficult to cold-work than is the case with ordinary steel; but it can be drawn into wire, rolled into sheets or strips, made into weldless drawn tubes, and pressed or stamped into various shapes. All this, however, provided the steel be more frequently softened between the successive stages of the mechanical working. Thus, the maximum stress in tons per sq. in., M.S.; and the reverse binding test, R.B., were found, for the hard-drawing of steel with 0·07 C, and 11·7 Cr, to be:

Diameter.		0·111	0·0804	0·0706	0·0568	0·0465
As drawn	M.S.	68	78	89	114	103
	R.B.	5	5	5	4	13
Tempered 500°	M.S.	59·5	64·5	61	67	61
	R.B.	6	7·5	9	11·5	22
Tempered 600°	M.S.	46	50	49	50·5	46
	R.B.	8	16·5	18	20	30
Tempered 700°	M.S.	36	39·5	38	40·5	39
	R.B.	9	15	18	27	11

S. H. Rees obtained the results given in Table LXXI, with stainless iron with 0·12 C and 12·0 Cr, and stainless steel with 0·40 C and 13·0 Cr. The indicated temp. refer to the temp. of annealing for one hour. The annealing of the iron at 300°–375°, and of the steel at 375°–450°, results in a marked improvement in the elastic properties of the cold-drawn rods. R. A. Hadfield observed that at −182°, the results are normal.

TABLE LXXI.—EFFECT OF ANNEALING ON THE PROPERTIES OF COLD-DRAWN RODS OF CHROMIUM IRON, AND CHROMIUM STEEL.

Treatment		Tensile				Compression		
		Elastic limit (tons per sq. in.)	Yield-point (tons per sq. in.)	Max. load (tons per sq. in.)	Elongation (per cent.)	Reduction of area (per cent.)	Elastic limit (tons per sq. in.)	Yield-point (tons per sq. in.)
Iron	Cold-drawn	7	32·0	37·2	28·5	70	9	28·0
	100°	8	32·0	37·2	28·0	70	9	28·0
	200°	14	32·5	37·6	27·0	70	12	27·0
	300°	22	33·0	38·0	24·0	69	18	30·0
	375°	22	26·0	34·0	32·0	73	20	26·0
	450°	19	26·0	34·0	32·0	72	19	26·0
	650°	18	20·0	32·8	37·0	74	16	21·0
Steel	Cold-drawn	9	39·0	50·8	21·0	50	7	35·0
	100°	10	39·0	50·8	21·0	52	10	34·0
	200°	17	40·0	51·2	19·0	50	17	36·0
	300°	24	43·0	50·8	20·0	52	22	37·0
	375°	29	40·0	50·4	21·0	52	26	35·5
	450°	28	39·0	50·4	22·0	53	25	35·0
	550°	26	35·0	49·2	22·0	55	26	33·5
	650°	24	32·0	38·4	25·0	57	23	32·5
	780°	24	31·0	47·6	26·0	57	25	31·5

The mechanical properties of stainless steel were discussed by E. Piwowarsky, P. Oberhoffer and E. Piwowarsky, R. S. Poister, T. L. Robinson, T. Matushita, J. Galibourg, A. Abraham, C. E. MacQuigg, and H. J. French; the effect of silicon on the mechanical properties of stainless steel were discussed by E. Kothny, H. H. Abram, and J. H. G. Monypenny; of nickel, by J. H. G. Monypenny, and B. Strauss and E. Maurer; of manganese, by L. Guillet, and J. H. G. Monypenny; of copper, by J. H. G. Monypenny, and L. Grenet; and of vanadium, by F. Rogers.

K. Ruf measured the thermal expansion of iron-chromium alloys between 0° and 250°. An anomalous expansion with iron occurs between 950° and 870°; with a 6 per cent. chromium alloy, between 830° and 770°; and with a 12 per cent. chromium alloy, between 845° and 810°; whilst no anomaly occurs with alloys having over 13 per cent. chromium. F. Stäblein found that the mean coeff. of thermal expansion decreases with an increase of chromium. J. A. N. Friend and R. H. Vallance found three samples of stainless steel had coeff. of thermal expansion between $0{\cdot}0_4110$ and $0{\cdot}0_4117$ at temp. between 10° and 100°. Observations were made by A. M. Portevin and P. Chévenard, H. Jüngbluth, P. Hidnert, P. Hidnert and W. T. Sweeney, J. B. Austin and R. H. H. Pierce, and H. J. French. W. H. Souder and P. Hidnert found the coeff. of thermal expansion of chromium steel—with C, 0·30 per cent.; Si, 0·11; Mn, 0·18; and Cr, 13·1—on hardened samples, and samples tempered at 760°. The average values respectively for hardened and tempered steels are $0{\cdot}0_599$ and $0{\cdot}0_4103$ between 20° and 100°; $0{\cdot}0_598$ and $0{\cdot}0_4107$ between 20° and 200°; $0{\cdot}0_599$ and $0{\cdot}0_4122$ between 200° and 400°; $0{\cdot}0_4138$ and $0{\cdot}0_4133$ between 400° and 600°; $0{\cdot}0_4134$ and $0{\cdot}0_4136$ between 600° and 800°; and $0{\cdot}0_4122$ and $0{\cdot}0_4121$ between 20° and 600°. B. Kjerrman, T. Matushita, and P. G. McVetty and N. L. Mochel made some observations on this subject. F. Stäblein found that the presence of chromium rapidly reduces the heat conductivity of iron, and alloys with 5 to 13 per cent. of chromium have only half the heat conductivity of iron. T. Matushita found the heat conductivity, k_1, of samples slowly cooled from 900°, and, k_2, of samples rapidly cooled from 1100°, to be:

Cr	0	0·5	2·0	5·0	10·0	13	20 per cent.
k_1	0·100	0·099	0·095	0·073	0·052	—	0·043
k_2	0·098	0·089	0·087	0·044	—	0·033	0·043

W. H. Hatfield found the thermal conductivity of stainless steel to be less than that of ordinary mild steel; the value for stainless or chromium steel is k=0·0363 to 0·0466 cal. per cm. per sec. per degree, when the value for iron is 0·1450, and for mild steel 0·1436 at 18°, and 0·1420 at 100°. The rate of heating of chromium or stainless steel is nearly the same as that of ordinary steel, so that if the rate of heating depends on the diffusivity, where the diffusivity=k/sD where s denotes the sp. ht., and D the sp. gr.—the conductivity k must increase with temp., or the product sD must decrease with temp. sufficient to satisfy observations. W. Brown found that the presence of chromium has little influence on the sp. ht., for with the percentage proportions of C and Cr—0·90 : 2·00, the sp. ht. was 0·1202; with 0·43 : 3·25, 0·1169; and with 1·09 : 9·50, 0·1206. F. Wüst and co-workers represented the mean sp. ht. by 0·10233+0·00003347θ, and the true sp. ht. at θ° by 0·10233 +0·00006694θ for temp. between 0° and 1500°. W. H. Hatfield gave 0·115 to 0·121 for the sp. ht. of chromium or stainless steel at ordinary temp. F. Osmond found that 44 per cent. ferrochromium ran a little at the point of contact with an iron area at 1355°, but the fusion was quite local, the sample melted at about 1430°; 66 per cent. ferrochromium liquated at 1440° into a fusible and a refractory part which did not melt at 1475°; while 90 per cent. ferrochromium did not melt at 1485°. The f.p. curve is indicated in Figs. 445 and 446. A. Ludgren noticed that there is a particularly strong evolution of heat during the annealing of hardened chromium steel, when the steel had previously been converted into austenite by quenching from a high temp.; if the structure is martensitic, no development of heat is perceptible because the breaking up of the martensitic structure proceeds so slowly. W. W. Coblentz and R. Stair measured the reflecting power of stainless steel; and H. Pincass, the spectrum of the Fe-Cr catalyst.

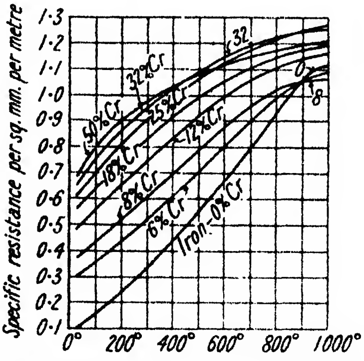


FIG. 448.—The Specific Resistance of Fe-Cr Alloys.

K. Ruf's values for the sp. resistance in ohms per sq. mm. per metre are shown in Fig. 448. J. Hopkinson found that the electrical resistance is lowered by annealing. The following values were obtained for the sp. resistance:

C	Cr	Hard-drawn	Annealed	Hardened in water
0·16 per cent.	0·29 per cent.	$0{\cdot}0_4 2234$	$0{\cdot}0_4 1917$	$0{\cdot}0_4 1903$
0·27 ,,	1·18 ,,	$0{\cdot}0_4 3351$	$0{\cdot}0_4 3305$	$0{\cdot}0_4 5706$
0·77 ,,	5·19 ,,	$0{\cdot}0_4 2012$	$0{\cdot}0_4 2234$	$0{\cdot}0_4 4062$
0·71 ,,	9·18 ,,	$0{\cdot}0_4 2315$	$0{\cdot}0_4 2401$	$0{\cdot}0_4 2843$

F. Stäblein found the sp. resistance of the iron-chromium alloys increases linearly up to 2 per cent. chromium, and then increases less rapidly. A. M. Portevin gave 5·4 microhms per cm. cube for the increase in the resistance of iron produced by 1 per cent. of chromium ; and he found that, at 15° to 20°, for samples with about 0·2 per cent. of carbon, the electrical resistance *R* microhms per cm. cube for chromium steel before and after hardening by quenching from 980° in water :

Cr . .	1·20	4·50	10·14	14·52	22·06	31·75
R Before .	16·3	33·2	49·7	62·9	56·0	63·7
R After .	18·0	35·0	50·8	69·7	57·7	66·3

Similarly with steels containing about 0·8 per cent. of carbon :

Cr . .	0·62	2·14	7·28	13·94	26·54	40·03
R Before .	23·1	27·8	39·6	65·4	67·1	71·5
R After .	43·5	54·0	62·2	72·5	68·4	73·5

C. Benedicks' formula was found to be applicable for steels with up to 2·67 per cent. of chromium. T. Spooner, F. K. Fischer, O. Boudouard, M. A. Hunter and A. Jones, T. Murakami, H. A. Dickie, W. F. Barrett and co-workers, and T. F. Russell made observations on this subject. C. A. Edwards and A. L. Norbury observed that there is a gradual increase in resistance by quenching from gradually increasing temp. above the Ac_1-point, and this increase takes place in the range over which the carbide of the pearlite gradually dissolves. The fully tempered stainless steel has a resistance of about 0·000050 to 0·000055 ohm per cm. cube, and this increases to about 0·00007 ohm when the steel is quenched from temp. high enough to dissolve all the carbide. C. Benedicks and R. Sundberg found unquenched specimens of stainless steel having practically the same resistance as hardened specimens when the carbon is low, this is taken to show that the chromium is in solid soln. ; on raising the proportion of carbon, the resistance is much lowered. If δR, microhms per cm. cube, denotes the differences observed between the quenched and unquenched samples, and $\delta R'$ the increase which would occur with the carbon going into soln., the higher values for δR indicate that much of the chromium is precipitated with the carbon in the slowly cooled samples :

Carbon . . .	0·07	0·20	0·28	0·34	0·45	0·47 per cent.
δR	3·0	11·8	16·0	12·6	17·4	16·2
$\delta R'$	1·9	5·4	7·5	9·1	12·1	12·6

F. K. Fischer found that the electrical resistance ranges from 43 to 53 microhms per cm. cube, and the value varies at the rate of 0·60 microhm for each per cent. of chromium added. G. Tammann and V. Caglioti discussed the recovery of the resistance after cold-work. A. Kussmann and B. Scharnoff observed no relation between coercive force and hardness.

G. Tammann said that assuming a chromium atom on the surface can render an adjacent iron atom passive to dil. acids, the (101)-face should become passive with 0·25th of a mol. of chromium, and the (100)- and (111)-faces, passive with ⅜th mol. Actually passivation occurs with 0·16 to 0·28 mol. of chromium : this is less than the predicted amount. Hence, other factors— *e.g.* the nature of the solvent— are involved. C. Benedicks and R. Sundberg found that the electrode potential, *E*, of unquenched steel—with 0·04 to 0·08 per cent. of carbon— in neutral $0{\cdot}82N\text{-}FeSO_4$, free from oxygen, rises from $E=-0{\cdot}711$ to $-0{\cdot}744$ volt when 8 per cent. of chromium is added, and the potential is sensibly baser than that of iron or carbon steel ; the addition of more chromium lowers the value of *E*, to a minimum with 13 to 14 per cent. of chromium, and with more chromium, *E* rises again. With chromium constant at 13 per cent., E is much lowered when the proportion of carbon is raised. With quenched specimens, E rises with increasing chromium, but with chromium constant at 13 per cent., E is reduced to $-0{\cdot}55$ volt on increasing the proportion of carbon. If the neutral soln. of $0{\cdot}82N$-$FeSO_4$ be partially oxidized by the addition of hydrogen dioxide, the electrode potential, E, is remarkably constant at 0·31 volt, and this is not affected by carbon or chromium over 8 per cent.; in quenched specimens with 0·04 to 0·08 per cent. of carbon, E' is reduced to $-0{\cdot}64$ volt with 8·05 per cent. of chromium, and to 0·31 for higher proportions of chromium. Quenched specimens with 13 per cent. of chromium have E' between 0·275 and 0·308 volt. The electrical resistance, sp. vol., and the electrode potentials, all indicate an abrupt change near 13 per cent. of chromium. This is thought to be due to the gradual fading out of the γ-region with the higher proportions of chromium, as indicated by E. C. Bain. According to C. Benedicks and R. Sundberg, a stainless steel with 0·10 per cent. of carbon and 13 per cent. of chromium, when immersed in N-KCl, assumes temporarily a higher or active potential, and a visible rusting occurs. A photoelectric cell was constructed by using two strips of stainless steel immersed in a soln. of ferrous sulphate. This cell is sensitive to light. The light causes an increase in the electrode potential rendering the steel slightly baser. G. Tammann and E. Sotter found that the electrode potential of iron-chromium alloys in $0{\cdot}1N$-H_2SO_4 is strongly positive to chromium with cathodic polarization, and only slightly so with anodic polarization. The end anodic potential is attained in accord with the exponential law, but with cathodic polarization the case is more complex, there being apparently three distinct periods. Polishing with emery, and heating at 400° decrease the electropositiveness of the alloys. The presence or absence of air bubbling through the soln. affects the potential but little, but the presence of a reducing agent, such as pyrogallol, phosphorus, or quinol, reduces the electropositiveness of cathodically polarized iron-chromium alloys to a remarkable extent. E. Newbery, and O. Meyer and K. Roesch also studied the potential of chromium steels, and their tendency to rust. According to B. Strauss, the potential of iron-chromium alloys in N-$FeSO_4$ soln. against a $0{\cdot}1N$-calomel electrode, ranges from $-0{\cdot}6$ volt to $+0{\cdot}2$ volt. The former value is the same as that of mild steel, and with low-carbon steels, the negative potential was found with less than 12 per cent. of chromium; both values with between 13 and 15 per cent. of chromium; and the positive potential with over 16 per cent. of chromium. With 0·8 per cent. of carbon, both values were given with steels having 13 to 15 per cent. of chromium, and a negative potential when more carbon was present. Steels with 20 per cent. of chromium gave a positive potential with up to 2 per cent. of carbon, and a negative potential with more carbon. E. Newbery, H. Stäger and H. Zschokke, R. Borchers, M. de K. Thompson and R. B. Morrissey, T. P. Hoar and U. R. Evans, and L. C. Bannister and U. R. Evans studied the electrode potentials of these alloys.

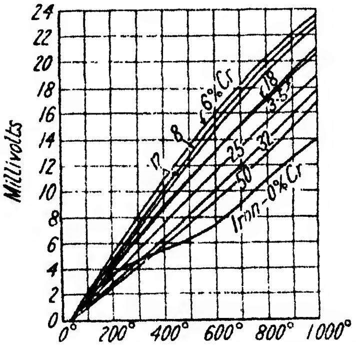


FIG. 449.—The Thermoelectric Force of Fe-Cr Alloys.

K. Ruf's values for the thermoelectric force of the alloys against platinum are indicated in Fig. 449. Observations were also made by M. A. Hunter and A. Jones, and P. Nicolau. T. S. Fuller found the thermoelectric force, E millivolts, against copper between 0° and 100° for alloys of iron and

Chromium .	10	18	20	23·5	29·5 per cent.
E . . .	1·20	1·04	0·43	8·32	0·31

E. L. Dupuy and A. M. Portevin measured the thermoelectric force of chromium steels against copper over a range of temp. from −80° to 100°. The results, expressed in millivolts, are indicated in Table LXXII. The blanks mean that the samples cracked.

TABLE LXXII.—THERMOELECTRIC FORCE OF CHROMIUM STEEL AGAINST COPPER.

Per cent.		Untreated		Annealed at 100°		Hardened by quenching from 1000°	
C	Cr	−80°	100°	−80°	100	−80°	100°
0·06	1·20	17·1	16·6	17·53	16·93	6·70	16·4
0·08	1·89	15·2	16·6	15·43	16·65	14·50	15·20
0·28	2·66	14·70	17·10	16·94	18·11	14·60	21·50
0·07	7·84	8·50	12·70	9·75	14·92	9·80	13·50
0·42	9·80	6·84	5·82	12·18	14·74	—	—
0·14	13·60	6·15	8·73	6·50	10·56	5·10	7·65
0·24	25·31	4·17	6·28	6·26	9·01	6·23	5·09
0·46	31·75	5·92	9·55	4·29	6·55	4·99	7·86
0·97	0·92	9·51	8·83	9·74	8·92	3·90	3·64
0·89	2·14	9·51	9·00	10·21	9·64	3·52	4·20
0·79	4·57	12·30	12·90	12·18	12·56	7·10	5·91
0·84	7·27	10·20	11·90	11·60	13·45	—	—
0·52	9·85	2·78	3·63	11·48	14·48	4·98	3·58
0·96	11·52	9·41	11·90	10·40	13·60	6·90	9·70
0·90	18·65	0·81	1·55	4·99	7·95	3·25	4·64
0·82	26·54	2·90	5·37	3·30	5·91	2·00	4·64
0·92	32·46	4·87	6·28	6·84	6·30	4·32	5·55

W. Treitschke and G. Tammann observed that all the iron alloys with up to 80 per cent. chromium are magnetic. J. Hopkinson found that ferrochromium with 8 to 28 per cent. chromium is strongly magnetic; with 44 per cent. chromium, it is feebly magnetic but is strongly magnetic when in the form of powder; and 66 per cent. ferrochromium is feebly magnetic. In general, the magnetism of ferrochromium alloys decreases with increasing chromium and carbon. J. Hopkinson obtained the results for the magnetic induction, *B*, per sq. cm., with different values for the magnetizing force, *H*, from which the following is a selection, for steel with 0·71 per cent. of carbon and 9·18 per cent. chromium:

Before heating	*H*	0·018	0·075	0·30	1·02	4·04	11·86	22·78	33·24
	B	0·75	1·53	6·2	23·4	93·1	286	603	978
After heating to 850°	*H*	0·17	0·07	0·38	1·16	4·05	11·72	22·7	31·67
	B	1·5	5·0	20·2	86·0	323	1070	7580	11,553

The induction, *B*, per sq. cm., for the same steel after heating to the temp. indicated:

H, 1·02		395°	558°	640°	701°	773°	839°	860°
	B	31	41	98	161	201	331	0
H, 4·04		416°	645°	717°	789°	823°	841°	860°
	B	113	416	603	1022	1462	1863	0
H, 11·9		438°	584°	661°	735°	807°	829°	860°
	B	340	661	2226	5489	6424	4943	0
H, 27·06		456°	616°	677°	746°	813°	834°	860°
	B	832	2891	7796	8728	7112	5375	0

R. Abt, H. A. Dickie, R. L. Dowdell, F. K. Fischer, E. Gumlich, W. S. Messkin and E. S. Tovpenjez, P. Oberhoffer and O. Emicke, J. H. Partridge, J. Safranek, S. Saito, E. H. Schulz and W. Jenge, H. Scott, T. Spooner, J. Würschmidt, E. A. Watson, C. E. Webb, and L. W. Wild measured the magnetic properties; and A. Kussmann and B. Scharnoff, E. Gerold, H. Scott, and S. Curie measured the coercive force, magnetic moments, and remanence of chromium steels. F. Stäblein found the coercive force of chromium-iron alloys rises to an ill-defined maximum with 10 per cent. of chromium, and then falls to a minimum with 17 per cent. of chromium. W. Brown found for the magnetic moment M per gram, and the percentage loss by percussion :

Cr . .	1·75	1·96	2·11	3·50	5·79	9·22 per cent.
M . .	38·2	50·4	52·5	41·7	38·7	42·2
Loss . .	1·9	0·5	2·2	7·9	7·0	1·3 per cent.

F. K. Fischer found that the magnetic properties of the alloys with 10 to 20 per cent. of chromium vary with the proportion of chromium and with the heat-treatment. Annealing produces the best magnetic results. The best magnetic results were obtained with alloys ranging from 17·5 to 18·7 per cent. of chromium—in the region of zero magnetostriction. The effect of quenching on the magnetic properties is to reduce the flux density by a large amount and to make practically permanent magnetic material out of the ring samples except those in the neighbourhood of zero magnetostriction. Baking the alloys at 500° after annealing was harmful to the properties as it reduced the permeability. The magnetic critical point varies from about 675° to 750°, the average being about 700°. The best alloy obtained was one of 18·7 per cent. chromium. When annealed, this alloy has a maximum permeability of about 2000 at approximately 6000 gausses. Its hysteresis loss for B_m=5000 is 1770 ergs per c.c. per cycle, or it has about the permeability and 4 times the hysteresis loss of Armco iron.

A. W. Smith and co-workers found the minimum reluctance—*i.e.* the reciprocal of the maximum permeability—occurs when the proportion of carbon approaches 0·8 per cent., and a maximum with about 0·5 per cent. R. L. Sanford and W. L. Cheney found that the maximum induction of oil-quenched chromium steel is 11,200, and the coercive force 53·5. G. Mars investigated the use of chromium steel in permanent magnets. His results are indicated in Table LXXIV.

TABLE LXXIII.—THE HARDNESS AND MAGNETIZATION OF CHROMIUM STEELS.

Composition				Hardening temp.	Brinell's hardness	Magnetization		
C	Si	Mn	Cr			Just after magnetization	After 8 days	Percentage loss
1·01	0·20	0·25	1·21	720	713	86	83·5	2·9
0·82	0·19	0·18	1·40	750	652	94	90	4·3
1·05	0·15	0·24	1·62	750	652	95	94	1·1
0·78	0·19	0·20	1·30	750	782	93·5	92·5	1·0
1·02	0·21	0·23	2·14	750	600	93	90	3·2
0·54	0·18	0·26	4·25	750	514	84·5	82	3·0
1·20	0·22	0·25	4·05	730	655	86	83·5	2·9
1·80	0·21	0·24	12·45	760	640	55	53·5	2·7
2·60	0·27	0·26	2·46	750	713	50·5	48·5	4·0

TABLE LXXIV.—MAGNETIC PROPERTIES OF CHROMIUM STEELS.

Cr (per cent.)	Residual magnetism	Intrinsic residual magnetism	Coercive force	Residual magnetism after percussion	Residual magnetism after heating and cooling	Percentage loss magnetism by percussion	Percentage loss magnetism by heating and cooling
1·0	660	295	28	275	245	6·8	9·5
4·05	600	374	39	354	334	5·3	5·3
8·0	580	385	46	371	364	3·6	1·9
12·0	435	332	54	328	322	1·2	1·8
16·0	340	286	56	284	278	0·7	2·1
20·0	320	252	44	239	235	5·2	1·5

The magnetic properties resemble those of high-carbon steels, and stainless steel when suitably hardened makes a good permanent magnet, which is not so good as the 6 per cent. tungsten steel commonly employed. M. B. Moir obtained hysteresis curves of annealed and quenched chromium steels, at 15° and at —190°, and found the value with the annealed alloy to be too small to be worth investigating for permanent magnetism, but the quenched specimens, while not ideal, make useful magnets, with the properties indicated in Table LXXIII.

L. Jordan and F. E. Swindells discussed the decarburization of ferrochromium by heating it in **hydrogen**; and E. Martin, the absorption of hydrogen and nitrogen by chromium steels. The commercial importance of the chromium steels as *rustless steels*, *non-corrosive steels*, or *stainless steels* was developed by H. Brearley, although the resistance of these steels to corrosion had been previously noted by B. Strauss and E. Maurer, and E. Haynes, and a mixture for a resistant chromium steel patented by the Firma Krupp for use as cutlery, propeller blades, etc. Indeed, over a century ago P. Berthier drew attention to the fact that chromium-iron alloys are less corrodible than iron itself, and analogous observations have been made by M. Faraday and J. Stodart. The subject was discussed by P. R. Kuehnrich. E. A. and L. T. Richardson also noted that chromium enhances the effect of copper in resisting corrosive influences.

The corrosion-resisting alloys were discussed by H. H. Abram, W. Ackermann, L. Aitchison, R. J. Anderson and G. M. Enos, P. A. E. Armstrong, J. A. Aupperle, E. C. Bain, M. Ballay, C. B. Bellis, C. Benedicks and R. Sundberg, J. S. de Benneville, H. N. Booker, P. Bres, A. Brunner, W. S. Calcott, C. W. Carnell, H. C. H. Carpenter, F. F. Chapman, P. Chevenard, T. H. Chilton and W. R. Huey, D. G. Clark, A. Christiansen, J. Clavier, J. Cournot, J. L. Cox, W. H. Creutzfeldt, K. Daeves, G. Dillner, T. W. Downes, G. A. Drysdale, R. L. Duff, V. Duffek, C. Duisberg, T. G. Elliot and co-workers, G. M. Enos, H. Esselbach, H. O. Forrest and co-workers, H. J. French, H. A. de Fries, J. Fritz and F. Bornefeld, T. S. Fuller, C. Griff, M. A. Grossmann, L. E. Gruner, W. Guertler, W. Guertler and W. Ackermann, W. Guertler and T. Liepus, L. Guillet, R. A. Hadfield and co-workers, J. F. Hardecker, W. H. Hatfield, W. H. Hatfield and H. Green, E. Haynes, J. G. Hopcraft, E. Houdremont, F. Hütte, A. C. Iebens, R. Irmann, K. K. Järvinen, C. M. Johnson, W. E. Jominy and R. S. Archer, B. Kalling, J. F. Kayser, B. Kjerman, P. Koetzschke, A. Krüger, P. R. Kuehnrich, C. Küttner, L. Losana and G. Reggiani, D. J. McAdam, J. W. McMyn and V. Edge, C. E. MacQuigg, P. G. McVetty and N. L. Mochel, A. Mangin, W. H. Marble, J. A. Mathews, C. Matignon, W. H. Melaney, P. S. Menough, C. G. Merritt, O. Meyer and K. Roesch, J. L. Miller, W. M. Mitchell, P. Monnartz, J. H. G. Monypenny, T. H. Nelson, F. Ormo, A. R. Page and J. H. Partridge, A. E. Perkins, A. Phillips and R. W. Baker, H. D. Phillips, J. Pomey and P. Voulet, V. and G. Prever, W. J. Priestley, H. S. Primrose, M. J. Prucha, H. S. Rawdon and A. I. Krynitsky, E. A. and L. T. Richardson, W. D. Richardson, H. Rieger, F. Rittershausen, K. Roesch and A. Clauberg, W. Rohn, A. Rys, B. D. Saklatwalla, M. Sauvageot and L. Lauprète, R. Schäfer, C. A. Scharschu, F. Schmitz, E. H. Schulz and W. Jengo, H. Stäger and H. Zschokke, B. Strauss, J. Strauss and J. W. Talley, R. Stumper, G. Tammann and co-workers, J. G. Thompson, N. S. Torsueff, S. Tungay, T. H. Turner, E. Valenta, J. S. Vanick and F. L. la Que, R. Waddell, B. Waeser, E. Wellman, H. Whitaker, H. Williams, T. R. Wilton, J. K. Wood, C. F. Würth, A. C. Yorke, and V. Zsak. E. C. Rollason discussed the intergranular corrosion of stainless steels.

J. F. Kayser said that most of the useful heat- and acid-resisting alloys of nickel, chromium, and iron fall within the area *abc*, Fig. 450, and the best of these within the shaded zone *def*. Alloys in the dotted region to the left are brittle; those to the right are difficult to work in the foundry, and when cast are unmachinable. The stainless irons fall in the region *gh*, and alloys falling in the region about *k* have been exploited. P. A. E. Armstrong found that the Cr-Fe-C alloys with a composition within the shaded area, Fig. 451, can be rendered immune to food acids by heating them about 300° above their upper transformation point, and cooling them rapidly. V. Duffek found the rate of corrosion to be faster, the higher the proportion of contained carbon. E. C. Bain and co-workers studied the intergranular corrosion of austenitic stainless steels; and J. Cournot and L. Halm, the effect of polish.

According to J. K. Wood, when chromium is added to steel, it forms a solid soln. with the iron, so lessening the tendency of the iron to go into soln. Sufficient chromium in an iron alloy will reduce its corrodibility to zero. All the chromium added does not, however, go to the making of the iron-chromium solid soln., but some is locked up in any carbides present, so that the higher the carbide-content the greater the amount of chromium necessary to confer immunity from corrosion. On the other hand, suitable heat-treatment will reduce the carbide-content by inducing a fine martensitic structure, and that will leave more chromium available to protect the iron. The action of chromium is to cause the eutectoid point to occur at a lower percentage of carbon; thus, with no chromium, the eutectoid carries 0·85 per cent. carbon; but with 4 per cent. chromium, the eutectoid carries only 0·56 per cent. carbon; and with 12 per cent. chromium, it carries only 0·31 per cent. carbon. Consequently, much less carbon is needed to produce the various structural changes in steel when chromium is present.

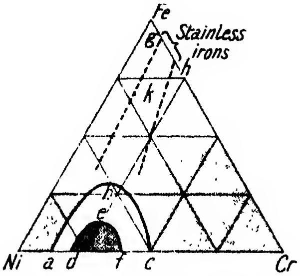


FIG. 450.—The Acid and Heat Resistance of the Ternary Alloys: Fe-Cr-Ni.

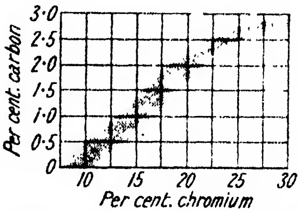


FIG. 451.—The Acid Resistance of the Fe-Cr-C Alloys.

The passivity of the iron-chromium alloys was studied by L. C. Bannister and U. R. Evans, C. Benedicks and R. Sundberg, R. Borchers, W. Guertler, J. Heibling, J. Hinnüber, E. Liebreich, E. Liebreich and W. Wiederholt, O. Meyer and K. Roesch, P. Monnartz, J. H. G. Monypenny, W. J. Müller, W. J. Müller and E. Noack, W. Oertel, H. Stäger and H. Zschokke, B. Strauss, B. Strauss and J. Hinnüber, B. Strauss and E. Maurer, J. Strauss, G. Tammann, and G. Tammann and E. Sotter.

According to J. H. G. Monypenny, a polished sample of stainless or about 12 per cent. chromium steel, when heated in **air**, assumes a series of temper colours similar to those of ordinary steel, but at a considerably higher temp.; a grey film appears on a polished surface at 750°–825°, but this interferes very little with the polish; above 825°, the steel begins to scale appreciably, but it is more resistant than nickel or vanadium steel. Increasing the chromium to 20 per cent. makes the alloy still more resistant to surface oxidation at high temp., and this is still more the case with 30 per cent. chromium. L. B. Pfeil observed that a three-layer scale—*vide supra*—is formed on stainless steel when it is heated for some hours in air; and that the inner layer contains 3·5 times as much chromium, as oxide, as the original steel, whilst the two outer layers contain only a fraction of that amount of chromium. P. Oberhoffer and K. Daeves observed that polished surfaces of steels with 0·3 to 0·5 per cent. carbon, and 15 to 20 per cent. chromium, preserved their polish when kept 18 hrs. at 800° in an oxidizing atmosphere. B. Strauss and E. Maurer also made observations on the resistance of high chromium steels to rusting. For the observations of H. O. Forrest and co-workers, *vide* corrosion. Y. Utida and M. Saito found that the gain in weight in grams per sq. cm. when samples are heated for an hour at 1100°; and the loss in weight in grams per sq. cm. when samples are immersed in 10 per cent. soln. of the acids for 24 hrs., were, for steels with 0·06 to 0·11 per cent. carbon, and

Chromium .	0	0·97	4·86	8·33	13·55	27·85	35·88 per cent.
At 1100° .	0·0212	0·0455	0·0510	0·0498	0·0407	0·0017	0·0004
HNO_3 .	0·9380	0·6240	0·5400	0·0181	0·0002	0·0000	0·0000
HCl . .	0·0712	0·2465	—	0·2801	0·3055	0·6158	0·7160
H_2SO_4 .	0·0990	0·1002	0·1110	0·2166	0·1248	0·0710	0·0132

H. Endo's results for 5 hrs.' action at ordinary temp. on steels with 0·28 to 0·35 per cent. of carbon, and the indicated proportions of chromium, are summarized in Fig. 452. J. A. N. Friend and co-workers noted that the resistance of chromium steels to corrosion by **sea-water** is better the higher the proportion of chromium—up to 5·3 per cent. Cr. The subject was discussed by J. Strauss and J. W. Talley, D. J. McAdam, H. H. Abram, W. Guertler and T. Liepus, P. S. Menough, L. Aitchison, W. Rohn, T. McKnight, W. B. Arness and J. N. Ostrofsky, and W. M. Mitchell. T. S. Fuller studied the action of steam on the endurance tests. F. M. Becket patented the use of high chromium alloys for resisting high temp., and the subject was discussed by C. E. MacQuigg. J. H. G. Monypenny found that the 12–13 per cent. chromium steel is corroded in towns, and particularly in the neighbourhood of factories, where the air contains distinct amounts of acid, and large amounts of dust, so that the metal becomes coated with dust which may adhere tenaciously. When the dust is removed, the polished surface may be marred by minute pitting, though the actual corrosion is exceedingly small, and out of all proportion with the rusting of ordinary steel. In the cleaner atm. of the country, or indoors, the metal retains its polish for long periods. W. G. Whitman and R. P. Russell studied the effect of oxygen dissolved in water on chromium steel. L. Gruner stated that the presence of chromium favours the corrosion of iron by humid air, sea-water, and acidulated water; but there is something amiss with this observation. P. Monnartz observed that steels with a high proportion of chromium—say, over 40 per cent.—resisted two years' exposure to a laboratory atmosphere without losing their bright lustre; and they also resisted **river-water** and sea-water—but alloys with less chromium are not so resistant. J. A. N. Friend and co-workers observed that if the corrosion factor for steel with 0·29 per cent. carbon and 0·39 per cent. manganese is 100, the values for alloys with 1·12, 3·58, and 5·30 per cent. of chromium are respectively 85, 58, and 43 for tap-water; 60, 26, and 23 for sea-water; and 93, 30, and 21 for steels subjected to alternate wet and dry conditions. J. H. G. Monypenny found that ordinary **tap-water** has no perceptible action during the exposure of either hardened or tempered steel; river-water, and well-water have usually no action; and sea-water is without action if the metal is wholly immersed, or alternately wet and dry; but under the prolonged action of spray, some pitting may be produced. J. A. N. Friend observed that 11·73 to 13·40 per cent. chromium steels resisted atm. corrosion almost perfectly; and they also resisted sea-water very well, although there were some severe localized pits developed by exposure to sea-water. J. H. G. Monypenny found that stainless steel resists the action of superheated steam remarkably well, even when the steel steam fittings are in contact with ordinary nickel or copper alloys used for the fittings. According to O. Meyer and K. Reesch, the rusting of 13 per cent. chromium steels commences whenever the potential falls below $E_H = -0{\cdot}015$ to $-0{\cdot}010$ volt. In acidic soln., the potential of chromium steels becomes more positive and the rate of corrosion decreases with an increase in the quenching temp. The higher the carbon-content of the steel the higher is the temp. from which the steel must be quenched in order to prevent rusting, as the more nearly the structure approaches a single solid soln. the greater is the chemical resistance; in this sense, therefore, carbon must be considered as an objectionable impurity in rust-resisting steels.

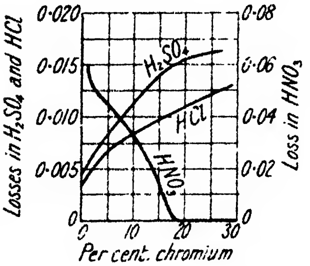


FIG. 452.—The Corrosion of Chromium Steels by Acids.

Soln. of **ammonia, alkali hydroxides,** or **alkali carbonates** have no perceptible action; and no attack occurs in damp atmosphere charged with gaseous ammonia. A. Krüger said that although chrome steels are attacked by hot, dil. acid soln., they resist boiling alkalies. The material also resists hydrogen dioxide, and soln. of sodium sulphide. According to J. H. G. Monypenny, 5 per cent. soln. of the following **salts,** during 4–5 weeks' action, produced no visible corrosion on immersed samples: alkali carbonates or hydrocarbonates; alkali nitrates, or sulphites; sodium chloride*, potassium chloride*, cyanide, chlorate, or dichromate; ammonium oxalate, persulphate or phosphate; copper acetate, nitrate, or sulphate; ferric nitrate or sulphate; ferrous sulphate; lead acetate, magnesium chloride* or sulphate*; and manganese sulphate. With the salts marked with an asterisk, corrosion may occur at the points of support of the metal below the surface of the soln. L. Aitchison observed that the losses in weight per 100 sq. cm. with chromium steels exposed 77 days in darkness to a 3 per cent. soln. of sodium chloride, were:

Cr	0·99	4·97	10·15	15·01	19·46	23·70 per cent.
Loss	1·31	1·38	0·79	0·91	0·00	0·24

J. H. G. Monypenny found that 12–13 per cent. chromium steel is slightly pitted by a dil. soln.—5 grms. per litre—of **ammonium chloride** in 10 days at 80° to 90°; while a piece of mild steel was badly corroded, and lost seven times as much weight. There was also a slight attack during two months' exposure to a conc. soln.—25 grms. per litre—at ordinary temp. Soln. of **ammonium sulphate** have no perceptible action when dil., but the chromium steel is slowly attacked by conc. soln. With 5 per cent. and a sat. soln. of **potash-alum,** stainless steel lost respectively 0·012 and 0·008 mgrm. per sq. cm. per hour, under conditions where mild steel lost respectively 0·065 and 0·035 mgrm. per sq. cm. per hour; similarly also with soln. of **ammonia-alum.** Soln. of **ferric chlorine,** even when fairly dil., attack the stainless steel; similarly also with soln. of **copper chloride**; the attack with soln. of **mercuric chloride** is fairly rapid. Dil. soln. of potassium or sodium sulphate have no action, but conc. soln. attack the metal—conc. soln. of these salts have an acidic reaction.

J. H. G. Monypenny observed that **hydrochloric acid** attacks stainless steel quite readily, and in 24 hrs. the loss in mgrms. per sq. cm. per hour with *N*-HCl and 5*N*-HCl was 0·82 and 5·00 respectively under conditions where the losses with mild steel were respectively 1·84 and 6·80. P. Koetzschke found that chromium decreases the corrodibility of cast-iron in hydrochloric acid. Y. Utida and M. Saito showed that chromium increases the corrosion of iron by hydrochloric acid—*vide supra*. W. H. Hatfield obtained the results indicated in Table LXXV for the losses in weight in grams per sq. cm. after 24 hrs.' immersion at 15°.

TABLE LXXV.—ACTION OF ACID ON CHROMIUM STEELS.

Composition					Condition	Brinell's hardness	HCl	HNO_3	H_2SO_4 10 per cent.
C	Mn	Ni	Cr	Si					
0·395	0·66	0·41	*nil*	0·19	Normalized as rolled	167	0·1812	0·5858	0·1032
0·38	0·18	0·10	5·10	0·09		157	0·3075	0·8989	0·2198
0·64	0·34	0·15	8·96	0·19	,,	180	0·1666	0·0005	0·3048
0·29	0·22	0·09	10·06	0·14	,,	180	0·1492	0·0001	0·2143
0·56	0·21	0·10	12·47	0·12	,,	209	0·1845	*nil*	0·2496
0·50	0·35	0·11	15·60	0·28	,,	255	0·2902	,,	0·4279
0·49	0·21	0·14	19·66	0·23	,,	223	0·1709	,,	0·3530
0·53	0·30	0·10	24·22	0·38	,,	209	0·2836	,,	0·4543
0·58	0·31	0·15	32·07	0·49	,,	216	0·3221	,,	0·5583

W. H. Hatfield found, in grams per sq. cm. in 24 hrs.:

	Hydrochloric acid			Sulphuric acid			Nitric acid	
	5	25	50	5	25	50	9	40 per cent.
15°	0·0162	0·0536	0·0626	0·0880	0·2558	0·0046	0·0032	*nil*
40°	0·0851	0·3640	0·0180	0·2902	0·6406	0·0115	0·0015	,,
60°	0·0812	0·4027	0·8066	0·4133	0·8787	0·0187	0·0076	,,
80°	0·1043	0·4326	0·8061	0·4592	0·7199	0·2246	0·0103	0·0005

W. Rohn observed the relative losses in weight in grams per sq. dm., with N=not annealed, and A=annealed steels, in 10 per cent. acids :

Fe : Cr		84 : 16		75 : 25		68 : 32		50 : 50	
		N	A	N	A	N	A	N	A
HNO_3	24 hrs. cold	0	0	0	0	0·006	0	0·002	0·002
	1 hr. hot	0	0·04	0·003	0·003	0	0	0·004	0·004
H_2SO_4	24 hrs. cold	9·5	7·5	11·9	9·6	13	18	45·6	—
	1 hr. hot	47	32	22	19	64·8	57·6	52·8	—
HCl	24 hrs. cold	35	6·5	12·3	6·2	18·5	17	11·5	15·8
	1 hr. hot	70	27	26	14	62·6	57·6	30·5	43·2
CH_3COOH	24 hrs. cold	0	0·03	0	0	0	0	0	0
	1 hr. hot	0·10	0·240	0	0·003	0	0	0	0
H_3PO_4	24 hrs. cold	0	0·04	0	0	0	0	0	0
	1 hr. hot	0	2·44	0	0·003	0·003	0	0·003	0·003

The presence of 0·25 per cent. carbon, or of 1 per cent. of manganese, or 1 per cent. of silicon increased the corrosion—*vide infra*, sulphuric acid. H. Gruber observed that plates 60×13×12 mm. of 25 per cent. chromium alloy gained in weight on on an hour's exposure to hydrogen sulphide :

	700°	800°	900°	1000°
Gain in weight	0·58	3·2	8·0	13·2

L. Vernitz and A. Kudinova found that the alloy resists the action of dry **sulphur chlorides**—S_2Cl_2, and SCl_2. J. H. G. Monypenny found that stainless steel is attacked by **sulphurous acid** owing partly to the sulphuric acid always present in commercial sulphurous acid. M. Faraday and J. Stodart, L. Gruner, and P. Berthier noticed that, in general, iron-chromium alloys are less readily attacked by acids than iron, and the attack is less the higher the proportion of contained chromium ; and similar observations were made by G. W. Heise and A. Clemente, E. Frémy, J. Fritz, and J. B. J. D. Boussingault. P. S. Menough, and Y. Utida and M. Saito observed that chromium lessens the attack by sulphuric acid. R. A. Hadfield exposed samples of chromium steel to 50 per cent. **sulphuric acid** for 21 days, and found the following percentage losses :

					Mild steel	Wrought iron
C	0·27	0·77	0·71 per cent.			
Cr	1·18	5·19	9·18 ,,			
Loss	3·32	4·78	5·64	Loss	7·48	44·7 per cent.

For the observations of Y. Utida and M. Saito, and of W. H. Hatfield, *vide supra.* J. A. N. Friend and co-workers found that when the corrosion factor with steel containing 0·29 per cent. of carbon and 0·39 per cent. of manganese is 100, the values for steels alloyed with 0·12, 3·58, and 5·30 per cent. of chromium are respectively 71, 68, and 68 for 0·15 per cent. sulphuric acid, and 223, 61, and 78 for 0·5 per cent. acid. W. Guertler and W. Ackermann represented the loss in mgrms. per sq. cm. per hr. in sulphuric acid of sp. gr. 1·005 by the curve Fig. 453. P. Koetzschke and E. Piwowarsky found that the addition of up to 1 per cent. of chromium in grey cast iron had a marked effect on the corrosion by acids, but not by salt soln. A. Carnot and E. Goutal found that steels with a small proportion of chromium are readily attacked by cold, dil. acids, but if the chromium steels are highly carburized they are attacked more slowly than when only a small proportion of carbon is present. W. Borchers and P. Monnartz patented an acid-resisting steel with 10 per cent. of chromium and 2 to 5 per cent. molybdenum. Observations were also made by J. A. N. Friend and co-workers, who noted that up to 5·3 per cent. chromium steels resisted attack better the higher the proportion of chromium. E. Jänecke noted that hot 1 : 1 sulphuric acid attacks the iron-

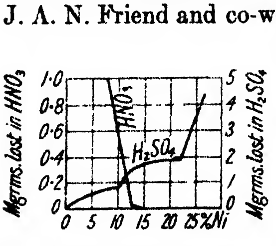


FIG. 453.—The Action of Sulphuric and Nitric Acids on Iron-Chromium Alloys.

chromium alloys. L. Aitchison found that chromium steels with about 0·85 per cent. carbon lost per 100 sq. cm. in 1 per cent. sulphuric acid for 77 days, and in 10 per cent. sulphuric acid for 45 days, in darkness:

Cr	. . . . .	0·99	4·97	10·15	15·02	19·46	23·70 per cent.
H_2SO_4	1 per cent. .	12·6	5·4	10·3	5·85	0·52	1·76
	10 per cent. .	15·9	11·0	18·3	33·6	29·0	23·7

J. H. G. Monypenny found that the loss in mgrms. per sq. cm. per hour at atm. temp. during 6 hrs.' attack with 5, 35, and 50 per cent. sulphuric acid were respectively 1·98, 15·8, and 0·50; with the 0·25 per cent. carbon and 12·1 per cent. chromium steel, and with mild steel, respectively 3·16, 11·55, and 0·23. In 24 hrs.' attack, with 50 per cent. sulphuric acid, on chromium steel and mild steel, the numbers were respectively 0·26 and 0·10. M. Sauvageot and L. Lauprète found that steels with about 13 per cent. of chromium were all practically unattacked by nitric acid of any conc. at any temp., but the nickel steel rapidly dissolved in hot, 1 to 25 per cent. nitric acid and slowly in cold acid of the same conc., although acid of a higher conc. than 30 per cent. was without action at any temp. The nickel steel was by far the most resistant to the action of hydrochloric acid, but all the samples were badly corroded by hot, 20 per cent. acid. Sulphuric acid had practically no action on the nickel steel whatever the temp. (up to 100°) or conc.: the other steels showed a maximum rate of dissolution in 40 to 45 per cent. acid. The subject was studied by J. Fritz.

Both copper and ferric sulphates occur in **mine-waters** along with sulphuric acid; with a soln. of 100 grms. of copper sulphate per litre, and a steel with 0·30 per cent. carbon and 12·6 per cent. chromium, no action occurs on the addition of sulphuric acid until 75–100 grms. of H_2SO_4 per litre is present, after that the rate of attack is determined by the conc. of the copper sulphate in soln.; if copper sulphate is gradually added to a dil. soln. of sulphuric acid, say, 100 grms. H_2SO_4 per litre, the attack on the steel increases rapidly. Flocculent copper is deposited on the steel and appears to set up electrochemical action. When nearly 20 grms. per litre have been added the attack falls off rapidly and soon ceases altogether. The amount of copper sulphate required to stop the reaction is relatively less, the smaller the concentration of the acid. The steel thus acquires a kind of passivity. W. H. Hatfield found that the amount of ferric sulphate required to prevent the attack of sulphuric acid is proportional to the conc. of the sulphuric acid. With hardened and tempered steel, no attack occurred if the conc. of the ferric sulphate is twice that of the free acid, while with hardened steel the same effect was produced when the conc. of the ferric sulphate is one-fifth that of the free acid. J. H. G. Monypenny made observations on this subject; and he also found mine-waters with copper 14·7 to 16 parts per 100,000; ferric iron, 71·2 to 188; ferrous iron, 160; free sulphuric acid, 14 to 30, did not act on stainless steel, though it rapidly attacked ordinary mild steel.

F. Adcock found that solid or molten alloys of iron and chromium take up **nitrogen,** and in quantities which increase with the proportion of chromium. Alloys with near 12 per cent. of chromium, in contact with nitrogen, acquire the martensitic structure closely resembling that with the iron-carbon alloys. The Brinell's hardness can be considerably modified by heat-treatment, and ranges from about 115 in the annealed state to 315 when quenched above the critical range. Most of the alloys containing nitrogen in the range 20 to 60 per cent. chromium, present a two-phase structure except in some cases where the material has been quenched at a temp. immediately below the m.p. Although one of these constituents invariably develops a structure of the sorbitic or pearlitic type on suitable heat-treatment, these changes are not accompanied by any great variation in hardness. This pearlitic or lamellar type of structure, which characterizes the alloys with 20 to 30 per cent. chromium containing nitrogen, is known to be absent from the corresponding pure iron-chromium alloys. Further, the deliberate addition of 0·05 per cent. of carbon to an alloy with approximately 28 per cent. chromium, free from nitrogen, fails to produce any signs of a lamellar structure in the furnace-cooled material, although a considerable amount of a second constituent is visible. Consequently, the presence of nitrogen in iron-chromium alloys can give rise to structures closely resembling those generally attributed to carbon in ordinary steel, and, further, that at high temp., the pure alloys of iron and chromium, whether solid or liquid, readily absorb nitrogen from the atmosphere. S. Satoh studied the nitridization of these steels by heating them in **ammonia** at 560° to 580°. E. Müller and H. Barck studied the action of **nitric oxide.**

P. Monnartz, and J. G. Thompson observed that the presence of chromium greatly increased the resistance of iron to **nitric acid ;** and with alloys containing up to 20 per cent. chromium, he concluded that the resistance of alloys with up to 4 per cent. chromium to dil. nitric acid decreases as the proportion of chromium increases, but the resistance to attack by the conc. acid is greater. The resistance of alloys with 4 to 14 per cent. chromium to dil. nitric acid increases rapidly as the amount of chromium increases; and as the proportion of chromium rises from 14 to 20 per cent., the resistance to attack by dil. acid increases slowly. W. M. Mitchell, E. S. P. Bellinger, G. Grube and W. von Fleischbein, W. R. Huey, W. H. Hatfield—*vide supra*—and Y. Utida and M. Saito observed that the introduction of chromium lessens the attack by nitric acid—*vide supra*. W. Guertler and W. Ackermann represented the loss in mgrms. per sq. cm. per hour in nitric acid of sp. gr. 1·005 by the curve Fig. 454. G. Grube and W. von Fleischbein observed that the rate of dissolution of the alloys in dil. nitric acid diminishes with increasing chromium-content; when this reaches 12·5 mol. per cent., the rate of dissolution of chromium diminishes suddenly; and when it reaches 25 mol. per cent., falls suddenly to zero; and the rate of dissolution of iron also shows a sudden drop to a low value. The iron dissolves more rapidly than the chromium relatively to its proportion in the surface layer. The protective effect of small proportions of chromium on the iron may be due to the dissolved chromic acid rendering the iron passive. The resistance of a bar is not diminished by rolling to half its initial diameter. E. Jänecke found that boiling conc. nitric acid is without action on the higher chromium alloys. J. H. G. Monypenny observed that at ordinary temp., the loss in mgrms. per sq. cm. per hour, during 5 hrs., varies with the proportion of chromium in the steel as follows:

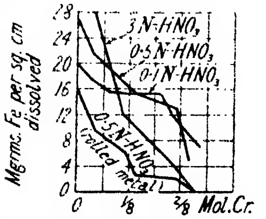


FIG. 454.—The Action of Nitric Acid on Iron-Chromium Alloys.

Carbon		0·16	0·14	0·16	0·09	0·09	0·13 per cent.
Chromium		0·00	4·72	10·0	12·0	14·0	17·5 „
Loss	N-HNO$_3$	16·2	15·65	2·1	0·35	0·03	*nil*
	HNO$_3$, sp. gr. 1·2	1·25	1·64	trace	*nil*	*nil*	*nil*

Thus, the attack by the conc. acid is greatly retarded when over 4·72 per cent. of chromium is present, and with dil. acid, when over 10 per cent. is present. At 80° to 85°, the results were:

Cr		10·6	11·1	12·2	13·3	14·4 per cent.
Loss	N-HNO$_3$	11·5	16·5	1·09	0·41	0·27
	$5N$-HNO$_3$	0·03	—	0·025	0·01	0·005

and with a steel with 12·2 per cent. chromium at 80° to 85°:

HNO$_3$	0·1N	0·2N-	0·5N-	N-	2N-	5N-
Loss	4·90	8·82	15·13	1·09	0·20	0·025

and at ordinary temp. in a 5 hrs.' and a 24 hrs'. attack the losses in mgrms. per sq. cm. per hour, were:

HNO$_3$		0·01N-	0·2N-	0·5N-	N-	2N-	2N-
Loss	5 hrs.	0·40	0·65	1·11	1·53	0·61	0·01
	24 hrs.	0·355	0·50	0·72	0·395	0·115	0·00

In general, the stainless steel with 12 to 13 per cent. chromium and 0·3 per cent. carbon is attacked by nitric acid at ordinary temp. only when the acid is very dilute—say, less than 5N-HNO_3 or 1·20 sp. gr.—and then the action is slow. By selecting a suitable steel, even this attack may be prevented. Hence, stainless steel may ultimately be useful in the manufacture and transport of nitric acid. The attack is augmented by raising the temp.; and it is decreased by raising the percentage of chromium in the alloy. As a result, a 15 per cent. alloy resists attack at ordinary temp. or at 85°. Thus the presence of chromium greatly increases the tendency of iron to become passive in nitric acid. The action of copper nitrate or ferric nitrate along with nitric acid resembles the effect of the corresponding sulphates on the attack by sulphuric acid. The presence of 8 grms. of copper as nitrate, or 5 grms. of iron as nitrate per litre, sufficed to prevent the attack of N-HNO_3 on steel with 0·3 per cent. carbon, and 12·6 per cent. chromium. W. M. Mitchell, and E. S. P. Bellinger discussed the use of stainless iron, or high chromium alloys of iron, in the construction of equipment for the manufacture and handling of nitric acid. G. Tammann tried the hypothesis that a chromium atom in the surface of iron can render an adjacent iron atom passive in dil. acids, so that the (101)-face of a crystal should become passive when 0·25 mol. proportion of chromium, and the (100)- and (111)-faces, passive with 0·375 mol. Passivation actually occurs with less, namely, 0·16 to 0·28 molecule of chromium. Hence, passivity is affected by other conditions—the nature of the solvent, previous treatment of the alloy, and the nature of the second component.

According to J. H. G. Monypenny, chromium steel is also slowly attacked by **phosphoric acid.** The losses in mgrms. per sq. cm. per hour with 5, 25, and 66·3 per cent. phosphoric acid were respectively 0·050, 0·20, and 0·47 with the chromium steel, and respectively 1·11, 2·60, and 4·62 with mild steel. The subject was studied by P. R. Kosting and C. Heins, and A. M. Portevin and A. Sanfourche. According to J. H. G. Monypenny, a soln. of 20·7 grms. of **boric acid** per litre had no action on this steel. H. R. S. Clotworthy recommended stainless steel for resisting the action of **carbon disulphide.** The action of dil. **acetic acid** or **vinegar** varies in that some vinegars contain appreciable amounts of sulphuric acid, while others are free from that acid. P. Kötzschke found that chromium decreases the corrodibility of cast iron in acetic acid. According to J. H. G. Monypenny, ordinary malt vinegar has 4 to 5 per cent. of acetic acid. The losses with 5, 15, 33 per cent. and glacial acetic acid, during 14 days, were respectively 0·014, 0·012, 0·012, and *nil* mgrm. per sq. cm. per hour, and with mild steel, respectively 0·067, 0·105, 0·115, and 0·124 mgrm. per sq. cm. per hour. Expressing the losses in mgrms. per sq. cm. per hour respectively with chromium steel and ordinary mild steel, 5 per cent. **carbolic acid,** with 14 days' exposure, had losses *nil*, and 0·005; 6 per cent. **citric acid,** in 7 days' action, had losses 0·011 and 0·260; 10 per cent. **formic acid** in 12 days' action, had losses 0·26 and 0·33; oleic acid had no action on the chromium steel during 14 days' exposure; normal **oxalic acid,** in 10 days' action, gave losses 0·021 and 0·036; 10 per cent. **tannic acid,** in 14 days' action, had losses *nil* and 0·0042; and in 14 days' action, normal **tartaric acid** had losses 0·0085 and 0·062, and 25 per cent. tartaric acid, 0·022 and 0·14. J. G. Thompson studied the action of aq. soln. of **urea** and of **ammonium carbonate.** J. H. G. Monypenny found that, in general, **fruit juices** have a similar action to that of vinegar, though their corrosive power varies. The pure acid, the same strength as the acid in fruit juice, has sometimes the greater action—*e.g.* vinegar and acetic acid, or lemon juice and citric acid. Possibly the natural fruit juice contains some colloid which acts as a retarding agent—*vide supra*, the corrosion of iron and steel. No action was observed with **lubricating oils, greases, paraffin, benzol,** or **petrol.** R. Tull discussed the resistance of the alloy to **smoke.**

General discussions on the use of chromium steels have been contributed by C. B. Bellis, E. Lievenie, T. Blair, J. Ohly, T. H. Nelson, T. H. Burnham, J. D. Corfield, W. M. Mitchell. The so-called **stainless steels** are essentially chromium steels containing from 12 to 15 per cent. of chromium, but their general properties are greatly affected by the carbon-content, which may vary from 0·1 to 0·5 per cent. The discovery of the non-corrosive properties of these steels was made by H. Brearley, in 1913, but, owing to counter-attractions, a British patent was not obtained, although they were obtained in Canada in 1915, and in the United States in 1916. He claimed an alloy steel with from 9 to 16 per cent. of chromium and less than 0·7 per cent. of carbon, and gave as an example an alloy with 0·30 per cent. of carbon, 0·30 manganese, and 13·0 chromium. A great variety of steels can be obtained by modifications of the central idea. Thus, by varying the proportion of carbon or manganese, and heat-treatment, steels of widely different hardness can be obtained, but all have the distinguishing property of great resistance to corrosion. According to J. H. G. Monypenny, with a fixed proportion of chromium, and the same heat-treatment, the resistance to corrosion will be greater the lower the proportion of carbon; and with a fixed proportion of carbon, and the other conditions equal, increasing the proportion of chromium augments the resistance. The mechanical properties of the steel, conditioned by the heat-treatment, are often as important as the degree of resistance to corrosion, and this restricts the permissible variations in composition. The cost of the chromium is also a factor to be considered. Hence, taking all things into consideration, H. Brearley considered that the proportions just indicated are best for commercial alloys. Silicon raises the temp. of the Ac_1-change, and also the temp. required for the complete dissolution of the carbide, and hence, higher hardening temp. are needed to obtain similar resistances to corrosion when silicon is present. H. H. Abram reported that high-silicon steels resist some chemical agents better, but their superiority over low-silicon steels for resisting the weather, and sea-water, is not evident, and it exists only in tempered, high-carbon steels. The effect of nickel favours the mechanical properties of steel; and up to 2 per cent. of nickel slightly favours resistance to attack by acids. Hence, additions of nickel can be made to suit the physical requirements. B. D. Saklatwalla showed that 0·5 to 1·5 per cent. of copper considerably improves stainless steel, and this was confirmed by J. H. G. Monypenny.

According to J. H. G. Monypenny, in general, a heterogeneous steel is more susceptible to attack than a homogeneous steel, so that when a steel is hardened by quenching, it consists almost wholly of martensite and is then in its most resistant form; while if the steel be annealed so as to produce a complete separation of carbide and ferrite, it is in its least resistant form. In the separation, the chromium has a tendency to accumulate in the carbide at the expense of the ferrite, and the ferrite is then more liable to attack; the separation also means that galvanic effects may be produced which hasten the corrosive actions. The greatest resistance to corrosion was obtained by quenching the steel from a temp. sufficiently high to dissolve all the carbide it contains. The hardness of these hardened steels persists on tempering up to 500°, and this does not markedly alter the martensitic structure of the steel, nor does it have any notable effect on the resistance to corrosion. As the tempering temp. is raised to between 500° and 600°, there is a marked fall in the hardness, and a slightly lessened resistance to corrosion. The martensitic structure changes, and small carbide particles coalesce to form larger ones; by tempering at 750° the effects at 600° are more marked. Similar remarks apply to material annealed at a high enough temp. to give a pearlitic structure. As indicated in connection with the corrosion of iron and steel—*vide supra*—most metals, including the chromium steels, have a greater tendency to corrode when they are distorted by cold-work. V. S. Polansky compiled a bibliography of the stainless steels; and observations on their corrodibility were made by L. Aitchison, H. Hubert, H. C. H. Carpenter, etc. A. Matsubara and J. Takubo found that copper pyrites in dil. sulphuric acid is decomposed cathodically into hydrogen sulphide, cuprous sulphide, and ferrous sulphate, and, ultimately, into metallic copper; preliminary anodic polarization produces the reverse effect of that observed with iron pyrites. Copper pyrites which yields but little hydrogen gives abnormal quantities of decomposition products. It is supposed that the fraction of the mineral which is dissolved directly by the acid exists in the solid in an ionized condition, the degree of ionization in various specimens of copper pyrites being 0·035 to 0·305.

O. K. Parmiter gave the following comparison of the effect of various reagents, at room temp., on carbon steel, stainless steel with 13 per cent. Cr, and stainless steel with 13 per cent. Cr and 8 per cent. Ni, respectively : 100 per cent. *acetic acid*, attacked, not attacked, not attacked ; 33 per cent. acetic acid, attacked, attacked, —— ; 5 and 15 per cent. acetic acid, attacked, attacked, not attacked ; 100 per cent. boiling acetic acid vapour, attacked, attacked, attacked ; 33 per cent. acetic acid vapour, attacked, attacked, slightly attacked ; 100 per cent. *acetic anhydride*, attacked, attacked, not attacked ; 100 per cent. *acetone*, attacked, slight corrosion, not attacked ; 10 per cent. *alum*, attacked, attacked, not attacked ; 1, 5, and 10 per cent. *aluminium sulphate*, attacked, attacked, not attacked ; *ammonia* (sp. gr. 0·880), not attacked, not attacked, not attacked ; 1, 5, 10, 20 per cent. *ammonium chloride* soln., attacked, slightly attacked, not attacked ; 5, 23, 47 per cent. ammonium chloride (boiling soln.), attacked, attacked, very slightly attacked ; 10 per cent. soln. of *ammonium nitrate*, attacked, not attacked, not attacked ; 10 per cent. soln. of *ammonium sulphate*, attacked, attacked, not attacked ; ammonium sulphate (sat. soln.) +5 per cent. sulphuric acid (at 50°), attacked, attacked, attacked ; *apples*, attacked, not attacked, not attacked ; *beer*, attacked, not attacked, not attacked ; *benzene*, not attacked, not attacked, not attacked ; aq. suspension of *bleaching powder*, attacked, attacked, slightly attacked ; 5 per cent. soln. of *boric acid*, attacked, not attacked, not attacked ; *bromine*, attacked, attacked, attacked ; 0·83, 1·65, 3·3 per cent. bromine water, attacked, attacked, attacked ; 0·165, 0·33 per cent. bromine water, attacked, attacked, very slightly attacked ; 10 per cent. soln. of *calcium chloride*, attacked, slightly attacked, not attacked ; *carbolic acid*, attacked, attacked, not attacked ; *carbon tetrachloride*, —— , not attacked, not attacked ; wet and dry *chlorine* gas, attacked, attacked, attacked ; conc. *chlorosulphonic acid*, attacked, attacked, not attacked ; 10 per cent. chlorosulphonic acid, attacked, attacked, attacked ; 0·5 per cent. chlorosulphonic acid, attacked, attacked, not attacked ; *cider*, attacked, not attacked, not attacked ; all concentrations of *citric acid*, attacked, attacked, not attacked ; conc. aq. extract of *coffee*, attacked, not attacked, not attacked ; Congo *copal* (370°), —— , attacked, not attacked ; *copal varnish*, not attacked, not attacked, not attacked ; sat. soln. of *copper carbonate* in ammonia, attacked, not attacked, not attacked ; 5 and 10 per cent. soln. of *copper chloride*, attacked, attacked, attacked ; 10 per cent. soln. of *copper sulphate*, attacked, not attacked, not attacked ; copper sulphate (10 per cent.) +2 per cent. sulphuric acid, attacked, not attacked, not attacked ; developers : (a) *hydroquinone*, attacked, not attacked, not attacked ; (b) *metolhydroquinone*, attacked, not attacked, not attacked ; (c) *pyrogallol*, attacked, very slightly attacked, not attacked ; 100 per cent. *ether* (ethyl), not attacked, not attacked, not attacked ; 100 per cent. *ethyl chloride*, attacked, not attacked, not attacked ; 5, 10, and 15 per cent. *ferric chloride*, attacked, attacked, attacked ; *food-pastes*, attacked, not attacked, not attacked ; 40 per cent. *formaldehyde*, attacked, not attacked, not attacked ; 5, 25, 50, and 100 per cent. *formic acid*, attacked, attacked, not attacked ; 50 per cent. formic acid (boiling), attacked, attacked, not attacked ; (40 hypo. 2·5 pot. met.) *fixing soln.* (acid), —— , attacked, not attacked ; *horse-radish cream*, attacked, slightly attacked, not attacked ; all concentrations of *hydrochloric acid*, attacked, attacked, attacked ; *hydrofluoric acid*, attacked, attacked, attacked ; *inks*, attacked, not attacked, not attacked ; *iodine* in 2 parts of potassium iodide, attacked, attacked, not attacked ; sat. *lactic acid*, attacked, attacked, not attacked ; *lemon*, attacked, not attacked, not attacked ; *lime-juice*, attacked, very slightly attacked, practically not attacked ; *lime* and *limestone*, attacked, not attacked, not attacked ; *lubricating oils*, not attacked, not attacked, not attacked ; 2 per cent. and conc. soln. of *lysol*, attacked, not attacked, not attacked ; 10 per cent. soln. of *magnesium chloride*, attacked, attacked, not attacked ; 10 per cent. soln. of *magnesium sulphate*, attacked, attacked, not attacked ; fresh and sour *milk*, attacked, attacked, not attacked ; ($65HNO_3$, $25H_2SO_4$, 10 water) mixed, or *nitric-sulphuric acid* (at 50°), attacked, not attacked, not attacked ; *nitric acid* (sp. gr. 1·42), not attacked, not attacked, not attacked ; nitric acid (sp. gr. 1·20), attacked, not attacked, not attacked ; up to 11 per cent. nitric acid, attacked, slightly attacked, not attacked ; *nitrous acid* (sp. gr. 1·41), attacked, slight staining, not attacked ; 5 per cent. nitrous acid, attacked, slightly attacked, not attacked ; 100 per cent. *oleic acid*, attacked, not attacked, not attacked ; *oranges*, attacked, attacked, not attacked ; 5 per cent. soln. of *oxalic acid*, attacked, attacked, not attacked ; *paraffin*, not attacked, attacked, not attacked ; *paregoric compound*, attacked, badly stained, not attacked ; *petrol*, not attacked, not attacked, not attacked ; 100 per cent. *phosphoric acid*, attacked, slightly attacked, not attacked ; 75 per cent. phosphoric acid, attacked, attacked, not attacked ; 5, 25, 50 per cent. phosphoric acid, attacked, slightly attacked, not attacked ; *pickles*, attacked, not attacked, not attacked ; *picric acid* (alcoholic), attacked, not attacked, not attacked ; 10 per cent. *potassium nitrate*, attacked, not attacked, not attacked ;

pyrogallol, attacked, not attacked, not attacked; *moist salt* (cerebos), attacked, attacked, not attacked; moist salt (ordinary), attacked, attacked, not attacked; *sauces*, attacked, not attacked, not attacked; *sea-water*, attacked, attacked, slightly attacked; sea-water (80°), attacked, attacked, not attacked; sea-water (agitated), attacked, attacked, not attacked; sea-water (intermittent spray), attacked, attacked, very slightly attacked; 100 per cent. *sebacic acid* (at 140°), attacked, attacked, attacked; 3, 5, 10 per cent. soln. of *sodium chloride*, attacked, slightly attacked, not attacked; 3·5 per cent. *sodium citrate*, ——, not attacked, not attacked; 33·66 per cent. soln. of *sodium hydroxide*, not attacked, not attacked, not attacked; sat. soln. of sodium sulphate, attacked, not attacked, not attacked; 10 per cent. *sodium sulphide*, attacked, not attacked, not attacked; 30 per cent. *sodium thiosulphate*, attacked, ——, ——; all conc. of *sulphuric acid*, attacked, attacked, not attacked; 5 per cent. *tannic acid*, attacked, practically not attacked, not attacked; 5, 10, 25, and 50 per cent. soln. of *tartaric acid* (all temp. up to boiling), attacked, attacked, not attacked; *vinegar*, attacked, not attacked, not attacked; *running water* (tap-water), attacked, not attacked, not attacked; 15° water (tap-water), attacked, not attacked, not attacked; liquid *zinc* (450°), attacked, attacked, attacked; *zinc chloride* (boiling), sp. gr. from 1·030 to 1·725, attacked, very slightly attacked, not attacked.

The use of alloys for resisting acidic and alkaline soln. in chemical plants has been discussed by A. E. Anderson and G. M. Enos,[23] P. A. E. Armstrong, F. M. Becket, T. H. Burnham, W. S. Calcott, W. S. Calcott and co-workers, C. M. Carmichael and co-workers, F. J. R. Carulla, F. F. Chapman, J. Cournot, G. A. Drysdale, U. R. Evans, H. J. French, E. D. Gleason, A. Grounds, W. Guertler, H. G. Haase, R. A. Hadfield, M. L. Hamlin and F. M. Turner, W. H. Hatfield, F. W. Horst, E. Houdremont and R. Wasmuth, W. E. Jominy and R. S. Archer, G. B. Jones, R. Lund, R. J. McKay, C. E. MacQuigg, W. R. Mott, T. H. Nelson, A. Portevin, H. Reiger, F. Ritterhausen, C. S. Robinson, K. Roesch and A. Clauberg, W. Rohn, F. W. Rowe, B. D. Saklatwalla, L. Sanderson, W. Schmidt, E. H. Schulz and W. Jenge, C. E. Sholes, R. Thews, G. Thompson, S. J. Tungay, A. Vacin, R. P. de Vries, H. F. Whittaker, E. C. Wright and K. E. Luger, and A. Zemanek. The subject is also discussed in more detail in connection with specific alloys.

B. D. Saklatwalla and A. W. Demmler,[24] E. H. Schulz, K. Sasakawa, and J. A. Jones studied the **chromium-copper steels.** The mechanical tests far exceed those of the plain, low-carbon, copper steels; the alloys can be rolled, forged, pressed, and stamped very well; and they also resist corrosion very well. V. and G. Prever also found that the alloys resist corrosion. E. Scheil and E. H. Schulz, C. Taillandier, and F. B. Lounsberry and W. R. Breeler studied the **chromium-aluminium steels.** L. Guillet recommended nitridized chromium-aluminium steels for the cylinders of internal combustion engines, and for propeller shafts. S. Sato studied the electrode potentials of the nitridized alloys. H. Gruber found that the aluminium-chromium-iron alloys are attacked by hydrogen at elevated temp. C. Casper, H. Moissan, J. B. Johnson and S. A. Christiansen, E. Valenta, W. Oertel and K. Würth, V. O. Homerberg and I. N. Zavarine, A. R. Page and J. H. Partridge studied the mechanical properties of **chromium-silicon steels,** and P. Bres, their resistance to corrosion; W. Denecke gave a ternary diagram of the system with up to about 30 per cent. each of chromium and silicon. The iron and chromium furnish a continuous series of solid soln. with minimum in the f.p. curves. No evidence was observed of the formation of the compound Fe_2Cr, or of a eutectic with 15 per cent. of chromium. The reaction between the solid soln. of iron and silicon, and the formation of FeSi, is accelerated by the presence of chromium. E. D. Campbell and H. W. Mohr studied the electrical resistance and the thermoelectric potentials; G. D. Newton, the shearing strength; H. H. Abram, J. N. Alcacer and G. Gayoso, T. G. Digges, H. J. French and W. A. Tucker, F. J. Griffiths, G. A. Hawkins and co-workers, W. Kahlbaum and co-workers, R. R. Moore and E. V. Schaal, T. Murakami and K. Yokoyama, T. L. Robinson, K. Roesch, S. C. Spalding, J. S. Vanick and co-workers, and C. F. Würth, the mechanical properties; and J. Cournot and K. Sasagawa, the viscosity. S. Sato studied the electrode potentials of nitrified **chromium-titanium steels,** and of **chromium-zirconium steels.** B. Stoughton and W. E. Harvey,

W. Kahlbaum and L. Jordan, T. Heczko, and H. M. Boylston investigated the physical properties, and J. G. Thompson and co-workers, and G. H. Keulegan and M. R. Houseman, the action of aq. soln. of urea and of ammonium carbamate on the **chromium-vanadium steels.**

Samples of iron alloyed with up to 28·49 per cent. of molybdenum were reported by C. J. Heine,[25] F. Stromeyer, A. Wehrle, H. A. L. Wiggers, and C. Steinberg. P. Berthier prepared **iron-molybdenum alloy, or ferromolybdenum,** with 2 per cent. of molybdenum which was as fusible as iron, but whiter, extremely hard, brittle and tenacious, and uneven and granular in fracture. J. J. Berzelius also described bluish-grey alloys with iron and molybdenum in the proportion 1 : 1 and 1 : 2. To prepare the iron-molybdenum alloys, J. Ohly recommended adding molten iron to a bath of fused molybdenum. H. Lautsch and G. Tammann prepared alloys by reducing a mixture of the oxides with aluminium. The strong affinity of molybdenum for oxygen, and the volatility of the molybdenum oxides may give large losses of the expensive metal molybdenum in the manufacture of alloys with iron or steel. Ferromolybdenum can be prepared in electric furnaces with 10 to 50 per cent. molybdenum, and at most 0·5 per cent. of carbon; and, by using ferromolybdenum, the losses in the preparation of molybdenum steels are smaller. S. S. Steinberg and P. S. Kusakin, O. J. Steinhart, R. Cazaud, F. M. Becket, R. M. Keeney, F. Peters, W. Guertler, G. P. Scholl, P. Girod, J. Pokorny, G. and E. Stig, and W. Borchers and R. W. Stimson prepared alloys of iron and molybdenum. W. R. Hulbert employed the thermite process. W. P. Sykes prepared alloys by heating together intimate mixtures of the constituent elements in a powdered form such as is produced by reduction in hydrogen. The mixture is compressed into bars which are sintered in hydrogen above 1440° until diffusion is complete. The bars are quenched and aged for several days above 600°—*vide* **11.** 61, 5. A. Stavenhagen and E. Schuchard obtained the alloys by the thermite process. C. F. Burgess and J. Aston discussed the working properties of these alloys. A. Kissock added calcium molybdate to steel. Some uses of molybdenum steels were discussed by M. H. Schmid, P. Oberhoffer, W. Borchers and R. W. Stimson, W. Heym, G. W. Sargent, G. T. Holloway, J. K. Smith, J. Escard, J. A. Mathews, J. W. Richards, F. W. Rowe, J. W. Evans, C. McKnight, V. L. Eardley-Wilmot, A. H. Hunter, A. Haenig, E. Lievenie, E. Schaaf-Regelman, G. Gin, P. Girod, W. Venator, and G. Surr.

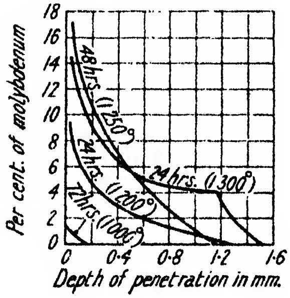


FIG. 455.—The Diffusion of Molybdenum in Iron.

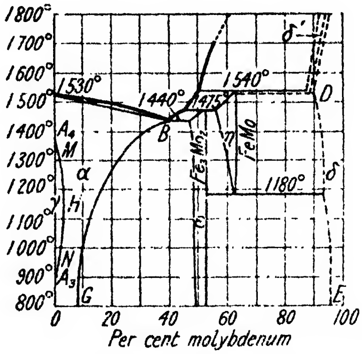


FIG. 456.—Equilibrium Diagram of the Iron-Molybdenum Alloys.

G. Grube and F. Lieberwirth, N. Agéeff and M. Zamotorin, and J. Laissus discussed the diffusion of molybdenum in iron. Fig. 455 has a selection from the results of F. Lieberwirth. The alloys were described by J. L. Gregg and H. W. Gillett. H. Lautsch and G. Tammann made a partial study of the binary system and found a eutectic with 43 per cent. molybdenum at 1360°. The breaks in the cooling curve indicated that a compound is formed which decomposes slowly at higher temp. The compound does not form mixed crystals with iron, and probably not with molybdenum, but the metals themselves form two series of mixed crystals. W. P. Sykes' diagram modified by T. Takei and T. Murakami is shown in Fig. 456. When alloys with up to 24 per cent. Mo are quenched from the solidus temp., large polyhedral grains of the solid soln. are formed; if cooled at a moderate rate, a second phase—**iron tritadimolybdide,** Fe_3Mo_2—appears, either as small globular grains, or as needle-like crystals. E. Vigouroux, and A. Carnot and E. Goutal observed the existence of this compound in alloys of iron and molybdenum free from carbon. T. Takei and T. Murakami also found a solubility of the ϵ-phase in the α-phase, *BG*, corresponding with 6 per cent. of molybdenum at room temp., and 38 per cent. at the eutectic 1440°. They observed solid phases named respectively α-, γ-, ϵ-, δ-, and δ'-; and in addition to iron tritadimolybdide, they found **iron molybdide,** FeMo, exists as the η-phase, and it is formed by the peritectic reaction: $\text{melt}+\delta'\rightleftharpoons\eta$ at 1540°, and it decomposes by a eutectoidal reaction, $\eta\rightleftharpoons\epsilon+\delta$, into the ϵ- and δ-phases at about 1180°. According to T. Takei and T. Murakami, the tritadimolybdide forms the ϵ-phase, and it is formed by the peritectic reaction: $\text{melt}+\eta=\epsilon$ between 1450° and 1500° on cooling, and it forms a eutectic with the α-phase. They also studied the lowering of the critical points of iron by molybdenum. H. Scott observed that molybdenum has but a slight effect on the temp. of transformation of martensite to troostite. V. N. Svechnikoff studied the γ-phase.

E. C. Bain's X-radiograms corresponded with hexagonal FeMo, and H. Arnfeldt observed that in the Fe–Mo system there is an intermediate trigonal phase with lattice parameters $a=4\cdot743$ A., and $c=25\cdot63$ A., or $c:a=5\cdot40$. The crystals have the composition of iron tritadimolybdide, Fe_3Mo_2. H. Lautsch and G. Tammann studied the microstructure of the alloys more or less carburized. W. P. Sykes observed that *BG* denotes the solubility curve of molybdenum in iron between 400° and 1440°. The eutectic is made up of iron tritadimolybdide and the sat. solid soln. of molybdenum in iron, and in alloys quenched from just below 1440°, it appears as a fine network, while with slower cooling, it has a distinctly lamellar structure. The solid soln. of molybdenum in iron is 24 per cent. Mo at 1440° and 7 per cent. at 600°. As the proportion of molybdenum rises above 35 per cent., massive areas of the tritadimolybdide appear. An alloy with 53 per cent. of molybdenum, when heated over 5 hrs. at 1450°–1500°, consists of only one phase, the tritadimolybdide. This alloy is porous, due to the vol. shrinkage accompanying the formation of this compound in the solid state. This alloy is non-magnetic, those with less molybdenum are magnetic. When alloys with 50 to 90 per cent. molybdenum are heated above 1540°, the tritadimolybdide dissociates into an iron-rich liquidus, and a solid soln. of iron in molybdenum. *DE* represents the solubility curve of iron in molybdenum. The line *MHN* is drawn through the Ar_4- and Ar_3-points during cooling. The point Ar_3 marks the change from γ-iron, with its face-centred cubic lattice, to α-iron, with its body-centred cubic lattice; and Ar_4 represents the change from δ-iron with its body-centred cubic lattice, to γ-iron, with its face-centred cubic lattice. The addition of 3 per cent. of molybdenum to iron lowers the Ar_4-point from 1400° to 1230°; and raises the Ar_3-point from 890° to 980°. The addition of molybdenum in iron thus tends to prevent the change from α- to γ-iron or from δ- to γ-iron in heating through Ar_3 or cooling through Ar_4 respectively; that is, additions of molybdenum to iron progressively restrict the range of temp. in which γ-iron is stable, until, with 4·0 to 4·5 per cent., the body-centred form prevails exclusively at temp. below the solidus. P. Oberhoffer observed a similar restriction of the range of γ-iron with 5 per cent. of silicon, but F. Wever placed it at 1·8 pet cent. of silicon. F. Wever also found the restriction occurs with about 2 per cent. of tin; E. Maurer, with 2·5 per cent. of vanadium; E. C. Bain, with about 14 per cent. of chromium; and W. P. Sykes, with about 6 per cent. of tungsten. T. Takei and T. Murakami found that with alloys having over 63 per cent. of molybdenum, there is an eutectoidal change, $\delta'=\delta+\eta$, at about

1500°. The A_2-arrest is slightly lowered by increasing proportions of molybdenum. S. Curie observed that the temp. of magnetic transformation on the heating curve is 720° to 730°, and the magnetic properties are regained on the cooling curve at 683° to 689°. H. C. H. Carpenter gave for the critical ranges on the cooling curve of molybdenum steels :

C	Mo	Initial Temp.	Critical ranges		
0·28	0·95	1020°	812°–870°	759°–744°	688°–658°
		1250°	836°–730° ;	617°–573° ;	546°–523°
0·57	9·25	900°	—	768°–724°	688°–618°
		1200°	—	783°–706° ;	592°–385°

Molybdenum is more powerful than tungsten in its action on iron. Less than 1 per cent. of molybdenum causes a widening and an alteration in the character of the critical ranges. Mild quenching in an air-blast caused the complete or almost complete suppression of the critical range. T. Swinden found that for alloys up to 8 per cent. molybdenum, if the initial temp. has not exceeded a certain minimum temp., normal points are obtained in the recalescence curves on cooling, and these are independent of the rate of heating, or time of soaking. The low temp. of recalescence is below the Ac_1-point with 8 per cent. molybdenum low-carbon steels. If the low temp. of recalescence has been exceeded, the normal Ar_1-point is lowered or split, and as the temp. increases, assumes a definite low position. There is in some cases an intermediate zone in which an equilibrium exists between the two points even with fairly slow heating, and a 2 hrs.' soaking. The position of the lowered recalescence temp. is a progressive function of the molybdenum-content, being more easily effected as the proportion of molybdenum increases, but a higher temp. and longer soaking is necessary to produce the full lowering effect. The temp. which first affects the point, and also that which produces the maximum lowering effect, is slightly higher as the carbon-content increases. The low temp. is not disturbed by slow cooling or arrested cooling at about 800° if the steel has been previously heated at 1200°. The recovery of the normal point is effected by repeated heating to below the lowering temp. It is not easily effected by a single slow heating and soaking. The normal Ac_1-point is found on heating, and no new point has been observed corresponding to the lowering temp. The subject was discussed by H. J. French, F. Lepersonne, and G. Burns.

E. Vigouroux obtained **iron tritadimolybdide,** Fe_3Mo_2, as an insoluble residue from alloys with 50 per cent. molybdenum. Its sp. gr. is 9·16 at 0°. It is attacked slowly by chlorine at ordinary temp., and vigorously at 250° ; oxygen, sulphur, and water-vapour react at a red-heat. Soln. of hydrochloric and hydrofluoric acids, as well as gaseous hydrogen chloride, have no appreciable action, but the compound is readily attacked by hot, conc. sulphuric acid, by dil. nitric acid, and by iodine suspended in water. Potassium hydroxide has no action in soln., but reacts readily in the fused condition. As indicated above, this compound was prepared by A. Carnot and E. Goutal ; and W. P. Sykes observed the conditions under which it is formed, Fig. 456. No other compound appears on the thermal diagram, but E. Vigouroux said that **iron hemimolybdide,** Fe_2Mo, of sp. gr. 8·90 at 0°, is obtained by the action of hydrochloric acid on alloys with less than 46·16 per cent. of molybdenum ; iron molybdide, FeMo, of sp. gr. 9·01 at 0°, from 54 to 63 per cent. alloys ; and **iron dimolybdide,** $FeMo_2$, of sp. gr. 9·41 at 0°, from 64 to 77 per cent. alloys. The existence of these three molybdides has not been confirmed. For the cementation of these steels, *vide supra.*

A. Carnot and E. Goutal found that molybdenum steels with 1·7–2·3 per cent. of carbon contained the **iron molybdenum carbide,** $Fe_3C.Mo_2C$. P. Williams prepared the same compound. J. O. Arnold and A. A. Read analyzed the residues obtained by treating molybdenum steels with acid, and found that with the 0·78 C and 2·43 Mo steel, the residue corresponds with 6FeC, Fe_3Mo_3C ; with the 0·75 C and 4·95 Mo steel, $7Fe_3C$, $3Fe_3Mo_3C$, 2C ; with the 0·71 C and 10·15 Mo steel,

Fe_3C, $3Fe_3Mo_3C$, C: with the 0·79 C and 15·46 Mo steel, Fe_3C, $8Fe_3Mo_3C$; and with the 0·82 C and 20·70 Mo steel, Fe_3Mo_3C. F. R. Morral and co-workers, and V. Adelsköld and co-workers observed the formation of the **molybdenum iron tritacarbide,** Fe_3Mo_3C. The observations of H. Lautsch and G. Tammann, and of W. P. Sykes, show that a part of the molybdenum in iron forms only one compound, and the remainder forms mixed crystals with the iron; in the presence of carbon, there may be formed the mixed crystals of iron and molybdenum —*molybdenoferrite*; iron molybdenum carbide; iron tritadimolybdide; and in hardened steels, molybdenum-austenite or martensite in which, with higher proportions of molybdenum, iron molybdenum carbide can be recognized; while, with annealed steels, intermediate forms between martensite and pearlite can also be recognized. L. Guillet found that the pearlitic steels have 0·20 per cent. of carbon and less than 2 per cent. of molybdenum, or 0·80 per cent. of carbon and less than 1 per cent. of molybdenum; and the carbide steels have a double carbide with over 2 per cent. of molybdenum and 0·20 per cent. of carbon, and over 1 per cent. of molybdenum with 0·80 per cent. of carbon. A. M. Portevin supposed that the double carbide is found in steels with over 5 per cent. of molybdenum and 0·2 per cent. of carbon; and with above 2 per cent. of molybdenum and 0·8 per cent. of carbon. H. le Chatelier supposed that the molybdenum is isolated in the mass of the metal as a solid soln.; and O. Boudouard, and C. A. Edwards made a similar assumption with respect to the existence of tungsten in tungsten steels; but measurements of the electrical resistance—*vide infra*—do not favour this hypothesis. C. A. Edwards supposed that the carbon exists as iron carbide. J. S. de Benneville prepared the complex iron **chromium molybdenum carbide,** $Fe_7(Cr_2Mo)_8C_4$, and called it *wahlite*. F. Roll, H. Sawamura, and F. L. Coonan found that molybdenum partly decomposes and partly preserves the cementite in cast iron. J. W. Donaldson studied the action of molybdenum in cast iron.

T. Swinden suggested that the molybdenum occurs in annealed steels as a compound of iron and molybdenum, and not in simple solid soln. When the steel is heated, the Fe_3C goes into soln. at Ac_1, and unless the lowering temp.—*vide supra*—is exceeded, is re-precipitated at the normal Ar_1-temp. on cooling. If the steel be heated beyond the lowering temp., the condition of the molybdenum compound behaves as if it passed into soln. The separation of Fe_3C from this soln. takes place at a lower temp. than the normal Ar_1. The actual temp. depends on the conc. of the molybdenum soln. When the steel has been cooling beyond the lowering temp., and then re-heated, the molybdenum gradually re-assumes its original condition if the temp. does not exceed that producing the lowering. When this change is complete, the normal Ar_1-temp. is regained in the cooling curve. T. Swinden also observed that specimens quenched from 800° contain normal martensite indicating that the carbide is partially soluble at this temp. Molybdenum steels quenched from 1200° are less easily attacked by acid, and in the case of certain steels with the higher proportions of carbon and molybdenum, they show white polyhedra. The structure of specimens heated to 1200°, and quenched at 600°, is essentially the same as that of those quenched at 1200°. Samples which have been air-cooled from 1200° show martensite and troostite, and the proportion of martensite is greater, the greater the proportion of carbon and molybdenum. J. O. Arnold said that a true molybdenum steel is formed when 18·3 per cent. of molybdenum and 0·7 per cent. of carbon are present. The 100 per cent. pearlite then consists of $24Fe+Fe_3Mo_3C$. The subject was discussed by G. W. Sargent, and E. L. Reed.

E. C. Bain discussed the X-radiograms; and E. P. Chartkoff and W. P. Sykes, the changes in the lattice parameters in solid soln. The scleroscopic and Brinell's hardnesses of molybdenum steels, measured by T. Swinden, are indicated in Table LXXVI. The normalized steel was obtained by heating it for 15 minutes at 900°, and free cooling in air. T. Swinden also examined the file hardness of molybdenum steels. W. P. Sykes found that the Brinell hardness of iron increases

Table LXXVI.—The Hardness of Molybdenum Steels.

Percentage composition		Brinell's Hardness						Scleroscopic hardness			
C	Mo	Annealed	Normalized	Hardened and tempered	Quenched 800°	Quenched 1200°	Air-cooled from 1200°	Annealed	Normalized	Hardened	Tempered
0·19	1·03	99	116	241	220	332	143	11	13	33	27
0·44	1·05	131	228	287	387	444	330	13	23	45	37
0·87	1·02	228	302	418	600	—	460	23	32	61	44
1·21	1·09	207	321	512	652	—	477	22	34	61	45
0·25	2·18	116	170	387	217	375	—	15	18	36	35
0·44	2·18	143	217	444	246	444	—	18	21	47	39
0·88	2·19	207	302	512	600	—	—	22	29	62	47
1·21	2·11	196	340	512	652	—	—	22	37	69	48
1·36	2·54	196	332	532	267	—	—	26	35	61	44
0·19	4·11	116	170	286	293	375	—	17	18	31	28
0·49	4·01	143	228	444	351	481	—	18	27	52	43
0·86	4·00	179	321	512	627	—	—	20	34	62	44
1·06	4·02	196	340	532	600	—	—	23	38	68	48
0·13	8·01	143	163	163	156	220	137	16	16	16	15
0·36	8·17	143	196	351	179	460	411	18	25	33	30
0·44	8·11	156	235	444	228	512	430	18	23	40	39
0·77	7·85	170	286	512	477	600	578	20	35	55	42
1·12	7·92	187	340	512	—	—	555	22	40	68	46

continuously with the addition of molybdenum up to about 40 per cent. by weight. The hardness of molybdenum is increased at a more rapid rate by the addition of iron up to about 15 per cent. The hardness of some of the alloys, water-quenched from just below the solidus, is increased by as much as 250 per cent. by ageing at temp. between 600° and 700°. In tempering or ageing at certain given temp. the hardness reaches a maximum and then decreases as ageing is prolonged. The higher the temp. of the ageing above a certain minimum temp., the more rapidly the hardness increases, but the lower is the maximum hardness attained. A shrinkage in vol. occurs during the ageing process, and, in general, its maximum coincides with that of the maximum hardness developed by ageing. The subject was discussed by G. Grube and F. Lieberwirth, and M. Ballay; and E. K. Smith and H. C. Aufderhaar observed that the Brinell's hardness, and tensile strength of cast iron were increased by adding 0 to 3·1 per cent. of molybdenum, but the machinability was decreased. G. Tammann and V. Caglioti discussed the recovery of hardness after cold-work.

Observations on the mechanical properties were made by W. von Lipin, J. K. Smith, R. Helmhacker, P. Marsich, S. B. Ritchie, A. L. Colby, L. Campredon, A. Rys, R. A. Hadfield, H. J. French, W. N. Bratton, K. Taniguchi, J. V. Emmons, E. L. Henderson, J. Cournot and J. Challansonnett, E. C. Clapp and F. C. Devereaux, H. J. French and T. G. Digges, P. Prömper and E. Pohl, F. L. Coonan, E. K. Smith and H. C. Aufderhaar, W. Liestmann and C. Salzmann, E. E. Thum, R. C. Good, A. L. Norbury, E. Kothny, J. H. Küster and C. Pfannenschmidt, I. Musatti and G. Calbiani, C. H. Lorig and F. B. Dahle, K. H. Müller and E. Piwowarsky, J. E. Hurst, E. L. Henderson, W. H. Phillips, A. C. Prulière, E. Piwowarsky, P. Blum, H. Fleck, O. Smalley, A. Campion, A. M. Portevin, and L. Guillet. The subject was summarized by H. W. Gillett and E. L. Mack. According to L. Guillet, the pearlitic steels have a high tensile strength and elastic limit which increases regularly with the percentage of molybdenum; while the elongation and resistance to shock diminish a little, but preserve high values. The carbide steels have a tensile strength and elastic limit which increase with the percentage of molybdenum; the elongation and reduction of area are low; while the brittleness increases with the percentages of carbon and molybdenum. The effect of heat-treatment resembles that with the tungsten steels—*vide infra.* T. Swinden obtained the results indicated in Tables LXXVII and LXXVIII.

TABLE LXXVII.—ELASTIC LIMIT AND TENSILE STRENGTH OF MOLYBDENUM STEEL.

Percentage composition		Elastic limit (tons per sq. in.)				Maximum stress (tons per sq. in.)			
C	Mo	As rolled	Annealed	Normalized	Hardened and tempered	As rolled	Annealed	Normalized	Hardened and tempered
0·19	1·03	22·40	13·90	22·29	21·04	83·52	26·15	30·22	40·24
0·41	1·05	34·40	18·36	37·81	75·28	54·40	35·71	52·44	94·00
0·84	1·02	52·00	26·00	45·77	86·48	80·0	54·05	67·66	107·36
1·27	1·09	—	26·05	52·18	91·04	58·67	42·65	70·96	124·56
0·25	2·18	—	14·10	29·24	51·52	52·5	29·05	40·63	76·40
0·44	2·18	—	19·38	35·67	66·56	67·4	36·73	49·30	94·40
0·88	2·19	57·6	24·45	51·24	79·84	88·8	47·80	71·53	116·44
1·21	2·11	75·6	27·55	63·40	—	96·8	42·50	85·71	120·96
0·19	4·11	33·64	14·05	28·39	29·68	53·2	28·30	38·15	39·36
0·49	4·01	53·6	18·85	36·17	62·40	84·0	34·40	53·51	84·32
0·89	4·00	—	20·50	58·20	91·04	102·8	42·10	47·62	115·20
1·06	4·02	80·32	19·00	60·69	119·20	106·8	41·50	79·85	126·00
0·13	8·01	—	18·60	26·11	24·00	41·2	35·30	36·46	36·64
0·36	8·17	—	15·50	31·46	33·68	66·2	34·40	45·80	47·04
0·44	8·11	68·80	17·25	38·16	34·72	96·0	37·15	52·28	56·88
0·77	7·85	66·56	20·15	41·29	96·86	86·56	39·10	65·42	110·40
1·12	7·92	84·80	21·80	66·37	—	109·60	41·20	90·30	80·0
1·36	2·54	76·80	21·00	—	—	82·24	40·00	53·06	—

TABLE LXXVIII.—ELONGATION AND REDUCTION OF AREA OF MOLYBDENUM STEEL.

Percentage composition		Percentage elongation on 2 ins.				Percentage reduction of area			
C	Mo	As rolled	Annealed	Normalized	Hardened and tempered	As rolled	Annealed	Normalized	Hardened and tempered
0·19	1·03	33·31	35·5	35·5	27·46	64·32	65·75	73·0	68·4
0·41	1·05	19·5	25·0	20·1	14·08	49·23	39·2	49·3	49·2
0·84	1·02	14·4	17·22	13·2	9·15	34·36	22·25	27·9	25·2
1·27	1·09	1·0	5·55	10·9	4·92	2·02	7·5	17·8	12·0
0·25	2·18	21·05	33·3	30·0	15·49	57·0	62·5	64·2	54·4
0·44	2·18	16·7	27·7	23·4	14·08	46·41	44·3	55·5	47·2
0·88	2·19	12·1	18·8	13·8	5·63	32·07	27·5	32·6	12·0
1·21	2·11	7·04	9·4	3·92	—	9·6	13·5	2·84	—
0·19	4·11	21·7	42·7	29·0	30·20	52·71	72·5	63·6	64·0
0·49	4·01	13·5	28·3	22·0	11·26	33·81	52·0	52·9	41·6
0·86	4·00	8·0	20·5	14·5	4·22	17·27	34·0	38·5	4·8
1·06	4·02	10·56	15·5	10·7	7·04	18·40	20·5	22·0	23·2
0·13	8·01	25·7	31·1	29·8	30·9	52·22	58·75	59·5	65·6
0·36	8·17	19·4	36·6	28·4	25·3	45·89	68·23	57·5	54·4
0·44	8·11	19·71	32·22	21·7	21·1	34·00	57·5	39·6	49·2
0·77	7·85	9·85	22·2	15·7	7·74	18·40	35·5	38·9	23·2
1·12	7·92	8·45	16·1	12·77	—	16·40	24·0	16·1	—
1·36	2·54	2·11	17·22	0·4	*nil*	2·4	7·5	1·5	*nil*

The rolled steels are not closely comparable, because of variations of treatment in the mill; but the influence of molybdenum in rendering the steel susceptible to cold-working is clearly shown. The annealed steels diminish in strength and ductility as the molybdenum increases from 1 to 8 per cent. This is very marked with steels having 0·9 per cent. or more carbon. The normalized steels are only slightly influenced by molybdenum. As the proportion of carbon increases, the influence of molybdenum is more marked. It produces an appreciable increase in tenacity with only a slightly reduced ductility. The effect of molybdenum on hardened and tempered steels is very marked, resulting in high tenacity with considerable elasticity. The most promising results are obtained with the series containing 1 and 2 per cent. molybdenum. T. Swinden observed no evidence of the softening of any steels by quenching as reported by L. Guillet for double carbide steels. W. P. Sykes found that the tensile strength, like the hardness, increases with ageing or tempering ; a decrease in ductility accompanies the increase in tensile strength. The development of secondary hardness in these alloys is accompanied by the precipitation of the compound Fe_3Mo_2. The particle-size of the separation remains sub-microscopic until the hardness has passed through its maximum value and has fallen off considerably. C. L. Clark and A. E. White measured the effect of temp. on the tensile strength. T. Swinden found that the bending tests show up the brittleness of the high-carbon annealed bars ; and, in general, they confirm the tensile tests. Molybdenum does not greatly increase the resistance of steels to alternating stresses with any heat-treatment. The annealed series gave fair results with a low percentage of carbon, but poor values with a high proportion of carbon notwithstanding the low tensile values. Crushing tests show that the molybdenum slightly stiffens the steel, but the effect is not marked. W. Giesen found that with molybdenum steel having 0 to 4 per cent. of molybdenum and 0·3 per cent. of carbon, or 0 to 2 per cent. of molybdenum and 0·95 per cent. of carbon, gave results approximating to those furnished by additions of tungsten so far as tensile strength, elastic limit, elongation, hardness, and brittleness, when the ratio of added molybdenum is to tungsten as 1 : 2·225. F. Robin observed that the addition of 1 to 2 per cent. of molybdenum in 0·8 per cent. carbon steels makes the resistance to crushing low, and it is about 5 kgrms. per c.c. at 1100°. The effect of molybdenum on cast iron, etc., was studied by F. L. Coonan, H. M. Boylston, and J. H. Jennings and E. L. Henderson.

T. Takei and T. Murakami observed an abrupt dilation in alloys with less than 2 per cent. of molybdenum ; this is due to the $\alpha \rightleftharpoons \gamma$ change. The dilation is not observed in alloys with over 4 per cent. of molybdenum. In the alloys containing more than 7·5 per cent. of molybdenum quenched at a high temp., an abrupt change at about 700°–720° is observable during heating, the magnitude of the dilation increases with the molybdenum-content. This change may also be attributed to the gradual deposition of the ϵ-phase from the supersaturated α-solid soln. F. Wüst and co-workers found the mean sp. ht. of molybdenum steel between 0° and $\theta°$ up to 1500°, to be $0{\cdot}06162+0{\cdot}0_4 1099\theta$, and the true sp. ht. at $\theta°$, is $0{\cdot}06162+0{\cdot}0_4 2198\theta°$.

According to T. Takei and T. Murakami, no marked change was observed in the effect of temp. on the electrical resistance of annealed specimens of iron-molybdenum alloys, except a slight bending and a break which is attributable to the change in solubility of the ϵ-phase. If, however, the specimens, consisting of the α- and ϵ-phases, are quenched from a high temp. they show an abrupt change in the electrical resistance on heating them at about 700°, and the greater the molybdenum-content, the more conspicuous is the change. This abnormal change corresponds with the deposition of the ϵ-phase, from a supersaturated α-solid soln. According to H. le Chatelier, the electrical resistance of steel is only slightly influenced by the addition of molybdenum, and this is taken to mean that the molybdenum is not dissolved in the iron. Some observations were made by A. M. Portevin ; and T. Swinden obtained the results indicated in Table LXXIX. A. M. Portevin gave 3·4 microhms per cm. cube for the increase in the resistance of iron produced by 1 per cent. of molybdenum. T. Swinden added that the influence of molybdenum on the annealed steels depends on the carbon-content. In the 0·20 per cent. carbon series, there is a slight increase with increasing proportions of molybdenum ; in the

0·45 per cent. carbon series, the resistance is unaffected; and with 0·9 to 1·20 per cent. carbon, there is a distinct decrease. Samples quenched at 800° give a resistance in agreement with the assumption that the carbon is in soln., and the molybdenum not in soln.; but samples quenched at 1200°, indicate that a considerable proportion at least of the molybdenum is in solid soln. G. Tammann and V. Caglioti discussed the recovery of the resistance after cold-work. E. L. Dupuy and A. M. Portevin found the thermoelectric force of molybdenum steel against copper, expressed in millivolts, to be:

C	0·19	0·16	0·14	0·29	0·77	0·81	0·81	per cent.
Mo	0·45	1·00	2·20	4·50	0·50	1·21	1·98	,,
Annealed −80° .	10·00	10·80	10·70	8·60	4·50	4·70	5·20	
Annealed 100° .	8·35	7·70	7·80	6·30	3·00	3·20	4·30	
Hardened −80° .	-	10·00	10·10	(−12·0)	−4·40	—	1·10	
Hardened 100° .	- -	8·00	7·92	3·98	−6·50	—	0·10	

G. Tammann and E. Sotter found that the electrode potentials of the alloys in $0{\cdot}1N\text{-}H_2SO_4$ show that they are electronegative to molybdenum with up to 65 per cent. of that element, and beyond that slightly electropositive.

TABLE LXXIX.—THE ELECTRICAL RESISTANCE OF MOLYBDENUM STEELS.

Percentage composition		Electrical resistance in microhms per cm. cube			
C	Mo	As rolled	Annealed	Normalized	Hardened and tempered
0·195	1·030	14·18	13·48	14·51	14·22
0·445	1·054	17·40	14·77	16·55	16·86
0·869	1·018	21·00	18·55	20·47	20·25
1·215	1·096	23·10	19·54	20·32	21·15
0·246	2·176	18·66	13·55	16·73	17·93
0·442	2·181	20·66	14·97	16·42	19·47
0·883	2·186	22·90	16·13	18·80	20·10
1·210	2·109	24·80	18·47	21·72	20·80
0·190	4·110	20·22	14·95	16·40	19·12
0·487	4·009	24·60	14·89	16·39	19·52
0·865	4·002	25·70	15·53	18·42	19·88
1·060	4·019	27·10	16·92	19·37	19·78
0·135	8·012	25·83	23·70	25·76	25·25
0·361	8·167	19·00	15·32	17·20	18·79
0·445	8·107	28·00	14·38	16·79	19·06
0·775	7·847	27·40	15·38	17·87	19·92
1·125	7·920	22·60	16·13	18·86	19·50
1·360	2·540	31·30	20·13	21·79	22·40

S. Curie found that molybdenum increases the coercive force and residual magnetism of steel, so that molybdenum steels make excellent magnets. These steels lose their magnetic qualities between 700° and 750°, and regain them on cooling at a temp. rather lower than that at which the loss occurs on heating. T. Takei and T. Murakami's observations on the intensity of magnetization in different fields are summarized in Fig. 457. By the addition of molybdenum, the intensity of magnetization is gradually decreased; the amount of decrease is small in the range of alloys consisting of the α-phase alone, whereas in those consisting of the two phases, α and ε, the decrease is conspicuous. For annealed specimens, the intensity of magnetization decreases gradually with the rise of temp., and rapidly at the critical point, which is only slightly lowered by the addition of molybdenum. The change at the critical point decreases in amount as the molybdenum-content increases, up to 50 per cent., owing to the fact that the magnetic α-phase in the specimen decreases and the non-magnetic ε-phase increases. Quenched specimens, with over 6 per cent. of molybdenum, *i.e.* consisting of the two phases

α and ϵ, at room temp., show a higher intensity of magnetization in the heating curve than in the cooling—that is, the intensity of magnetization of the quenched specimen decreases on annealing, the amount of the decrease being much greater on increasing the molybdenum-content and raising the temp. of quenching. This fact may be explained as follows: As mentioned above, in an annealed state the intensity of magnetization of alloys gradually decreases in the case of those consisting of the α-phase alone as the molybdenum content increases, while in alloys consisting of the α- and ϵ-phases the decrease is conspicuous, owing to the increase of the non-magnetic ϵ-phase. If the specimen is quenched from a high temp., the α-phase increases in amount, dissolving the ϵ-phase in supersaturation, and hence, the intensity should be increased, owing to the decrease of the non-magnetic phase. If, however, the specimen is heated, the ϵ-phase is deposited from the supersaturated α-phase, and hence, the intensity should be decreased, owing to the increase of the non-magnetic phase. The amount of deposition is greater, as the molybdenum-content increases and the quenching temp. rises. The intensity of magnetization of these quenched specimens gradually decreases at first with the rise of temp., and an abnormal change, or an increase of the intensity, takes place at a temp. above 700°. The amount of the abnormal change increases as the molybdenum-content increases, and also with rise of quenching temp. From the change of microstructure of the quenched specimen on heating, it is definitely inferred that the abnormal change of magnetization is to be attributed to the deposition of the ϵ-phase—that is, if the quenched specimen is heated to about 800°, the ϵ-phase separates extensively, whereas no change is observable if the heating temp. is less than 650°. Since the magnetic critical point of the α-phase is gradually lowered with the increase of the molybdenum-content, it is probable that the critical point of the supersaturated α-phase would be lower than that in the sat. state, and hence, the subsequent heating of the quenched specimen, or the deposition of the ϵ-phase, should result in the rise of the critical point. Hence, the abnormal change observable on the heating of the quenched specimen may be attributed to the superimposed effect of the following two factors. The decrease in the magnetization begins at the lower temp. in the quenched specimen, owing to the lowering of the critical point. If, however, the deposition of the ϵ-phase occurs, the critical point rises and the magnetization should be increased. When the deposition is completed, the change of the intensity is that of the sat. α-phase and it rapidly falls at the critical point. Besides these changes, there is a small increase in the intensity of magnetization above 100°. This is attributed to the removal of strains acquired during quenching. The magnetic properties of molybdenum steels were studied by T. Takei, E. Gerold, and A. F. Stogoff and W. S. Messkin; and the effect of cold-work on the magnetic properties—*vide supra*, iron—by W. S. Messkin.

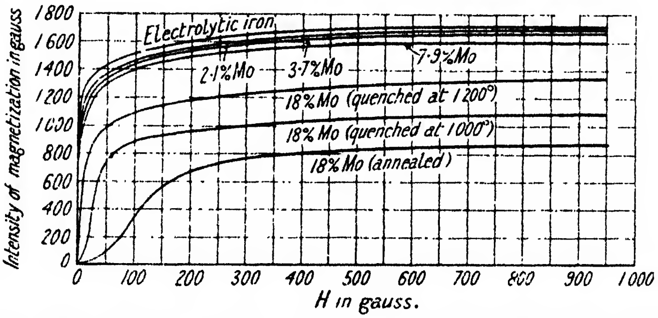


FIG. 457.—The Intensity of Magnetization of the Iron-Molybdenum Alloys in Different Magnetic Fields.

E. Martin studied the absorption of hydrogen and nitrogen by molybdenum steels. J. A. N. Friend and C. W. Marshall tested the effect of molybdenum on the corrodibility of steel, and concluded that (i) molybdenum up to 4 per cent. does not exert any marked influence on the corrodibility of steel by tap-water, salt soln., and dil. sulphuric acid. The results with 0·5 per cent. sulphuric acid are nearly the same as the mean of those with other corroding agents. The resistance of steel to corrosion by alternate wetting and drying, increases with the percentage of carbon, but increasing the proportion of molybdenum increases the corrosion. Hence, the presence of over 1 per cent. of molybdenum is undesirable where steels have to resist corrosion. L. Aitchison found that the addition of molybdenum to carbon steel results in a definite increase in corrodibility by tap-water, 3 per cent. sodium chloride soln., and 1 and 10 per cent. sulphuric acid, until a high proportion of molybdenum—approximately 15 per cent.—has been added. W. A. Dew and H. S. Taylor studied the adsorption of ammonia in the alloy; and S. Satoh studied the nitridization of these steels by heating them in ammonia at 560° to 580°. The corrosion of the alloys was studied by G. Tammann and E. Sotter, H. J. French, C. Duisberg, W. Oertel and K. Würth, W. Guertler and T. Liepus, F. Lieberwirth, and J. S. de Benneville. H. Endo, Fig. 459, found for the losses, in grams per sq. cm., during 5 hrs.' action, at ordinary temp., with alloys containing 0·27 to 0·34 per cent. of carbon, and

Molybdenum .	2·05	3·06	5·10	8·51	13·25	17·02	25·08	31·49%.
Loss H_2SO_4 .	0·00564	0·00449	0·00295	0·00190	0·00232	0·00289	0·00223	0·00324
Loss HCl .	—	0·00114	0·00062	0·00048	0·00035	0·00070	0·00047	0·00032
Loss HNO_3 .	0·07891	0·07652	0·06317	0·06200	0·05785	0·05622	0·02775	0·02033

G. Grube and F. Lieberwirth's values for the number of milligrams of iron (dotted lines, Fig. 458), and of molybdenum (continuous lines) dissolved per sq. mm. in 24 hrs., at 20°, by 0·1*N*-HCl and 0·1*N*-H_2SO_4 per sq. cm. of surface, are summarized in Fig. 458. J. G. Thompson and co-workers studied the action of aq. soln. of urea and of ammonium carbonate. M. Wiessner studied some **copper-molybdenum-iron alloys**; R. Scherer, some **tungsten-vanadium-iron alloys**; F. T. Sisco and D. M. Warner, M. Baer, K. F. Starodubоff and F. M. Gorbacheva, H. Franz, K. H. Müller and E. Piwowarsky, A. C. Prulière, W. Rohn, and C. F. Würth, the **chromium-molybdenum-iron alloys**; W. H. Cunningham and J. S. Ashbury, **aluminium-chromium-molybdenum-iron alloys**; W. Guertler and T. Liepus studied the corrodibility of the **iron-molybdenum-vanadium alloys** (52 : 20 : 28); and W. Kahlbaum and L. Jordan, **vanadium-chromium-molybdenum-iron alloys**; A. Rys, H. J. French, and J. S. de Benneville prepared some molybdenum-chromium steels, and the corrodibility of the iron-chromium-molybdenum alloys was studied by H. C. Cross, C. N. Dawe, T. G. Digges, H. J. French and W. A. Tucker, M. A. Grossmann, W. Guertler and T. Liepus, W. Oertel and K. Würth, E. W. Pierce, V. and G. Prever, H. B. Pulsifer and O. V. Greene, and C. F. Würth. T. L. Robinson investigated the endurance qualities of these steels; and M. Okochi and co-workers found erosion to be severe in guns made from molybdenum steel.

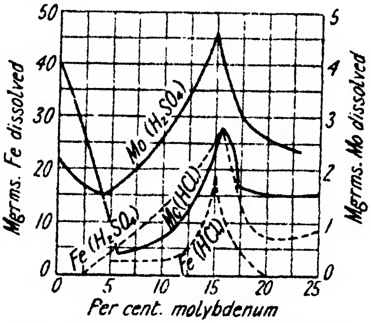


FIG. 458.—The Solubility of Iron-Molybdenum Alloys in Acids.

J. J. and F. de Elhuyar [26] prepared a dense, greyish-white, hard, **iron-tungsten alloy**, or *ferrotungsten*, in 1783; nearly half a century later, P. Berthier obtained an alloy approximating Fe_6W, which he said is a whiter grey colour than iron; is brilliant, hard, and more brittle than cast iron; has a lamellar structure, and contains bubbles or pores. H. de Luynes prepared various kinds of damasked steel with up to 1 per cent. tungsten. According to L. Gruner, M. Koeller and J. Jacob first prepared tungsten steel about 1855; and about this time, too, F. Mayr obtained tungsten steel on a commercial scale. In 1857, R. Oxland obtained ferrotungsten by heating wolframite with charcoal in a closed crucible; and adding the resulting powder of tungsten, iron, manganese, and carbon to molten iron or steel. In 1857–59, R. F. Mushet prepared ferrotungsten which he employed for making tungsten steels; and in 1860, A. Delvaux de Fenffe described the use of tungsten *par l'amélioration de l'acier et de la fonte de fer.* In 1860, M. Siewert, and F. A. Bernoulli described the properties of a number of tungsten alloys; and, in 1867–69, P. le Guen reported attempts made to use tungsten steel rails. Observations were reported by T. Kellermann, R. Volkmann, F. Kick, R. N. Riddle, J. E. T. Woods and J. Clark, and H. A. Levallois. In 1886, G. Heppe emphasized the need for studying the tungsten steels. He said that improved rails, railway axles, and cutting tools can be obtained by adding a small proportion of tungsten to steel. V. Leepin, in 1897, examined some mechanical properties of tungsten steels. The manufacture was described by G. Surr, C. R. Schröder, J. B. Nau, K. P. Grigorovitch, G. T. Holloway, W. Heym, G. and E. Stig, W. Borchers and R. W. Stimson, F. C. A. H. Lantsberry, E. C. Bain and Z. Jeffries, M. A. Grossmann, J. W. Weitzenkorn, H. K. Ogilvie, A. H. d'Arcambal, S. S. Steinberg, F. Peters, J. K. Smith, G. A. Meerson, H. W. Hutchin, R. C. McKenna, R. M. Keeney, J. W. Richards, J. Escard, C. McKnight, F. M. Becket, R. Cazaud, H. G. Batcheller and J. O. Kelley, W. H. Wahl, J. Castner, P. Girod, P. Oberhoffer, O. J. Steinhart, E. Vigouroux, P. Müller, W. Venator, A. Haenig, W. Giesen, J. Percy, P. Nicolardot, and R. A Hadfield; and the general uses and properties of the alloys were described by J. Ohly, W. Guertler, A. C. Ross, H. Alterthum, H. Behrens and A. R. van Linge, and E. Lievenie.

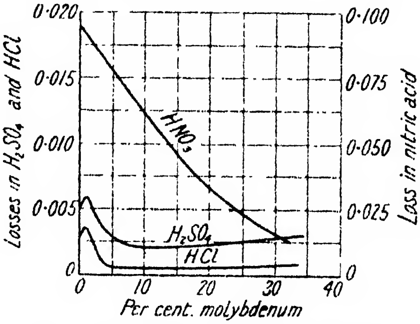


FIG. 459.—The Corrosion of Molybdenum Steels by Acids.

J. Laissus, G. Grube, G. Grube and K. Schneider, N. Ageeff and M. Zamotorin, and W. Geiss and J. A. M. van Liempt discussed the diffusion of tungsten in iron. H. List said that the two metals do not form true alloys. The preparation of ferrotungsten has been discussed in connection with the preparation of tungsten. Portions of the equilibrium diagram were studied by H. Harkort, who obtained alloys by melting ferrotungsten and iron in magnesia crucibles. He found that the temp. of the transformation of α-iron into β-iron was not influenced by the addition of tungsten; but the temp. of the transformation of β-iron to γ-iron rises rapidly from 871° for iron to 933° for an alloy with 10 per cent. of tungsten. Solid soln. were formed, and evidence was obtained of the separation of a compound of iron and tungsten from solid alloys rich in tungsten; the compound being in soln. when the alloys are quenched from a high temp. G. Grube and K. Schneider found that the diffusion coeff. of tungsten in iron at 1280°, 1330°, and 1440° are respectively $3{\cdot}2\times10^{-6}$, 21×10^{-5}, and 26×10^{-5} per sq. cm. per day. D. Kremer made some observations on the solid soln. of tungsten in iron, and of iron in tungsten. K. Bornemann constructed a hypothetical diagram based largely on H. Harkort's observations; and K. Honda and T. Murakami proposed a possible equilibrium diagram based largely on a microscopical study of the alloys. This was discussed by A. Hultgren, and modified by S. Ozawa. The modified diagram is shown in Fig. 460, where it is assumed that **iron hemitungstide,** Fe_2W, is formed in accord with the suggestion of K. Honda and T. Murakami, and H. Harkort. With up to about 10 per cent. of tungsten, the f.p. is raised a little and then gradually lowered. The alloy with 33 per cent. of tungsten freezes at 1510°. The solubility curve of tungstide in ferrite is connected with the A_3-transformation, and at ordinary temp., it corresponds with about 9 per cent. tungsten. A. M. Portevin obtained a lower value for the solubility. The A_2-transformation point, at 790°, is not affected by the tungsten. The line is dotted in Fig. 460 because it does not represent a change of phase. W. P. Sykes found rather different results; they are summarized in Fig. 461. Iron holds about 33 per cent. of tungsten in solid soln. at 1525°, and about 8 per cent. at 600°. The 33 per cent. alloy melts about 10° below the m.p. of iron. An alloy with 33 per cent. or less of tungsten contains large polyhedral grains of the solid soln., and if cooled very slowly, another phase is formed. This same phase appears if this alloy be heated for some time near 1200°; it appears scattered through the solid soln.; and it is probably **iron tritaditungstide,** Fe_3W_2. H. Harkort represented this compound as a hemitungstide, Fe_2W–*vide supra*. The curve *BG* represents the solubility of tungsten or the tritaditungstide. When the tungsten exceeds 33 per cent., this tungstide appears in specimens quenched from the solidus; the alloy with 49 to 51 per cent. iron appears to be the eutectic, of f.p. 1525° to 1527°. Long needles of the tungstide are formed in an excess of solid soln. with alloys having 33 to 49 per cent. of tungsten. With higher proportions of tungsten, there is a rapid rise in the liquidus, so that an alloy with 55 per cent. of tungsten did not fuse until 1600°. The compound can be formed by heating the alloy for, say, 20 hrs. at 1550°–1575°. As the compound forms in the solid soln., there is a considerable shrinkage which makes the alloy more or less porous. If the compound be heated to 1650° or over, it is decomposed. The 62 per cent. alloy is not magnetic after heating for 30 hrs. at 1550°. The solubility of iron in tungsten at 1600° is about 1·20 per cent. The critical point Ar_4 is lowered from 1400° to 1200°, and Ar_3 raised from 890° to 980° by the addition of 5·5 per cent. of tungsten. F. Stäblein said that the A_3-transformation cannot be detected when over 5 per cent. of tungsten is present. S. Takeda found an ϵ-phase corresponding with W. P. Sykes' tritaditungstide; the eutectic of the ϵ- and δ-phases lies at 33 per cent. of tungsten; and the peritectic reaction in which the ϵ-phase is formed occurs with alloys having over 43 per cent. of tungsten, as in S. Ozawa's diagram. Indications of a phase *x* were obtained; it may be formed pericectically from the melt and tungsten or a ζ-phase. T. Murakami and S. Takeda studied the formation of ferrite in tungsten steels. According to H. Harkort, as the tungsten-content increases, there is a corresponding decrease in the amount of γ-iron, *i.e.* the face-centred cubic iron; and when the proportion of tungsten exceeds 6 per cent., only the body-centred cubic lattice is present at any temp. S. L. Hoyt, and N. H. Aall studied this subject.

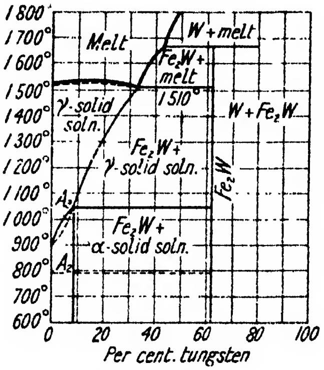


FIG. 460.—Equilibrium Diagram of the Iron-Tungsten Alloys.

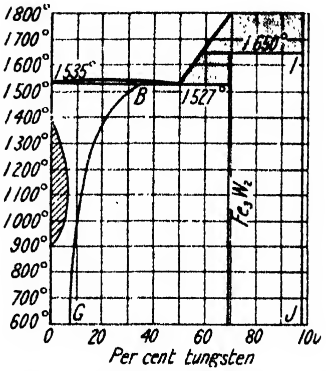


FIG. 461.—Equilibrium Diagram of the Iron-Tungsten Alloys.

A. Carnot and E. Goutal found that when **tungsten** steels are treated with dil. acids, there remains undissolved **iron tritatungstide,** Fe_3W. This same compound was assumed by T. Swinden to occur in the **tungsten steels.** J. O. Arnold and A. A. Read supposed that iron hemitungstide, Fe_2W, occurs in steels, and this compound was assumed by K. Honda and T. Murakami, and S. Ozawa to be formed—Fig. 461. H. Behrens and A. R. van Linge found octahedral crystals of Fe_2W in ferrotungsten. T. Poleck and B. Grützner observed trigonal, hard, silver-grey prisms of **iron ditungstide,** FeW_2, were formed in the crevices of a lump of iron-tungsten alloy derived from Bohemian wolframite. E. Vigouroux obtained iron tritaditungstide, Fe_3W_2, as a residue when dil. hydrochloric acid acts on tungsten steel; and W. P. Sykes' diagram, Fig. 461, shows the conditions under which it can exist in the steel. E. Vigouroux said that the compound forms brilliant plates of sp. gr. 13·89 at 0°; it is not attracted by a magnet; it is readily attacked by chlorine at 350°; by oxygen, or the alkali carbonates at a bright red-heat; by potassium hydrosulphate at a dull red-heat; while aqua regia, sulphuric acid, and fused potassium chlorate have very little action. J. S. de Benneville, E. Vigouroux, and P. Berthier reported products corresponding with Fe_4W, Fe_5W, and Fe_6W, but there is nothing to show that they are chemical individuals. The subject was discussed by N. H. Aall, and W. Zieler.

E. C. Bain's X-radiograms of the ferrotungstens corresponded with hexagonal carbide, FeW. H. Arnfeldt observed at least two intermediate phases in the ferrotungstens. One of them has a hexagonal structure, and when it is in equilibrium with the iron phase its lattice is defined by the parameters $a=4·727$ A. and $c=7·704$ A.; $c/a=1·630$. Its composition corresponds to the formula Fe_2W. There are four groups of Fe_2W in the unit cell. It seems to be unstable at higher temp., and has a decomposition temp. lying between 1000° and 1150°. Another intermediate iron-tungsten phase has a trigonal lattice with the parameters $a=4·731$ A. and $c=25·76$ A.; $c/a=5·44$. The unit cell probably contains 40 atoms. Crystals of this phase have been isolated and they have a composition corresponding with Fe_3W_2. A. Carnot and E. Goutal found that when dil. hydrochloric acid acts on tungsten steels with 2·0 to 2·2 per cent. of carbon, and 6·6 to 7·8 per cent. of tungsten, in the absence of air, there is formed **iron tungsten carbide,** $Fe_3C.WC$; and P. Williams obtained the complex carbide, $2Fe_3C.3W_2C$, by heating tungsten carbide and iron in an electric furnace. The crystalline powder is magnetic, and has at 18° a sp. gr. 13·4. It is attacked by fused potassium hydroxide, and is insoluble in cold, conc. hydrochloric acid. A. Westgren and G. Phragmen found octahedral crystals of Fe_4W_2C in ferrotungsten; and F. R. Morral and co-workers, and V. Adelsköld and co-workers observed the formation of **tungsten iron tritacarbide,** Fe_3W_3C. W. Zieler, and F. Rapatz studied these carbides. J. O. Arnold and A. A. Read assumed that tungsten steels contained the complex carbide, $Fe_3C.WC$. W. A. Wood and co-workers found that the X-radiograms indicated the presence of tungsten carbide and of the complex carbide, Fe_4W_2C, but no cementite. S. Ozawa observed no evidences of this in his study of the ternary system. L. Guillet, K. Däves, and P. Oberhoffer and K. Däves studied the solubility curve of tungsten in the iron-carbon alloys. A. Hultgren assumed that the complex carbides, FeWC, and Fe_2W_2C, can exist in the system. The latter is stable in the presence of a moderate proportion of carbon, while the former is easily decomposed into the carbide, WC, and austenite. Low-carbon steels are supposed to contain Fe_nW. Cementite is supposed to dissolve a certain amount of the carbide, WC, and the carbide W_3C is supposed to exist only in the tungsten-carbon alloy, but not in tungsten steels. Sudden changes in the physical properties of tungsten steels are correlated with changes of composition involving the passage from one side to the other of this limiting curve. The appearance of so-called double carbides of iron and chromium or of iron and tungsten, observed by different workers, is attributed to the same cause. Small amounts of tungsten in steel raise the melting-point, but larger amounts depress it. For the cementation of these steels, *vide supra,* observations. The subject was studied by S. Takeda, E. Houdremont and co-workers, and E. L. Reed. J. S. de Benneville prepared the complex **iron chromium tungsten carbide,** $Fe_7(Cr,W)_6C_4$, and called it *garrisonite.*

O. Böhler concluded that tungsten lowers the m.p. of iron. S. Ozawa, and S. Takeda studied the thermal changes of the ternary system. Tungsten affects the position of the recalescence points of steel as indicated by W. P. Sykes in connection with the equilibrium diagram, Fig. 461. F. Osmond observed that with steels carrying up to 1·53 per cent. of tungsten, and up to 0·13 per cent. of carbon, the positions of the Ar_3- and Ar_2-points remain normal; while Ar_1 is lowered as the tungsten increases, provided the steel has been heated to a sufficiently high temp. He therefore concluded that tungsten has no appreciable action on the allotropic changes of iron, but it causes the carbon change to occur at a lower temp. than the normal one. J. O. Arnold found that with a steel carrying 0·08 per cent. of carbon and 1·41 per cent. of tungsten, the Ac_3-point was absent, Ac_2 occurred at 729°, and Ac_1 was absent; and on cooling from 1150°, Ar_3 was faint at 834°—a little below its normal position; Ar_2 occurred at 729°; and Ar_1 at 590°—about 50° below normal. F. Osmond then noted that with steels having 0·13 to 0·46 per cent. of carbon, and 0·20 to 8·33 per cent. of tungsten—manganese about 0·25 per cent.—that if the initial temp. is not above 850°, the curve resembles that with steels having no tungsten; if the initial temp. exceeds 1040°, the Ar_1-point is sharply lowered, while the Ar_3- and Ar_2-points do not move; if the initial temp. is 1300°, Ar_3 and Ar_2 are lowered in turn, and tend to rejoin Ar_1; while under certain conditions, Ar_1 divides into two portions. O. Böhler found that a steel with 0·85C, and 7·78W had two critical points—about 700° and 550°. The former was visible if the initial temp. did not exceed 1100°, and the latter appeared only if 1000° was passed. Both critical points appeared in the interval, and both were said to correspond with the formation of pearlite. The tungsten facilitates this duplication of the points, and as the proportion of tungsten increases, a higher initial temp. is needed for the doubling, and at the same time, the temp. of the second recalescence point is lowered. In high-speed steels, the chromium and tungsten were said to lower the second recalescence point below ordinary temp., and thus the softening of the metal due to the formation of pearlite is avoided. H. Pommerenke and R. Deivert, H. Scott, P. Dejean, E. Maurer and W. Haufe, W. Zieler, and A. Merz discussed this subject. F. Osmond showed that with hypereutectoid or supersaturated steels, both tungsten and chromium impede during cooling the segregation of the cementite to such a degree that the rate of cooling can be neglected. The transformation points are lowered during cooling, even slow cooling, more and more as the original content is raised above that of the eutectoid. If the lowering is sufficient, the transformations remain more or less incomplete, and quenching is no longer necessary. The proportion of carbon dissolved is then a function of the temp. of heating and indirectly of the chemical composition. The homogeneous distribution of the carbon, however, is not instantaneous—the dissolution on heating and its segregation on cooling are difficult. If the temp. is not high enough, areas of unequal carburization are produced, and if cooling then commences, each fraction acts as if it were alone, and has a recalescence temp. dependent on the carbon-content, so that the recalescence temp. may appear doubled; and the result is dependent on the initial temp. H. Scott found that tungsten has but a slight effect on the temp. of the transformation of martensite to troostite. H. Sawamura, and F. Roll observed that tungsten promotes the graphitization of cast iron.

H. C. H. Carpenter found that when a steel containing 0·63C and 0·94W is cooled from 1000°, the ranges occur in their normal positions, but when cooled from 1250°, there is a slight lowering of Ar_1 to 664°, and there is a prolonged range from 801° to 706°. The alloy is restored to its original state at 1000°. The heating curve is also dependent on the free-heating for it shows the lower range from 696° to 716° only after being heated to 1250°. When a steel with 0·63C and 10·56W is cooled from 1207°, the beginning of the critical range is not lowered, but the lower limit drops about 260°. The upper range, $Ar_{2,3}$, is quite distinct. The drop in temp. occurs only with the lower limit, thus widening the range. The results are the same whether the alloy be cooled at once from the given temp., or after soaking for a long time at that temp., showing that not many minutes are necessary for equilibrium to be attained. Fairly wide differences in the rate of cooling gave similar results. H. C. H. Carpenter concluded that the action of tungsten or molybdenum consists in hindering or preventing changes in the iron-carbon alloys which result in the softening of the material. Air-quenched high-speed alloys consist almost entirely of white polyhedra resembling austenite. T. Swinden found that below a certain initial " lowering temp.," all the steels examined have the same critical points as carbon steels. In steels below 0·35 per cent. carbon, heating beyond this initial temp. lowers Ar_1 to a definite low point; Ar_2 is practically unaffected; and Ar_3 is gradually suppressed in its normal position, but appears again below Ar_2 forming the upper maximum of the low point. With between 0·35 and 0·9 per cent. carbon, Ar_1 is first lowered, and then increased; heating displaces $Ar_{3,2}$ towards Ar_1; beyond 0·9 per cent. carbon, the $Ar_{3,2,1}$-point is lowered as a whole by heating beyond the lowering temp., and produces a single low point. As the carbon increases, a higher initial temp. is needed for the critical lowering to be effected. The low point is practically constant at 570° for 3 per cent. tungsten steels. The rate of cooling does not affect the position of the low point after lowering has once taken place. The range of the recalescence is not merely widened, but the critical point is at a distinctly lower temp. At Ac_1, on heating, a change of a similar nature to the carbon change occurs; and at the critical lowering temp., a further change in constitution occurs, the reverse of which is at the low point. No recalescence occurs at the critical lowering temp. The microstructure, cooling curves, and hardness of the tungsten steels confirm these conclusions, and indicate that the critical lowering temp. marks a definite reaction in which the tungsten is involved.

As a working hypothesis, H. C. H. Carpenter attributed the low point in tungsten steels to a special carbide containing iron, and either tungsten or manganese, or both; and C. A. Edwards concluded that the low point is not the Ar_1 or the iron carbide change depressed by tungsten, but is due to the slow formation at 1200° of a tungsten carbide which has a critical temp. quite independent of Ar_1. T. Swinden concluded that the similarity in the form of the cooling curve from 1200° to the curve from 900°, the maximum intensity of the low point at 0·9 per cent. carbon, and the general evidence of the microstructures indicate that the low point is not due to the deposition of a tungsten carbide or of a double or triple carbide. The low temp. change in the 3 per cent. tungsten steels is really a separation of cementite from decomposing martensite. It is assumed that iron tungstide, Fe_3W, is formed in the mass and thus passes into soln. at the lowering temp., and the carbide, Fe_3C, is dissolved in this soln. The iron tungstide does not separate until the low point is reached, and the carbide, Fe_3C, immediately follows. The increased electrical resistance beyond the lowering temp. is due to the increase in the proportion of dissolved impurity. S. N. Brayshaw discussed the range of the Ac_1-arrest; and W. Eilender and co-workers, the temper hardness.

L. Guillet found that tungsten steels with 0·20 per cent. of carbon are pearlitic with less than 9 per cent. of tungsten, and show carbide formation with over that proportion of tungsten; while the steels with 0·80 per cent. carbon are pearlitic with less than 4·5 per cent. of tungsten and show carbide formation with over that proportion of tungsten. Quenching exerts the same effect on pearlitic steels as it does on ordinary carbon steels, but the difference which exists between the properties of the steel as annealed, and as quenched, is the more marked as the proportion of tungsten becomes greater. Quenching at 850° produces in steels containing a double carbide an exceedingly fine martensitic structure, and leaves a portion of the carbide undissolved, if the percentages of carbon and tungsten are fairly high. The higher the quenching temp. above 850°, the lower the proportion of carbide remaining unaltered by quenching. Quenching raises the tensile strength, elastic limit, and hardness. Steels containing the double carbide are superficially affected by liquid air-quenching; somewhat coarse needles of martensite are formed when the steel is heated to near 100° and subsequently cooled in air. Annealing slightly softens all tungsten steels, and furthers the formation of grains of carbide. By suitably case-hardening a pearlitic tungsten steel, it is possible to cause the double carbide to appear even when the percentage of carbon in the outer layer is below 0·85 per cent. J. O. Arnold said that a true tungsten steel is formed, with 100 per cent. pearlite, when 11·3 per cent. of tungsten and 0·72 per cent. carbon are present. The pearlite consists of 26Fe+WC. J. P. Gill and L. D. Bowman, P. Oberhoffer and K. Däves, and K. Däves studied the structure of these steels.

R. A. Hadfield observed that the fracture of cast, and of forged, unannealed pieces with a low content of carbon up to 0·20 per cent. changes when about 1·49 per cent. of tungsten has been added, when it becomes finely crystalline. The fine grain increases with increasing proportions of carbon and tungsten, so that when the carbon exceeds about 1 per cent., the fracture becomes silky, and this peculiar fracture is not possessed to the same degree, if at all, by other steels. The molten metal is only slightly less fluid than ordinary steel. The malleability when hot is fairly good, but not equal to that of ordinary commercial steel, and some difficulty was experienced in forging some of the bars with a rather low proportion of manganese. The presence of tungsten—as well as of manganese, chromium, silicon, aluminium, and nickel—in an iron alloy greatly hinders or prohibits the welding of the metal. C. F. Burgess and J. Aston discussed the working properties of the iron-tungsten alloys.

A. Westgren and A. Almin calculated from the X-radiogram data that the vol. per atom of alloys of iron and the contraction are as follow:

Tungsten . . .	0	13·3	40	100 atom per cent.
Volume per atom . .	11·70	12·42	12·48	15·45 A³.
Contraction . . .	—	4·3	5·5	—

A. Osawa and S. Takeda studied the X-radiograms of the alloys and their carbides. Z. Nishiyama found the lattice parameter, *a*; the sp. gr.; and the elastic modulus, *E* kgrms. per sq. cm., at 13·6° to 15·6°, to be:

W . .	1	2	3	4	5	6	7	7 per cent.
a . .	2·861	2·866	2·866	2·866	2·868	2·863	2·869	2·869 A.
Sp. gr. .	7·9112	7·9577	7·9895	8·0430	8·1005	8·1008	8·1495	8·2119
$E\times10^{-6}$.	2·164	2·157	2·153	2·174	2·101	2·134	2·085	2·150

—*vide infra.* E. C. Bain, and E. P. Chartkoff and W. P. Sykes measured the lattice parameters of the solid soln. R. A. Hadfield found the sp. gr. of an alloy with 0·15 C and 0·20 W to be 7·676; with 0·21 C and 1·49 W, 7·683; with 0·28 C and 3·40 W, 7·792; with 0·46 C and 8·33 W, 8·109; and with 0·78 C and 16·18 W, 8·602. W. Brown found with 0·16 C, 0·11 Mn, and 1·0 W, the sp. gr. and sp. vol. were respectively 7·9365 and 0·12600; with 0·28 C, 0·28 Mn, and 3·5 W, 8·0645 and 0·12400; with 0·38 C, 0·20 Mn, and 7·5 W, 8·2918 and 0·12060; and with 0·76 C, 0·28 Mn, and 15·5 W, 8·7720 and 0·11400. With up to 15 per cent. of tungsten, therefore, the sp. vol. decreases by 0·0009 c.c. per 1 per cent. of tungsten. A. S. Townsend found the sp. gr. of tungsten steels to vary with the proportion of contained tungsten in the following manner:

Sp. gr. .	8·60	8·63	8·66	8·69	8·72	8·75	8·78	8·80
W . .	15·92	16·53	17·14	17·76	18·37	18·98	19·59	20·00 per cent.

with an error of ±0·30 per cent. F. Stäblein found that the sp. gr. of the tungsten-iron alloys increases by 0·048 for every 1 per cent. of added tungsten. C. Benedicks and co-workers, J. O. Arnold, and B. Simmersbach made some observations on this subject. C. Benedicks studied the sp, vol.

R. A. Hadfield made some observations on the hardness of tungsten steels quenched from 750°, 950°, and 1200° in cold water. Observations were also made by C. A. Edwards, W. Zieler, O. Böhler, H. Scott, G. Mars, K. Taniguchi, etc. W. P. Sykes observed that Brinell's hardness increases continuously with the addition of up to about 50 per cent. of tungsten. The hardness of some alloys when water-quenched from 1500° is increased as much as 130 per cent. by annealing at 600°–700°. In the annealing at a given temp., a maximum hardness is attained, and this decreases as the annealing is prolonged. The higher the temp. of annealing above a certain minimum temp., the more rapidly the hardness increases, but the lower the temp. at which maximum hardness is attained. The development of the secondary hardness is accompanied by the separation of iron tritaditungstide. *Vide infra*, Table LXXXII, for some data. F. Osmond observed that a steel with 0·48 C and 6·0 W, remained soft when slowly cooled from a white-heat, and had an arrest between 505° and 485°, but when heated at 555°, it became glass-hard. L. Guillet found that with pearlitic steels, the hardness increases rapidly as the proportion of tungsten is raised; and with the carbide steels, the hardness increases as the proportion of carbon is raised. No self-hardening was observed, but T. Swinden observed that self-hardening occurred with a 3 per cent. tungsten steel, and a high initial temp. S. N. Brayshaw found that a 1·19 C and 0·57 W steel, when quenched from 731°, which is below the hardening temp. 738°, did not increase in hardness, but other steels heated above the hardening temp. for 10 mins., and then kept from 30 to 240 mins. below the hardening temp. and quenched in water, were hardened. Thus, with the first heating at 760°, and the second at 731° for 30, 120, and 240 mins., the Brinell's hardnesses were respectively 600, 477, and 241, and the scleroscopic hardnesses respectively 103, 88, and 53; again, with the first heating at 890°, and the second at 725°, for 30, 120, and 240 mins., the Brinell's hardnesses were respectively 418, 207, and 187; and the scleroscopic hardnesses respectively 82, 51, and 38. The transformation from the hard to the soft state is completed within a range of six degrees of the hardening temp.; the hardening temp. is represented by an arrest on the heating curve; if the quenching temp. is over 20° or 30° above the hardening temp., the steel becomes softer. E. G. Herbert, W. P. Sykes and A. C. Ellsworth, H. B. Pulsifer, and L. Grenet discussed the hardening of these steels. G. Tammann and V. Caglioti discussed the recovery of the hardness after cold-work. E. C. Bain and Z. Jeffries suggested the following explanation of the red-hardness of these steels:

> The changes which cause the martensite in carbon steel to soften are grain-growth of the ferrite and growth of the carbide particles above critical size. Similar changes in high-speed steel take place only at a red-heat. The outstanding reasons for the retention at red-heat of fine grains in the ferrite of high-speed steel are the increased resistance to growth, due to the elements in atomic dispersion in the ferrite and the copious presence of obstructing carbide particles. The reason for retention at red-heat of carbide particles of critical size is the great stability of the iron-tungsten carbide and the large size of the tungsten atom. The great stability of this double carbide favours its formation to the exclusion or elimination of other carbides when the necessary atoms are available. The large size of the tungsten atom prevents its diffusion in the ferrite space-lattice until a temperature corresponding to a red-heat is reached. The double carbide is an intermetallic compound, which owes its existence entirely to crystallization. The formation of a particle of this carbide, therefore, requires a number of tungsten atoms, which must be supplied by diffusion through the ferrite lattice. The precipitation and growth of the double carbide in quenched high-speed steel at a dull red-heat is, therefore, somewhat comparable to the precipitation and growth of cementite in quenched carbon steel below 300°.

A. M. Portevin found that the hardness of tungsten steel increases with the quenching temp., and with the time of heating at this temp. Thus:

Per cent.		Minutes heated	Hardness when quenched from			Hardness when annealed
Carbon	Tungsten		800°	950°	1050°	
0·09	5·30	2	216	263	—	158
		30	284	289	—	
0·06	13·54	2	192	183	291	180
		30	212	200	315	
0·70	10·29	2	260	501	—	223
		30	473	600	—	
0·66	15·03	2	414	664	766	265
		30	670	695	--	

—*vide infra*, magnetization. The so-called *tungsten carbide steels*, produced by the cementation of tungsten steels, are valued for their hardness. They were discussed by R. D. Prosser, L. L. Wyman and F. C. Kelley, C. M. Thompson, C. Sellers, T. G. Digges, M. Nakamura, and J. L. Gregg and C. W. Küttner.

In his experiments on the effect of alloying different metals with steel, R. F. Mushet, about 1868, observed that while ordinary steel is hardened by abrupt cooling from a red-heat, as it is quenched in water, some bars of steel alloyed with tungsten seemed to have the property of becoming hard after heating, without the usual quenching. Indeed, the unquenched tungsten steel was harder without the usual quenching than ordinary steel which had been quenched. Hence, R. F. Mushet investigated this alloy with the idea of producing a superior tool steel which could be employed for cutting at speeds above those at which ordinary steel tools become overheated by friction near the cutting edge, with a consequent drawing of the temper, the rubbing away of the edge, and the ruin of the tool. It was soon found that the cooling of the bars of the tungsten steel exposed in a draught of air gave a better steel than if cooled where there was no draught; and still better results were obtained by cooling the metal in an air-blast. The composition of one of R. F. Mushet's steels is C, 2·0; W, 5·0; Cr, 0·5; Mn, 2·5; and Si, 1·3 per cent., and a steel of this character is sometimes known as a **Mushet steel.** The steels were then called **self-hardening steels,** and also **air-hardening steels.** M. A. Grossmann and E. C. Bain, and D. M. Giltinan discussed the history of these steels. O. M. Becker gives the following for the percentage composition of self-hardening steels:

	C	W	Cr	Mn	Si	P	S
High .	2·4	11·6	3·4	3·5	1·04	0·080	0·050
Low .	1·1	4·5	0·07	0·08	0·16	0·016	0·004
Mean .	1·8	7·3	1·6	1·8	0·56	0·032	0·015

One sample was reported with 4·58 per cent. molybdenum. The excellence of the steel is dependent on the care exercised in subjecting it to the required heat-treatment when it is being prepared. F. W. Taylor, and others observed that the capacity of these self-hardening steels for cutting at high speeds is considerably enhanced when subjected to a heat-treatment at temp. which would ruin ordinary steels. The superheated steels, in fact, stood up to their work much better than when given the usual treatment. In fact, it was found that the heat-treatment could be carried up to nearly the m.p. and it would give better results than when the temp. of the heat-treatment is lower. Beyond 925°, a slight increase in the hardening temp. raises the cutting power in an extraordinary way. Hence the term **high-speed steels,** and **rapid steels.** The high-speed steels are partially self-hardened. O. M. Becker gave for the composition of high-speed steels:

	C	W	Mo	Cr	V	Mn	Si	P	S
High .	1·28	25·45	7·6	7·20	0·32	0·30	1·34	0·029	0·016
Low .	0·32	14·23	0·0	2·23	0·00	0·03	0·43	0·013	0·008
Mean .	0·75	19·00	3·5	4·00	0·30	0·13	0·22	0·018	0·010

The vanadium was found in three of the steels analyzed. The difference between the self-hardening and the high-speed steels is more of degree than kind, so that the Mushet steel becomes a high-speed steel if it has been subjected to the superheating process. In ordinary steel, the austenitic structure can be obtained only under special conditions, because it changes so rapidly to the martensitic structure. Martensite, however, passes into pearlite comparatively slowly. The martensitic structure is obtained by suddenly quenching the metal from a bright red-heat. Martensite is hard and brittle, so that for the sake of durability some hardness is sacrificed by tempering the metal so as to let it down to any degree towards the pearlite stage where the metal is soft and tough. The presence of tungsten hinders the passage from austenite to pearlite, so that in order to obtain the pearlite structure in the presence of, say, 7 per cent. of tungsten, the cooling must be extremely slow. Martensite is not stable in ordinary steel unless the metal is kept cool. In the presence of over 7 per cent. of tungsten, the stability of martensite becomes so great that the steel can be heated above the ordinary tempering heats before the martensite begins to change into pearlite.

J. H. Andrew and G. W. Green, A. H. d'Arcambal, J. O. Arnold and co-workers, G. Auchy, H. W. Baker and A. H. Gibson, R. K. Barry, O. M. Becker. A. E. Bellis, C. Benedicks, C. H. Benjamin, C. P. Berg, F. Bischoff, P. Blum, O. Böhler, W. V. Brandt, S. N. Brayshaw, L. P. Breckenridge and H. B. Dirks, G. R. Brophy and R. H. Harrington, W. Brown, A. Campion, H. C. H. Carpenter, J. Castner, H. le Chatelier, C. Codron, A. L. Colby, C. E. Corson, C. Day, P. Dejean, L. Demozay, M. Denis, J. W. Donaldson, F. W. Duesing, H. Eckardt, W. Eilender and co-workers, P. Eyermann, H. Fleck, E. L. French, H. J. French and J. Strauss, G. Gabriel, F. L. Garrison, G. Gherardi, J. P. Gill and M. A. Frost, J. P. Gill, D. M. Giltinan, C. S. Gingrich, J. M. Gledhill, P. Goerens, R. C. Good, A. W. F. Green, M. A. Grossmann, M. A. Grossmann and E. C. Bain, R. A. Hadfield, A. Hänig, G. Hailstone, O. E. Harder and H. A. Grove, D. Hattori, A. Heller, R. Helmhacker, E. G. Herbert, H. D. Hibbard, J. M. Highducheck, H. H. Hill, R. Hohage and A. Grützner, R. Hohage and R. Rollett, K. Honda and T. Matsushita, E. Houdremont and H. Kallen, G. J. Horvitz, J. E. Hurst, Z. Jeffries, J. A. Jones, L. M. Jordan, W. Kahlbaum and co-workers, K. Kellermann and O. Schliessmann, S. Kern, F. Kick, A. H. Kingsbury, P. Kirwadi, G. Klein and W. Aicholzer, E. Kothny, F. C. A. H. Lantsberry, J. W. E. Littledale, P. Mabb, R. C. McKenna, P. Marsich, J. A. Mathews, E. Maurer and W. Haufe, E. Maurer and G. Schilling, G. Z. Nesselstrauss, J. Miley, K. H. Müller and E. Piwowarsky, I. Musatti and G. Calbiani, J. T. Nicholson, A. L. Norbury, E. R. Norris, G. L. Norris, W. Oertel and E. Pakulla, W. Oertel and F. Pölzguter, H. K. Ogilvie, F. Osmond, A. R. Page, C. Pendlebury, E. Piwowarsky, F. Pölzguter and W. Zieler, H. Pommerenke and R. Dewert, F. Rapatz, F. Rapatz and H. Kallen, F. Rapatz and H. Pollack, F. Reiser, E. W. Rettew, E. L. Rhead, E. D. Rogers, H. W. Rushmer, K. Sasagawa, G. Schlessinger, E. Schulz and co-workers, H. Scott, F. Seiler, B. F. Shepherd, E. Sievers, O. Smalley, E. K. Smith and H. C. Aufderhaar, J. Spüller, A. Stockall, M. Vasvari, J. Wagner, F. Walker, J. W. Weitzenkorn, W. H. Wills, A. J. Wilson, A. D. Wilt, W. Wrazei, W. Zieler, and E. Zingg and co-workers made observations on the mechanical properties of tungsten steels. V. Ehmcke studied the influence of silicon and manganese on the properties of high-speed steel.

F. Robin studied the acoustic properties of tungsten steels. F. W. Harbord said that additions of up to 1·5 per cent. of tungsten had no appreciable effect on the mechanical properties of mild steel. Z. Nishiyama's observations on the elastic modulus are indicated above. L. Guillet observed that the pearlitic tungsten steels had a tensile strength and elastic limit which becomes higher in proportion as the percentage of tungsten increases, while the elongation, reduction of area, and resistance to shock diminish as the proportion of tungsten rises. With the carbide steels, the tensile strength and elastic limit vary little with the proportion of tungsten, if anything they diminish. They become higher as the proportion of carbon increases. W. P. Sykes found that the tensile strength is affected by annealing very like the hardness, and that a decrease in ductility accompanies an increase in tensile strength. T. Swinden's results on normalized steel are indicated in Table LXXX. The tests show the toughening influence of tungsten as the

TABLE LXXX.—MECHANICAL PROPERTIES OF TUNGSTEN STEEL.

Percentage composition		Elastic limit (tons per sq. in.)	Maximum stress (tons per sq. in.)	Elongation (per cent. in 2 in.)	Reduction of area (per cent.)	Compression (per cent. under 100 tons per sq. in.)	Alternating stress (alternations)
C	W						
0·144	3·25	24·44	34·27	28·5	62·8	50·50	218
0·218	3·24	25·27	33·19	27·5	61·0	50·66	226
0·270	2·92	29·00	39·30	24·1	59·8	(53·9)	232
0·480	3·11	41·54	53·75	16·0	45·5	34·82	95
0·530	3·18	45·08	55·82	16·0	47·9	31·83	104
0·570	3·17	44·56	57·76	14·5	44·2	31·04	92
0·890	3·08	48·87	62·00	13·5	29·2	25·80	42
1·07	3·09	40·37	50·82	15·5	28·2	30·24	30
1·24	3·02	46·10	56·00	9·5	16·9	—	22

proportion of carbon increases. The compression is rather less than is usual with steels without tungsten. Tungsten imparts no beneficial influence to the resistance of steel to repeated impact. An average boiler-plate gives about 350 alternations. K. Honda and T. Terada gave for the coeff. of elasticity, *E*, of tungsten steel from $1{\cdot}928\times10^{12}$ with a load, 1758 grms. per sq. mm., to $1{\cdot}945\times10^{12}$ with a load of 11,523 grms. per sq. mm. The coeff. of rigidity is $0{\cdot}608\times10^{12}$ at 14·0°. For the effect of magnetization on the elastic constants, *vide infra.* W. Giesen observed that pearlitic steels with 0 to 15 per cent. of tungsten and 0·3 per cent. of carbon, or 0 to 8 per cent. of tungsten and 0·95 per cent. of carbon, show an increase in tensile strength, limit of stretch, and breaking load with increasing proportion of tungsten, but the ductility diminishes. The hardness is generally a little greater than carbon steels with the same proportion of carbon. The brittleness remains unchanged even when the proportion of tungsten is 15 or 18 per cent. in the presence of respectively 0·3 and 0·95 per cent. carbon. With this high proportion of tungsten, the only properties that vary are elastic limit, and ductility, which increase but slightly, and breaking load, which rises with the content of carbon and tungsten. Pearlitic steels with 0·25 per cent. carbon and over 9 per cent. tungsten, or 0·85 per cent. of carbon and over 4 per cent. tungsten, increase in hardness as the proportion of tungsten rises. Tungsten steels with double carbide attain sufficient hardness only when the carbon content is high, but the great fragility remains the same. C. L. Clark and A. E. White measured the effect of temp. on the tensile properties; V. Ehmcke studied the effect of nickel and manganese on high-speed steels. R. A. Hadfield observed no abnormal behaviours when the steel is cooled to —182°. The observations of K. Honda and T. Matsushita on the modulus of elasticity and rigidity of tungsten steels, in dynes per sq. cm., are summarized in Figs. 462 and 463. The dotted curves refer to steels heated to 1100° and quickly cooled, and the maximal values due to the presence of carbide, as in the conductivity-concentration curves. F. Pölzguter and W. Zieler studied the effect of annealing on the properties of tungsten steels.

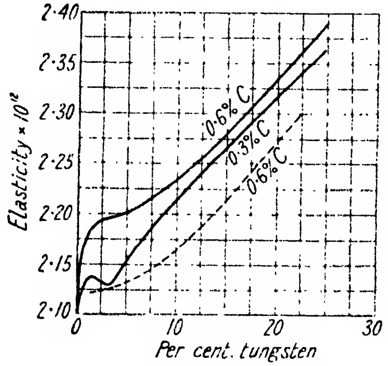


FIG. 462.—The Elasticity of Tungsten Steels.

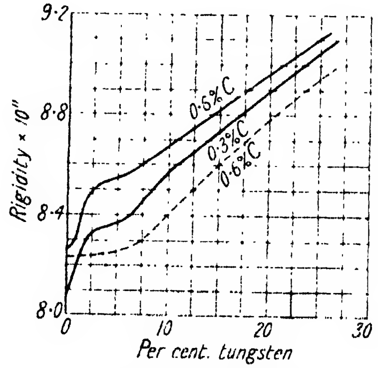


FIG. 463.—The Rigidity of Tungsten Steels.

K. Honda and T. Matsushita measured the coeff. of thermal expansion, and the results at 100°, 500°, and 850° are shown in Fig. 464. The values at 100° and 500° resemble the conductivity curves (*q.v.*). Here there are two maxima, one corresponding with the presence of the double carbide. F. Stäblein found that the mean coeff. of thermal expansion decreases with increasing proportions of tungsten; and the heat conductivity is but little affected by increasing proportions of tungsten. The electrical and thermal conductivity curves are shown in Fig. 465. The samples were annealed at 900° and then slowly cooled to room temp.

Generally speaking, a metallic compound has a less conductivity for electricity and heat than one of its components; thus cementite, tungsten carbide, and the double carbide all possess much less conductivity than pure iron. Hence, as the content of tungsten increases, the conductivity of the tungsten steels increases in virtue of the diminution of cementite, and decreases owing to the increasing content of tungsten carbide, and of double carbide and tungstide. The variation of the conductivities of the tungsten steels with the conc. of tungsten is then the resultant of these effects. But in steels whose tungsten-content is less than 5 per cent., the quantity of the double carbide is large as compared with other compounds, and therefore the variation of the conductivities is principally effected by the double carbide. The quantity of the carbide increases from zero, reaches a maximum at 1·84 per cent. of tungsten, and then decreases; hence, with the addition of tungsten, the conductivities must at first rapidly and afterwards slowly decrease, until they reach a minimum at 1·84 per cent. of tungsten and then slightly increase. These theoretical conclusions are in exact agreement with the observed facts. The steady decrease of the two conductivities after reaching a small maximum, as actually observed, is attributed to the increasing content of tungsten carbide and tungstide at the cost of pure iron. In the series of tungsten steels containing 0·3 per cent. of carbon, the quantities of the carbides are only half as large as in the former series. Hence, the minimum and maximum in the conductivity-concentration curves in this series must be much less conspicuous than in the last case; this conclusion also agrees with the observed facts. W. Brown found that the sp. ht. of a 0·16 C, 0·11 Mn, and 1·0 W steel is 0·1162; 0·28 C, 0·28 Mn, and 3·5 W, 0·1136; 0·38 C, 0·20 Mn, and 7·5 W, 0·1100; and 0·76 C, 0·28 Mn, and 15·5 W, 0·1041. There is an increase in the sp. ht. of steel by 0·0028 by the addition of 1 per cent. of tungsten, and with 3·5 per cent., the sp. ht. is the same as that of iron; while with the addition of 15 per cent., the sp. ht. is lowered 0·0093. F. Wüst and co-workers gave for the mean sp. ht. between 0° and θ° up to 1500°, $0{\cdot}03325+0{\cdot}000001 07\theta$; and for the true sp. ht. at θ°, $0{\cdot}03325+0{\cdot}00000214\theta$.

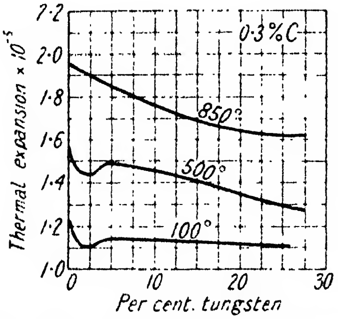


FIG. 464.—The Thermal Expansion Curves of Tungsten Steels.

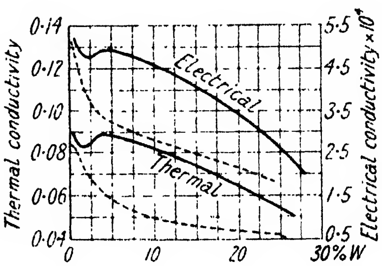


FIG. 465.—The Thermal and Electrical Conductivities of Tungsten Steels.

Observations on the electrical resistance, *R*, of tungsten steel were made by W. F. Barrett and co-workers, L. Guillet, O. Boudouard, etc. W. F. Barrett and co-workers gave 1·1 microhms, and A. M. Portevin, 1·5 microhms per cm. cube for the increase in the resistance of iron produced by 1 per cent. of tungsten. F. Stäblein found that the sp. resistance increased linearly with up to 7 per cent. of tungsten, and then remained nearly constant. A. M. Portevin gave for the resistance, *R* microhms per cm. cube, for steels with less than 0·28 per cent. of carbon:

W . .	0·41	0·93	1·75	6·90	11·89	14·37	20·71	27·05 per cent.
R {normal .	12·8	13·5	15·8	25·3	20·9	22·6	23·1	20·7
R {quenched .	13·8	14·3	17·1	23·4	24·5	24·6	25·3	25·8

For the electrical conductivity, *vide* Fig. 465. The results agree with C. Benedicks' formula with up to 7 per cent. of tungsten, indicating that the tungsten is in solid soln. With 0·8 carbon steels :

W . .	0·40	0·95	2·75	4·68	9·99	14·75	19·25 per cent.
R normal .	22·4	20·9	24·3	28·1	26·9	26·5	25·3
R quenched .	39·1	39·6	40·9	41·2	39·5	32·3	31·0

The agreement with C. Benedicks' formula with up to 5 per cent. of tungsten is taken to mean that this amount of tungsten is in solid soln. H. le Chatelier found :

	0·6 C, 5·0 W				0·76 C, 2·7 W.			
Quenching .	760°	800°	850°	1100°	730°	780°	850°	1100°
R . .	21·0	29·4	31·5	37·8	25·9	29·6	31·5	35·2

The increased resistance on quenching beyond the lowering temp. agrees with the assumption that a tungsten compound passes into soln. This was also observed by T. Swinden, who obtained :

C . . .	0·144	0·218	0·27	0·48	0·53	0·57	0·89	1·07 per cent.
W . . .	3·25	3·24	2·92	3·11	3·18	3·17	3·08	3·09 ,,
R annealed .	17·31	17·50	—	18·87	18·40	18·56	17·64	16·97
R normalized .	16·68	17·63	17·63	19·12	18·46	19·98	18·76	18·43
R hardened .	19·24	19·33	20·20	23·87	25·64	26·68	36·6	38·70

G. Tammann and V. Caglioti discussed the recovery of the resistance after cold-work. P. W. Bridgman studied the press. coeff. of the resistance. E. L. Dupuy and A. M. Portevin found the thermoelectric force of tungsten steel against copper, expressed in millivolts, to be :

C . . .	0·18	0·11	0·20	0·22	0·86	0·66	0·81	0·71%
W . . .	0·41	1·75	14·37	20·71	0·40	0·95	9·99	14·74%
Annealed −80° .	9·00	7·60	7·60	7·85	1·80	2·50	4·90	2·70
Annealed 100° .	6·30	5·24	6·40	6·30	−0·08	0·50	3·00	0·60
Hardened −80° .	8·40	6·70	7·80	7·90	−1·60	1·10	2·80	0·00
Hardened 100° .	5·70	4·75	7·40	7·25	−4·15	−1·70	1·30	−1·40

S. Curie found that tungsten increases the coercive force and residual magnetism of steel. On heating, it still loses its magnetic properties between 700° and 750°, and regains them on cooling, but at a rather lower temp. than that at which the loss occurs on heating. L. W. Wild, A. Abt, S. Saito, C. C. Trowbridge, C. Chistoni and G. G. de Vecchi, E. Gumlich, R. L. Dowdell, J. Würschmidt, E. A. Watson, S. Evershed, G. Hannack, A. M. Parkin, T. Spooner, K. G. Brecht and co-workers, N. I. Spiridovich, and B. Hopkinson made observations on the magnetic properties of tungsten steels. W. F. Barrett observed that as the carbon and tungsten increased, the coercive force increased, while the maximum induction, for $H=45$, decreased ; thus :

		Intensity of Magnetization		
C	W	Maximum	Remanent	Coercive force
—	0·00	1335	778	1·66
0·22	1·20	1320	568	3·23
0·28	3·40	1305	998	5·73
0·38	7·47	1266	1081	9·02
0·76	15·65	920	766	13·92

The retentivity or remanence of the steel with about 7·5 per cent. tungsten steel is high, in agreement with the observation that the tungsten is specially well suited for making permanent magnets. R. A. Hadfield said that one peculiar effect of tungsten in high-carbon steel is the great increase in retentiveness ; but with steels low in carbon the effect is not so marked. This is taken to mean that the action of tungsten is indirect in causing the carbon present to become very intimately combined. Tungsten in the presence of low-carbon steel interferes with the permeability much less than chromium, nickel, and other elements. Probably, therefore, tungsten steel with high carbon, more readily permits the steel to become permanently magnetized, so that in its presence the intimate union of carbon and iron in the quenched steel enables the imparted magnetic energy to be retained. T. Swinden made a series of observations on approximately 3 per cent. tungsten steel, normalized by heating it to 950° for 15 mins. and cooling freely in air; annealed by heating 3 hrs. at 950°, and kept between 930° and 960° for 90 mins. and cooled over 8 hrs. in the muffle; hardened, by heating to 900° and quenching in water; and tempered at 60°–75° for 14 hrs. A selection from the results is summarized in Table LXXXI. In Table LXXXI, A. denotes annealed; N., normalized; H., hardened; and T., tempered. As the proportion of carbon increases, the maximum induction decreases, and the maximum remanent intensity is unimpaired by the 3 per cent. of tungsten. The remanent magnetism is higher than for quenched carbon steels. With lightly annealed tungsten steels, the coercive force is almost identical with that of comparable carbon steels. S. Curie observed that with steels with a higher proportion of tungsten, the coercive force is increased irrespective of carbon. F. Stäblein found that the coercive force of iron-tungsten alloys rises sharply with up to between 5 and 10 per cent. of tungsten, reaching a well-defined maximum at 15 per cent. of tungsten. The subject was discussed by F. W. Harbord; and W. F. Barrett and co-workers obtained better results for magnetic steels when manganese was absent. T. Swinden found that annealed, 3 per cent. tungsten steels gave hysteresis losses very little different from carbon steels, while with the normalized steel, the losses were higher, and still higher with hardened steel. J. O. Arnold inferred that in iron containing 0·1 to 0·9 per cent. of carbon, and quenched, the permanent magnetism is directly proportional to the hardening carbon. The ratio of the remanent and permanent magnetism increases steadily with up to 0·53 per cent. carbon with the annealed and normalized

TABLE LXXXI.—MAGNETIC PROPERTIES OF TUNGSTEN STEEL ($H = 150$ C.G.S. UNITS).

Composition		Heat-treatment	Remanence				Coercive force		Permanence after shocks	
C	W		Permeability	Intensity	Induction	Intensity	Before shocks	After shocks	Induction	Intensity
0·144	3·25	A.	127	1508	9,150	730	3·85	—	—	—
		N.	126	1490	9,250	737	5·65	5·1	—	—
		H.	112	1320	11,370	906	19·40	17·1	2080	166·0
		T.	139	1532	14,100	1124	12·10	—	1410	112·3
0·218	3·24	A.	127	1500	9,200	734	6·80	—	—	—
		N.	123	1460	9,450	753	16·30	—	—	—
		H.	109	1280	10,970	873	39·50	39·4	2490	199·0
		T.	125	1475	13,200	1052	18·50	—	1580	126·0
0·480	3·11	A.	124	1475	9,550	761	7·40	—	—	—
		N.	118	1406	11,350	905	18·20	17·2	1730	—
		H.	104	1223	11,350	905	43·40	42·9	7670	137·9
		T.	126	1486	14,770	1177	18·90	—	2870	612·0
0·57	3·17	A.	122	1440	11,850	945	—	—	—	228·5
		N.	116	1372	11,630	298	9·20	14·8	2510	—
		H.	101	1198	10,870	868	17·40	59·2	7000	200·0
		T.	124	1471	14,750	1175	58·80	—	2690	538·0
0·89	3·08	A.	117	1380	12,100	965	21·70	—	1540	214·5
		N.	112	1324	12,020	960	—	—	6490	—
		H.	73	868	7,330	584	—	66·1	3910	119·5
		T.	123	1459	148	1183	10·90	—	—	517·8
1·07	3·09	A.	106	1258	11,640	930	14·40	—	1250	311·5
		N.	109	1282	11,800	940	64·90	—	5700	—
		H.	59	693	6,020	480	—	—	4690	99·7
		T.	113	1340	12,080	964	26·50	—	—	454·0

bars; the tempered steel gave a uniform increase up to 0·9 per cent. carbon; and the hardened steel gave a maximum with 0·4 per cent. carbon. In general, a steel which is physically hard has a high coercive force and a high remanent magnetic intensity. G. Mars discussed this subject, and his results for tungsten steel are summarized in Table LXXXII, the data for the magnetization refer to arbitrary units on the magnetometer, and to steels quenched, from the temp. named, in water at 10° to 15°. He also obtained results for chromium-tungsten steels. These steels were also examined by L. Guillet, F. Osmond, and W. Brown. U. Adelsberger discussed the hysteresis losses. The magnetic properties of the tungsten steels were examined by J. Trowbridge and S. Sheldon, H. Scott, W. Siemens, and C. W. Siemens. R. L. Sanford and W. L. Cheney observed the maximum induction of oil-quenched tungsten steel to be 11,200, and the coercive force, 68·0. W. A. Wood found that the coercive force may be reduced to a fifth of its optimum value at about 950°, and it can be restored by heating to 1250°. The hardness varies in the same way. The decrease in magnetic quality and hardness at about 900° is due to the disappearance of lattice distortion, and the recovery at 1250° is due to the re-introduction of the distortion. Lattice distortion is the main factor in the spoiling and recovery of tungsten magnet steels.

TABLE LXXXII.—THE HARDNESS AND MAGNETIZATION OF TUNGSTEN STEELS.

Composition				Hardening temp.	Brinell's hardness	Magnetization		
C	Si	Mn	W			Just after magnetizing	After 8 days	Percentage loss
1·15	0·20	0·23	0·68	780°	600	69·5	68·5	2·9
1·16	0·19	0·20	1·20	750°	744	76·5	76·0	1·3
0·64	0·25	0·26	1·12	820°	713	76·5	73·5	3·9
0·62	0·22	0·20	1·96	800°	782	85·5	84·5	1·8
1·20	0·28	0·29	3·22	740°	782	66·5	65·5	4·5
0·57	0·18	0·26	5·47	930°	782	90·5	90·5	0
1·25	0·27	0·30	8·65	930°	782	61·0	58·5	4·1
1·25	—	—	30·0	850°	578	19·0	—	—

K. Honda and S. Shimizu found that the intensities of magnetization, I, with different field-strengths, H, at −186° were:

H	1·37	5·89	12·40	28·8	62·7	272·4	570
I	13	64	254	1035	1236	1468	1557

and at 30·7°:

H	2·16	6·91	10·35	25·8	111·2	333	557
I	21	104	376	1064	1326	1463	1509

K. Honda and S. Shimizu measured the magnetostriction of tungsten steel. K. Honda and T. Terada found the change in the coeff. of elasticity, $\delta E/E$, by magnetization is small, gradually increasing as the strength of the magnetic field increases; $\delta E/E \times 10^2$ rises from 0·08 with $H=245$, to 0·10 with $H=380$. The magnetostriction or elongation, $\delta l/l$, by magnetization increases at first rapidly, then slowly, and finally decreases. With a load of 1693 grms. per sq. mm., $\delta l/l \times 10^6$ rose from 0·03 to 1·39 as H changed from 10·0 to 24·9, and from 1·39 to 3·72 as H changed from 24·9 to 167·2, and it fell to 3·28 as H rose to 399. With a load of 5762 grms. per sq. mm., $\delta l/l \times 10^6$ rose from 0·03 to 1·05 as H increased from 8·9 to 25·0; it then rose to 2·51 as H was raised to 166·0, and fell to 1·93 as H changed to 397. The increase in the rigidity, $\delta k/k \times 10^2$, with magnetization is small, rising from zero with $H=136$ to 0·51 with $H=429$. The change in Poisson's ratio, $\delta\sigma/\sigma \times 10^2$, rose from zero with $H=100$ to 0·3 with $H=300$. The change of magnetization, δI_i, with initial loading, and δI_c, with cyclic loading, for loads in tension, T grms. per sq. mm., is :

	T	1625	4837	8092 grms. per sq. mm.
$H = 4{\cdot}08$	δI_i	0·4	2·6	6·5
	δI_c	0·2	0·4	0·7
$H = 341$	δI_i	−0·3	−1·5	−2·8
	δI_c	−0·3	−1·7	−3·4

K. Honda and T. Terada also found that with a constant tension the magnetization increases rapidly in low fields, and gradually approaches saturation. They also examined the effect of a twist, and of a combined twist and tension on the magnetization. In all cases the reciprocal nature of the changes of strains by magnetization and of the changes of magnetization by strain were established. For instance, magnetic elongation under constant tension, and of magnetization under constant tension ; of elongation by tension under a constant field, and the change of magnetization by tension under a constant field ; of magnetic twisting under a constant couple, and magnetization under a constant twist ; and of the change of rigidity under a constant field ; and the change of magnetization by twist under a constant field.

E. Martin studied the absorption of hydrogen and nitrogen by tungsten steels ; and L. Losana and G. Reggiani, the corrosion of tungsten steels. According to R. A. Hadfield, the percentage losses in weight which occurs after the metal has been immersed for 21 days in 50 per cent. sulphuric acid, were :

C	0·15	0·21	0·28	0·38	0·76	0·78 per cent.
W	0·20	1·49	3·40	7·47	15·65	16·18 ,,
Loss	5·01	3·50	2·25	4·50	5·75	5·50 ,,

when the percentage loss with ordinary steel was 3·97 ; with mild steel, 2·09 ; and with 99·80 per cent. iron, 4·52.

L. B. Pfeil observed a three-layer scale—*vide supra* - is formed when tungsten steel is heated for several hours at 1000° in air. The tungsten is about twice as concentrated in the innermost layer as it is in the original steel ; tungsten also occurs in the middle layer, but very little is present in the outer layer. Some tungsten oxide is volatilized, but not enough to explain the impoverished outer layer. C. Chappell said that the presence of 3 per cent. of tungsten has practically no effect on the corrodibility of carbon steels by sea-water. Y. Utida and M. Saito found the gain in weight, in grams per sq. cm., when the tungsten steel with about 0·07 per cent. of carbon is heated for an hour at 1100° ; and the loss in weight, in grams per sq. cm., when the metal is immersed in 10 per cent. acid for 24 hrs. :

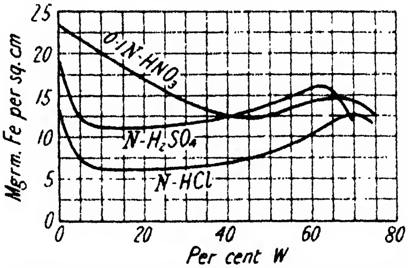


FIG. 466.—Corrosion of Iron-Tungsten Alloys by Acids.

Tungsten	0	0·40	0·73	2·85	4·63	6·63	8·24 per cent.
At 1100°	0·0212	0·0397	0·0344	0·0291	0·0221	0·0227	0·0306
HNO_3	0·9380	0·5890	—	0·5642	0·5207	0·4545	0·3175
HCl	0·0712	0·1427	0·1222	0·0576	0·0335	0·0183	0·0117
H_2SO_4	0·0990	0·9796	0·0638	0·0476	0·0328	0·0278	0·0172

H. Endo's results, shown in Fig. 466, represent the losses, in grams per sq. cm., in 5 hrs. at ordinary temp., with alloys containing 0·50 to 0·56 per cent. of carbon, and the given amounts of tungsten. The results of G. Grube and K. Schneider showed that the greatest attack occurs with the alloy corresponding with the compound Fe_3W_2. C. F. Burgess and J. Aston found that the progress of the corrosion of alloys of tungsten and iron, expressed in grams per sq. dm., by

20 per cent. sulphuric acid for an hour; and by exposure to weather conditions for 162 days from July to February, expressed in kgrms. per sq. metre, is as follows:

W .	0·406	0·925	2·334	3·553	5·982	9·849	13·641	23·866 per cent.
Acid .	0·363	0·088	0·086	0·332	0·304	0·398	0·365	0·183
Air .	0·371	0·302	0·302	0·308	0·293	0·195	0·329	0·215

L. Aitchison found for the loss in weight per 100 sq. cm. of tungsten, with nearly 3 per cent. of tungsten:

C	0·47	0·20	0·58	0·88	1·08 per cent.
NaCl 3 per cent. .	1·56	1·68	1·83	1·04	1·70
H_2SO_4 1 per cent. .	2·16	2·87	6·4	3·69	3·98
10 ,, .	2·80	5·37	4·95	5·13	4·83

and for steels with nearly 0·7 per cent. of carbon:

W . .	2·36	5·37	9·74	14·96	21·5	26·3 per cent.
Tap-water .	0·970	0·930	0·976	1·100	0·940	0·970

S. Satoh studied the nitridization of these steels by heating them in ammonia at 560° to 580°; and O. Bauer, J. S. de Benneville, C. Duisberg, R. A. Hadfield, and W. H. Hatfield studied the retarding effect of tungsten on the corrosion of steel. F. Osmond studied the corrosion of a Mushet's chromium-tungsten steel with 1 per cent. sulphuric acid. G. Mars, and O. Bauer also made observations on this subject. Y. Utida and M. Saito found that tungsten decreases corrosion, but L. Aitchison said that it does not appreciably reduce corrosion when it is present in the carbide phase.

E. Maurer and W. Haufe discussed some **tungsten-silicon-iron alloys**; and J. Swan, the effect of silicon on some tungsten magnet steels; H. J. French, W. Kahlbaum and co-workers, A. Schevchenko, and H. Pommerenke and R. Dewert, the **chromium-tungsten-vanadium steels.** According to E. Maurer and co-workers, the addition of chromium increases the solubility of tungsten in steel. A. Schevchenko, and L. Guillet prepared **tungsten-chromium steels** containing from 0·124 to 0·849 per cent. of carbon, 0·94 to 20·44 per cent. of chromium, and 1·98 to 20·3 per cent. of tungsten. The structures which the hypoeutectoidal tungsten-chromium steels can assume are: pearlite, martensite, martensite and carbide, carbide with a background probably of sorbite, and carbide with a background of γ-iron. The influence of tungsten may be superadded to that of chromium with the production of martensite. The most frequently occurring structure is that with grains of carbide more or less numerous on a background of what is thought to be sorbite. When tungsten is added to a pearlitic chromium steel, it adds its influence to the chromium to form martensite; if an excess be added, martensite is not formed, but troostite or sorbite. If the percentage of carbon reaches 0·5, a carbide, probably a triple carbide, is formed. If tungsten be added to a martensitic chromium steel, the steel remains martensitic so long as the proportion of tungsten is small; if otherwise, carbide is formed with a background of probably sorbite. The addition of tungsten to a chromium steel already containing carbide has the effect of increasing the proportion of carbide only. Quenching at 850° transforms pearlitic steels into martensitic steels, and partly so with steels containing carbide. When a tungsten-chromium steel containing carbide is quenched from 850°, in water at ordinary temp., the amount of carbide is somewhat diminished, but the carbide does not all disappear; if the steel contains troostite, it becomes martensitic, but with steels containing high proportions of carbon and tungsten, part of the troostite persists; if the steel is martensitic, it remains so, but a little γ-iron may be formed; and if it contains γ-iron, that constituent remains. If steels be heated to 1250°, the longer the period of heating, previous to quenching, the greater the proportion of carbide which is destroyed. Half an hour's heating at 1200° was sufficient to cause the carbide to disappear in all the cases examined. Similar effects can be obtained by heating the steel for a longer time at a lower temp. Annealing has no perceptible effect on the microstructure, excepting that the carbide, if present, becomes a little better defined. Cooling in liquid air, or subjecting the steel to stresses, produced no change in the microstructure. The case-hardening of all the carbide steels increases the proportion of carbide, and a martensitic steel containing carbide undergoes in the case-hardened portion a transformation into troostite or sorbite; whilst martensitic steels not containing carbide have, after case-hardening, carbide embedded in a background of troostite. J. S. de Benneville, K. Honda and T. Murakami, and A. Michel and P. Bénazet studied the structure of the chromium-tungsten steels. A. E. White and C. L. Clark found that a steel with 7·93 per cent. of chromium, and 7·70 per cent. of tungsten, quenched from 1232°, had the highest proportional limit yet recorded at 538°, namely, 100,000 lbs. per sq. in.

L. Guillet found that the mechanical tests on the normalized steels show that with the pearlitic steels, the tensile strength, elastic limit, and resistance to shock are raised, and the elongations are lowered. The martensitic steels have a high tensile strength and elastic limit, and a low elongation; they are also hard and brittle. Steels containing both carbide and martensite have a high tensile strength, a low elastic limit, and a medium elongation; they are hard and brittle. Similarly also with steels containing carbide and sorbite. Here the mechanical properties vary but little with the proportions of the various elements present, except the elastic limit which slowly increases as the carbon and chromium increase, and is reduced when the proportion of tungsten is high. Steels containing carbide, and polyhedra of γ-iron, have a low tensile strength, elastic limit, elongation, and reduction of area, while the brittleness is high. On quenching from 850°, when the proportions of chromium and tungsten are fairly constant, the hardness increases as the percentage of carbon is raised; when the proportion of tungsten alone varies, the hardness reaches a maximum with 8 per cent. tungsten—carbon $>$0·73 per cent.; and when the proportion of chromium alone varies, the hardness is reduced as the percentage of chromium increases owing to the fact that it becomes increasingly difficult to dissolve the triple carbide. When the steel is quenched from 1200°, the hardness of all steels containing carbide is increased owing to the dissolution of the carbide, and prolonging the period of heating before quenching increases the hardness to a maximum. A similar result is obtained at a lower temp. if the duration of heating be prolonged. The more energetic the quenching medium, the lower the degree of hardness owing to the presence of γ-iron. Annealing at a high enough temp., 900° to 1200°, increases the grains of carbide and induces extreme brittleness, lowers the tensile strength and elastic limit, and reduces the elongation and reduction of area. W. Kahlbaum and co-workers, E. Maurer and W. Haufe, and W. Schneider and E. Houdremont studied the mechanical properties. F. Robin found that the high-speed, sorbitic, chromium-tungsten steels offer the highest resistance to crushing. This resistance rises rapidly at reduced temp., and at −185° is very high; a fall in resistance occurs at about 500°; and at high temp. the curve is almost linear—at 1100° the resistance is nearly double that of mild steel. The subject was discussed by L. Grenet. F. Robin discussed the acoustic properties of the chromium-tungsten steels; but observed no specially noteworthy characteristics. C. F. Würth also examined the effect of tungsten on the corrodibility of chromium steels. L. Guillet, and W. Kahlbaum and L. Jordan discussed the nitridization of the **chromium-tungsten-vanadium-iron alloys.** J. S. de Benneville, and J. V. Emmons studied the **molybdenum-tungsten-iron alloys.**

The **iron-uranium alloys** have not been closely investigated. Uranium, like molybdenum and tungsten, is considered to be an alloying element; and it also forms carbides, and possibly enters into combination with the cementite of steel.[27] A. Stavenhagen and E. Schuchard prepared the alloys by the thermite process, and F. Peters by electrometallurgical processes. Uranium is readily oxidized, and, according to G. K. Burgess and R. W. Woodward, is liable to leave its oxide in the steel. H. W. Gillett and E. L. Mack also found that it segregates badly. Up to 2 per cent., it has no marked effect on the critical ranges of steel; nor does it increase the tendency to hardening to any great extent. E. L. Reed studied the subject. H. S. Foote said that 0·60 per cent. is advantageous, and E. P. Poluskin added that while it increases the strength and toughness of steel, it does nothing which cannot be as well accomplished by less costly elements. Alloys with over 40 per cent. of uranium are decomposed by water. There may be present uranium, the carbides UC, $Fe_3C.U_2C_3$, U_2C_3, Fe_6U, and the oxide U_3O_8. H. S. Foote observed no useful effect with cast iron. The alloys were discussed by F. F. Mueller and R. W. Harris, J. M. Flannery, P. A. Heller, J. Ohly, I. Musatti and G. Calbiani, H. S. Foote, E. V. Britzke and co-workers, P. Blum, P. Girod, A. Haenig, H. Fleck, P. Oberhoffer, E. Lievenie, H. J. French and W. A. Tucker, G. and E. Stig, W. Borchers and R. W. Stimson, H. C. H. Carpenter, O. J. Steinhart, J. Johnson, R. M. Keeney, J. W. Richards, J. Escard, A. F. Braid, G. J. Horvitz, F. M. Becket, R. P. Neville and J. R. Cain, and H. W. Gillett and E. L. Mack. F. Roll showed that uranium favours the graphitization of cast iron. J. Laissus discussed the diffusion of uranium in iron. S. Satoh studied the nitridization of these steels by heating them in ammonia at 560° to 580°.

Soon after the discovery of manganese in the eighteenth century, S. Rinman[28] obtained an impure **iron-manganese alloy,** or ferromanganese, by melting grey pig-iron with an equal weight of manganese ore. The alloy was brittle; the fracture, white; and the manganese deprived the iron of its usual magnetic properties. W. Sowerby stated that old Persian steel blades were made from a kind of manganiferous iron-stone, tempered in oil; and in Spain, the Toledo blades were also manufactured from a manganiferous iron-stone. T. Bergman gave for his analyses of Swedish iron and steel:

	Ferrum crudum (cast iron)		Ferrum cusum (forged iron)		Chalybs (steel)	
	Min.	Max.	Min.	Max.	Min.	Max.
Silicon . . .	1·0	3·4	0·05	0·3	0·3	0·9
Carbon . . .	1·0	3·3	0·05	0·2	0·2	0·8
Manganese . .	0·5	30·0	0·50	30·0	0·5	30·0
Iron . . .	63·3	97·5	99·50	99·4	68·3	99·0

This, said D. Mushet, attracted the attention of the manufacturers of iron and steel at the beginning of the nineteenth century, and attempts were made to alloy manganese with iron. The use of manganese in the manufacture of iron and steel was patented by W. Reynolds in 1799; by J. Wilkinson in 1808; by J. M. Heath in 1839; and by R. F. Mushet in 1856. A legal case arising from the infringement of J. M. Heath's patent was discussed by T. Webster, and J. Percy. D. Mushet thus summarized his observations on the subject:

> I was now satisfied that ores of manganese might be smelted with success along with our common argillaceous iron-stone in the blast-furnace, with a considerable augmentation of metallic produce; and much pleased to have discovered the fact that iron alloyed with manganese, in certain proportions (22 per cent.), ceases to be obedient to the magnet. This fact alone renders it extremely probable that the presence of manganese is not essential to the formation of good steel; and that those irons analyzed by T. Bergman, contain no notable quantity, seeing that the strongest and most durable magnets are made from steel manufactured from such iron.

C. J. B. Karsten said that manganese is a very common companion of iron, but the most he had observed was 1·85 per cent. To-day, the manganese finds its way in Bessemer and open-hearth steels during the addition of the decarburizer, and, as emphasized by A. L. Baikoff, it can be regarded as a normal constituent of steels. One important result of the addition of manganese is to remove sulphur, so that the greater proportion of the manganese added passes into the slag as manganese sulphide. According to E. F. Law, that remaining in the steel is readily recognized by covering the surface with gelatin mixed with an acidic soln. of a cadmium salt. The acid attacks any exposed manganese sulphides, liberating hydrogen sulphide, which produces yellow cadmium sulphide in the gelatin. In 1865, H. Bessemer emphasized the use of manganese in iron; in 1865, W. Henderson manufactured ferromanganese with 25 to 35 per cent. manganese; and in 1871, F. Kohn discussed the prôduction of alloys of iron and manganese, with particular reference to the manufacture of spiegeleisen. The manufacture of manganese steel by W. Henderson's process was taken up by A. Pourcel in the Terr-Noire Co. in France in 1867; and in 1876, F. Gautier predicted:

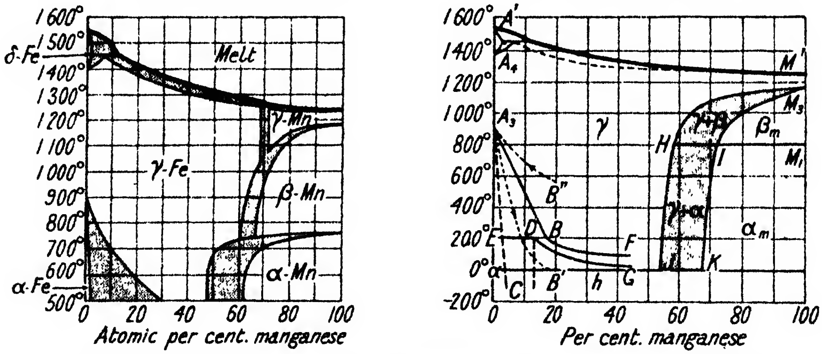
> The judicious combination and treatment of the different elements which are at the disposal of the metallurgist will attract more attention in the future, as only little is known on this question at present. Amongst the elements which may be most readily used for admixture is manganese; it is found plentifully and is a most active element.

Great improvements in the manufacture of manganese steels, and a detailed examination of the properties of the metal were made by R. A. Hadfield in 1888 and subsequent years. In consequence, there is now available a great deal of information on the strength and weakness of these alloys. The subject has been discussed by H. M. Howe, and others. The manufacture and uses of manganese iron, steels, etc., were discussed by R. J. Anderson, E. S. Bardwell, L. J. Barton, C. Benedicks, E. Büttgenbach, R. Cazaud, D. Clark and J. Coutts, H. I. Coe, E. F. Cone, E. Decherf, S. H. Dolbear, B. Egeberg, J. Escard, T. Fujiki, F. L. Garrison, W. H. Greene and W. H. Wahl, C. D. Grier, K. P. Grigorovich and V. S. Yemelyanoff, W. Guertler, A. Hänig, J. H. Hall, W. Hampe, J. Harden, W. Heym, G. Hofer, J. H. Hruska, W. G. Imhoff, E. Indenkempen, J. E. Johnson, M. Kauchtschischwili, R. M. Keeney and J. Lonergan, R. M. Keeney and co-workers, E. F. Kern, B. G. Klugh, R. Korten, V. G. Kotelnikoff, E. Kothny, E. F. Lake, W. S. McKee and J. M. Blake, G. P. Messenger, E. Monaco, P. Oberhoffer, F. Peters, J. W. Richards, P. H. Royster, H. K. von Schiele, G. P. Scholl, F. Schroedter, E. L. Shaner, O. Simmersbach, O. J. Steinhart, G. and E. Stig, S. R. Stone, G. Surr, R. R. Tatlock and R. T. Thomson, H. Thaler, E. E. Thum, P. M. Tyler, W. Venator, F. M. Walters, J. D. Weeks and G. L. Stone, C. M. Weld, and R. S. Wile. W. R. Hulbert used the thermite process. The methods of preparing ferromanganese were indicated in connection with manganese. F. Sauerwald, and A. N. Campbell prepared alloys electrolytically. G. Oishi, F. Körber and W. Oelsen, and G. Tammann and W. Oelsen studied the distribution of manganese between the slag and molten steel.

According to R. A. Hadfield, manganese steel is not as liable to honeycomb as ordinary steel, and the counter-agent silicon is unnecessary. The molten metal is very fluid, and it can be run in thin sections; but it cools more rapidly than ordinary steel, and its contraction is greater. Hence its tendency to piping and settling, both in ingots and castings, unless proper head or runners are employed. The steel is manufactured by ordinary processes. Highly heated or molten ferromanganese is added to molten decarbonized iron or mild steel. The proportion of carbon should not exceed 1 per cent. or the product will be inferior. About 0·5 per cent. of the manganese is oxidized during the preparation of the steel – *vide infra*. According to R. A. Hadfield, when less than 0·10 per cent. of manganese is added to decarbonized iron, it is very difficult to roll or forge the ingots, but above this they become malleable; mild steel with 0·2 per cent. of manganese is unsound, and rises in the ingot moulds, the honeycombs, however, close up on being forged, rolled, or otherwise reduced. As the proportion of manganese is increased, the material becomes sounder, but on exceeding 1 per cent., the steel becomes tender, the elongation is much reduced, and the material is of doubtful commercial value. The steel becomes brittle and rotten with about 2·5 per cent.; and with between 2·5 and 7·5 per cent. manganese, the cast material is brittle, like glass; and although ductile when hot, it can, when cold, be reduced to powder by a hand-hammer.

When the cast material is heated, and hammered or forged, it gains considerably in strength, and the grain of the bar is coarse and white; but if re-heated, and cooled in air, it acquires a close-grained texture, and this self-hardening manganese steel is suitable for turning tools and cutters. When the proportion of manganese passes beyond 7·5 per cent., the peculiar brittleness and hardness begin to disappear, and the steel becomes hard enough to compete with chilled iron for articles to resist wear and tear. The increase in toughness continues up to about 14 or 15 per cent., when a decrease in toughness but not in transverse strength occurs. Beyond 20 per cent. manganese causes a rapid decrease in toughness. In the hot forging of the manganese steel, there is a tendency for surface oxidation, so that some carbon is burnt off. N. Czako said that steel with a high percentage of manganese can be welded. The working qualities of the alloys were discussed by C. F. Burgess and J. Aston, H. P. Evans, and W. S. McKee.

A. Fry, J. Cournot, N. Agéeff and M. Zamotorin, and F. C. Kelley discussed the diffusion of manganese in solid iron; and W. F. Holbrook and co-workers, in molten iron. According to M. Levin and G. Tammann, the f.p. curve indicates the absence of any compound of iron and manganese; there is only an unbroken series of solid soln. of the two metals. Under the microscope, there seem to be two structural elements, but this is due to the fact that during rapid cooling, equilibrium is not established between the liquid alloy and the solid soln., so that crystals richer in iron separate first and then become surrounded by others richer in manganese. The magnetic permeability of the 100 per cent. iron alloy disappears at 950° and returns at 750°; that of the 90 per cent. iron disappears at 820° and returns at 715°; and that of the 80 per cent. iron disappears at 750° and returns at 720°. G. Rümelin and K. Fick also studied the equilibrium diagram; and P. Goerens combined the two sets of results in the one diagram. E. Oehman also examined the alloys by means of the X-radiograms and summarized his results in Fig. 467. The ranges of stability of the various solid soln. are indicated. The face-centred, cubic γ-iron, and the face-centred, tetragonal γ-manganese are said to form a continuous series of solid soln., but there may be a break at about 70 at. per cent. manganese where the cubic structure becomes tetragonal—*vide infra*. The vol. per atom is a linear function of the composition, and increases from 11·32 A³. for pure γ-iron, to 12·56 A³. for pure γ-manganese. The solubility of iron in β-manganese increases from 0 per cent. at 1191°, the transformation point of γ-Mn$\rightarrow\beta$-Mn, to 35 at. per cent. at 730°, by saturating the alloy with iron, the lattice parameter decreases from 6·305 A. to 6·251 A. The transformation point of β-Mn$\rightarrow\alpha$-Mn is but little affected by iron. The solubility of iron in α-Mn is very little affected by the temp. At 490°, it amounts to about 37 at. per cent., and at 690°, to 34 at. per cent. By the dissolution of 36 at. per cent. of iron, the lattice parameter changes from 8·904 A. to 8·864 A. The vol. per



Figs. 467 and 468.—Equilibrium Diagrams of the Binary System: Fe–Mn.

atom for β-manganese is 12·53 A^3., and for α-manganese, 12·17 A^3. The β-Mn$\rightarrow$$\alpha$-Mn transformation is accompanied by a considerable change of vol. The lattice dimensions of α-manganese are smaller per atom than those of the other modifications, and it is also less affected by the introduction of iron atoms in the lattice. The break in the solid soln. series between α-manganese and γ-iron extends over the range of 15 at. per cent. The break in the solid soln. between β-Mn and γ-Fe is narrow—at 800° it amounts to about 4 per cent. The ϵ-phase with a close-packed, hexagonal lattice extends over 12 to 23 at. per cent. manganese, and probably to 30 at. per cent. manganese. The ϵ-phase is not stable over 500°. The ϵ-phase with 22·9 per cent. manganese has a space-lattice with $a=2·541$ A., $c=4·106$ A., and $a:c=1:1·616$. There is a considerable decrease in vol. in passing from γ-Fe to the ϵ-phase. The solubility of manganese in α-iron is very small. The break between the γ-Fe and the α-Fe phases increases as the temp. falls, and the limits cannot be followed beyond 500°, and beyond 30 at. per cent. The system was also studied by V. N. Krivobok. A. Osawa found that the hexagonal, close-packed lattice observed by T. Ishiwara has the axial ratio $a:c=1:1·61$, and corresponds with iron pentitamanganide, Fe_5Mn. Manganese quenched from 1200° has a face-centred, tetragonal lattice with the axial ratio $a:c=1:0·961$, and alloys with 7·96 to 38·62 per cent. of iron, similarly treated, have the face-centred, tetragonal lattice with $a:c$ varying from $1:0·96$ to $1:1$. Five phases were observed in the iron-manganese system: the body-centred phase extending from 91 to 100 per cent. iron; the hexagonal phase extending from 78 to 84 per cent. of iron; and α- and β-manganese extending from 0 to 35 per cent. The solid soln. made by γ-iron, and γ-manganese occurs throughout the whole series of alloys at a high temp.

T. Ishiwara's results are summarized in Fig. 468. The alloys with less than 17 per cent. of manganese undergo the $\gamma\rightarrow\alpha$ or the A_3-transformation at positions corresponding with the dotted curve A_3B'; but, on the heating curve, with the dotted curve A_3B''. Hence, as shown by H. Esser and P. Oberhoffer, the progressive addition of manganese to iron results in the progressive lowering of the A_3-transformation, and there is also a steady increase in the temp. hysteresis of the transformation. The true boundary curve is estimated to be represented by A_3B. The curve A_3C represents the solubility of manganese—about 3 per cent.—in iron at the temp. indicated. A. Sauveur said that, in accord with the work of C. R. Wohrman, a solid soln. of 3 per cent. manganese in γ-iron may occur at a high temp., and that the resulting manganese-austenite breaks up on slow cooling into α-iron, which may retain some manganese in soln., and of a pearlitic constituent—manganese pearlite. T. Ishiwara, however, said that the alleged pearlitic structure is not present in carbon-free alloys; and when it is present, it corresponds with the structures belonging to the iron-carbon system with alloys containing over 17 per cent. of manganese; another transformation, γ to h-solid soln., begins on cooling at 140° to 20° and ends at about 50° to −60°, and on heating, it begins at 100° to 230° and ends at 170° to 280°. The mean temp. of the γ–h transformation are represented by the curves BF and DG. The γ–h transformation occurs with alloys containing 17 to 30 per cent. of manganese. The alloys at first show a remarkable change in vol., which finally diminishes and becomes inappreciable; the alloys also, at first, have a Widmannstätten structure, characteristic of the h-state; and finally, a uniform austenitic structure. The γ–h transformation is reversible; and the boundary curve of the γ–phase is closed by the curve A_3BF. Alloys with a concentration between E and B should show two transformations, the peritectoid change γ–h, and the A_3 change γ–α. Alloys with between 55 and 68 per cent. of manganese consist of the γ and α_m solid soln. in the range of temp. below about 800°, and of the γ and β_m solid soln. above this temp. The heterogeneous alloys with both phases are bounded in the region JHM_3IK. An alloy with 68 per cent. of manganese furnishes a uniform solid soln. α_m, and when heated it passes into the β_m state, a change accompanied by an abrupt expansion. When further heated, this alloy passes into the upper portion of the JHM_3IK-region, and afterwards enters the field of the γ-solid soln. At high temp., iron and manganese are miscible in all proportions to form the γ-solid soln. Iron has a face-centred, cubic lattice at these temp., and manganese has a face-centred, tetragonal lattice at temp. above M_3. Hence, there is nothing to show that these elements correspond with one another to give rise to a homogeneous solid soln. A. Osawa showed that the axial ratio $c:a$ of the tetragonal lattice of manganese is less than unity, but it gradually increases with the addition of iron, finally to merge into that of the face-centred, cubic lattice. The subject was also discussed by H. Esser and P. Oberhoffer, E. L. Reed, W. Schmidt, T. Murakami and M. Mikami, and C. H. M. Jenkins and M. L. V. Gayler. J. A. M. van Liempt said that it is doubtful if the X-radiograms support the view that iron and manganese form a continuous series of solid soln.

According to W. S. Potter, in the cooling of steel containing 10 to 20 per cent. manganese, and 1 per cent. carbon, γ-iron begins to freeze at about 1370°, and is for the most part frozen at about 1270°. The eutectic freezes at 1125°–1080°, or perhaps at a little higher temp. with low-carbon and manganese mixtures. The mechanical break-up of austenite begins at 850° to 825°. Carbides separate between the grains at 710° to 650°. The magnetism increases at 550° to 525° with further carbide separations between the grains, and there is a further mechanical separation at 430° to 420°. In heating, if the steel is originally austenitic, there is a preliminary break-up at 350°, a further break-up at 450° to 470°, and a complete break-up at 575°, with the separation of magnetic carbides of iron or manganese at 475° to 575°. In rolled steel, separated carbides begin to re-dissolve at about 725°, and this is completed at 850° to 870° with the re-formation of austenite. Slight re-separation of carbides occurs along the grain outlines as the m.p. of the eutectic is approached, beginning at about 1025°, and continuing to 1100° or over. This is most noticeable in ingot metal, and taken together with the fact that the outlines of the original freezing structures persist in the cast steel at temp. below 1125° or thereabout, the remarkable tenderness of ingots between 1025° and 1125° is made clear. In cast ingot steel, the melting of the eutectic occurs at 1120° to 1140° if the heating is slow; and at about 1100° to 1130° if the heating be rapid. The complete re-solution of constituents and a re-formation of grains with the first formation of uniform austenite occurs above 1150°. Cementite re-separates out extensively at about 1250°. The mass melts at 1350° to 1375° or lower, depending on its composition. The subject was discussed by J. S. Lloyd, N. H. Aall, B. Kjerrmann, J. Strauss, J. H. Hruska, V. N. Krivobok, O. von Keil and F. Kotyza, E. C. Bain and co-workers, J. H. Hall, J. H. Andrew and H. A. Dickie, and H. Scott and J. G. Hoop. P. Schafmeister and R. Zoja found that the proportions of carbon in the eutectoid decreases with increasing proportions of manganese, being 0·83 per cent. carbon with 1 per cent. of manganese; about 0·77 with 2 per cent. of manganese; and about 0·71 with 3·1 per cent. manganese. The percentage of ferrite in the steels decreases with the rate of cooling, and with an increase in the proportions of manganese. The effect produced by the cooling is greater the higher is the percentage of manganese. H. A. Schwartz and A. N. Hird observed that manganese when present of the order of magnitude of 0·25 per cent. freezes out with the austenite; any sulphide freezes out at the beginning, and may be entrapped with the ledeburite eutectic.

The manganese carbides were discussed in connection with the carbides, **5**. 39, 20. J. O. Arnold and A. A. Read said that part of the iron in iron carbide is replaced by manganese in steels with a high proportion of manganese to form a **manganese iron carbide**; and J. E. Stead also made similar observations with respect to the carbide residue remaining after a manganese steel had been dissolved in dil. acid. F. Mylius and co-workers also obtained a complex carbide from steel; and A. Carnot and E. Goutal stated that when over 74 per cent. ferromanganese is treated with dil. acid, it furnishes the complex carbide $Fe_3C.4Mn_3C$; that 60 to 74 per cent.

ferromanganese furnishes $Fe_3C.2Mn_3C$; and that 30 to 60 per cent. ferromanganese yields $2Fe_3C.Mn_3C$. The last carbide crystallizes in large plates during the cooling of ferromanganese blocks. J. O. Arnold and A. A. Read observed that in steels with up to 4 per cent. manganese, the carbide residues are simply mixtures; possibly a true double carbide, $3Fe_3C.Mn_3C$, is present in steels with 11·21 to 13·38 per cent. manganese; and in steels with over 15 per cent. manganese, the carbide $2Fe_3C.Mn_3C$, or a mixture of carbides, is present. It was inferred that at ordinary temp. the manganese carbide is less stable than the iron carbide because, according to C. Benedicks, and O. Ruff and E. Gersten, the iron carbide of cementite is endothermal, and that of manganese carbide is exothermal. Carbon is assumed to have a stronger affinity for iron at the high temp.; and, conversely, at the low temp., the manganese is easily displaced by iron from manganese carbide. F. Wüst found that the effect of manganese is to impart exceptional stability to the solid soln., so that beyond *afd*, Figs. 467 and 468, no double phases occur, but only homogeneous solid soln. H. Lütke considered that manganese does not affect the percentage of carbon in solid soln. until more than 49 per cent. of manganese is present. H. Scott found that manganese has a marked effect on the temp. of transformation of martensite to troostite. A. Matsubara and J. Takubo found that cathodic polarization of iron pyrites in dil. sulphuric acid causes the ionization of one or both atoms of sulphur, which then combine with the hydrogen ions present to form hydrogen sulphide. If the material is first made the anode, subsequent cathodic polarization gives rise to an abnormal amount of hydrogen, and certain natural specimens behave similarly without previous treatment. The current yield is, in general, smaller when much hydrogen is evolved. F. Roll observed that manganese in cast iron makes the cementite more stable.

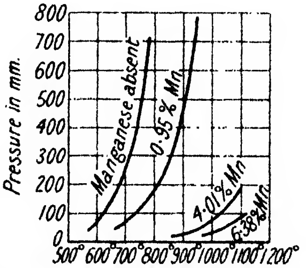


FIG. 469.—The Effect of Manganese in Iron on the Equilibrium: $2CO = CO_2 + C$.

The influence of carbon monoxide on solid soln. of iron and manganese was studied by R. Schenck and H. Semiller. The results for the press., *p* mm., of the gas at different temp. are as follow: (i)

	634°	672°	691°	722°	734°	774°	779°
p .	83	131	195	298	341	562	657

(ii) with an alloy of 0·95 per cent. of manganese, 96·6 per cent. of iron, and 2·15 per cent. of carbon:

	629°	679°	731°	751°	820°	900°	959°
p .	28	41	86	101	180	396	802

(iii) with an alloy of 4·01 per cent. of manganese, 93·0 per cent. of iron, and 2·99 per cent. of carbon:

	853°	911°	965°	1010°	1088°	1093°
p . . .	17	28	46	74	162	170

and (iv) with an alloy having 6·38 per cent. manganese, 93·2 per cent. of iron, and 1·32 per cent. of carbon:

	943°	956°	981°	1031°	1086°	1093°	1110°
p. .	15	20	20	34	62	68	96

The results are plotted in Fig. 469, and they show the lowering which the equilibrium point undergoes at any given temp., say 950°, with increasing proportions of manganese. This lowering is relatively great for even small proportions of manganese. For the cementation of manganese steels, *vide supra*, cementation; and for observations of E. Adamson, A. Allison, J. H. Andrew, J. O. Arnold and F. K. Knowles, O. Bauer and K. Sipp, H. H. Beeny, S. S. Beliaeff, P. P. Berg and M. S. Pshonik, E. Maurer and W. Bischof, A. F. Braid, J. R. Cain, A. Campion, E. Decherf,

C. H. Desch, J. W. Donaldson, A. L. Feild, H. E. Field, A. O. Fulton, F. Giolitti, R. C. Good, E. H. Graef, J. H. Hall, C. H. Herty, C. H. Herty and G. R. Fitterer, C. H. Herty and J. M. Gaines, H. D. Hibbard, T. E. Holgate, E. Houbaer, H. M. Howe, E. C. Hummel, J. E. Hurst, C. A. Jacobsen, W. Jellinghaus, J. E. Johnson, A. Jung, O. von Keil and co-workers, E. Killing, F. Körber, I. Kotaira and M. Maeda, E. C. Krekel, V. N. Krivobok, B. M. Larsen, K. Lehmann, E. Leuenberger, S. L. Levin, F. A. Matthewman, E. Maurer, R. P. Neville

FIG. 470.—Manganese Steel (×100). Quenched from 1200°. (G. Mars.)

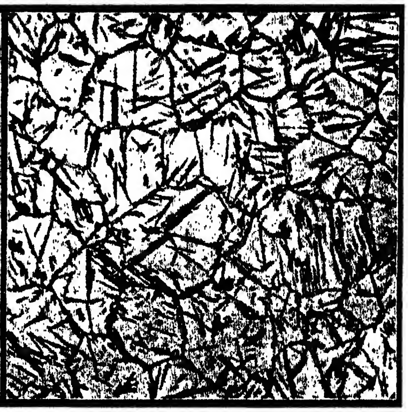


FIG. 471.—Manganese Steel (×100). Slowly cooled from 1200°. (G. Mars.)

FIG. 472.—Manganese Steel (×400). Slowly cooled from 1020° and tempered at 200°. (F. Schaffer.)

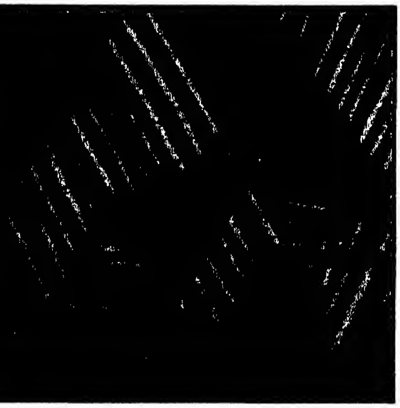


FIG. 473.—Manganese Steel (×1200). Slowly cooled from 1020°. (F. Schaffer.)

and J. R. Cain, A. L. Norbury, P. Oberhoffer and H. Schenck, G. Oishi, E. Oughterbridge, E. Piwowarsky, A. Pohl, W. E. Remmers, R. T. Rolfe, D. Saito and K. Nishiwara, H. Schenck, J. Shaw, N. W. Shed, G. Sirovich, A. E. M. Smith, S. C. Spalding, E. R. Taylor, E. Thews, B. Thomas, O. Wedemeyer, E. A. Wheaton, F. Wüst and co-workers, etc., on the effect of manganese on cast iron, steel, etc., *vide supra.*

The polyhedral crystals of the ferrite in manganese steel are illustrated by Figs. 470 and 471 (×100). Their outlines are not so rounded as in the case of the ferrite of, say, electrolytic iron. The steel illustrated in Figs. 472 and 473 contained 10 per cent. of manganese, and 1·15 per cent. of carbon; that in Fig. 470, was quenched from 1200°; and that in Fig. 471, was slowly cooled from that temp. The ferrite of alloy steels contains the special constituents—*e.g.* manganese-forming *manganoferrite*—in soln., and in this respect is related to martensite. The polyhedral form is best developed by cooling the steel from a high temp.; and the changes which occur in the heat-treatment of the alloy steel are in some respects rather simpler than with ordinary steels. Both diagrams show the polyhedral crystals with cleavage cracks, and in the slowly cooled sample, the carbide separations accumulate between the grains. The steel illustrated in Fig. 472 (×400) contains 20·43 per cent. manganese, and 1·08 per cent. of carbon; after forging, it was heated 45 mins. at 1020°, slowly cooled, and kept for 200 days at 200°. The steel illustrated by Fig. 473 (×1200) contains 20·98 per cent. of manganese, and 1·2 per cent. of carbon. After forging, it was heated 45 mins. at 1020°, and slowly cooled. The remarkable twinning of the crystals is clearly shown. According to C. R. Wohrman, the Widmanstätten structure and martensitic patterns with the iron-manganese alloys result from the breaking up of a solid phase into two. The latter structure is finer, less well defined, and less regular than the former. On thorough annealing there is formed an aggregate consisting of a ferritic constituent, an intermetallic compound rich in manganese. An eutectoid of the two (6 per cent. Mn) is also believed to exist, at first martensitic and then pearlitic. H. M. Howe and A. G. Levy discussed the hypothesis that the deformation lines in manganese steel are slip-bands, though it is possible they may be due to twinning. T. W. Hogg found crystals of titanium cyanonitride in ferromanganese.

F. Osmond observed that the curve representing the effect of manganese on the A_3-transformation of steel merges into the curve representing the martensite-pearlite transformation when 2·5 to 3·5 per cent. of manganese is present. The transformation with a steel having 4 per cent. manganese lies between 200° and 300°; with a steel having 5 per cent. manganese, it is near 100°; and with one having 7 per cent. manganese, it is below 0°. Unlike ordinary steel, therefore, alloys with over 7 per cent. of manganese, when heated above 700°, show no recalescence when cooled down to ordinary temp.—*vide supra*, martensite. R. A. Hadfield examined the heating and the cooling curves of a forged steel with 1·26 per cent. carbon, and 13·38 per cent. manganese, and of a cast steel with 1·16 per cent. carbon, and 10·88 per cent. manganese, and obtained no evidence of the existence of critical points when cooled down from or heated up to about 1300°. There is not the slightest evidence of any internal change of structure during heating or cooling. The same results are obtained if the material is cooled slowly, or quickly by quenching in water. This in spite of the fact that the physical properties are markedly influenced by the rate of cooling. Thus, by slowly cooling manganese steel, it remains brittle and non-magnetic, but by quick cooling, the material becomes very ductile, and non-magnetic. R. A. Hadfield continued:

> Whereas with all ordinary as well as hardening or self-hardening steels, the critical points are of considerable importance in guiding heat-treatment, with manganese steel, the heating and cooling curves are apparently of no value in this respect, and do not give any clue to the extraordinary change of structure which goes on in this material when it is transferred from its original and brittle state into that condition in which it possesses ductility unequalled by any other alloy of iron and steel.

R. A. Hadfield and B. Hopkinson found that a steel containing 1·26 per cent. of carbon, and 13·38 per cent. of manganese, becomes magnetic when heated several hours at 500°, and it loses its magnetism rapidly at about 700°. The heating curves show a heat absorption corresponding with this change. The range 650° to 750°, thus corresponds with the critical range in which ordinary carbon steel loses its magnetism. The reverse transformation—non-magnetic to magnetic—is so slow that it cannot be detected on the cooling curve. It is probable that as the temp. falls the alloy has a tendency to assume its equilibrium state in which it becomes magnetic, but the change is too slow for the alloy to acquire a state of stable equilibrium. The effect of manganese is to retard the attainment of equilibrium, rather than to produce any marked shift of the position of the critical range. R. A. Hadfield and B. Hopkinson added that the attainment of equilibrium in manganese steel at temp. below the change point, is opposed not only by resistances of the nature of fluid viscosity, which can be overcome by a very small force if continued long enough, but it is also opposed by a resistance of the nature of solid friction, which requires a force of a definite amount to be exerted before motion takes place at all. Thus, magnetic manganese steel at 650° ultimately attains a magnetism about twice as great as that reached by the non-magnetic variety heated at the same temp. Hence, the final condition at this temp. is different according as it is approached, so to speak, from above or below; and, so far as it is possible to judge from observed facts, these two limiting conditions could never be brought into coincidence, however much the heating were prolonged. E. Gumlich observed that a steel with 12·4 per cent. manganese began its magnetic transformation at −8°, and ended it at −109°. If this steel be re-heated, it loses its magnetism between 600° and 700°. Hence, between 0° and 600°, the same steel can be either magnetic or non-magnetic. Steels with 14·4 and 15·7 per cent. of manganese did not become magnetic at the temp. of liquid hydrogen.

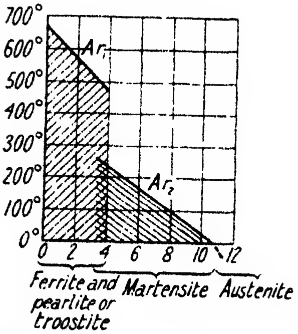


Fig. 474. — Constitution of Manganese Steel—0·3 to 0·4 per cent. Carbon.

L. Guillet observed that with a steel containing 0·20 per cent. of carbon, the pearlite structure obtains when the proportion of manganese is less than 5 per cent.; the martensite-troostite structure, with alloys having 5 to 12 per cent. of manganese; and the polyhedral γ-iron structure, with alloys having over 12 per cent. manganese; whereas with a steel having 0·80 per cent. carbon, the pearlitic structure occurs with alloys having less than 3 per cent. manganese; the martensite-troostite structure with alloys having between 3 and 7 per cent. manganese; and the polyhedral γ-iron structure with alloys having over 7 per cent. manganese. Free cementite occurs with alloys having over 1·65 per cent. carbon. This proportion of carbon in ordinary carbon steels was considered by F. Osmond to give the maximum proportion of austenite. According to A. M. Portevin, by annealing, followed by very slow cooling of steels containing 7 per cent. manganese, and 0·5 to 1·0 per cent. carbon, it is possible to obtain lamellar pearlite with martensite. With a steel containing 12 per cent. manganese, and 1 per cent. carbon, by very slow cooling the co-existence of lamellar pearlite and austenite, separated by a thin border of troostite, can be obtained. By ordinary annealing the whole becomes austenitic. Using a steel containing 9·8 per cent. manganese, and 0·66 per cent. carbon, by slow cooling it was possible to find the complexes troostite-pearlite-martensite-austenite, the martensite arising from a polymorphic transformation of the austenite. P. Dejean found that steels containing 0·3 to 0·4 per cent. of carbon, and 0 to 3·5 per cent. of manganese are pearlitic, and give the point Ar_1; those with 3·5 to 11 per cent. manganese are martensitic, and give the point Ar_2; and those with intermediate proportions 3·5 to 4·0 per cent. manganese, show both critical points, and consist of martensite and troostite. As the proportion of carbon rises to 0·7 to 1·0 per cent., the intermediate zone becomes of importance, since, with equal proportions of manganese, the temp. of the point Ar_1 rises, and that of Ar_2 falls, and finally, by suitable cooling, it is possible to produce the point Ar_1 in steels for which the point Ar_2 is below 0°, and the steels are troostitic and martensitic, Fig. 474. According to H. Meyer, the presence of manganese lowers the temp. of Ar_3 at which ferrite separates, thus:

Mn . .	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0 per cent.
Lowering Ar_3	5°	10°	15°	20°	26°	32°	38°	45°	52°	60°

H. I. Coe observed that the manganese arrests the carbon in lowering the primary freezing, so that with 13 per cent. of manganese, the f.p. is 40° lower than with the corresponding iron-carbon alloy. The effect of manganese on the critical temp. is as follows:

TOTAL CARBON	MANGANESE	SILICON	FIRST ARREST	SECOND ARREST	PEARLITIC CHANGE
3·14	0·025	0·01	1285°	1139°	700°
3·15	3·75	0·27	1270°	1141°	645°
3·37	7·95	0·17	1247°	1140°	525°
3·47	13·60	0·22	1204°	1140°	—
3·84	16·80	0·26	1160°	1141°	—
4·00	21·63	0·33	1140°	1130°	—
4·05	28·80	0·41	—	1125°	—
4·45	32·42	0·42	1133°	1125°	—

As pointed out by F. Wüst, the pearlitic change is thus materially affected by manganese, so that with 8 per cent. of manganese it can scarcely be detected. J. O. Arnold said that manganese does not form a true steel having 100 per cent. pearlite. F. Wüst and H. Meissner observed that in the presence of 1·5 per cent. of silicon, and 2·7 to 3·9 per cent. of carbon, below 0·3 per cent. of manganese favoured the separation of graphite, but with 0·3 to 2·5 per cent. of manganese, no perceptible effect on the condition of the carbon was observed. H. I. Coe observed that in the presence of silicon, the effect of manganese on the pearlitic change in cast iron is more marked. Thus, the addition of 4·45 per cent. of manganese, in the absence of silicon, changed the pearlitic arrest from 700° to about 600°, whereas in the presence of silicon, the arrest was lowered to 350°. Large proportions of manganese, even in the presence of silicon, keep the solid soln. of combined carbon more stable, and favour the production of hard, white cast iron. A. Merz, J. A. Jones, F. Kjerrman, H. S. Rawdon and F. Sillers, H. Scott and J. G. Hoop, G. Tammann, and J. J. A. Jones discussed the Ac_1-range in manganese steels; R. Austin, H. M. Boylston, A. Allison, W. Eilender and H. Diergarten, F. M. Walters and C. Wells, M. Hamasumi, Z. Shibata, V. N. Krivobok and co-workers, P. Schafmeister and R. Zoja, H. S. Rawdon and F. Sillers, H. Sawamura, C. R. Wohrman, H. Schenck, P. Oberhoffer and co-workers, T. Swinden, F. Giolitti, E. Killing, A. L. Feild, C. H. Herty and J. M. Gaines, K. Hilgenstock, B. M. Larsen, H. E. Field, F. W. Lürmann, T. Naske and A. Westermann, A. K. Silin, and J. O. Arnold and G. B. Waterhouse, the deoxidizing or desulphurizing action *vide* the action of oxygen on iron. L. Goldmerstein tried manganese and other fluorides for removing phosphorus, sulphur, etc., as fluorides.

According to W. S. Potter, during the cooling of steels with 1 to 2 per cent. of carbon and 10 to 20 per cent. of manganese, γ-iron begins to freeze out at about 1370°, and is for the most part frozen at about 1270°; the eutectic freezes at 1125° to 1080°—and at a rather higher temp. with low-carbon and manganese mixtures. The mechanical break-up of austenite occurs at about 850° to 825°; carbides separate between the grains at 710° to 650°; the magnetism increases at 550° to 525° with a further separation of carbide between the grains; and there is a further separation of carbide at 430° to 420°. In heating a steel, originally austenitic, there is a preliminary break-up at 350°, a further break-up at 450° to 470°, and a complete break-up at 575°, with the separation of magnetic carbides of iron or manganese at 475° to 575°. In rolled steel, the separated carbides begin to be re-dissolved at about 725°, and this is completed at 850° to 870° with the re-formation of austenite. There is a slight re-separation of carbides along the grain outlines as the m.p. of the eutectic is approached, beginning at about 1025° and continuing to 1100° or over. This is very marked with ingot metal; and, considering that the outlines of the original freezing structures persist in the cast steel at temp. below about 1125°, this explains the tenderness of ingots between 1025° and 1125°. In cast ingots, the melting of the eutectic occurs at about 1120°

to 1140° if the heating is slow, and at about 1100° to 1130° if the heating be rapid. The complete re-solution of the constituents, and new grain-formation with the production of austenite occurs above 1150°; cementite separates extensively above 1250°; and the mass melts at 1350° to 1375° or less, according to its composition.

B. M. Larsen showed that manganese tends to extend the temp. range of stability of γ-iron or austenite; manganese forms a carbide more stable than cementite; and manganese atoms cannot well diffuse through the iron space-lattice at ordinary annealing temp. at which carbon atoms diffuse freely. In steels containing more than 1 per cent. of manganese, dendritic segregation causes a marked dendritic pattern in cast sections, and a fibrous pattern in rolled or forged bars. The proportion of manganese is higher in the dendritic fillings. Heat-treatment up to 1100° is ineffective, but an hour's heating at 1300° causes the manganese to diffuse to a uniform concentration throughout. As a cast bar with 1 to 3 per cent. of manganese cools through the critical range, the Ar_3-point is attained first by the lower manganese axes of the dendrites. If the cooling rate is below 5° to 7° F. per minute, the carbon tends to segregate in the high-manganese fillings between the dendrites. With a total carbon-content of 0·3 per cent. or less, a dendritic pattern is formed by the pearlite or sorbite areas in cast sections, and a marked banded structure in rolled or forged bars; the ferrite areas always correspond to the dendritic axes. Phosphorus and arsenic tend to cause these same patterns, but as these elements raise the Ar_3-point of pure iron, the ferrite areas formed correspond to the dendritic fillings. Above the Ar_3-point, the carbon atoms are probably uniformly distributed in the γ-iron lattice. With an increasing percentage of manganese, a manganese-cementite tends to form, perhaps containing an increasing proportion of mols. of Fe_2MnC. Up to 2 per cent. manganese, finer-grained pearlite and sorbitic areas are formed. Above 2 per cent. manganese, the carbides separate in a fine-grained distributed structure that may be linked together through the manganese atoms scattered through the iron space-lattice. The eutectoid point of pure iron-carbon alloys containing about 0·9 per cent. carbon appears to widen with an increase in the amount of manganese into a eutectoid range which, with 3 per cent. of manganese, extends from 0·6 to 0·92 per cent. carbon. This apparent eutectoid range is probably the result of a very small temp. interval between the Ar_3- and Ar_1-points in the given range of carbon-content. H. M. Howe did not agree with T. Mukai that manganese causes the retention of carbon in the non-hardened state, and he summarized the effects of sudden cooling on manganese and carbon steels as follows:

	CARBON STEEL	MANGANESE STEEL	EFFECTS
Hardness	Large increase	Slight increase	Alike
Per cent. total combined carbon.	Large increase	Moderate increase	Alike
Specific gravity	Decrease	*Nil* or increase	Opposite
Size of grain	*Nil* or decrease	Increase	Opposite
Separation components . .	Decrease	Increase	Opposite
Ductility	Large decrease	Large increase	Opposite
Tensile strength	Increase	Increase	Alike

In 1878, E. Mallard showed that the crystal form is dependent on the proportion of manganese, and that with 52 to 55 per cent. the crystal form changes. B. Rathke showed that the crystals rich in manganese are hexagonal, or pseudohexagonal, and those with smaller proportions are rhombic prisms. F. Wever observed that with manganese steels ranging from 19·08 per cent. manganese and 0·30 per cent. carbon to 2·06 per cent. manganese and 1·90 per cent. carbon, the lattice parameter, a, of austenite varied from 3·597 to 3·643 A.; the sp. vol. from 0·1262 to 0·1288 for high and low manganese respectively; and $a=3{\cdot}578+0{\cdot}00050[\mathrm{Mn}]+0{\cdot}00645[\mathrm{C}]$, where the symbols represent atomic percentages. V. N. Svetchnikoff, and T. Mukai studied the microstructure of the manganese steels; M. L. V. Gayler, the constitution; and for the observations of E. Persson and E. Oehman, and Z. Nishiyama on the X-radiograms of these alloys, *vide* manganese. E. C. Bain,

M. Gensamer and co-workers, J. B. Friauf and M. Gensamer, and V. N. Krivobok and C. Wells discussed this subject. W. Schmidt's X-radiograms of the iron-manganese alloys showed that the α-solid soln. is present up to 20 per cent. of manganese, when the lattice parameter, a, increases from 2·857 A. for iron alone, to 2·871 A. for iron with 20·1 per cent. of manganese. Alloys with 16 to 60 per cent. of manganese contain the γ-solid soln., with a cubic, face-centred lattice having a=3·586 A. for iron with 15·7 per cent. of manganese to a=3·616 A. for iron with 55·85 per cent. manganese. Alloys with 60 to 98 per cent. of manganese have the structure of β-manganese, with a lattice parameter increasing from 6·24 A. for 62·7 per cent. of manganese, to 6·28 A. for 87·25 per cent. manganese; alloys with more manganese have the structure of α-manganese. In the alloys with 12 to 29 per cent. of manganese, there is an ϵ-phase having a hexagonal, close-packed lattice, with a=2·532 A. to 2·543 A., and c=4·061 A. to 4·082 A., according to the manganese-content. The way the lattice parameters change shows that no definite chemical individual, as a compound of iron and manganese, exists. Since the α-, γ-, and ϵ-phases can co-exist in the same alloy, one of them must be metastable in the range 12 to 29 per cent. of manganese. No transition points were observed by thermal or dilatometric analysis. For E. Oehman's observations on the X-radiograms, *vide* manganese. H. Perlitz discussed the distance apart of the atoms. Z. Nishiyama found the lattice parameter a; the sp. gr.; and the elastic modulus, E kgrms. per sq. cm., at 14·8° to 15·6°, to be:

Mn .	0	0·5	1·0	1·5	2	3	4	6	8 per cent.
a . .	2·866	2·863	2·865	2·864	2·867	2·873	2·871	2·867	2·872 A.
Sp. gr. .	7·8596	7·8555	7·8404	7·8416	7·8430	7·8402	7·8292	7·8163	7·8003
$E \times 10^{-6}$.	2·151	2·128	2·138	2·125	2·128	2·122	2·108	2·072	2·044

R. A. Hadfield found the sp. gr. of cast, 13·75 per cent. manganese steel to be 7·83, and when drawn into wire, 7·81–7·83. W. Brown found for the sp. gr., and sp. vol.:

C .	0·20	0·24	0·41	0·36	0·15	1·20	0·26	1·54 per cent.
Mn .	0·50	1·00	2·25	4·00	5·40	7·00	13·00	18·50 ,,
Sp. gr.	7·8456	7·8354	7·7983	7·8352	7·8411	7·9028	7·9970	7·9075
Sp. vol.	0·12746	0·12762	0·12823	0·12763	0·12753	0·12654	0·12605	0·12646

so that with up to 2 per cent. manganese, the sp. vol. increases 0·00026 c.c. for 1 per cent. manganese, and with 2 to 18·5 per cent. manganese, the sp. vol. decreases 0·00015 c.c. per 1 per cent. manganese. J. O. Arnold, H. A. Dickie, A. Osawa, H. Meissner, H. Tomlinson, and O. Simmersbach discussed this subject. C. Benedicks and co-workers studied the sp. vol. E. Gumlich found the sp. gr. gives an abrupt increase when 8 to 10 per cent. of manganese has been added, Fig. 476, and that the sp. gr., with p per cent. manganese, up to 1 per cent., decreases in accord with $7{\cdot}873-0{\cdot}008p$. F. Wever gave for the sp. vol., v, of manganese steel, $v=0{\cdot}1246+0{\cdot}0004[\mathrm{Mn}]+0{\cdot}0041[\mathrm{C}]$, where the symbols represent atomic percentages. The results of K. Tamaru are summarized in Fig. 475; and those of C. Benedicks, in Fig. 186. H. I. Coe found that the shrinkage curve of the manganiferous, white cast irons showed minima corresponding with the formation of carbides: Fe_3C; $8Fe_3C.Mn_3C$; $2Fe_3C.Mn_3C$; and $3Fe_3C.2Mn_3C$; and with grey cast irons the increasing shrinkage with increasing proportions of man-

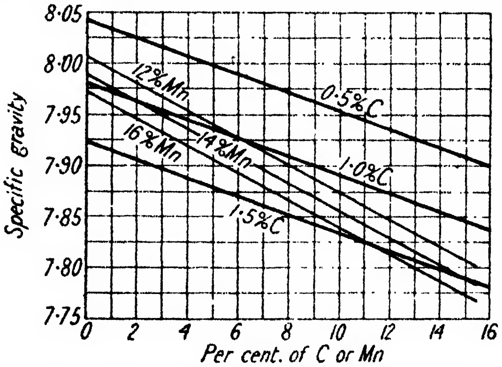


FIG. 475.—Specific Gravities of Manganese Steels.

ganese is more uniform. Some peculiarities observed by R. A. Hadfield in connection with the hardness of manganese steels have been indicated above. R. A. Hadfield pointed out that the hardness varies considerably in degree. It is most intense in cast material containing 5 to 6 per cent. of manganese, for no tool will face or touch this steel; a gradual decrease in hardness occurs as manganese is added, so that when the proportion has attained 10 per cent., the softest condition is reached; an increase in hardness again occurs as the proportion of manganese rises to 22 per cent., when the hardness is not so great as it was with 5 per cent. By heating at 831° a specimen with 1·17 per cent. carbon, and 12·46 manganese for 10 days, the steel became magnetic, and its Brinell's hardness decreased from 532 to 241. H. I. Coe found variable results with the scleroscopic hardness of manganiferous, white cast irons. The hardness rises from 57 to 80 as the proportion of manganese rises to about 6 per cent., there is then a fall to a minimum 52 with about 11 per cent. of manganese, a rise to a maximum of 66 with 16 per cent. manganese; a fall to 60 with about 18 per cent. of manganese, and a very gradual rise from 70 as the proportion of manganese exceeds 22 per cent. With grey cast irons, there is a maximum of 40 with 1·5 per cent. manganese, a fall to 52 with 2·7 per cent. manganese, a sudden rise to 52 with 4 per cent. manganese, and a slower rise with higher proportions of manganese. M. Hamasumi, and K. Taniguchi studied Brinell's hardness of these alloys. The results of L. Guillet are summarized in Fig. 477. The hardness of pearlitic tungsten steel is approximately the same as that of the corresponding carbon steels; the martensitic steel shows the maximum hardness, and the steel with the polyhedral structure is softest. T. Murakami and K. Hatsuta, T. Kase, H. A. Dickie, H. O'Neill, A. Osawa, and A. Wahlberg also measured the hardness of the manganese steels. R. A. Hadfield found for low-carbon, manganese steels, the values for Brinell's hardness:

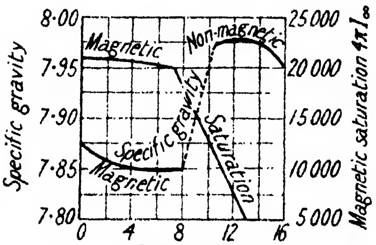


FIG. 476.—The Specific Gravity of Manganese Steel.

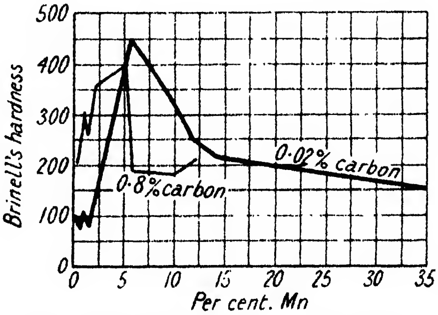


FIG. 477.—Brinell's Hardness of Manganese Steel.

Mn . .	1·10	3·13	4·10	5·50	10·50	12·90	15·90	19·85 per cent.
Hardness .	143	430	418	418	444	302	192	235

The value for iron alone is about 90; and for the hardest steel known, 800, or perhaps a little higher. With high-carbon, manganese steels:

Mn . . .	1·16	3·10	4·98	10·07	15·11	19·59 per cent.
Hardness. . .	650	600	286	179	196	192

W. Giesen said that pearlitic steels with 0 to 7 per cent. of manganese and 0 to 5 per cent. of carbon, or 0 to 5 per cent. of manganese and 0·95 per cent. of carbon, differ very little from ordinary steels with the same carbon-content, in respect to tensile strength, ductility, yield-point, elongation, hardness, and brittleness. Martensitic and troostitic steels with 7 to 15 per cent. of manganese and 0·3 per cent. of carbon, or 5 to 9 per cent. of manganese and 0·95 per cent. of carbon, have a high limit of about 165,000 lbs. per sq. in. for the stretching and breaking strains; the ductility and brittleness are very low, and the hardness is extremely high. Generally, a manganese steel consisting of martensite, exhibits a great brittleness and high tensile strength; and if the structure is polyhedral, the hardness is very great. Steels with the γ-iron structure having 7 to 18 per cent. of manganese and 0·3 per cent. of carbon, or 5 to 11 per cent. of manganese and 0·95 per cent. of carbon, have a high ductility, low elastic limit, low brittleness, and medium breaking strength. A steel with 5·5 to 11 per cent. manganese is more brittle and harder than one in which the manganese-content is higher or lower. It is rare to find that the hardness and brittleness of steels high in manganese are diminished, instead of increased, by quenching, but this does occur with a manganese steel low in carbon when the manganese reaches 19·5 per cent., and with 7·5 per cent. manganese in high-carbon steels. F. Robin studied the acoustic properties of manganese steels. The martensitic steels show a fall in resonance up to 300°, when the metal is aphonic.

Observations on the mechanical properties of manganese steel were made by K. Amberg, P. Bardenheuer and G. Schitzkowsky, C. F. Burgess and J. Aston, L. Campredon, A. Capron, C. L. Clark and A. E. White, H. I. Coe, A. L. Colby, V. Deshayes, H. A. Dickie, V. Ehmcke, F. L. Garrison, H. Guédras, L. Guillett, R. A. Hadfield, J. H. Hall, J. H. Hall and G. R. Hanks, J. J. Hall, G. A. Hawkins and co-workers, J. H. Hruska, G. R. Johnson, J. A. Jones, W. Kahlbaum and L. Jordan, W. J. Keep, V. N. Krivobok, G. Lang, A. Ledebur, E. Leuenberger, E. Lievenie, H. C. Loudenbeck, P. Marsich, R. P. Neville and J. R. Cain, A. M. Portovin, W. S. Potter, F. Rapatz and H. Pollack, H. W. Roberts, A. D. Ross, R. Scherer, W. Schneider and E. Houdremont, A. Schulze, H. J. Schuth, H. Souther, J. F. Springer, A. Stadeler, B. Stoughton and W. E. Harvey, J. Strauss, V. N. Svetchnikoff, E. E. Thum, H. Tomlinson, T. D. West, M. H. Wickhorst, and F. Wüst and H. Meissner.

H. I. Coe observed that the addition of the first 5 per cent. of manganese to white cast iron produces no appreciable change in brittleness, but increases up to 13 per cent. make the metal more brittle. With higher proportions of manganese, the metal becomes stronger, and with 19 per cent., there is an increase in toughness. With 30 per cent. and over, the metal partakes of the nature of spiegeleisen and becomes weak and brittle. Z. Nishiyama's observations on the elastic modulus are indicated above. R. A. Hadfield observed that the cast manganese steel is so brittle that it does not seem to be a steel at all. This cold-short material, however, is ductile when hot, and can then be drawn into any desired size. The brittleness is intensified by the peculiar crystallization of the cast samples. When forged, there is a marked increase in strength, but the steel is still brittle. The grain of the forged steel is coarse and open. If re-heated and cooled quickly in air, a fine, close grain is produced, and this is the state of the metal which is made into boring cutters, and other tools. The tensile strengths, in kgrms. per sq. mm., and the percentage elongations of forged steel and of steel heated to a high temp. and cooled in air, oil, or water, are indicated in Table LXXXIII. J. O. Arnold and F. K. Knowles obtained the results indicated in Table LXXXIV, and they consider that they prove that, although the influence of carbon is considerable, the dominating factor is the presence of manganese. M. Hamasumi measured the tensile strength of the alloys; and C. L. Clark and A. E. White, the effect of temp. on the tensile strength. A. M. Portevin found that when the percentage of manganese increases from 0·5 to 5 per cent., the resistance to shear and the elastic limit increase until the former is 61 kgrms. and the latter 46 kgrms., but the contraction on shearing diminishes slightly. Steels with over 5 per cent. manganese show a nearly constant resistance to shear of nearly 50 kgrms., the elastic limit remains low, between 10

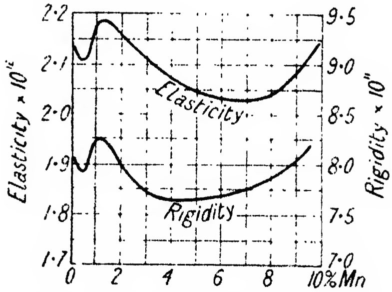


FIG. 478.—The Elasticity and Rigidity of Manganese Steel.

and 20 kgrms., and the contraction on shearing has high values ranging from 20 to 30. The first class of steels are pearlitic and troostitic, and the second class have γ-iron. So long as the steels are simply pearlitic, the resistance to shear and elastic limit are small, but they attain comparatively high values with 5 per cent. manganese. T. Matsushita's results for the elastic modulus and rigidity of manganese steel; in dynes per sq. cm., are summarized in Fig. 478. R. A. Hadfield examined the effect of reducing the temp. to —182° on the mechanical properties of manganese steel. With 0·08 C and 3·50 Mn, the tenacity is increased and all ductility is lost. The metal does not appear to be modified when the temp. returns to normal. Steels with 0·41 C and 2·23 Mn, and 1·66 C and 11·53 Mn all behaved normally. A steel with 1·23 C and 12·6 Mn had a slightly raised tensile strength and suffered a 2·5 per cent. decrease in elongation. The cooling to —182° thus embrittles or de-toughens the material. When the steel is cooled to —182° and allowed to return to normal temp., the de-toughening is merely temporary, for the steel exhibits an increase in toughness. When quenched in liquid air from 620° to —182°, the steel is toughened as if it had been cooled to ordinary temp., showing that the toughening occurs in the fall of the first 150°–250°. In no case did the steels at —182° show any change in magnetic properties. F. Robin found that the resistance of manganese steels to crushing resembles that of nickel steels (*q.v.*) with the corresponding structure. For C. L. Clark and A. E. White's observations on the proportional limit, *vide* Fig. 481, nickel-chromium steels.

TABLE LXXXIII.—EFFECT OF HEAT-TREATMENT ON TENSILE STRENGTH AND ELONGATION OF MANGANESE STEEL.

Percentage composition			Tensile strength				Elongation			
				Quenched in				Quenched in		
C	Si	Mn	Forged	Air	Oil	Water	Forged	Air	Oil	Water
0·47	0·44	7·22	42·5	42·5	39·4	39·4	2	5	3	2
0·85	0·28	10·60	53·6	64·5	66·2	63·0	4	17	19	17
1·10	0·16	12·60	61·4	58·3	78·8	86·7	2	11	28	27
0·85	0·28	14·01	56·7	75·6	86·6	105·5	2	14	27	44

TABLE LXXXIV.—THE MECHANICAL PROPERTIES OF MANGANESE STEEL.

Percentage composition		Elastic limit (tons per sq. in.)	Maximum stress (tons per sq. in.)	Elongation (per cent.)	Reduction of area (per cent.)	Alternating impact tests (alternations endured)
C	Mn					
Below 0·1	1·10	19·04	24·48	43·5	79·5	350
	3·13	34·56	41·42	25·0	63·2	180
	4·10	20·56	53·48	25·5	42·4	225
	5·50	38·68	65·96	28·5	38·1	207
	10·50	30·80	57·88	1·0	0	6
	12·90	19·80	56·12	6·5	4·6	44
	15·70	37·80	63·72	17·5	20·6	290
	19·85	—	—	30·0	33·5	212
0·85	1·16	25·75	52·76	10·5	11·7	161
	3·10	39·48	59·64	5·0	5·2	89
	4·98	33·96	54·64	2·0	2·0	28
	10·07	30·12	42·22	1·0	1·4	8
	15·11	28·00	49·88	9·5	9·7	241
	19·59	24·68	52·16	23·5	19·5	249

A. Schulze studied the coeff. of thermal expansion of the iron-manganese alloys between 20° and 100°. T. Matsushita's results for the coeff. of thermal expansion are shown in Fig. 479. The continuous lines refer to pearlitic or martensitic steels, and the dotted lines to austenitic-martensitic steels. The hysteresis loop at the critical temp. widens as the proportion of manganese increases. J. A. N. Friend and R. H. Vallance gave $0{\cdot}0_4183$ for the coeff. of expansion of manganese steel between 10° and 100°. Observations were made by A. M. Portevin and P. Chévenard, and M. Gensamer and co-workers. A. Schulze gave 0·03 for the coeff. of thermal conductivity. W. S. Potter found the sp. ht. of manganese steels to range from 0·15 at ordinary temp. to 0·20 at 1200°. W. Brown gave :

C .	0·20	0·24	0·41	0·36	0·15	1·20	0·26	1·54	per cent.
Mn .	0·50	1·00	2·25	4·00	5·40	7·00	13·00	18·50	,,
Sp. ht.	0·9258	0·8987	0·9007	0·9128	0·9189	0·9357	0·9796	0·9884	

so that the sp. ht. first decreases up to 1 per cent. manganese, and then increases 0·0006 per 1 per cent. of manganese up to 18 per cent. A. Eucken and H. Werth measured the sp. ht. of manganese-iron alloys, and the values for the at. hts. under constant press. and constant vol., and for Debye's constant $\ominus$—the x of **1.** 13, 15—are as follow :

50 per cent. Mn	T° K .	15·65°	18·37°	46·93°	88·65°	115·80°	173·13°	205·46°
	C_p .	0·05628	0·07510	0·8590	2·890	3·895	5·144	5·645
	C_v .	0·05628	0·07510	0·8587	2·883	3·878	5·101	5·583
	$\ominus$.	316	338	369	366	356	310	235
30 per cent. Mn	T° K .	15·32°	17·66°	42·45°	83·00°	114·50°	186·94°	215·94°
	C_p .	0·05008	0·05863	0·5885	2·634	3·756	5·438	5·830
	C_v .	0·05008	0·05863	0·5884	2·529	3·741	5·386	5·761
	$\ominus$.	322	352	386	378	368	267	177
19·4 per cent. Mn	T° K .	19·95°	22·00°	40·55°	83·90°	118·63°	176·25°	205·40°
	C_p .	0·0780	0·1157	0·5506	2·813	4·090	5·532	6·048
	C_v .	0·0780	0·1157	0·5505	2·807	3·562	5·481	5·977
	$\ominus$.	361	350	378	363	354	229	—

F. Wüst and co-workers represented the mean sp. ht. between 0° and θ° up to 1070°, by $0{\cdot}12037+0{\cdot}0_4 2541\theta$; between 1130° and 1210°, by $0{\cdot}17700-7{\cdot}41\theta^{-1}$; and between 1230° and 1250°, by $0{\cdot}19800-3{\cdot}8\theta^{-1}$; where the true sp. ht. between 0° and 1070° is $0{\cdot}12037+0{\cdot}0_4 5082\theta$. H. Klinkhardt studied the sp. ht. of manganese steels. Manganese suffers an allotropic change between 1070° and 1130° which has a thermal value of 24·14 Cals. R. A. Hadfield showed that the thermal conductivity of manganese steel is less than that of ordinary steel ; A. Schulze gave for a 10 per cent. manganese steel, $\lambda=0{\cdot}03$; and W. S. Potter found the thermal conductivity up to 600° is about one-third of that of ordinary steel. T. Matsushita's results for the thermal conductivity, in c.g.s. units, and electrical conductivity, in mhos, of manganese steel are summarized in Fig. 480.

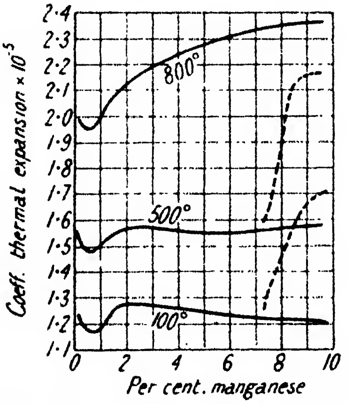


FIG. 479.—Thermal Expansion of Manganese Steels.

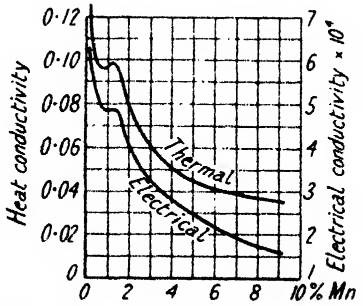


FIG. 480.—Thermal and Electrical Conductivities of Manganese Steel.

J. T. Littleton found the reflecting power, R, the coeff. of extinction, k, and the index of refraction, μ, for light of wave-length 5893, and an alloy with 50, 75, and 100 per cent. manganese, to be respectively, R=61·0, 62·5, and 64·0; k=3·70, 3·77, and 3·88; and μ=2·42, 2·43, and 2·41. S. Shimura and K. Wada studied the spectral analysis of the alloys; and H. Pincass, the spectra of the Fe-Mn catalyst.

W. F. Barrett, and J. H. Partridge found that the electrical resistance of steel is increased by the introduction of manganese, so that manganese steel can be used for making resistance coils; and E. Hopkinson observed that a steel with 13·95 per cent. manganese had a resistance eight times as great as that of iron. W. F. Barrett said that the increased resistance with rise of temp. is 0·136 per cent. per degree, while with iron, the increase is 0·5 per cent. W. S. Potter said that the resistance of manganese steel is roughly 3·4 times that of Bessemer steel. According to H. le Chatelier, the resistance of steel increases 5 microhms for each per cent. of manganese; and the resistance of magnetic steel with a high proportion of manganese is much less than the same steel in the non-magnetic state. Observations were made by T. Matsushita, H. A. Dickie, and H. Tomlinson. O. Boudouard saw that the proportion of carbon does not affect the resistance of manganese steel, and that the resistance, R microhms per cm. cube, attains a maximum with 12 to 13 per cent. of manganese; thus:

Mn .	0·43	2·15	6·14	10·51	12·92	14·40 per cent.
R .	15·5	25·4	59·8	73·1	75·8	72·5

K. Tamaru found that the electrical resistance of rods slowly cooled from 1050° increase at first linearly with increasing proportions of manganese, Fig. 481; the increase is rapid between 3 and 5 per cent. Mn, and then again linearly with the increase of manganese. This rapid increase is caused by the increasing content of austenite intermingled with ferrite. The linear increase of resistance above 5 per cent. of manganese-content shows that the resistance of austenitic steel increases linearly with the content of manganese; hence, when this linear portion of the curve is extrapolated to manganese-content zero, the corresponding ordinate gives the electrical resistance of austenitic carbon steel containing 0·5 per cent. of carbon at room temp., its sp. resistance being $32{\cdot}7\times10^{-6}$ ohm. The linear portion below 3 per cent. of manganese shows the electrical resistance of pearlitic steel; it intersects with the ordinate at a point 20×10^{-6} ohm when extrapolated to manganese zero, this value being sp. resistance of pearlitic steel containing 0·5 per cent. of carbon, and in good agreement with the result found by H. Masumoto. E. Gumlich represented the resistance of alloys with p per cent. manganese—up to 9 per cent. Mn— by $R=0{\cdot}1+0{\cdot}05p$; and with over 10 per cent. of manganese, by $R=0{\cdot}506\times0{\cdot}007(p-10)$. There is a break in the resistance curve, R microhms per cm. cube; and also in the curve showing the percentage decrease in the temp. coeff. of the resistance of manganese steel slowly cooled from 800°. T. Matsushita's results for the electrical conductivity, in ohms, of manganese steels are shown in Fig. 482. H. le Chatelier gave 5·0 microhms per cm. cube for the increase in the

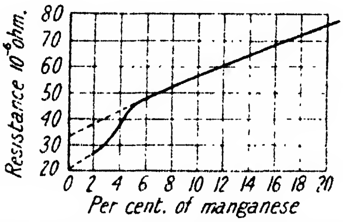


FIG. 481.—Electrical Resistance of Manganese Steels.

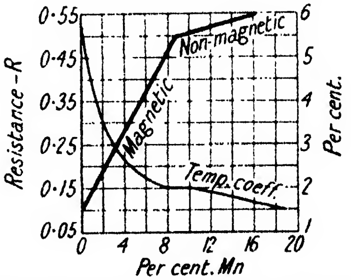


FIG. 482.—Electrical Resistance Curve of Manganese Steels.

resistance of magnetic, and 3·5 microhms for non-magnetic steels by the addition of 1 per cent. of manganese; W. F. Barrett, and E. Gumlich and P. Goerens gave 5·0; G. Lang, and T. Matsushita, 5·5. H. Tomlinson found that the electrical resistance is decreased by annealing hard-drawn wires, and that the resistance is increased by a longitudinal pull, and by longitudinal magnetization.

G. Tammann and E. Vaders found the e.m.f. of the cell Fe : 0·1*N*-$MnCl_2$: $Mn_nFe_{(100-n)}$, where *n* represents the percentage by weight:

n	19·53	29·37	36·58	58·94	69·24	78·89	100 per cent.
E immediately	0·035	0·290	0·260	0·248	0·475	0·465	0·520 volt
E after 40 hrs.	0·005	0·080	0·050	0·120	0·160	0·130	0·300 ,,

A. N. Campbell discussed the anodic behaviour of 77·9 per cent. ferromanganese in *M*-soln. of manganese sulphate, nitrate and chloride, and in ferrous sulphate. Passivity was absent in soln. of ferrous chloride with a slight excess of acid. At ordinary temp., passivity was found to occur in all the soln., but it was not complete; it was specially marked with manganese sulphate soln. The potential of the visible oxygen discharge from a neutral electrolyte at the ordinary temp. is about +2·15 volts (abs.). This is near the potential required for the formation of permanganate in an electrolyte of manganese sulphate. The passivity is destroyed at 25°, and also by activating the anode by charging it with hydrogen or by etching it with sulphuric acid. The passivity is reduced by a superposed alternating current. In *N*-potassium hydroxide electrolyte at 15° and 75° there is no formation of manganate, and nothing enters into soln.; but heavy slimes are formed. In other cases, both components entered into soln.; the efficiency is often less than 100 per cent., possibly owing to soln. being followed by immediate precipitation. Under a gas discharge the anode disintegrates, and ferromanganese is thus useless as an insoluble anode. C. Wells and J. C. Warner, and M. de K. Thompson and R. B. Morrissey studied the potential of ferromanganese.

E. Sedström, and J. Galibourg studied the thermoelectric properties of the alloys. E. L. Dupuy and A. M. Portevin found that the thermoelectric force against copper, in millivolts, with steels having 0·84 to 0·96 per cent. of carbon, is as follows:

Mn		0·40	1·03	3·08	12·09 per cent.
Annealed	−80°	−0·30	−0·70	−2·60	−9·60
	100°	−3·10	−2·80	−4·70	−11·80
Hardened	−80°	−0·00	−5·40	—	−10·00
	100°	−2·00	−6·65	—	—

As indicated above, S. Rinman, and D. Mushet noticed that manganese diminishes or destroys the magnetic properties of steel even when there is eight or nine times as much iron as manganese present. R. A. Hadfield added that the material behaves in the same manner in its forged or cast state, and water or oil quenching makes practically no difference. J. Hopkinson observed that the small quantity of manganese present enters into what must be regarded, for magnetic purposes, as the molecule of iron, and completely changes its properties. Twelve per cent. of manganese annihilates the magnetic properties of iron. J. A. Ewing and W. Low said that even under the magnetic forces amounting to 10,000 c.g.s. units, the resistance which 13·95 per cent. manganese steel offers to magnetization suffers no break-down in any way comparable to that which occurs with wrought-iron, cast iron, or ordinary steel, at a very early stage in the process of magnetization. On the contrary, the permeability is approximately constant under large and small forces, and may be therefore concluded as being only fractionally greater than that of copper, brass, or air. As indicated above, R. A. Hadfield noted that the magnetization disappears at 700°; and when the non-magnetic steel is heated several hours at 500°, it becomes magnetic. W. F. Barrett found that when the magnetization of ordinary iron is represented by 100,000, that of manganese steel is 20, and its susceptibility or induced magnetization is about as low as that of zinc or other non-magnetic metals. Observations were made by H. A. Dickie, L. T. O'Shea, H. Tomlinson, R. A. Hadfield and co-workers, W. F. Barrett, A. Abt, A. D. Ross, J. J. Porter, E. Griffiths, etc. S. Hilpert and W. Mathesius, T. Matsushita, J. H. Partridge, F. Goltze, H. F. Parshall, P. Kapitza, E. Gerold, and C. F. Burgess and J. Aston gave for the magnetic induction of alloys of manganese and iron the results indicated in Table LXXXV. The annealed alloys show a marked decrease in permeability with increasing proportions of manganese. Annealing at 675° improves the permeability, but a second annealing at 1000° lessens it. Quenching restores the 4·51 per cent. alloy to its best condition obtained by a first annealing at 675°. The values for coercive force and retentivity, Table LXXXVI, follow closely the fluctuations in the permeability.

TABLE LXXXV.—MAGNETIZATION OF IRON-MANGANESE ALLOYS.

Per cent. Mn	$H=10$				$H=100$			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°
0·50	9850	13,000	11,300	10,700	18,300	18,400	17,900	18,150
1·00	4850	9,700	5,400	—	18,200	18,000	17,800	—
2·00	1350	3,100	1,100	—	15,700	16,700	15,350	—
3·00	650	1,150	900	—	12,200	14,550	14,650	—
3·50	1100	850	950	—	13,700	13,600	13,550	—
4·51	150	800	500	900	12,100	16,800	10,600	16,400
6·00	200	—	—	—	10,150	—	—	—
8·00	150	150	50	—	5,450	6,100	1,750	—
10·00	0	50	150	0	500	1,400	1,300	—
10·42	0	0	0	0	0	300	300	500

TABLE LXXXVI.—THE COERCIVE FORCE AND RETENTIVITY OF IRON-MANGANESE ALLOYS.

Per cent. Mn	Coercive Force				Retentivity			
	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°	Not annealed	Annealed at 675°	Annealed at 1000°	Quenched from 900°
0·50	6·5	5·7	4·5	4·8	11,000	12,500	9700	10,100
1·00	9·6	6·9	7·0	—	10,800	14,700	9000	—
2·00	19·2	12·5	16·0	—	10,500	11,600	8800	—
3·00	28·7	23·0	24·0	—	8,500	9,800	9000	—
3·50	20·8	28·0	24·5	—	7,600	10,600	8900	—
4·51	41·5	23·0	45·2	23·9	8,600	15,000	8000	12,900
6·00	50·8	—	—	—	9,200	—	—	—
8·00	58·7	57·5	65·0	—	5,200	6,100	2000	—
10·00	90·1	70·7	80·0	—	1,100	1,800	1900	—
10·42	None	103·0	121·0	78·5	None	400	500	800

W. Mathesius investigated and measured the magnetization, the coercive force, and the saturation of manganese steels with 0·45 to 20·8 per cent. of manganese, and 0·21 to 2·18 per cent. of carbon, after they had been subjected to different heat-treatments. The results are summarized in Table LXXXVII. E. Gumlich represented his observations on manganese steels with 0·23 per cent. carbon, and quenched from 800°, by Fig. 476; the discontinuity in the curve corresponds with that obtained for the sp. gr., and for the sp. resistance, Fig. 482. The magnetic state was obtained by cooling the specimens to —193°, and the non-magnetic state by cooling or quenching from Ac_2. The sp. gr. of the non-magnetic steel is much greater than that of the magnetic; and the sp. resistance of the non-magnetic steel is less than that of the magnetic. R. A. Hadfield and co-workers found the magnetic susceptibility increases as the proportion of carbon diminishes (manganese constant); and with carbon constant, the effect of manganese is small. The mass susceptibility increases as the [C]/[Mn] ratio decreases. The mass susceptibility of manganese steels ranges from 17×10^{-6} to 259×10^{-6}, so that the alloys are paramagnetic. With the [C]/[Mn] ratio constant, 2·57 to 19 per cent. of nickel raises the susceptibility in the ratio 23 : 67 ; 0·74 per cent. of tungsten raises the susceptibility in the ratio 18 : 29 ; 3·5 per cent. of chromium raises the susceptibility 10 per cent. ; 2·5 per cent. of copper raises the susceptibility of a manganese-nickel steel 19 per cent. ; and the addition of silicon to a manganese steel makes the steel more ferromagnetic. No relation between the sp. gr. and mass susceptibility or composition was observed.

TABLE LXXXVII.—SATURATION VALUES FOR $4\pi I$.

Heat-treatment	Field strength (c.g.s. units)	Saturation values $4\pi I$				
		C 0·27 Mn 4·58	C 0·29 Mn 11·67	C 0·34 Mn 20·80	C 1·33 Mn 11·80	C 2·18 Mn 11·70
4 hrs. at 750° and slowly cooled	50	3,020	140	70	105	235
	100	8,410	225	105	175	510
	300	13,080	450	140	380	1150
	800	15,520	720	195	720	1840
3 hrs. at 700° and quenched in salt-water at 20°	50	5,420	85	25	40	40
	100	11,970	180	40	70	70
	300	15,800	430	80	120	105
	800	17,850	755	95	140	115
3 hrs. at 900° and quenched in salt-water at 20°	50	6,400	80	20	—	—
	100	11,640	230	40	—	—
	300	15,750	580	60	—	—
	800	17,990	1090	60	—	—
2 hrs. at 1200° and quenched in salt-water at 20°	50	9,110	485	65	370	—
	100	13,290	1380	115	770	—
	300	17,460	3070	185	1560	—
	800	19,340	4410	235	2310	—
Like the second above but tempered at 400°	50	10,580	905	70	315	900
	100	14,540	2570	100	800	3140
	300	17,540	4808	115	1910	5580
	800	18,790	6440	125	2760	6740
Like the fourth above but tempered at 400°	50	11,110	1490	105	865	—
	100	14,760	4200	170	1950	—
	300	18,310	7200	220	3620	—
	800	19,640	9030	225	4950	—
Like the second above but cooled in liquid air	50	3,150	750	60	240	530
	100	9,800	2000	85	610	2180
	300	14,360	4170	100	1640	4840
	800	16,830	5830	100	2440	6150

R. A. Hadfield studied the temp. of the critical magnetic change in the alloys. With over 16 per cent. manganese the alloys have no magnetic transformation, but with the magnetic alloys there is a transformation at 767° to 776° on cooling, and 765° to 780° on heating. H. K. Onnes and co-workers studied the magnetic properties of these steels at a low temp. E. Gumlich assumes that there are two allotropic states involved. He found that non-magnetic, high per cent. manganese steel becomes magnetic with a martensitic structure when dipped in liquid air.

E. Gumlich obtained the hysteresis loop shown in Fig. 483 for steel with 12·4 per cent. manganese, and 0·23 per cent. carbon. The magnetization of the steel cooled to −78° is comparable with that of a feebly magnetic steel; and the improvement observed in heating the steel for 24 hrs. at 800° in vacuo is attributed to the surface oxidation by traces of residual air in the vessel.

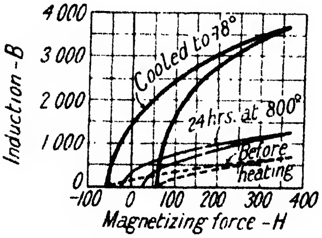


FIG. 483.—Hysteresis Loop of 12·4 per cent. Manganese Steel.

G. Mars, discussing the low magnetic properties of the manganese steels, said that the magnetism depends not so much on the kind of molecule present as on the structure of the molecule, *i.e.* not on the chemical nature of the body, but on the space left free between the molecules, or on the form of this space. This intermolecular space, which is assumed to be filled with æther, and which acts as the magnetic medium, is, in the case of iron, cobalt, and nickel, of such a nature that it causes a mechanical disturbance of the metal mols., the effect of which is to produce magnetic attraction or repulsion. This intermolecular space of a magnetic metal is changed when the metal is alloyed with another magnetic or non-magnetic metal. Thus, even when two magnetic metals, like iron and nickel, are melted together, the result may be non-magnetic metal; whereas two non-magnetic metals, like manganese and aluminium, may give a strongly magnetic alloy— *e.g.* the Heustler alloys. Consequently, the magnetism of one and the same magnetic metal may be reduced by heating it to a certain temp., because the mols. are thus driven farther apart, and the cohesion between them is reduced; again, any treatment which disturbs the arrangement in space of the mols. of a magnetic metal *e.g.* cold-working—may alter considerably the magnetism of the metal. A. Schulze measured the magnetostriction of alloys. Observations were also made on the effect of the magnetic intensity and concentration on the magnetostriction of iron-manganese alloys.

R. Dubois observed that a ferromanganese, with about 80 per cent. of manganese, disintegrated on exposure to air. G. Tammann and E. Vaders, and A. N. Campbell studied the passivity of these alloys. B. H. Thwaite found that steels with 0·684 and 12·55 per cent. manganese, and respectively 0·16 and 0·067 per cent. of carbon, were attacked by dil. nitric acid (1 : 9), so that the former lost 0·1475 and the latter 0·1735 grm. per sq. cm. when exposed for the same time. The increase in corrodibility of steel when manganese is present was also noted by P. Berthier, C. W. von Siemens, T. Turner, E. Heyn and O. Bauer, G. J. Snelus, C. F. Burgess and J. Aston, C. H. Desch and S. Whyte, L. Aitchison, R. Finkener, and A. S. Cushman. R. A. Hadfield and J. A. N. Friend found that in the absence of sulphur, manganese is not a particularly objectionable element in steel. L. B. Pfeil observed that a three-layer scale—*vide supra*—is formed when manganese steel is heated to 1000° for a few hours in air. With a 0·71 and a 3 per cent. manganese steel, the manganese in the innermost layer was about two-thirds of that present in the original steel, whilst in the middle and outer layers a little more manganese was present than was contained in the original steel. Usually, with other alloy steels, more foreign element is contained in the innermost layer than in the middle layer. E. Heyn and O. Bauer noted that with cast iron containing 3·5 C, 2·5 Si, and 0·07 P and S, and exposed to tap-water, the relative corrodibilities were:

Mn . . .	0·46	0·70	0·99	1·90	2·83	3·08 per cent.
Corrosion . .	100	92	100	94	96	89

C. F. Burgess and J. Aston found that the corrosion of manganese-iron alloys in grams per sq. dm., on exposure for an hour to 20 per cent. sulphuric acid, and the corrosion in kgrms. per sq. metre per year, on exposure to the weather for 162 days from July to February, were:

Mn . .	0·505	1·000	2·000	3·000	10·419
Acid . .	0·560	0·520	0·725	1·110	0·352
Air . .	0·268	0·390	0·302	0·327	0·435

Y. Utida and M. Saito measured the loss in weight, in grams per sq. cm., when manganese steels with about 0·05 per cent. of carbon are immersed for 24 hrs. in 10 per cent. acid:

Manganese . . .	0	0·95	4·36	8·41	13·75	16·55 per cent.
HNO_3	0·9380	0·5090	0·6464	0·7720	0·8263	0·7570
HCl	0·0712	0·2191	0·5015	0·5520	0·8930	0·8570
H_2SO_4	0·0990	0·1854	0·3055	0·5999	2·5850	3·0120

W. Guertler and T Liepus, J. Aston, E Maurer, O. Bauer, R. Dubois, O. W. Storey, E. A. and L. T Richardson, R. A. Hadfield, C. Duisberg, H. G. Haase, V. V. Kendall and E. S. Taylerson, and C. H. Charles studied the corrodibility of the iron-manganese alloys. S. Satoh studied the nitridization of these steels by heating them in ammonia at 560° to 580°. H. Endo's results, Fig. 484, represent the loss in grams per sq. cm., during 5 hrs.' action, at ordinary temp. on alloys with 0·47 to 0·52 per cent. of carbon, and the proportions of manganese indicated. R. A. Hadfield and J. A. N. Friend found with steels containing 0·10 to 0·9 per cent. of manganese, a slight increased resistance to corrosion by tap-water, and wet and dry tests occur with carbon up to about 0·5 per cent. From this point upwards, the manganese affords, generally, a slight protection which is decided in the wet and dry tests, but is not invariable with sea-water tests. The manganese raises the corrodibility by sulphuric acid; and E. A. and L. T. Richardson observed that manganese enhances the effect of copper in iron in resisting the attack of the alloy by corrosive influences. K. Hilgenstock studied the action of hydrogen sulphide and of sulphur dioxide on red-hot ferromanganese. R. Schenck and A. Kortengräber studied the dissociation press. of alloys in nitrogen. J. A. N. Friend noted the effect of manganese in masking the increased corrodibility caused by the addition of carbon to steels. C. H. Desch and S. Whyte observed no definite influence in the corrosion of manganese steels in 5 per cent. sodium chloride. The manganese was preferentially dissolved. L. Aitchison found that the losses of weight in grams per 100 sq. cm. are:

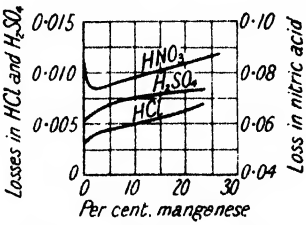


FIG. 484.—The Corrosion of Manganese Steels by Acids.

C	0·28	0·48	0·76	0·87 per cent.
Mn	0·94	0·91	1·01	0·83 ,,
NaCl 3 per cent. . .	1·82	1·94	2·50	1·88
H_2SO_4 { 1 per cent. .	8·16	9·70	4·67	7·08
H_2SO_4 { 10 per cent. .	8·05	8·80	12·3	6·12
Tap-water . . .	0·900	0·960	1·43	0·872

R. A. Hadfield and J. A. N. Friend also measured the effect with tap-water; L. Aitchison, C. Chappell, and R. A. Hadfield and J. A. N. Friend, sea-water; R. A. Hadfield and J. A. N. Friend, the effect when alternately wet and dry; and in 0·5 per cent. sulphuric acid. C. Chappell also observed the effect of dil. sulphuric acid. R. A. Hadfield and J. A. N. Friend thus summarized their observations:

> (1) The addition of from 0·03 to 1·63 per cent. of carbon to iron containing less than 0·2 per cent. of manganese results in (*a*) a steadily increasing rate of corrosion both in tap-water and sea-water, slight maxima being observed in the neighbourhood of 0·6 to 0·8 per cent. carbon; (*b*) an initial fall in corrosion, with a rapid rise to a maximum with 1·05 per cent. of carbon; (*c*) a rapid rise in corrosion to a maximum with 0·8 per cent. of carbon when exposed to the action of dil. sulphuric acid. There is some difference in the behaviour of steel towards all the corroding media in the neighbourhood of the eutectic composition, either a tendency to increased corrosion, or a decided increase in corrosion. (2) The addition of 0·7 per cent. manganese to all the steels resulted in (*a*) a very slightly increased corrosion in tap-water, sea-water, and in wet and dry tests, with a carbon-content up to

0·4 to 0·5 per cent. From this point upwards, the manganese, in general, affords a slight protection which is very decided in the wet and dry tests, but is not invariable in the sea-water tests. (*b*) An enormously increased corrosion in dil. sulphuric acid. This is important, since in commercial steels the manganese frequently ranges from 0·2 to 0·7 per cent., and the latter are therefore unsuited to acidic corroding media. A point of maximum corrosion occurs with a smaller per cent. of carbon than in steels with less manganese. (3) By increasing the proportion of manganese to 2 per cent. upwards, (*a*) the corrodibility of the steel in neutral soln. is greatly increased, particularly when the carbon-content exceeds 0·5 per cent. (*b*) The corrodibility in dil. sulphuric acid is greatly augmented.

N. Parravano [29] studied the ternary **iron-manganese-copper alloys,** and his results are summarized in Fig. 485. The gap in the binary copper–iron system is reduced by the addition of manganese, so that with 50 per cent. manganese, the solid solubility is complete. The continuous lines are liquidus curves, the dotted lines, solidus curves. F. Ostermann examined the manganese-copper steels, with 0·1 to 1·0 per cent. of carbon. The iron and copper are miscible in all proportions when 20° above the liquidus line. When carbon is added a two-layer system is formed in which most of the carbon collects in the layer rich in iron; on introducing manganese, the two-layer system is changed back to a single-layer phase. E. L. Nichols studied the electrical resistance of the iron-manganese-copper alloys. A number of these alloys had the remarkable property of decreasing in resistance each time that they were subjected to a change of temp.; an alloy containing 80·82 per cent. of copper and 19·12 per cent. of ferromanganese, when heated and cooled from 100° to 20°, diminished in resistance with each operation, the diminution being still perceptible at the end of the seventh cycle. On being then raised to a red-heat and allowed to cool, a still more marked diminution in the resistance of the above alloy was found to have taken place. The temp. coeff. of this alloy was positive, and continued to increase as the heating and cooling process was repeated. With an alloy consisting of 70·65 parts of copper and 29·35 parts of ferromanganese, a similar behaviour was observed. After being brought into a condition of stability such that further heating and cooling through a range of 80° had but little permanent effect upon its conductivity, it still showed, when hard-drawn, an appreciable negative temp. coeff. It was then annealed three times at red-heat, the sp. resistance and temp. coeff. being determined for the range of 20° to 100° after each annealing. The results were as follow:

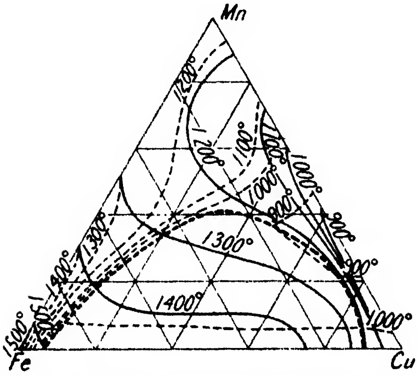


FIG. 485.—The Ternary System: Mn–Fe–Cu.

		Resistance			
		20°	100°	20°	Temperature coefficient
Hard		46·10	45·99	46·09	−0·000024
Annealed	once	45·10	45·18	45·09	+0·000021
	twice	44·07	44·33	44·06	+0·000068
	thrice	42·70	43·58	42·74	+0·000192

A number of similar alloys showed, when hard-rolled, a temp. coeff. very near to zero, sometimes positive, sometimes negative. After annealing at 300° to 400°, a well-defined negative coeff. was produced. It was found that the positive coeff. produced by annealing could be reduced again by rolling the alloy. With 10 per cent. of ferromanganese, the change of resistance is less than 1 per cent. for 100°. Alloys containing from 15 to 20 per cent. of ferromanganese have exceedingly small temp. coeff., the coeff. at 18 per cent. being practically zero. The coeff. may be made to undergo a considerable alteration by varying the temper of the metal.

The marked influence of temper upon the conductivity of these alloys renders it difficult to determine the precise law of the change in sp. resistance with the composition. It would, however, appear from the results that the resistance increases nearly in direct proportion to the percentage of ferromanganese.

T. W. Hogg prepared some **iron-manganese-aluminium alloys,** and observed that the alloy from 5·56 lbs. aluminium, and 50 lbs. of 82 per cent. ferromanganese, after standing twelve months, is completely disintegrated. G. Craig suggested that the disintegration is due to oxidation. The alloy was magnetic. Both manganese and aluminium reduce or destroy the magnetic property of iron, but raise the magnetic property when both are present. The mechanical properties were studied by P. E. McKinney.

L. Guillet studied the **manganese-silicon steels** with 0·104 to 0·620 per cent. carbon, 0·457 to 2·310 per cent. silicon, and 0·450 to 14·760 per cent. manganese. E. Kothny also studied a couple of these alloys. Steels with about 2 per cent. of manganese, 0·1 of carbon, and 0·5 to 1·5 of silicon, and also those with 0·5 per cent. carbon, 0·5 manganese, and up to 1·8 silicon, are pearlitic, with the grains of ferrite the closer the higher is the proportion of silicon. The other steels have polyhedra of γ-iron in some cases—*e.g.* 0·2 C, 2 Mn, and 1·5 Si—with fairly well-marked cleavage planes, and a few needles of martensite on the borders. Quenching from 850° renders the pearlitic steels martensitic. The γ-iron steels remain polyhedral, though the 0·2 C, 2 Mn, and 1·5 Si steel becomes wholly martensitic; this steel also becomes martensitic on annealing at 950° to 1200°, and when cooled in liquid air. The other steels were not changed by cooling in liquid air. The ferrite of the pearlitic steels becomes coarser on annealing, while the other steels remain unchanged. No precipitation of carbon was observed. The case-hardening of the pearlitic steels leaves a core of pearlite, a zone of troostite, and an outer zone of γ-iron. If carried far enough, pearlite and cementite are formed on the exterior. The mechanical tests on the normal steels show that silicon raises the tensile strength and elastic limit, and lowers the elongation, reduction of area, and resistance to shock. The variation in the elastic limit of the γ-iron steels was small. As silicon alters the mechanical structure, corresponding alterations occur in the mechanical properties, but the addition of silicon is, in general, injurious to manganese steels. Quenching raises the tensile strength and elastic limits, but reduces the elongation, reduction of area, and resistance to shock. Annealing softens all the steels excepting that with 0·2 C, 2 Mn, and 1·5 Si. G. Burns, B. Stoughton and W. E. Harvey, E. W. Colbeck and D. Hanson, G. H. Keulegan and M. R. Houseman, G. A. Hawkins and co-workers, W. Riede, S. Heuland, A. B. Kinzel, K. T. Kürten, W. Venator, and E. Mallard discussed the iron-manganese-silicon alloys. P. Nicolau examined their thermo-electric properties. F. Kohlhaas patented a *manganese-silicon-titanium steel*—0·9 to 1·0 C, 0·4 to 0·7 Si, 9·8 to 10·3 Mn, and 0·2 to 1·4 Ti.

L. Guillet prepared **manganese-chromium steels** with 0·128 to 0·923 per cent. carbon: 1·92 to 14·02 manganese; and 2·87 to 5·25 chromium. The microstructure shows that these steels may contain (i) pearlite (or troostite) if the proportions of manganese and chromium are not too high; (ii) martensite—with or without carbide; and (iii) polyhedra of γ-iron—with or without carbide. The alterations in structure show that the effect of chromium is superadded to that of the manganese, and when the proportion of chromium is high, a carbide is formed. Quenching renders the steels with pearlite wholly martensitic, it may render some with polyhedral γ-iron martensitic, and it may cause cleavage-planes to appear in some of the polyhedra. Annealing has very little effect on the martensitic or troostitic steels, but it produces transformations in the γ-iron, rendering it martensitic or troostosorbitic—*vide* the nickel chromium steels. Cooling in liquid air has very little influence. Stressing in the cold converted the steel with γ-iron and martensite into a martensite steel. The case-hardening of the martensitic steel left a central core of martensite, then a zone of troostite intermixed with martensite, and then a thin zone of γ-iron. In general, the mechanical properties correspond with the structure. The normal martensitic steels have a high tensile strength and elastic limit, a low elongation and reduction of area, high brittleness, and an enormous hardness. The troostitic steels have less strongly marked properties, while those with γ-iron have a high tensile strength but low elastic limit, a fairly high elongation, a high resistance to shock, and a medium hardness. The presence of carbide diminishes the resistance to shock. The changes in the mechanical properties which occur on quenching correspond with the microstructure. The hardness, tensile strength, and elastic limit generally increase; the elongation, reduction of area, and resistance to shock are reduced. Steels with γ-iron are softened by quenching—the elastic limit is reduced, and the resistance to shock is increased. Annealing has, in general, but little effect on the mechanical properties, though in some cases the hardness, tensile strength, and elastic limit are raised, while the elongation, and reduction of area, and resistance to shock are reduced. F. M. Beckett, J. M. Becket, A. B. Kinzel and W. B. Miller, and C. L. Clark and A. E. White studied the mechanical properties of these steels. W. Rohn found that the corrodibility of a Fe : Cr : Mn (60 : 25 : 15) alloy – normal and annealed —expressed as a loss in weight in grams per sq. dm., with 10 per cent. acids, is :

	HNO_3		H_2SO_4		HCl	
	N	A	N	A	N	A
24 hrs. cold .	0·02	0	0·28	0·82	0·34	0·15
1 hr. hot .	0·02	0	2·8	3·81	1·40	0·49

W. Guertler and T. Liepus also studied the corrodibility of the iron-manganese-molybdenum alloys. W. F. Rowden, and G. Burns studied the **manganese-molybdenum-iron alloys** ; and P. Berthier, and V. Ehmcke, **manganese-tungsten-iron alloys** ; A. Stavenhagen and E. Schuchard prepared **manganese-uranium-iron alloys** by the thermite process; and W. C. Hamilton examined some **manganese-vanadium-iron alloys.**

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§ 28. Ferrous Oxide and its Hydrate

The supporters of the phlogiston theory knew that the calx of iron unites with different proportions of phlogiston. Thus, in 1777, C. W. Scheele[1] said :

> I dissolved 2 ounces of martial vitriol in 32 ounces of water, and precipitated the soln. with a caustic lye. The precipitate being settled, I decanted the clear liquor, and I put the deep green precipitate of iron, together with the remaining liquor, into a bottle and corked it well. After a fortnight (during all of which time I shook the bottle frequently), the green calx of iron had acquired the colour of *crocus martis*, and out of 40 parts of air, 12 were lost.

J. Priestley made some observations on the oxidation of iron based on the phlogiston theory.

At the end of the eighteenth century, A. L. Lavoisier recognised two stages in the oxidation of iron ; and, near the beginning of the nineteenth century,

C. L. Berthollet believed that a great many oxides of iron exist—indeed, he was inclined to believe that the iron and oxygen form a continuously progressing series of indefinite compounds; but J. L. Proust considered that the various oxides so-called were mixtures or combinations of ferrous and ferric oxide. C. F. Bucholz, and J. Dalton favoured J. L. Proust's hypothesis; J. F. d'Aubuisson, and L. J. Thénard, favoured C. L. Berthollet's. J. L. Gay Lussac recognized an intermediate variety between ferrous and ferric oxides; and J. J. Berzelius at first supposed that there are only two oxides, but later proved that there are three definite oxides, namely *iron monoxide*, or **ferrous oxide,** FeO; *ferrosic oxide*, Fe_3O_4; and *ferric oxide*, Fe_2O_3. The oxides with a composition between those of ferrous and ferrosic oxides are considered to be solid soln., and have been named *wüstite;* those with a composition between ferrous oxide and iron have been called *oxyferrites*, and if the iron is also associated with carbon and cooled rapidly, *oxyaustenites;* and likewise, also, with those oxides having a composition between those of ferrosic and ferric oxides—*vide infra*; they form solid soln. which have been called *martites* —*vide* ferric oxide. Salts of the unknown *iron dioxide*, FeO_2, and of the unknown *iron trioxide*, FeO_3, have also been prepared; the former are called *perferrites*, and the latter *ferrates;* whilst the salts of ferric oxide are called *ferrites*. There is also the supposed *iron tetroxide*, FeO_4, and the salts of the corresponding acid, namely, the *perferrates*.

A. Brun reported that volcanic lava passing from the vitreous to the crystalline state traverses a period in which ferrous oxide is deposited as a new mineral which he called **iozite.** The presence of iozite in the lava is taken to indicate that water was absent at the time of its formation. The ferrous oxide content of a lava is reduced by the oxidizing action of air or steam. Hence, the magma in the crater is probably less highly oxidized than the lava outside. The subject was discussed by G. Ponte. The individuality of iozite is not yet established as a definite mineral species.

According to R. F. Marchand, when iron is burnt in the oxyhydrogen flame, the product of combustion is not the scaly oxide obtained when the metal is burnt in oxygen gas, but a fused, malleable mass which dissolves in hydrochloric acid with the evolution of hydrogen to form ferrous chloride. R. F. Marchand found that the analysis agreed with the assumption that *eine Verbindungen des Eisenoxyduls mit metallischen Eisen*, $Fe_3(FeO)$, or *ferrous suboxide*, or *iron tetritoxide*, Fe_4O, is formed. This has not been confirmed; it is thought that the alleged suboxide is a mixture or solid soln. of iron and ferrous oxide, or, possibly, ferrosic oxide. R. Schenck obtained a product with the ultimate composition Fe_3O, *iron tritoxide*, by the action of a mixture of equal parts of carbon monoxide and dioxide on a mixture of magnesia and finely-divided iron at about 650° and atm. press., but the work of R. Schenck and co-workers, G. Lepetit, and J. Müller showed that the product is really a solid soln. of ferrous oxide and magnesia. I. L. Bell supposed that an *iron hemioxide*, Fe_2O, is formed by the action of carbon monoxide on ferric oxide, and L. Dusart, that a similar oxide is produced by the oxidation of the hemisulphide with steam at 60°; but R. Akermann and C. G. Särnström showed that the product obtained by the action of carbon monoxide is a mixture of iron, ferrous oxide, and ferrosic oxide. W. Galbraith, and F. R. Eichhoff assumed that a product approximating Fe_7O, occurs as an inclusion in iron. C. R. Wohrmann discussed the ferrous oxide inclusions in iron. W. G. Mixter obtained a product approximating Fe_5O_4 by the action of a current of nitrogen on ferrous oxalate at 900°, but it was considered to be a mixture of iron and ferrous oxide. J. B. Ferguson, in his study of the action of water vapour on heated iron, obtained no evidence of the formation of any oxide of iron lower than ferrous oxide.

The solubility of iron in ferrous oxide, observed by A. Matsubara, and E. D. Eastman, was found by H. Groebler and co-workers not to exist; the solubility of iron in solid ferrous oxide is inappreciable when examined by the X-radiogram process. F. S. Tritton and D. Hanson reported that molten ferrous oxide dissolves about 1 per cent. of iron. H. le Chatelier and B. Bogitsch noticed that oxygen can dissolve in solid iron; and the subject was examined by J. E. Stead, and J. H. Whiteley. E. D. Eastman found that ferrous oxide is unstable with respect to iron below 550°; but although iron is not appreciably soluble in ferrous oxide, ferrous oxide is soluble in iron to the extent of 20 to 25 molar per cent.—*i.e.* 6 to 8 per cent. of oxygen. F. S. Tritton and D. Hanson obtained an equilibrium diagram for iron containing from 0·1 per cent. oxygen up to approximately 22 per cent., represented by the compound FeO. There is a large range of immiscibility of the two components, which in the molten state separate into two liquid layers. C. H. Herty and J. M. Gaines found that arrest points for δ-, γ-, and β-iron are not affected by the presence of from 0·12 to 0·21 per cent. of oxygen. The solubility of ferrous oxide in γ-iron is rather greater than it is in α-iron, because the A_3-arrest is lowered by the presence of the oxide. The lowering of the A_3-arrest is accompanied by the raising of the A_4-arrest. K. Schönert gave for the solubility of oxygen as ferrous oxide in α-, β-, and γ-iron respectively 0·03, 0·13, and 0·15 to 0·19 per cent. The proportion dissolved in α-iron increases with a rising temp., so that in molten iron at the f.p. the solubility is 0·21 per cent., and the f.p. is depressed to 1509°. When more oxygen is present, two solid phases are formed, the phase rich in oxygen contains about 0·21 per cent. of oxygen, and it consists mainly of ferrous oxide, a little ferric oxide, and 0·99 per cent. of free iron. The m.p. is lowered from 1535° to 1530° with the dissolution of 0·21 per cent. of oxygen; beyond this conc. of oxygen two liquid layers are formed. The solubility of oxygen in solid iron is taken to approximate to 0·05 per cent. oxygen; and the solubility of iron in the oxide about 1 per cent. C. Benedicks and H. Löfquist represented the equilibrium diagram by Fig. 486. The diagram is based on the observations of R. Akermann and C. G. Särnström on the solid phases in the system; of L. Wöhler and co-workers on the reduction of iron oxide with carbon monoxide; of R. B. Sosman and J. C. Hostetter on the equilibrium conditions when steam acts on iron; and on the assumed existence of solid soln. between the phases Fe and FeO, FeO and Fe_3O_4, and Fe_3O_4 and Fe_2O_3, discussed by W. Mathesius, P. Goerens, H. Moissan, etc.—*vide infra.* In C. Benedicks and H. Löfquist's diagram the m.p. of iron is lowered to *B* by the presence of dissolved ferrous oxide, and *BD* represents the solubility curve of ferrous oxide in molten iron determined approximately by C. C. de Coussergues, and more exactly by C. H. Herty. In the higher ranges of temp., liquid ferrous oxide and iron are only partially miscible, and it is estimated that the two solubility lines meet near 2000°, when the two phases become completely soluble. The f.p. of ferrous oxide is considered to be near 1370°, so that the curve *CGM* extends at least to 1370°, and *M* falls to the right of the wüstite area. The eutectic *N* was observed by P. Oberhoffer and K. d'Huart to occur at about 1200°, with about 24 per cent. of oxygen. S. Hilpert and others examined the system FeO–Fe_2O_3, but the data are somewhat indefinite. Although R. B. Sosman and J. C. Hostetter consider that there is a continuous series of solid soln. between Fe_2O_3 and Fe_3O_4, C. Benedicks and H. Löfquist consider that the great difference in the crystal structure of the two oxides favours the view that the miscibility is partial. The polymorphic forms of

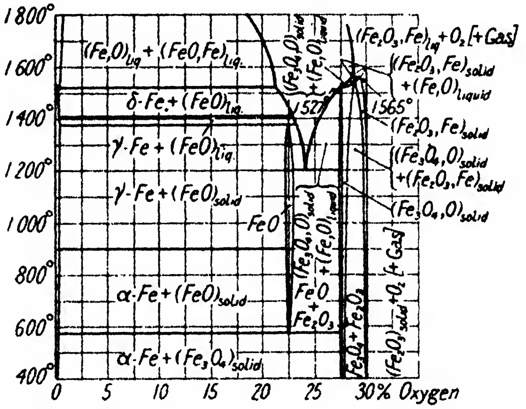


FIG. 486.—Equilibrium diagrams of the Iron-Oxygen System.

ferric and ferrosic oxides are not included in the diagram. The diagram was discussed by R. Schenck and T. Dingmann, P. Oberhoffer, E. Jänecke, R. Akerman, W. Austin, E. D. Eastman, E. W. Ehn, A. Matsubara, H. Monden, J. A. Picard, J. A. Picard and F. M. Potter, R. B. Sosman and J. C. Hostetter, J. E. Stead, A. E. White and J. S. Vanick, F. Sauerwald and W. Hummitzsch, and J. H. Whiteley.

The solubility of oxygen or ferrous oxide in molten iron was examined by A. Ledebur, P. Oberhoffer and K. d'Huart, F. Schmitz, A. Wimmer, and L. Romanoff. A. Ledebur found a maximum solubility of 0·24 per cent. of oxygen in liquid steel; F. S. Tritton and D. Hanson, K. Schönert, and C. H. Herty gave 0·21 per cent. at 1530°, and above that temp. the mixture separates into two layers; and A. Wimmer, 0·20 per cent. for iron at 40° or 50° above its m.p. C. H. Herty and J. M. Gaines gave for the solubility at 1535°, 0·94 per cent. of FeO, or 0·21 per cent. of oxygen; at 1600°, 1·36 per cent. of FeO, or 0·304 per cent. of oxygen; and at 1700°, 2·02 per cent. of FeO, or 0·452 per cent. of oxygen. H. le Chatelier observed that the dissociation press., p, of ferrous oxide dissolved in iron is $p\times10^{-8}=(1{\cdot}1C)^2$, where C denotes the conc. of the dissolved ferrous oxide. C. C. de Coussergues gave zero at 1400°, 1 per cent. at 1700°, and 3 per cent. at 1800°.

R. Schenck and T. Dingmann found a solubility of 2·8 per cent. ferrous oxide in solid iron at 1000°, and 2·05 per cent. at 700°. R. Schenck and co-workers later said that this result is only apparent, and is due to the formation of unstable wüstite; the solubility is 0·4 per cent. at 800° and 1000°; and they assumed a solubility of 0·8 per cent. at 700°. E. D. Eastman and R. M. Evans obtained a 5 per cent. solubility in iron at 772°; and A. Matsubara 6 to 7 per cent. For the solubility of oxygen in α-iron A. Wimmer gave 0·035 per cent., T. D. Yensen 0·4 per cent.; F. S. Tritton and D. Hanson gave 0·055 per cent. and P. Oberhoffer and co-workers 0·05 per cent. The solubility of oxygen in so-called β-iron was estimated by A. Wimmer to be 0·13 per cent., and a eutectic structure could be detected in iron with this proportion of oxygen. W. Dünwald and C. Wagner said that the solubility of oxygen in α- and γ-ferrites between 800° and 1000° is less than 0·01 per cent. The subject was discussed by H. Esser. The solubility of oxygen in γ-iron was measured by W. Austin, E. L. Reed, H. Monden, A. McCance, K. Schönert, P. Oberhoffer and co-workers, C. Benedicks and H. Löfquist, L. von Friesen, and J. C. W. Humfrey. The high values are based on equilibrium measurements, and the low values on the microstructure. Observations based on X-radiograms were made by H. Groebler and co-workers; and the magnetic measurements of J. Huggett and co-workers show no appreciable solubility of ferrous oxide in iron. W. Krings and J. Kempkens showed that the high values for the solubility of oxygen in iron are probably wrong, and they obtained 0·11±0·015 per cent. at 715°, and 0·095 ±0·010 per cent. at 800°. Even this is higher than the observed values for the quantity of oxygen in commercial iron, where the proportion is of the order 0·05 per cent. The results obtained by heating iron in mixtures of steam and hydrogen for 24 to 65 hrs. at 715°, when the estimated partial press. of the oxygen was p, were as follow:

Steam . . .	28·0	24·0	18·5	10·0	2·5	trace per cent.
$p\times10^{21}$ atm. .	0·87	0·57	0·305	0·0707	0·0038	—
Oxygen in iron .	0·0862	0·0832	0·0832	0·0832	0·0678	0·0185 per cent.

The limiting value is extrapolated to be 0·11 per cent. The results are in harmony with those obtained for the equilibrium: $FeO+H_2\rightleftharpoons Fe+H_2O$—*vide supra.*

R. Schenck studied the solid soln. of small quantities of ferrous oxide in iron, and he called them **oxyferrite,** or rather *oxoferrite;* if the ferrite be replaced by austenite, then the corresponding solid soln. is called **oxyaustenite.** Ferrous oxide does not occur as a solid phase, but it is part of a series of solid soln. of FeO and Fe_3O_4 called **wüstite.** Ferrous oxide is the dominant constituent of wüstite. At higher temp. the solid soln. wüstite approximates FeO. R. Schenck and co-workers found that in the reaction $FeO+CO \rightleftharpoons Fe+CO_2$, the proportions of stable oxyferrite, and wüstite formed are those indicated in Table LXXXVIII and Fig. 487. Wüstite can exist as a homogeneous solid soln. of variable composition only above 570° and all mixtures intermediate between oxyferrite and magnetite, below 570°, split into these components to form a heterogeneous mixture. Wüstite, however, may occur as a metastable phase down to about 420°. Oxyferrite also occurs as a homogeneous stable phase. Any mixture of intermediate composition cannot exist as a stable, homogeneous phase, but splits up into two solid soln., wüstite and oxyferrite. The mixture at the oxyferrite side will be oxyferrite saturated with wüstite, and that at the wüstite side will be wüstite saturated with oxyferrite or iron. There is a similar heterogeneous phase between wüstite and magnetite. There is a doubt whether R. Schenck has adopted the correct position for the wüstite area; E. D. Eastman and R. M. Evans placed their wüstite area astride the portion of the diagram corresponding with FeO. The subject was also studied by C. H. Mathewson and co-workers, U. Hofmann and E. Groll, and R. Schenck and E. Hengler. E. R. Jette and F. Foote studied the homogeneity of wüstite, and found that it decomposes between 565 and 570 ; they also showed that all samples had the space-lattice of FeO.

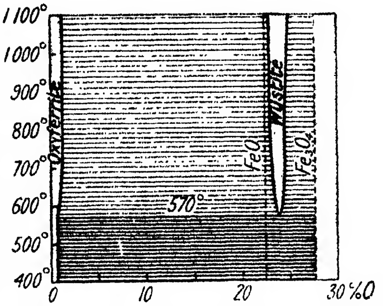


FIG. 487.—Iron–Oxygen System (Stable).

O. C. Ralston said that if R. Schenck's position for wüstite be accepted, no one could possibly prepare ferrous oxide by gas reduction or oxidation methods, and hence it is better to shift the position of the wüstite area to the left so that it includes ferrous oxide. R. Schenck's diagram does not show any difference between the solubility of wüstite in α-iron and in γ-iron. K. Schönert, and O. C. Ralston suggested that the lower slope of the oxyferrite boundary between 570° and 800° is associated with the properties of α-iron, and with those of γ-iron at a higher temp. By re-plotting R. Schenck's data, O. C. Ralston obtained the curves, Fig. 488, in which the lower one represents the solubility of ferrous oxide in α-iron, and the upper curve its solubility in γ-iron. The A_3-arrest is presumably lowered by the presence of ferrous oxide down to a eutectoid which had not been located but is somewhere in the range between 700° and 800°.

TABLE LXXXVIII.—THE IRON–OXYGEN SYSTEM.

	CO Per cent.	CO_2 Per cent.	Wüstite				Oxyferrite	
			Per cent. Fe	Per cent. O	Per cent. Fe	Per cent. O	Per cent. Fe	Per cent. O
600°	52·6	47·4	75·76	24·24	76·59	23·11	—	—
650°	56·9	43·1	75·71	24·29	76·83	23·17	—	—
700°	59·8	40·2	75·65	24·35	76·94	23·06	—	—
800°	65·2	34·8	75·65	24·35	77·05	22·95	99·6	0·4
900°	68·9	31·1	75·49	24·51	77·16	22·84	—	—
1000°	71·6	28·4	75·38	24·62	77·21	22·79	99·6	0·4
1100°	73·6	26·4	75·22	24·78	77·33	22·67	—	—

O. C. Ralston plotted the pressure data of R. B. Sosman and J. C. Hostetter, and of L. Wöhler and R. Günther in the theoretical diagram of A. Smits and

J. M. Bijvoet, and obtained the diagram Fig. 489, which does not show the region occupied by the solid soln. oxyferrite and wüstite—*cf.* Figs. 487 and 488.

Ferrous oxide is metastable at ordinary temp. It is stable above approximately 570°, but below that temp. G. Chaudron and co-workers showed that it breaks up in accord with the equation $4FeO \rightleftharpoons Fe_3O_4 + Fe$. The invariant or triple point was given at 570° by G. Chaudron, A. Smits and J. M. Bijvoet, R. B. Sosman, W. Reinders, P. van Groningen, E. D. Eastman and R. M. Evans, and L. Wöhler and R. Günther; J. B. Ferguson gave 578°; and M. Tigerschiöld, 535°. Obviously, therefore, in preparing ferrous oxide by the reduction of a higher oxide with hydrogen or carbon monoxide, the temp. must exceed this invariant point, 570°, for below that temp. ferrous oxide is metastable with respect to $Fe + Fe_3O_4$, and instead of reducing ferrosic oxide to ferrous oxide, the tendency will be for ferrosic oxide to pass directly to iron without the intermediate stage, ferrous oxide, appearing at all. This brings under suspicion all the alleged preparations of ferrous oxide by the gaseous reduction of the higher oxides where these limitations have not been taken into consideration; and it shows a reason for the difficulty in preparing ferrous oxide free from magnetite and iron. Further, the equilibrium diagram, Fig. 486, shows that stable ferrous oxide cannot separate in a pure condition from a melt; it loses its identity at its m.p., 1370°, and it is metastable below 570°.

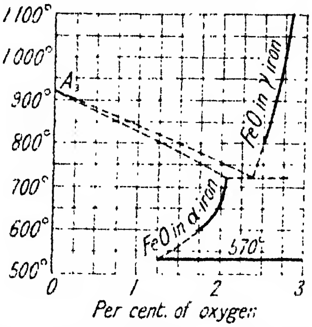


FIG. 488.—The Oxyferrite System.

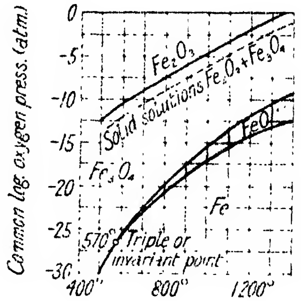


FIG. 489.—Pressure-Temperature Diagram for the System Fe–O.

According to J. B. Ferguson, and G. Chaudron and H. Forestier, the dissociation of ferrous oxide is reversible, for the reaction products—magnetite or ferrosic oxide, and iron—recombine to form ferrous oxide at temp. exceeding 570°. J. B. Ferguson kept a sample of ferrous oxide between 300° and 570° to allow complete decomposition to take place, and he then kept portions of the material at different temp. exceeding 570° for 5 hrs., and the results show that the iron and ferrosic oxide recombine to form ferrous oxide at temp. exceeding 570°; similarly, samples of ferrous oxide kept for 5 hrs. at different temp. below 570° slowly broke up at 536°, and the percentage decomposition increased as the temp. was lowered, until at 436° there was a 65 per cent. decomposition. This shows that the ferrous oxide must be super-cooled some distance below 570° before the rate of decomposition is appreciable during 5 hrs. G. Chaudron and H. Forestier found that about 78 per cent. ferrous oxide was decomposed in 8 hrs. at 445°. The rate of decomposition of ferrous oxide is a maximum at 480°, when about 80 per cent. decomposed in 24 hrs., and below 300° virtually no decomposition occurs during that period. Unlike J. B. Ferguson, G. Chaudron and H. Forestier obtained only a 50 per cent. recombination in 12 hrs. at 600°. The speed of decomposition is in accord with $dx/dt = k(100 - x)^4$, where x denotes the percentage decomposition in the time t, and k is a constant. The rate of decomposition is thus proportional to the 4th power of the concentration of the undecomposed ferrous oxide: $4FeO \rightleftharpoons Fe + Fe_3O_4$. The unit crystal cubic lattice contains four FeO molecules. According to

J. B. Ferguson, the invariant point 570° is lowered when ferrosic oxide is in solid soln. in the ferrous oxide, so that the new invariant point is between the solid soln., ferrosic oxide, iron, and gas.

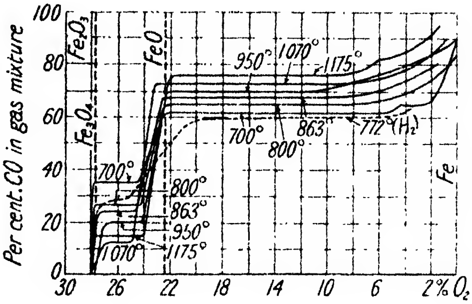


Fig. 490.—The Isothermal Reduction of Ferric Oxide.

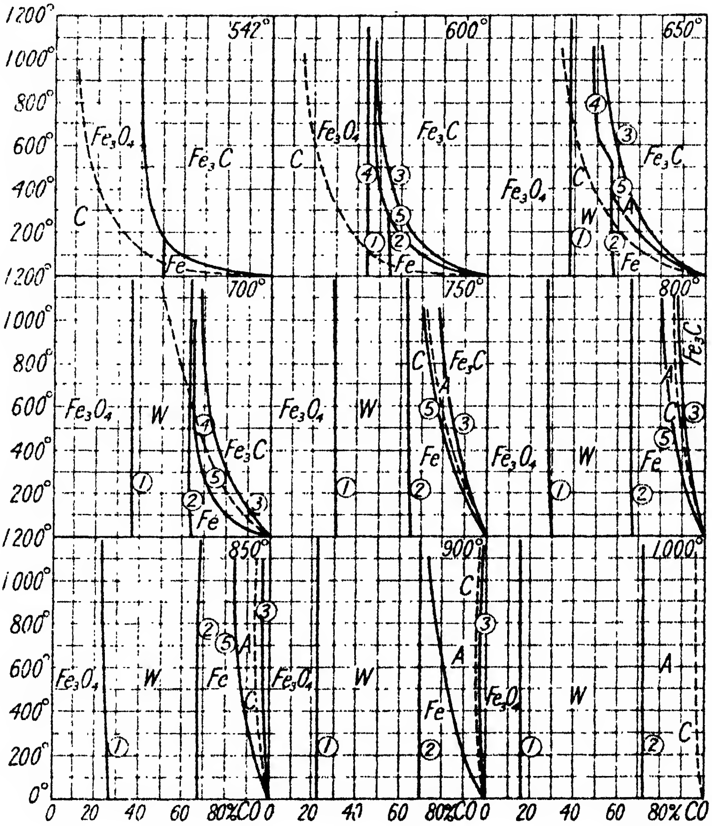
It follows from these observations that ferrous oxide prepared at high temp. can be safely cooled to room temp. without appreciable decomposition provided it be cooled rapidly through the range 570° to 300°; but if the product be slowly cooled, it will be contaminated with more or less ferrosic oxide and iron. At ordinary temp. the oxide is in a metastable state, and it can be preserved indefinitely provided it be protected from atm. oxidation. The preparation of ferrous oxide by the oxidation of iron or by the reduction of ferric or ferrosic oxide was discussed by S. Hilpert and J. Beyer, G. Chaudron and H. Forestier, J. B. Ferguson, L. Wöhler and R. Günther, L. E. Gruner, and G. Lepetit. The curves for the isothermal reduction of ferric oxide by carbon monoxide by R. Schenck at 700°, 800°, and 950°, and by A. Matsubara at 863°, 1070°, and 1175°, are shown in Fig. 490. The curves show the progress of the deoxidation at these temp. R. Schenck found that the mixture of ferrous and ferrosic oxides obtained at different temp. contained

p	$CO : CO_2$	650°	700°	720°
1 atm.	25 : 75	95·35	100	100 per cent. Fe_3O_4
	50 : 50	5·4	2·6	3·4 ,, ,,
atm.	75 : 25	—	91·87	91·23 ,, ,,

The curves show complications caused by the carburization of the iron when the proportion of oxygen in the solid has been reduced to about 8 per cent. R. Schenck's interpretation of the equilibria in the reaction between iron oxide and carbon monoxide, at one atm. press., is illustrated by Figs. 491 to 499. The dotted line refers to the producer gas equilibrium; *C* refers to the bivariant equilibrium: $2CO \rightleftharpoons C + CO_2$. The various fields of bivariant equilibria are numbered 1 to 5; (1) refers to Fe_3O_4, wüstite, and gas; (2) wüstite, oxyferrite, and gas; (3) Fe_3C, oxyaustenite, and gas; (4) wüstite, oxyaustenite, and gas; and (5) oxyferrite, oxyaustenite, and gas. *W* refers to the wüstite field; *Fe*, to the oxyferrite field; and *A* to the oxyaustenite field.

The increase in the proportion of carbon monoxide required for the reduction, that is, the lessened activity of the ferrous oxide near the iron-edge of the diagram, Fig. 490, is attributed to the disappearance of the pure ferrous oxide phase, and to the fact that the remaining ferrous oxide exists in solid soln. in the iron, and is then more difficult to reduce to metal. J. B. Ferguson suggested that two different forms of ferrous oxide may be concerned in the phenomenon. This is the region where R. Schenck's oxyferrite is formed. The subject was discussed by O. C. Ralston. H. Groebler and P. Oberhoffer obtained by the reduction process 97·8 per cent. ferrous oxide at 800°. They also attempted to remove iron from the product of the reduction by chemical agents, but the results were not good; a 95 per cent. ferrous oxide was so obtained. A. Smits and J. M. Bijvoet have discussed this subject from another aspect—*vide infra*, ferric oxide. The work of E. Baur and A. Glässner, L. Wöhler and O. Balz, P. P. Fedotéeff and T. N. Petrenko, R. Schenck and co-workers, M. Levin, H. Nippert, H. Kamura, J. B. Ferguson, H. J. van Royen, V. Falcke, E. Terres and A. Pongracz, A. Matsubara, and G. Chaudron on the equilibrium $K = [CO_2]/[CO]$, in the presence of iron and its oxides, at the absolute temp. *T*, summarized by E. D. Eastman, is indicated in

Fig. 502. According to O. C. Ralston, the horizontal lines represent equilibria between pairs of phases of approximately constant composition, whether pure compounds or solid soln. The portions curving away from the horizontal are obtained when the relative amount of one phase or another is small. Between Fe_3O_4 and FeO the isotherms show a horizontal portion which does not quite reach Fe_3O_4 or FeO, but is cut off by sloping portions of the curve. In this case, on the side next to FeO the change in direction is at the point where all of the free Fe_3O_4 is exhausted, and only a solid soln. of Fe_3O_4 in FeO is left in equilibrium with the gas; and then for every decrease in the amount of dissolved Fe_3O_4, gas of increased reducing power



FIGS. 491 to 499.—Space Model of the System: Fe–C–CO.

is necessary until all of the Fe_3O_4 is gone. Similarly, on the sloping branch of the curve next to the composition of Fe_3O_4, the FeO dissolves in the Fe_3O_4 in solid soln., as Fe_3O_4 is reduced to FeO, reducing the activity of the Fe_3O_4 and requiring gas of higher reducing power for the next step until enough FeO has been formed to saturate the Fe_3O_4. Afterwards the curve runs horizontally, excess FeO merely dissolving Fe_3O_4 to form a sat. soln. of Fe_3O_4 in FeO. The horizontal part of the curve is therefore actually one of equilibrium between two sat. soln., one mainly made up of magnetite and the other of FeO. The ends of the horizontal portions of the curves give directly the analyses of the sat. soln.

The dotted curve, Fig. 490, summarizes E. D. Eastman and R. M. Evans's results for the oxidation of iron by water vapour at 772°—when hydrogen is substituted for carbon monoxide as ordinate. The solid phase is here free from carbides, and again the phenomenon due to a decrease in the activity of the ferrous oxide, observed with carbon monoxide, occurs near the iron-edge of the diagram. The oxidation begins at about 750° with a gas mixture containing a less ratio than 0·54 of water vapour to hydrogen; below this temp., slightly oxidized specimens are reduced. The work of H. St. C. Deville, G. Preuner, G. Chaudron, P. P. Fedotéeff and T. N. Petrenko, P. H. Emmett and J. F. Shultz, L. Wöhler, and E. Schreiner and F. B. Grimnes on the equilibrium $K=[H_2O]/[H_2]$, in the presence of iron and its oxides, at the absolute temp. T, summarized by E. D. Eastman, is indicated in Fig. 501. These diagrams show the regions of stability of ferrous and ferrosic oxides at different temp., and in the presence of the respective gases. M. Tigerschiöld found that ferrous oxide is more readily reduced by hydrogen above 800°, and by carbon monoxide below that temp. W. Biltz and H. Müller gave values for the ratio $K=P_{H_2O}/P_{H_2}$; for Fe_3O_4/Fe, $K=0·2$ to 0·4 between 430° and 550°; for FeO/Fe, $K=0·5$ to 1·0 between 620° and 1000°; for Fe_3O_4/FeO, $K=0·6$ to 10 between 590° and 1050°; and for Fe_2O_3/Fe_3O_4, $K=7·5$ to 18 between 350° and 950°.

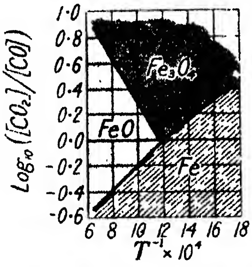


FIG. 500.—Equilibrium of the Solid Phases in the System with Iron, Iron Oxide, and Carbon Oxides.

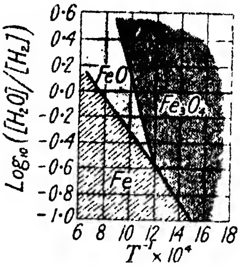
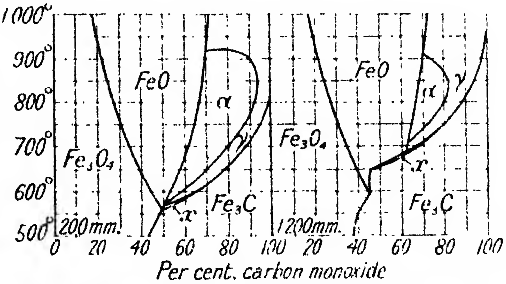


FIG. 501.—Equilibrium of the Solid Phases in the System with Iron, Iron Oxides, Hydrogen, and Steam.

E. Scheil and E. H. Schulz developed a series of curves from R. Schenck's data showing the effect of press. on the equilibrium, and the isobars for 200 and 1200 mm. are shown in Figs. 502 and 503. x refers to another phase (solid soln.).



FIGS. 502 and 503.—Isobars for the System : C-Fe-O.

The preparation of ferrous oxide.—Ferrous oxide of a high degree of purity has not been prepared. R. B. Sosman and J. C. Hostetter always obtained a product containing iron or iron carbide, magnetite, or some oxide intermediate in composition between FeO and Fe_3O_4. S. Hilpert and J. Beyer obtained a product free from metallic iron but in which some magnetic oxide was present. As just indicated, the failure to prepare ferrous oxide free from ferrosic oxide is attributed to the formation of a solid soln. of the two oxides, and A. Smits and J. M. Bijvoet also suggested that over a particular range of temp. ferrous oxide has a higher dissociation press. than ferrosic oxide, so that the reaction: $4FeO=Fe_3O_4+Fe$ may occur as in the analogous case of iridous oxide: $2IrO=IrO_2+Ir$ observed by L. Wöhler and co-workers. On account of the instability of ferrous oxide if heated above or cooled below 570°, E. D. Eastman, R. W. G. Wyckoff and E. D. Crittenden, R. Schenck, and L. Wöhler and R. Günther consider that ferrous oxide cannot be deliberately prepared without some decomposition; whilst K. Hofmann held that ferric oxide reduced by hydrogen at 564° consists essentially of ferrous oxide. The subject was discussed by G. Chaudron, S. Hilpert and J. Beyer, and R. Schenck and T. Dingmann.

According to the analyses of A. L. Lavoisier, J. L. Proust, J. W. Döbereiner, J. J. Berzelius, L. J. Thénard, J. L. Gay Lussac, and C. F. Bucholz, the proportions of iron in samples prepared by the oxidation of iron or the reduction of ferric oxide have from 73 to 78 per cent. of iron when the theoretical value for FeO is 77·14 per cent. R. Schenck, and O. Pattenhausen said that commercial ferrous oxide is mainly ferrosic oxide, Fe_3O_4.

According to C. F. Bucholz, ferrous oxide is a product of the action of steam on red-hot iron, and G. Chaudron stated that the reaction $Fe+H_2O\rightleftharpoons FeO+H_2$ occurs at 570°. H. Nippert, and L. Wöhler and R. Günther studied the reaction—*vide supra*. J. A. N. Friend said that ferrous oxide is produced by heating iron in steam at 350°; and H. Debray, that ferric oxide is reduced to ferrous oxide by one vol. of water vapour mixed with one to three vols. of hydrogen. According to S. Hilpert and J. Beyer, the ferrous oxide is formed in an increasing proportion as the temp. is raised; thus, at 700°, the product contains 85 per cent. of FeO, and at 800°, 92 per cent., but pure ferrous oxide is not obtained even at 1100°; nor was it possible to obtain pure ferrous oxide by the oxidation of reduced iron in a mixture of steam and hydrogen. R. M. Bozorth also observed that when steam acted on iron at 700°, he found a 2×10^{-2} cm. inner layer of ferrous oxide, a 2×10^{-4} cm. layer of ferrosic oxide, and an outer 2×10^{-5} cm. layer of ferric oxide.

According to G. Tissandier, iron can be oxidized to ferrous oxide by heating it to bright redness in a current of carbon dioxide. I. L. Bell obtained a similar result by using a mixture of equal vols. of carbon monoxide and dioxide; A. Laurent said that the product is ferrosic oxide; and H. Nippert, that at 720° ferrous oxide is produced. The reaction has been previously discussed by G. Lepetit, R. Schenck and T. Dingmann, etc., in connection with the blast furnace.

G. Chaudron and co-workers observed that at a temp. exceeding 570°, iron reacts with ferrosic oxide to form ferrous oxide, so that at 592°, 24 per cent. was transformed in 24 hrs., and 51 per cent. at 600°. P. Oberhoffer and H. Schenck said that the reaction is nearly complete at 1600°. C. N. Schuette and C. G. Maier, and C. T. Anderson studied the reaction. L. Wöhler and R. Günther did not notice the reaction $Fe_3O_4+Fe=4FeO$, because their mixture was too coarse-grained. W. Mills obtained an impure product by heating ferric oxide with iron: $Fe+Fe_2O_3=3FeO$; and R. W. G. Wyckoff and E. D. Crittenden obtained impure ferrous oxide by fusing magnetite with iron—analysis: 0·54, Fe; 78·40, FeO; 20·32, Fe_3O_4. R. W. Millar tried unsuccessfully to purify the sample, but he did succeed in raising the ferrous oxide to 82·95 per cent. J. H. Whiteley, F. S. Tritton and D. Hanson, and C. H. Herty also obtained analogous products. G. Tammann and E. Kordes observed that the reaction $Fe+PbO=Pb+FeO$ begins at about 460°, and $Fe+CuO=FeO+Cu$ at 610°.

P. Sabatier and J. B. Senderens said that ferrous oxide is formed at 200° when nitrous oxide is passed over iron; and F. Emich added that ferric oxide is the end-product of this reaction. J. Férée stated that ferrous oxide is produced when iron amalgam is slowly oxidized by exposure to air, but this reaction is not to be regarded seriously as a method of preparation. W. Vaubel obtained ferrous oxide as a product of the action of ammonium nitrate on iron; F. Martin and P. Fuchs, as a product of the reduction of alkaline earth sulphates with iron; and A. de Méritens, by the anodic oxidation of iron.

According to F. Stromeyer, H. W. F. Wackenroder and F. Stromeyer, and G. Magnus, ferric oxide, at the softening temp. of glass, is reduced by hydrogen to ferrous oxide; and M. Siewert added that the reduction to ferrous oxide occurs at 280° to 300°—*vide infra,* the action of hydrogen on ferric oxide. The ferrous oxide produced at this low temp. is pyrophoric, but it loses this property if kept in hydrogen for about 12 hrs. The product is very liable to be contaminated with ferrosic oxide, but H. Moissan said that he obtained a product of a high degree of purity by heating ferric oxide at 500° in hydrogen for 20 mins. As indicated above, the reaction involves some complex equilibria, discussed previously in connection with the blast furnace. H. Debray obtained ferrous oxide by reducing ferric oxide with a mixture of one to three vols. of hydrogen, and one vol. of steam at a red-heat. The equilibrium conditions with water vapour were discussed by S. Hilpert and J. Beyer, J. Beyer, L. Wöhler and R. Günther, and G. Chaudron—*vide supra.*

H. Moissan obtained ferrous oxide by reducing ferric oxide in a current of dry carbon monoxide at 500°; and H. Debray, I. L. Bell, and F. Leplay and A. Laurent employed a mixture of equal vols. of carbon monoxide and dioxide; C. R. A. Wright and A. P. Luff said that the product at a bright red-heat has the composition $Fe_{16}O_{17}$. O. Pattenhausen said that with a mixture of equal vols. of carbon monoxide and dioxide, ferric oxide heated at first to 775° and then to 825° yields a product with 83 to 84 per cent. FeO; and at 850° to 870°, one with 84·5 per cent. FeO; G. Chaudron obtained ferrous oxide at 800° to 1000° after 3 hrs.' exposure to the mixture of equal vols. of carbon monoxide and dioxide. L. Wöhler and R. Günther said that the product is not to be regarded as pure ferrous oxide; but H. Groebler and P. Oberhoffer, and H. Groebler obtained a product with 99·3 per cent. FeO and only 0·7 Fe_3O_4. R. Schenck could not obtain ferrous oxide as an independent solid phase by reducing ferrosic oxide with carbon monoxide up to 1100°, although he did get a feebly magnetic sample with 0·1 per cent. of iron in excess of that required for ferrous oxide by reducing ferric oxide at 800° with the equilibrium mixture of 66·66 per cent. of carbon monoxide and 33·33 per cent. of carbon dioxide. The equilibrium conditions in the reaction were studied by R. Schenck and co-workers, J. Müller, G. Lepetit, etc.—*vide supra.* C. H. Herty and G. R. Fitterer heated ferric oxide in a graphite crucible in an electric furnace, removed the iron and iron carbide by a magnet, and found the remaining product contained 98·9 per cent. FeO. The preceding observations weaken confidence in the old methods which have been reported for preparing ferrous oxide. J. von Liebig said that ferrous oxide is formed when dry ferrous oxalate is heated to 150° or 160°, in the absence of air, and cooled in an atmosphere of carbon dioxide. A. Vogel, and G. Magnus obtained pyrophoric ferrous oxide by a similar process; and the products of this reaction were discussed by C. F. Rammelsberg, and J. W. B. Döbereiner. According to H. Moissan, and W. G. Mixter, in order to avoid the separation of carbon, or the formation of a carbide, it is an advantage to heat the ferrous oxalate gradually up to 520° in a current of nitrogen, and finish off at about 900°. The product contains a little iron. S. Birnie, M. Herschkowitz, V. Falcke, and H. Nippert were also of the opinion that the products of the reaction are iron, ferrous and ferrosic oxides, carbon, and possibly undecomposed oxalate. H. le Chatelier reported ferrous oxide to be formed when a mixture of ferrous carbonate and oxalate is heated in a current of equal vols. of hydrogen and carbon dioxide; but O. Ruff and E. Gersten always obtained a product contaminated with ferrosic oxide and carbon. H. Moissan said that ferrous oxide, along with some ferrosic oxide, is produced when ferrous carbonate is rapidly heated. R. Böttger said that ferrous oxide is formed when ferrous oxalate is added to a boiling soln. of potassium hydroxide; and J. Riban, when a 5 per cent. soln. of ferrous formate or acetate is heated in a sealed tube at 175°, but in both cases some ferrosic oxide is formed.

Ferrous oxide has been reported by F. Bode to be formed in J. Hollway's process of desulphurizing copper pyrites in the Bessemer converter; by L. Benedek, when pyrites is heated to 300° or 400° in water vapour; by A. Brun, when basic volcanic glasses are heated to 800° in vacuo; and by E. Diepschlag and H. Fliegenschmidt, when ferrous silicate is heated to 1200° in the presence of an excess of lime. It is common to find that the metal oxides produced at a low temp. are more chemically active than those which have been heated to a high temp. This, for instance, is the case with alumina, chromic oxide, ferric oxide, etc. In some cases there is an evolution of heat as the oxide is transformed into the insoluble form—*vide* **5**. 33, 10; and *vide infra*, the caloresence of ferric oxide. R. W. Millar's sp. ht. curve, Fig. **504**, has a peak at −170°. H. Moissan said that ferrous oxide can exist in two **allotropic forms** according as it has been produced at a high or at a low temp. He said that the variety produced below 600° is more chemically active, for on exposure to air it unites with oxygen so rapidly that the whole mass may become incandescent; it decomposes water slowly in the cold, but more rapidly at the b.p.; it is readily soluble even in dil. acids such as acetic acid; it easily displaces ammonia from its salts; and it begins to be reduced by hydrogen at about 280°. On the other hand, ferrous oxide which has been heated above 1000° is no longer pyrophoric on exposure to air; it does not decompose water; it is not soluble in dil. acetic acid; it is not reduced by hydrogen below 330°. F. Glaser gave 370° for the temp. of reduction of ferrous oxide by hydrogen. The two varieties when oxidized to ferrosic oxide give products which show some differences (*q.v.*). G. Chaudron suggested that two varieties are in the one case ferrous oxide stable above 570° and in the other case a mixture of ferrosic oxide and iron: $4FeO \rightleftharpoons Fe_3O_4 + Fe$, which has a transition temp. at about 570°—*vide infra*, magnetic properties of ferrous oxide.

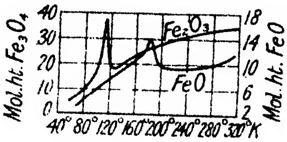


FIG. 504.—The Molecular Heats of Ferrous and Ferric Oxides.

The physical properties of ferrous oxide.—Ferrous oxide, when prepared by gaseous reduction, is a black powder, and when obtained by fusion processes, it is black and massive. Polished surfaces were found by H. E. Merwin to show the presence of magnetite by heat etching—the ferrous oxide at a red-heat assumes a matt appearance, whilst magnetite remains unaffected. The **crystals** are cubic. H. Groebler and P. Oberhoffer examined the **X-radiogram** of solid soln. with ferrosic oxide (*q.v.*). R. W. G. Wyckoff and E. D. Crittenden observed that the X-radiogram of ferrous oxide corresponds with a space-lattice of the sodium chloride type; the length of unit cube is $a=4{\cdot}2944$ A., V. M. Goldschmidt and co-workers found $a=4{\cdot}27$ A., and G. Natta, 4·28 A. D. W. Murphy and co-workers obtained $a=4{\cdot}289$ A. at temp. near the m.p. R. W. G. Wyckoff and E. D. Crittenden concluded that the unit cell contains 4 mols. of FeO. The unit cube of ferrous oxide containing some magnetite is slightly larger than is the case with ferrous oxide alone. The calculated **specific gravity** is 5·99, whereas the observed value making corrections for the ferrosic oxide impurity is 5·72. S. Hilpert and J. Beyer reported the sp.gr. of 97·83 per cent. ferrous oxide obtained by reducing ferric oxide in hydrogen to be 5·9, and if corrected for ferrosic oxide 5·92. W. Biltz studied the mol. vol.; and F. Sauerwald and G. Elsner, the adhesion of the compressed powder.

M. Mayer and B. Havas calculated values for the coeff. of **thermal expansion** from the addition rule for ferrous oxide in silicate glasses; and G. Chaudron and H. Forestier observed an anomaly in the thermal expansion corresponding with the change $4FeO \rightleftharpoons Fe_3O_4 + Fe$ below 570°. O. Kresta observed that the compressed powder, apparent sp. gr. 2·240, at about 49·8° has a **thermal conductivity** of 0·00133 cal. per cm. per second per degree. A. B. Lamb found the **specific heat** to be 0·1660 at 25° to 100°, or 0·1625 at 25°. If the temp. coeff. is the same as it is for iron, it would require 11,385 cals. to heat a gram of ferrous oxide from 25° to 727°. W. P. White gave for the true sp. ht. $c_p=0{\cdot}17508+0{\cdot}0000027\theta$, at temp. between 30° and 900°. M. Tigerschiöld calculated $C_p=10{\cdot}90$, at 17°, from the equilibrium relations $FeO+CO \rightleftharpoons Fe+CO_2$; and 10·64 from Kopp's rule. H. J. van Royen also made observations on this subject. R. W. Millar gave for the sp. ht., c_p, and the **molecular heat,** C_p, of a sample with 82·96 per cent. FeO, 14·54, Fe_3O_4, and 2·5, Fe:

	−202·3°	−182·8°	−160·0°	−122·4°	−105·0°
c_p . . .	0·04588	0·07020	0·09720	0·13970	0·16130
C_p . .	3·296	5·042	6·984	10·4	11·59
	−67·9°	−30·5°	−13·0°	1·6	28·8°
c_p . . .	0·16700	0·16280	0·16840	0·16730	0·17480
C_p . .	11·75	11·70	12·09	—	—

The results are plotted in Fig. 504. F. S. Tritton and D. Hanson gave 1370° for the **melting-point;** O. Ruff and O. Goecke, 1419°; C. H. Herty and G. R. Fitterer, 1355°; H. Groebler and P. Oberhoffer estimated 1377°; J. H. Andrew and co-workers, 1410°; B. Garre, 1530°; and F. Schönert, 1380°. As indicated above, G. Chaudron showed that ferrous oxide is unstable below 570°, decomposing in accord with $4FeO=Fe_3O_4+Fe$, and the thermal value of the reaction at 570° is $4\times66{\cdot}15$ Cals. L. Wöhler and R. Günther observed that the reaction is very slow at 550° in vacuo, for only 50 per cent. decomposed in 3 days. G. Chaudron and H. Forestier said that the reaction begins at 300° and attains a maximum speed at 480°. The **dissociation pressure** of ferrous oxide has not been measured directly. The values of the dissociation press. of the oxygen calculated indirectly are $8{\cdot}9\times10^{-22}$ atm. at 727° by H. J. van Royen; 4×10^{-21} to 5×10^{-21} atm. at 727° by O. Sackur; 10^{-21} atm. at 727° by G. Chaudron; and 10^{-8} atm. at 1327° by H. le Chatelier. H. Styri gave log $p=-7{\cdot}6$ for the dissociation press. of $2FeO=2Fe+O_2-131{,}400$ cals. L. Wöhler and R. Günther obtained:

	600°	800°	1000°	1200°	1400°
p . .	5×10^{-27}	3×10^{-21}	3×10^{-17}	3×10^{-14}	$6{\cdot}3\times10^{-12}$ atm.

H. von Jüptner calculated for the dissociation press. of the oxygen, in $2FeO=2Fe+O_2$, $\log[O_2]=-28752T^{-1}+1{\cdot}75\log T+2{\cdot}8$—*vide infra*; and values calculated from this equation are:

	600°	1000°	1400°	1800°	2200°	2400°
$\log[O_2]$.	$0{\cdot}0_{40}5151$	$0{\cdot}0_{20}1986$	$0{\cdot}0_{12}5869$	$0{\cdot}0_{7}3338$	$0{\cdot}0_{4}3803$	$0{\cdot}0_{3}5344$

A. Matsubara gave $\log p=-28{\cdot}752T^{-1}+1{\cdot}79\log T+13{\cdot}427$, and O. C. Ralston $\log p=2{\cdot}76-26750T^{-1}+0{\cdot}946\log T+0{\cdot}00072T^2-0{\cdot}0_81616T^3$. The dissociation press. approaches 1 atm. at about 4000°. No confidence can be given to extrapolation at such high temp. from equations derived from data collected at about 1000°. The dissociation press. of ferrous oxide at room temp. is of the order 10^{-42} atm. Observations on the subject were made by N. Parravano and G. Malquori, E. Baur and A. Glässner, L. Wöhler and O. Balz, K. Hofmann, E. Schreiner and F. B. Grimnes, A. McCance, G. Chaudron, F. Wüst and P. Rütten, and A. B. Lamb. C. H. Herty and co-workers estimated that the **melting-point** is not far above 1355°; P. Oberhoffer and O. von Keil gave 1390°; and D. W. Murphy and co-workers obtained 1360°±10°, and found that the oxide is stable above and below its m.p. when it has a constant lattice parameter of 4·289 A. The **heat of fusion** is 28 Cals. per grm., or 5 Cals. per mol.

J. Thomsen gave for the **heat of formation,** [Fe,O], 68·3 Cals.; H. le Chatelier, 64·6 Cals.; O. Ruff and E. Gersten, 60·4; G. H. Brodie and co-workers, 63·56 Cals.; M. Tigerschiöld, 66·3 Cals.; W. A. Roth and co-workers, 64·25 Cals.; J. Jermiloff, 66·713 Cals.; W. D. Treadwell, 66·6 Cals. at 1000°, or 68·6 Cals. at 25°; L. Wöhler and R. Günther, 63·35 Cals.; H. von Jüptner, 65·7 Cals.; W. G. Mixter, 64·3 Cals.; H. J. van Royen, 65·891 Cals.; E. D. Eastman, 63·73 Cals.; O. Doepke, 68·00 Cals.; and E. Baur and A. Glässner, 67·35 Cals. at 680° and at a constant press. P. A. Favre and J. T. Silbermann's value is too low. The results by W. D. Treadwell were calculated from the e.m.f., 0·040 volt, of the cell Fe,FeO: electrolyte: O_2,Ag with fused glass or borax as the electrolyte at 800° to 1193°; and those of M. Tigerschiöld, and L. Wöhler and R. Günther, from the equilibrium data of the system: $FeO+H_2\rightleftharpoons H_2O+Fe$. Observations were also made by M. Berthelot, and A. McCance, whilst E. Baur and A. Glässner said that there is a minimum value at 680°. The best representative value approximates 64 Cals. at 25°, per mol. FeO. W. A. Roth and co-workers gave $FeO+Fe_2O_3=Fe_3O_4+7{\cdot}0$ Cals.; and $2FeO+SiO_2$ (quartz)$=Fe_2SiO_4+8{\cdot}1$ Cals. J. Thomsen gave for the **heat of hydration** (Fe,O,Aq.) 68·9 Cals., or (Fe,O,H_2O), 68·28 Cals.; and for the **heat of neutralization** in acids 10·7 Cals. in N-HCl; 9·9 Cals. in N-$CH_3.COOH$; 12·5 Cals. in N-H_2SO_4; 5·0 Cals. in N-H_2CO_3; and 7·3 Cals. in N-H_2S. Observations were made by M. Berthelot. E. Petersen gave 13·265 Cals. for hydrofluoric acid. E. D. Eastman calculated for the **free energy** of ferrous oxide:

	600°	700°	800°	900°	1000°
Free energy .	−49,700	−48,075	−46,445	−44,840	−43,255 cals.

O. Sackur, G. Bodländer, H. J. van Royen, E. Baur and A. Glässner, and G. Beck studied the subject. F. Wüst and P. Rütten gave −49,000 cals. at about 600°; 43,000 cals. at about 900°; and 31,000 cals. at about 1500°. W. J. Sweeney gave −120·92 Cals. for the free energy of formation of $Fe(OH)_2$ from its elements; and W. G. Whitman and co-workers, −57,200 cals. G. N. Lewis and M. Randall, and O. C. Ralston gave: free energy $=-61{,}250+0\cdot94T\log T+0\cdot00165T-0\cdot0_637T^3+6\cdot82T^{-1}$, and this gives −57,472 cals. at room temp., and −42,083 cals. at 1000°. J. Chipman gave for the free energy, between 1550° and 1770°, of the reaction: $FeO+H_2=Fe+H_2O$, where $\log K=6200T^{-1}-3\cdot28$, $\delta F=-28400+15T$; and for the reaction: $Fe+\frac{1}{2}O_2=FeO$, $-31200-1\cdot0T$. The **entropy** of formation calculated for $Fe+\frac{1}{2}O_2=FeO$ is −21·3 Cals.; and for the absolute entropy of ferrous oxide 10·01 cals. per degree; R. W. Millar and J. D. Sullivan gave 12·7 cals. per degree at 25°. K. K. Kelley, and G. Beck studied the subject.

The effect of ferrous oxide on the **transmission of light** of short wave-length by glass is discussed in connection with ferric oxide. G. A. Dima said that the **photoelectric effect** with ferrous oxide is greater than it is with ferric oxide. W. A. Douglas-Rudge found that the powdered oxide acquires a negative charge when it is agitated in air. O. Kresta found that the compressed powder at 49·8° has an **electrical conductivity** of 0·00133 mho. G. Tammann and F. Westerhold made observations on the subject. A. B. Lamb calculated that an oxygen electrode and an iron electrode plunged in a sat. soln. of ferrous hydroxide would give zero **electromotive force** when the press. of the oxygen over the oxygen electrode is $4\cdot4\times10^{-90}$ atm. With the oxygen at atm. press., the e.m.f. of the cell would be $E=0\cdot01475\log 8\times10^{88}=1\cdot279$ volt; that of the cell $Fe|M\text{-}Fe^{\cdot\cdot}|1\cdot35\times10^{-5}M\text{-}Fe^{\cdot}|Fe$, −0·144 volt; and that of the cell $O_{2\text{atm.}}|M\text{-}OH'|2\cdot7\times10^{-5}M\text{-}OH|O_{2\text{atm.}}$, 0·269 volt. E. Baur and co-workers measured the e.m.f. of cells FeO,Fe (fused borax, glass or porcelain), CuO,Cu_2O at 700° to 1300°; and W. D. Treadwell, of the cell Fe,FeO(electrolyte of fused glass),O_2,Ag, and found 1·040 volts between 800° and 1193°. For W. D. Treadwell's cell, *vide supra*.

	800°	875°	940°	1000°	1100°	1180°
E.m.f. .	1·081	1·071	1·048	1·040	1·018	0·978 volts

and 1·06 volts was obtained for the potential Fe : FeO from the values obtained for the cell FeO,Fe | electrolyte | CuO,Cu_2O. Observations were also made by G. Chaudron, and E. Baur and A. Glässner. G. Schmidt, H. Debray, G. Lepetit, S. Hilpert and J. Beyer, S. Hilpert, S. Veil, and R. W. G. Wyckoff and E. D. Crittenden said that ferrous oxide is practically **non-magnetic.** H. Moissan obtained a magnetic variety at a temp. below 600°, and G. Chaudron observed that this is because the ferrous oxide decomposes: $4FeO=Fe_3O_4+Fe$ at a temp. between 550° and 580°, and this is evidenced by observations on the magnetic behaviour. J. B. Ferguson argued that since iron, ferric oxide, and ferrosic oxide undergo magnetic changes at 790°, 678°, and 530° respectively, ferrous oxide might be expected to behave similarly. Ferrous oxide containing ferrosic oxide was reduced to free iron and in the subsequent combination of the free iron the decrease in magnetic permeability did not correspond with the decrease in the free iron content of the sample. No evidence was obtained of the existence of a magnetic form of ferrous oxide. R. W. G. Wyckoff and E. D. Crittenden said the upper limit of the magnetic susceptibility is 0·00052 mass unit. Observations were made by S. Meyer, and E. F. Herroun and E. Wilson. A. Brun said that the mineral iozite is magnetic.

The chemical properties of ferrous oxide.—L. Wöhler and O. Balz observed only three equilibria in the reduction of ferric oxide with **hydrogen,** $K=[H_2O][H_2]$, for Fe_2O_3 to Fe_3O_4, 7·5 at 350° to 17·9 at 950°; for Fe_3O_4 to FeO, 1·3 at 640° to 5·07 at 950°; and for FeO to Fe, 0·62 at 750° and 0·92 at 990°. P. H. Emmett and J. F. Shultz found that the equilibrium constant, *K*, of the reaction $FeO+H_2 \rightleftharpoons Fe+H_2O$ is $K=p_{H_2O}/p_{H_2}$, and

	600°	700°	800°	900°	1000°
K . .	0·332	0·422	0·499	0·594	0·669

The subject was studied by J. Chipman, and by E. Schreiner and F. B. Grimnes—*vide* the blast-furnace reactions. For the temp. at which the reaction begins, *vide supra*. H. Moissan observed that in **oxygen** pyrophoric ferrous oxide burns to ferric oxide, but in consequence of the large evolution of heat, the temp. of combustion is high, and ferrosic oxide is formed. W. Eitel discussed the reaction $2FeO+\frac{1}{2}O_2 \rightleftharpoons Fe_2O_3$. According to L. Wöhler and R. Günther, finely-divided ferrous oxide readily oxidizes at room temp., and when heated to 200° or 250°, it readily burns in atm. **air,** as indicated above, to form ferrosic oxide. Observations were also made by M. Siewert, S. Birnie, H. Moissan, F. Glaser, and S. Hilpert and J. Beyer. A. G. Doroschevsky and A. Bardt observed that dry ferrous oxide does not oxidize in dry air at ordinary temp., but it is slowly oxidized in moist air below 100°. J. Férée found that the pyrophoric oxide oxidizes in air at 350° to form ferrosic oxide; H. Debray, and G. Tissandier also observed the formation of ferrosic oxide when ferrous oxide is heated in air. G. Schikorr studied the action of hydrated ferrous oxide on **water**—*vide infra*, the corrosion of iron. H. Moissan, and W. Eitel observed that the reaction with steam can be symbolized: $3FeO+H_2O \rightleftharpoons H_2+Fe_3O_4+15{,}400$ cals. J. Férée found that the pyrophoric oxide reacts with aerated water to form ferrosic oxide; and H. Moissan, that the pyrophoric oxide decomposes water slowly at ordinary temp., and rapidly at 100°. J. Riban found that when ferrous oxide and water are heated in a sealed tube, ferrosic oxide is formed. L. J. Thénard found that **hydrogen dioxide** oxidizes it to ferric oxide. A. V. Pamfiloff and N. N. Petin studied the influence of ferrous oxide on the liberation of iodine from an iodide by the action of hydrogen dioxide; and as a result they concluded that the mechanism of the action of ferrous oxide, typical of inductors in general, is probably based on its spontaneous oxidation, and the retarding influence exerted on the reaction by acidity is related to the great stability of ferrous ions in an acid soln.

Ferrous oxide dissolves in **acids** to form a well-defined series of ferrous salts. H. Moissan observed that the pyrophoric oxide dissolves readily in dil. acids. H. Moissan observed that **fluorine** does not act in the cold on ferrous oxide, but when gently warmed a reaction sets in with incandescence, and a skin of white fluoride is formed. A. Michael and A. Murphy found that ferrous oxide reacts at −18° with **chlorine** dissolved in carbon tetrachloride: $6FeO+3Cl_2=2Fe_2O_3+2FeCl_3$. R. Weber observed that chlorine acts on ferrous oxide to form ferric chloride, and, according to H. Schulze, a higher oxide is also produced. R. Wasmuht found that ferrous oxide alone reacts with chlorine at 150°. L. Mathesius found that ferrous oxide, prepared at 600°, is not attacked by an aq. soln. of **bromine**; and I. L. Bell, that the oxide prepared at a red-heat is not attacked by a cold aq. soln. of **iodine.** H. St. C. Deville found that ferrous oxide reacts slowly with **hydrogen chloride,** forming ferrous chloride and ferrosic oxide. L. Wöhler and R. Günther said that the oxide prepared at 700° or 800° is easily dissolved by dil. **hydrochloric acid**; G. Tissandier, that the oxide prepared at a red-heat dissolves easily in hydrochloric acid; R. W. G. Wyckoff and E. D. Crittenden, that the oxide prepared by a fusion process dissolves very slowly in boiling hydrochloric acid.

According to D. L. Hammick, when ferrous oxide, prepared at 300°, is heated in **sulphur dioxide,** the mass becomes incandescent, and clouds of sulphur and sulphur trioxide are formed, and the solid contains sulphide, ferric oxide, and ferrous and ferric sulphates. A. C. Halferdahl calculated for the reaction $6FeO+SO_2=2Fe_3O_4+\frac{1}{2}S_2$, the free energy −30,000 cals. at 600°, and +4300 cals. at 1400°;

for $4FeO+SO_2=2Fe_2O_3+\frac{1}{2}S_2$, −14,700 cals. at 600°, and +20,400 cals. at 1400°; and for $7FeO+SO_2=3Fe_2O_3+FeS$, −29,300 cals. at 600°, and +29,400 cals. at 1400°. R. W. G. Wyckoff and E. D. Crittenden found that the oxide prepared by the fusion process is almost insoluble in **sulphuric acid**; and N. J. Harrar observed that in 40 and 60 days, at 25°, sulphuric acid dissolved respectively 67·205 and 95·045 mgrms. of iron from ferrous oxide per 100 c.c. of soln.

S. Hauser studied the reduction of ferrous oxide by **ammonia.** F. Haber observed that the oxidizing and reducing action of **hydroxylamine** may be illustrated by adding hydroxylamine hydrochloride to a hot emulsion of ferrous hydroxide precipitated by means of sodium hydroxide. The greenish mass rapidly becomes reddish-brown, owing to the oxidation of the hydroxide. If now the liquid be acidified and a fresh quantity of hydroxylamine hydrochloride added, the latter acts as a reducing agent, and rapidly converts the ferric into ferrous salt, the change being rendered evident by the disappearance of the yellow colour. A. Smits found that **magnesium nitride** reacts vigorously with ferrous oxide; and O. Meyer likewise found that **titanium nitride** is vigorously attacked by ferrous oxide at a high temp. L. Santi said that a soln. of **ammonium chloride** converts ferrous oxide into chloride with the evolution of ammonia; and H. Moissan also observed that ferrous oxide liberates ammonia from the ammonium salts, but S. Hilpert and J. Beyer did not agree. H. Moissan found that when the pyrophoric oxide is gently warmed with **nitric oxide,** ferric oxide is produced, and similarly with **nitrogen dioxide**; whilst with **nitric acid** the pyrophoric oxide becomes incandescent. H. Debray found that ferrous oxide prepared at a red-heat dissolves in nitric acid with the evolution of nitrous fumes, and G. Tissandier also observed that the oxide prepared at a red-heat dissolves in nitric acid. H. Schackmann and W. Krings represented the action of **phosphorus** by $5FeO+2P\rightleftharpoons P_2O_5+5Fe$; and by $8FeO+2P\rightleftharpoons(FeO)_3P_2O_5+5Fe$; and W. Krings and H. Schackmann, the action of **iron phosphide,** by $8FeO+2Fe_3P\rightleftharpoons(FeO)_3P_2O_5+11Fe$.

V. Falcke and co-workers observed that when ferrous oxide is heated with purified **carbon,** no reaction occurs below 650°, but above this temp., reduction occurs. The speed of the reaction depends upon the form of carbon employed; thus, sugar-charcoal is relatively inert, for it does not begin to react until about 800°, whereas carbon obtained by burning acetylene in chlorine begins to react at 650°. W. Baukloh and R. Durrer observed that ferrous oxide is reduced by carbon only above 700°, and the rate of the reaction is the same as that at which carbon diffuses through iron, showing that the reaction proceeds from the surface inwards. N. Parravano and G. Malquori gave for the gas reaction: $2FeO+C=2Fe+CO_2$, $\log p_{CO_2}=4{\cdot}95$. Observations were made by J. R. Cain and L. Alder, H. Nippert, and R. Schenck and co-workers—*vide supra*, and also *infra*, magnetite. A. L. Feild assumed that the equilibrium constant K of the reaction $FeO+C\rightleftharpoons Fe+CO$ in molten steel is of the order $K=0{\cdot}010$, where $K=xy$, when x denotes the percentage weight of carbon and y that of iron oxide. It is assumed that the mass of the iron is constant, and that the press. of the carbon monoxide is a constant and equal to one atmosphere. C. H. Herty at first gave 0·040, but later 0·016. A. B. Kinzel and J. J. Egan obtained $K=0{\cdot}0005$ at 1550°. O. Meyer observed that ferrous oxide is attacked by **carbides**—*e.g.* silicon, chromium, and molybdenum—at 1500°. O. Houghton said that the reaction with silicon carbide begins at 1300°. The reaction was studied by E. H. Schulz and A. Kanz. R. Akermann and C. G. Särnström observed that a mixture of **carbon monoxide** and dioxide (10 : 4) reduces ferrous oxide at 850°—*vide supra* for the reducing action of carbon monoxide. The mean of A. C. Halferdahl's values for the free energy of the reaction $FeO+CO=Fe+CO_2$, can be represented by $-63{\cdot}265+16{\cdot}279T$, and the value at 25°, is −58,410 cals. H. Moissan, and W. Eitel discussed the reaction between **carbon dioxide** and pyrophoric ferrous oxide: $3FeO+CO_2\rightleftharpoons Fe_3O_4+CO$; or $2FeO+CO_2\rightleftharpoons Fe_2O_3+CO$. N. J. Harrar found the amounts of ferrous oxide, expressed in milligrams Fe per 100 c.c. of soln., at 25°, dissolved in 40 and 60 days by **formic acid** to be respectively 5·792 and 6·337 ; **acetic acid,** 0·520 and 0·491 ; **propionic acid,** 0·449 and 0·456 ; **oxalic acid,** 42·525 and 42·995 ; **malonic acid,** 31·734 and 47·451 ; **succinic acid,** 0·794 and 0·973 ; **lactic acid,** 12·398 and 13·871 ; **tartaric acid,** 14·022 and 28·084 ; **citric acid,** 31·122 and 42·226 ; **benzoic acid,** 2·022 and 2·148 ; and **salicylic acid,** 14·627 and 14·953. H. Moissan observed that ferrous oxide which has been heated to 1000° does not dissolve in dil. acetic acid. M. Juschkewitsch found that ferrous oxide dissolves very slowly in a 7 per cent. soln. of **potassium cyanide** at ordinary temp. A. G. Doroschevsky and A. Bardt found that **alcohol** vapour is oxidized to aldehyde in the presence of ferrous oxide ; and P. Sabatier discussed ferrous oxide as a catalytic agent in organic chemistry. C. H. Herty found that the deoxidation of iron by **silicon** proceeds $Si+2FeO \rightleftharpoons SiO_2+2Fe$, and when the metal is saturated with silica, $K=[Si][FeO]^2$, or $K=1{\cdot}49\times10^{-4}$. G. Tammann and G. Bätz observed that ferrous oxide reacts exothermally with quartz at about 700° or 800°, and with precipitated and calcined **silica,** at 800°. M. Rüger observed no combination with silica between 900° and 1200°. N. L. Bowen and J. F. Schairer, and F. Sauerwald and W. Hummitzsch studied the $FeO-SiO_2$ system. R. Sachsse and A. Becker found that ferrous oxide opens up the **silicates** by rendering them susceptible to attack by analytical reagents. G. Rauter observed that when ferrous oxide is heated with **silicon tetrachloride** in a sealed tube, ferrous chloride and ferric oxide are formed. P. Ramdohr studied the system with **titanic oxide:** $FeO-Fe_2O_3-TiO_2$. F. Halla noted the formation of the spinel **ferrous titanite,** $FeO.Ti_2O_3$, at 1000° ; the lattice parameter of this salt is $a=8{\cdot}47$ A., and the sp. gr. 4·68.

P. Oberhoffer represented equilibrium conditions of the reaction with **manganese,** $FeO+Mn \rightleftharpoons Fe+MnO$, by the curve Fig. 505. Observations on the subject were made by H. le Chatelier, R. Schenck, H. Styri, A. McCance, W. Krings and H. Schackmann, H. Giersch, and C. H. Herty. W. Krings and H. Schackmann found that the equilibrium constant $K=[Mn][FeO]/[Fe][MnO]$ is 0·0032 at 1550° to 1560°. B. Garre found that the reaction with **magnesium** begins at 575°, and 78·2 Cals. of heat are evolved. G. L. Clark and co-workers found **ferrous aluminate** is of the special type with unit cell having the parameter $a=8{\cdot}119$ A., and **ferrous chromite,** with $a=8{\cdot}344$ A.—*vide* aluminates and chromites. H. zur Strassen gave for the action of **nickel** $Fe+NiO=FeO+Ni+6{\cdot}4$ to 14·2 Cals. W. Jander and H. Senf studied the reaction. F. Sauerwald and W. Hummitzsch studied the system with **calcium oxide.** F. de Carlo found that **lead dioxide** converts ferrous oxide at 250° to 300° into a higher oxide. The miscibility of ferrous oxide with **iron** has been previously discussed ; and its miscibility with **ferrosic oxide** is discussed in connection with the last-named oxide. P. Oberhoffer and O. von Keil determined the m.p. of some mixtures of **manganous oxide** and ferrous oxide. They found :

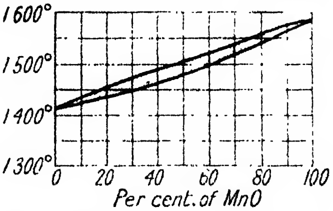


FIG. 505.—Equilibrium Diagram of the System : FeO–MnO.

FeO . . .	100	75	50	25	0 per cent.
Melting-points .	1390°	1470°	1513°	1650°	(1700°)

C. Benedicks and H. Löfquist have constructed a provisional equilibrium diagram on the basis of these meagre data ; and from the work of M. Matwéeff, and P. Oberhoffer and K. d'Huart, it is assumed that complete miscibility occurs in the liquid state. F. Sauerwald and W. Hummitzsch studied the reaction. C. Benedicks and H. Löfquist also constructed a provisional equilibrium diagram of the ternary system : Mn–Fe–O. According to G. Tammann and F. Westerhold, ferrous oxide reacts when heated with **molybdenum trioxide** to form ferrous molybdate ; and with **tungsten trioxide** to form ferrous tungstate. G. Tammann and W. Rosenthal studied the action of ferrous oxide on **uranium trioxide ;**

V. Lepiarczyk, its action on **calcium sulphide,** and on **calcium sulphate**; and C. Montemartini and A. Vernazza, its action on soln. of **chromic sulphate.**

Ferrous hydroxide, or **hydrated ferrous oxide.**—A. F. de Fourcroy observed that green *précipités martiaux* is formed when caustic alkalies are added to soln. of iron in acids. The precipitate was examined by G. F. Rouelle, C. W. Scheele, J. L. Proust, J. L. Gay Lussac, M. Darso, C. F. Bucholz, and J. J. Berzelius. L. J. Thénard obtained a white precipitate under similar conditions, and for a time it came to be called *Thénard's white oxide.* L. J. Thénard's idea that the precipitate obtained by the addition of alkali-lye to a soln. of a ferrous salt is a peculiar oxide was shown to be wrong by J. L. Proust, C. F. Bucholz, and J. J. Berzelius; M. Darso, C. F. Bucholz, and T. Thomson regarded it as a basic sulphate. J. L. Proust, H. Davy, and J. J. Berzelius at first considered the white or green precipitate to be a hydrate of ferrosic oxide, but later, J. J. Berzelius showed that it is a *monohydrate* of ferrous oxide, $FeO.H_2O$, or **ferrous hydroxide,** $Fe(OH)_2$. According to F. Hart, an impure *dihydrate,* $FeO.2H_2O$, occurs in the clay near Cuxhaven, in hard, yellowish-brown lumps which crumble on exposure to air.

The formation and preparation of ferrous hydroxide.—According to A. Ackermann, A. Bineau, H. Wölbling, R. Stumper, W. R. Dunstan and J. R. Hill, J. A. N. Friend, F. W. Durkee, W. G. Whitman and co-workers, and W. A. Tilden, ferrous hydroxide is formed as an intermediate stage in the rusting of iron; and when iron is in contact with aerated waters, or waters containing carbonic or sulphuric acid. A. Kaufmann observed that it is formed in green flecks when iron or solid ferrous salts are kept in contact with a sat. soln. of ammonium nitrate. P. de Clérmont and J. Frommel showed that ferrous hydroxide is produced by the action of boiling water on ferrous sulphide. O. Baudisch and co-workers found that the hydroxide is produced in the hydrolysis of ferrous hydrocarbonate; R. Fink, by treating a soln. of ferrous sulphate with basic copper sulphate; D. Vitali, by the action of silver oxide on a soln. of ferrous nitrate; and G. Kassner, by the action of potassium hydroxide on a soln. of ferrous cyanide, or, according to S. U. Pickering, on ferrous tartrate. O. Baudisch and L. W. Bass found that white, glistening crystals are formed when an alkaline normal soln. of potassium ferrocyanide, free from oxygen, is exposed for some hours to sunlight; and M. Volmar found that ferrous hydroxide and tartrate are produced when a soln. of potassium ferrous tartrate is exposed to ultra-violet rays.

H. E. Patten and G. H. Mains found that hydrated ferrous oxide is precipitated by ammonia or sodium hydroxide when the H˙-ion conc. is $p_H=5{\cdot}5$ to $6{\cdot}0$. Observations were also made by J. H. Hildebrand. H. T. S. Britton found that in the electrometric titration of 100 c.c. of $0{\cdot}025M$-$FeSO_4$, with $0{\cdot}0990N$-NaOH, the results shown in Fig. 506 were obtained. Precipitation began when 0·8 c.c. of the alkali soln. had been added, and when the H˙-ion conc. was $p_H=5{\cdot}49$; and it was complete when 1·71 eq. of alkali had been added. S. U. Pickering observed that complete precipitation had taken place from ferrous sulphate soln. at the point where they became alkaline to phenolphthalein, and this was when sodium hydroxide had been added in amounts which varied from 1·77 to 1·86 eq. He considered this sufficient justification for the assertion that the precipitate was a definite basic salt, $10FeO.SO_3$. H. T. S. Britton found that precipitation usually occurs somewhere near the point of the first inflexion, although often at a p_H which was a little less than that at which the main precipitation took place. This was probably due to the precipitate having been formed at a point in the liquid where the precipitation value of p_H had been temporarily exceeded, and time not having been allowed for its re-solution. If, therefore, the two straight portions of the curve be produced, it is probable that the point of intersection corresponds more nearly

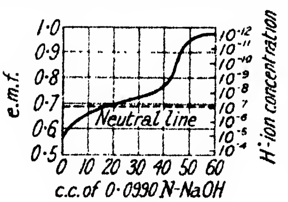


FIG. 506.—Electrometric Titration of Solutions of Ferrous Sulphate.

to the amount of alkali which had to be added to produce incipient precipitation, and also to the actual hydrion concentration at which precipitation under ideal conditions would commence. This point represents the limiting conditions necessary to form a precipitate. The conc. of the metal ions is then $p_{H^{\cdot}}=5{\cdot}77$, $p_{OH'}=8{\cdot}37$; and 0·6 c.c. 0·0990*N*-NaOH are required and $C_{Fe^{\cdot\cdot}}=3{\cdot}0\times10^{-4}$, so that $[Fe^{\cdot\cdot}][OH']^2=4{\cdot}5\times10^{-21}$—*vide infra*, solubility product.

G. Schmidt prepared ferrous hydroxide by mixing a soln. of a ferrous salt, free from ferric salt, with soda-lye or potash-lye freed from air by boiling, and performing the operation in a vessel from which air is excluded. The vessel is filled with boiling water and closed. The white flakes must be preserved from contact with air during washing and drying. The precipitate is allowed to settle, and the liquid decanted with a syphon; the vessel is again filled with boiling water, poured in slowly so as not to disturb the precipitate, and afterwards shaken and closed. This purification by alternate subsidence and decantation must be performed as quickly as possible, since hydrated ferrous hydroxide is decomposed by prolonged contact with water. The pale green precipitate is then placed in a retort with ether vapour, and the beak of the retort dipped under mercury. Air is expelled by the ether as the retort is warmed, and the water is afterwards driven off. The product can be preserved in hydrogen out of contact with air. If aq. ammonia is employed in place of potash-lye, the precipitate after long standing gives off hydrogen and is converted into black ferrosic oxide containing adsorbed ammonia. As commonly prepared, ferrous hydroxide is a bulky, greenish-grey substance, very liable to oxidation to greenish-black hydrated ferrosic oxide and finally to red ferric hydroxide. According to E. Divers and T. Haga, if, after the precipitation, the supernatant mother-liquor is poured off and solid potassium hydroxide dissolved in the remaining mother-liquor, the ferrous hydroxide diffused through it undergoes in the course of a few hours a very considerable diminution in vol., and then forms a pale greenish-grey pulverulent precipitate, although the gelatinous precipitate may have been of a much darker colour. This dense hydroxide is much more stable, and in oxidizing does not form the black hydroxide before becoming ferric hydroxide. According to E. Deiss and G. Schikorr, when gaseous ammonia is passed into a soln. of ferrous chloride, completely protected from oxygen, a pure white pulverulent precipitate is obtained, resembling in appearance calcium hydroxide. If the precipitate stands in contact with the mother-liquor for a long time, it may be partly peptized. The precipitate is washed with air-free water. O. Baudisch and P. Mayer, and O. Baudisch and L. A. Welo described a special apparatus for washing the precipitate while it is protected from air. The precipitate was found by W. R. Dunstan and T. S. Dymond to retain ammonia very tenaciously, and they added that the precipitation is incomplete (peptization). The hydroxide was obtained by the ammonia precipitation by A. Quartaroli, and K. Endell and R. Rieke; the alkali-lye precipitation, by W. R. Dunstan and T. S. Dymond, O. Baudisch and co-workers, J. Woost, S. Hilpert, A. Krause, M. Kuhara, G. Schmidt, and E. Deiss and G. Schikorr; and milk-of-lime, by W. von Zorn, and W. R. Dunstan and T. S. Dymond. A. B. de Schulten treated a soln. of ferrous chloride with an excess of potassium hydroxide and heated the mixture for a long time in a current of coal gas; and on cooling the green soln., obtained the hydroxide in green hexagonal prisms.

L. Brugnatelli, and R. Saxon obtained the hydroxide electrolytically using iron as an anode. R. Lorenz used a platinum cathode, an iron plate as anode, and an aq. soln. of sodium chloride, sulphate, or nitrate as electrolyte. The liquid was kept stirred during the electrolysis. H. Buff, F. Förster and co-workers, B. la Croix von Langenheim, P. Krassa, J. Woost, C. Monnet, R. Kremann and J. Lorber, M. Tichwinsky, O. Faust, O. Pattenhausen, and M. Roloff also obtained the hydroxide in an analogous manner. H. J. M. Creighton produced the *rhythmic precipitation* of ferrous hydroxide by passing an electric current, of potential gradient 0·0093 volt, through a 2-in. U-tube containing in the horizontal part 10 per cent. agar-agar mixed with small quantities of phenolphthalein and sodium chloride. The ends were filled with a dil. soln. of sodium chloride, with iron nails as electrodes. In a few days' time green discs of ferrous hydroxide appeared separated from one another by a pink jelly.

E. Deiss and G. Schikorr precipitated white ferrous hydroxide from a soln. of ferrous chloride by means of ammonia gas, and then by repeated centrifugal separation washed the precipitate with air-free water until it formed a **hydrosol of ferrous hydroxide.** A. Schmauss also obtained the hydrosol by electrical spluttering of iron wires under water containing a little gelatin in soln. E. Deiss and G. Schikorr found that the soln. is colourless by reflected light and red by transmitted light. The concentration is about 4 grms. per litre, and it cannot be kept longer than 6 days without flocculation. The particles are positively charged, and are flocculated by electrolytes. A. Schmauss's sol is green and unstable; it becomes yellow, by oxidation, on exposure to air. The hydrosol is cataphoretic, and it is flocculated by the positively charged hydrosol of ferric hydroxide. The absorption spectrum shows bands from $496\mu\mu$ to $662\mu\mu$.

The properties of ferrous hydroxide.—The dried, amorphous ferrous hydroxide is brittle, friable, and green. J. von Liebig and F. Wöhler said that the green colour is probably due to incipient oxidation. A. B. de Schulten obtained the hydroxide in green hexagonal prisms by crystallization from a conc. soln. of sodium hydroxide—*vide supra.* O. Baudisch and co-workers, E. Deiss and G. Schikorr, and M. Kuhara obtained the white hydroxide by carefully excluding oxygen during its preparation. According to G. Natta and E. Casazza, the **crystals** of ferrous hydroxide belong to the holohedral class of the rhombohedral system; and X-radiograms show that the crystals have a lattice structure like brucite. The elementary cell has one molecule, and the dimensions a=3·24 A., and c=4·47 A., so that the axial ratio $a:c$=1 : 1·38; and the calculated density is 3·40. H. Seifert studied the subject. G. Natta discussed the isomorphism of the bivalent hydroxides from the point of view of the space-lattice, and the atomic radii. J. Thomsen gave for the **heat of formation** of the hydroxide (Fe,O,H_2O)=68·28 Cals.; and M. Berthelot, 69·00 Cals. J. Thomsen gave for the **heat of neutralization** of the hydroxide with sulphuric acid, 24·92 Cals., and with hydrochloric acid, 21·39 Cals.; and M. Berthelot gave 21·4 Cals. with dil. hydrochloric acid. J. Thomsen found the **heat of oxidation,** $Fe(OH)_2 \rightarrow Fe(OH)_3$, to be 27·29 Cals. R. Dallwitz-Wegener discussed the **free energy** of the compound. M. Randall and M. Frandsen gave −115·4 Cals. for the free energy of formation of the hydroxide, and for $Fe+2H_2O=Fe(OH)_2+H_2$, −2·28 Cals.

F. Allison and E. J. Murphy studied the magneto-optic properties. F. Förster and V. Herold gave −0·740 volt for the **electrode potential** of ferrous hydroxide against a hydrogen electrode at 20°; O. Faust, −0·75 volt; and J. Woost for the electrode potential with 2·85N-KOH, hydrogen electrode unity, −0·835 to −0·845 volt at 0°; −0·825 to −0·840 volt at 20°; −0·820 to −0·835 volt at 50°; and −0·80 volt at 75°. O. Pattenhausen said that ferrous hydroxide shows two potentials—namely, −0·66 volt, and −0·55 to −0·53 volt—corresponding with two different stages in the hydration of ferrous oxide at ordinary temp. and with a current of 0·07 ampère. S. Miyamoto found the electric potentials of cells with N-, 2N-, 4N-, and 5N-NaOH soln. at 25° using platinized platinum. In the case of $Pt \mid NaOH,Fe(OH)_2,Fe_3O_4.nH_2O \mid NaOH \mid HgO,NaOH \mid Hg$, the potential $E=0{\cdot}8030-0{\cdot}0015 \log C'_{NaOH}$; with the cell $Pt,H_2 \mid NaOH \mid HgO,NaOH \mid Hg$, $E=0{\cdot}9270-0{\cdot}00332 \log C_{NaOH}$; and with the cell $Pt \mid NaOH,Fe(OH)_2,Fe_3O_4.nH_2O \mid NaOH \mid H_2,Pt$, $E=0{\cdot}1240+0{\cdot}00332 \log C_{NaOH}-0{\cdot}0015 \log C'_{NaOH}$. S. Hilpert, and J. von Liebig and F. Wöhler said that ferrous hydroxide is non-magnetic. A. Quartaroli gave $\chi=30\times10^{-6}$ to 60×10^{-6} for the **magnetic susceptibility** of the hydroxide precipitated by aq. ammonia; and $\chi=20\times10^{-6}$ to 30×10^{-6} mass unit. Observations were also made by G. Wiedemann.

A. Bineau prepared a soln. of ferrous hydroxide by means of iron and purified water, slightly aerated, and found that the **solubility** is such that one part of ferrous hydroxide dissolves in 150,000 parts of water, or $7{\cdot}5\times10^{-5}$ mol per litre; W. G. Whitman and co-workers gave $6{\cdot}7\times10^{-5}$ mol per litre, a value higher than that for ferric hydroxide. E. Müller and F. Kapeller calculated from the ferric-ferrous potential the **solubility product** $[\mathrm{Fe}^{\cdot\cdot}][\mathrm{OH}']^2=1{\cdot}69\times10^{-14}$, and the solubility was calculated to be $1{\cdot}6\times10^{-5}$; H. T. S. Britton obtained $4{\cdot}5\times10^{-21}$ for the solubility product—*vide supra*. B. Schrager calculated for $[\mathrm{Fe}^{\cdot\cdot}][\mathrm{OH}']^2$, 7×10^{-13}. Ferrous hydroxide shows amphoteric qualities, for it dissolves slightly as an acid in aq. soln. of sodium hydroxide owing to the reaction $\mathrm{Fe(OH)_2}+\mathrm{OH}'\rightarrow\mathrm{Fe(OH)'_3}$, where $K=[\mathrm{Fe(OH)'_3}]/[\mathrm{OH}']=5\times10^{-5}$. P. Krassa calculated, from the ferrous ion concentration in 20 per cent. potash-lye, the solubility product $8{\cdot}7\times10^{-14}$, and the solubility was calculated to be $2{\cdot}8\times10^{-5}$; J. W. Shipley and I. R. McHaffie calculated from the rate of corrosion of iron $3{\cdot}9\times10^{-15}$, and the solubility was calculated to be 1×10^{-5} mol per litre; and A. B. Lamb found, by conductivity methods, the conc. of the ferrous ion in a sat. soln. of ferrous hydroxide to be $1{\cdot}35\times10^{-5}$. G. Bodländer's values $2{\cdot}5\times10^{-21}$ for the solubility product, and $1{\cdot}7\times10^{-7}$ for the solubility in gram-equivalents per litre are not in good agreement with the others. W. G. Whitman and co-workers found 3·75 parts of iron per million, or $6{\cdot}7\times10^{-5}$ mols of ferrous hydroxide per litre for the solubility. The $\mathrm{H}^{\cdot}$-ion concentration of the soln. is represented by $p_{\mathrm{H}}=9{\cdot}6$, or $[\mathrm{OH}']=4\times10^{-5}$ and $[\mathrm{Fe}^{\cdot\cdot}]=2\times10^{-5}$. The **degree of ionization** in a sat. soln. where $p_{\mathrm{H}}=9{\cdot}6$ at 25° $\mathrm{Fe}^{\cdot\cdot}/\mathrm{Fe(OH)_2}$ is 30 per cent.; when $p_{\mathrm{H}}=9{\cdot}2$, 29 per cent.; and $p_{\mathrm{H}}=8{\cdot}2$, 24 per cent. The **ionization constant** $[\mathrm{Fe}^{\cdot\cdot}][\mathrm{OH}']^2/[\mathrm{Fe(OH)_2}]$ is $6{\cdot}8\times10^{-6}$ for the sat. soln. at 25°; and for soln. with $p_{\mathrm{H}}=9{\cdot}2$, $6{\cdot}0\times10^{-10}$; and for $p_{\mathrm{H}}=8{\cdot}2$, $1{\cdot}15\times10^{-10}$. S. Veil, and O. Baudisch and L. A. Welo studied the **magnetic properties** of the hydroxide.

The white hydroxide rapidly becomes green on exposure to air, then black owing to the formation of hydrated ferrosic oxide, and finally reddish-brown owing to the production of hydrated ferric oxide. These changes were discussed by L. J. Thénard, O. Baudisch and co-workers, J. J. Berzelius, C. F. Bucholz, M. Darso, H. Davy, E. Divers and T. Haga, O. Faust, P. Fireman, and J. von Liebig and F. Wöhler. A. B. de Schulten observed that even after the crystals have been washed with alcohol, and ether, and dried out of contact with air, they oxidize immediately on exposure to oxygen, developing much heat, and yielding ferric oxide. According to G. Schmidt, if the moist hydroxide be exposed to air, it quickly forms dingy green hydrated ferrosic oxide, and then yellowish-brown hydrated ferric oxide; but if the dried amorphous hydroxide be exposed to air, it is instantly converted into ferric oxide, and the change is attended by an evolution of heat, which often makes the mass red-hot. If the liquid in which the white flakes of hydroxide have been precipitated is boiled, the colour becomes black, due, said J. von Liebig and F. Wöhler, to the formation of ferrosic oxide by the action of the air. R. G. Knowland recommended ferrous hydroxide as an agent for removing dissolved oxygen from water. A. A. Bonnema showed that ferrous oxide or hydroxide form nitrite on exposure to air.

As just indicated, ferrous hydroxide readily **oxidizes** when exposed to air, but only under certain conditions does the end-product correspond with ferric hydroxide. P. Fireman observed that the colour of the product varies from yellow to brown to black according to the proportion of ferric hydroxide produced, and A. Krause showed that the colour of the oxidation product is darker the greater the proportion of contained ferrous hydroxide. S. Miyamoto found that the rate of oxidation is reduced by the presence of alkalies; and that the coeff., k, of the rate of oxidation of ferrous hydroxide suspended in soda-lye is independent of the quantity of ferrous hydroxide present, and its value is identical with that for the oxidation of sodium sulphite and stannous hydroxide in alkaline soln. The value of k is only slightly affected by temp., but decreases with increasing concentration of sodium hydroxide, since the velocity is probably determined by the speed of dissolution of oxygen, which is decreased by the sodium hydroxide. On the other hand, A. Krause found that the speed of oxidation is greatly favoured by a rise of temp. W. Gluud and W. Riese observed the rate of oxidation of suspensions of ferrous hydroxide in various solutions by a current of air. In soln. of sodium or ammonium hydrogen carbonate increase of alkalinity favours oxidation of ferrous hydroxide. With the former, however, increase of salt concentration reduces the oxidation rate. The addition of sodium sulphate or other neutral salt renders it more difficult to remove the carbon dioxide by air-blowing the sodium hydrogen carbonate soln. Ammonium sulphate facilitates the removal of both carbon dioxide and ammonia.

S. Miyamoto also showed that sodium hydroxide retards the oxidation, even though the reducing power of ferrous hydroxide increases with the conc. of HO′-ions; and A. Krause observed that ferrous hydroxide is oxidized to ferric hydroxide only when the alkali present does not exceed the mol. ratio $NaOH : FeSO_4 = 1 : 1$; if more alkali be present, the oxidation of the ferrous hydroxide by air is incomplete; and this the more the higher the proportion of alkali, but the mol. ratio of ferrous to ferric hydroxide does not exceed $FeO : Fe_2O_3 = 0{\cdot}3 : 1$. The water-content of the dried product decreases with increasing proportions of ferrous hydroxide. The oxidation of ferrous hydroxide by air is dependent on the H˙-ion conc. of the liquor from which it is precipitated. Reddish-yellow metaferric hydroxide or ferroferrite may be formed. The iso-electric point of hydrated metaferric oxide, corresponding with an air-dried product $Fe_2O_3.2H_2O$, is $p_H = 5{\cdot}2$. If the p_H is greater than 5·2, $(Fe_2O_3.aq.)'$ is formed; with p_H less than 5·2, $(Fe_2O_3.aq.)^{\cdot}$ is formed; and with p_H less than 0·3, the ferrous salt is stable in air. The oxidation of ferrous hydroxide to a ferrous ferrite, when the p_H is greater than 5·2, is shown by oxidizing ferrous hydroxide in the presence of magnesium hydroxide, for then the oxidation to magnesium ferrite is complete. Hydrated metaferric hydroxide differs in chemical and physical properties from orthoferric oxide with an isotectic point of $p_H = 7{\cdot}7$. E. Deiss and G. Schikorr also considered that a ferrous ferrite is formed as an intermediate stage in the reaction. The production of an intermediate peroxide of the type $FeO_2(OH)_2$ was discussed by W. Manchot and H. Schmid, G. Just, C. Sandonnini, and O. Baudisch and co-workers. According to C. Sandonnini, black ferrite is formed when a dil. suspension of the ferrous hydroxide is boiled in presence of air, or at the ordinary temp. when the hydroxide is protected by a deep layer of water. In the presence of chromic or aluminium hydroxides, however, no ferrite is formed even under these conditions. In an atmosphere of pure oxygen ferrous hydroxide is oxidized practically quantitatively to ferric hydroxide. A suspension of ferrous hydroxide in water which has been boiled for a long time in an atmosphere of hydrogen is oxidized directly to ferric hydroxide when subjected to the conditions which normally would give the black ferrite. W. Manchot, and W. Manchot and F. Glaser said that during the oxidation of ferrous hydroxide some oxygen is activated, and is taken up by an acceptor—say arsenious acid. N. R. Dhar found that the oxidation of ferrous hydroxide can be induced by the presence of a number of organic and inorganic substances. Ferrous hydroxide, precipitated by hydrolysis or by the action of hydroxyl ions from a soln. of ferrous hydrogen carbonate reacts in the nascent state with molecular oxygen to form a compound exhibiting a very high oxidation and reduction potential. With the oxidation process as a primary reaction, there are the oxidation of potassium oxalate and of nickel hydroxide as secondary reactions.

For the chemical action of ferrous hydroxide on **water**, *vide infra*, ferrous chloride. A. Bineau said that the aq. soln. of ferrous hydroxide rapidly becomes turbid on exposure to air; and, according to J. von Liebig and F. Wöhler, and G. Schmidt, ferrous hydroxide can decompose water, slowly in the cold, and rapidly when heated. O. Baudisch and L. A. Welo, E. Deiss and G. Schikorr, and W. Traube and W. Lange said that ferrous hydroxide remains unchanged when kept in contact with air-free water, and E. Deiss and G. Schikorr added that the oxidizing action reported by G. Schmidt is due to the action of dissolved oxygen from the air. If reducing agents be present, W. R. Dunstan and T. S. Dymond, and W. Manchot found that the water may be decomposed by the hydroxide; for example, W. Traube and W. Lange observed that in the presence of a trace of palladious chloride, there is a slow development of hydrogen, and black ferrosic oxide is formed. E. Berl and F. van Taack observed that when heated with water in a bomb, under press., black ferrosic oxide is formed and hydrogen is evolved.

The dehydration curve obtained by G. F. Hüttig and H. Möldner for white hydrated ferrous oxide is derived from the data for $FeO.nH_2O$:

	114°	220°	228°	230°	234°	261°	270°	277°	336°
n .	1·018	0·933	0·858	0·773	0·697	0·621	0·536	0·463	0·382

As the reaction $FeO.H_2O \rightarrow FeO + H_2O$ proceeds, the colour becomes black. There is also a side reaction $3(FeO.H_2O) \rightarrow Fe_3O_4 + 2H_2O + H_2$. The X-radiograms are indicated in Fig. 507.

A. B. de Schulten said that ferrous hydroxide is readily soluble in soln. of the **alkali hydroxides,** and also in aq. ammonia, so that ferrous hydroxide is not completely precipitated from soln. of ferrous salts by ammonium hydroxide, even in the presence of ammonium chloride. If the soln. of ferrous hydroxide in these menstrua be exposed to air or oxygen, the ferrous hydroxide is rapidly converted into hydrated ferric oxide. On the other hand, E. Deiss and G. Schikorr, and O. Baudisch said that the hydroxide is insoluble in sodium and potassium hydroxides; so that the alleged solubility is a case of peptization to form a hydrosol. S. H. Carsley found that ferrous hydroxide is partially peptized by boiling it with conc. alkali-lye. The rate of settling of hydrated ferrous oxide in neutral and dil. alkali soln. is greatly increased by boiling, owing, it is supposed, to the partial dehydration and coagulation of the particles. According to W. G. Whitman and co-workers, the solubilities of ferrous hydroxide in various **salt solutions**—calcium, sodium, ammonium, and magnesium chlorides, and in sodium sulphate, chromate,

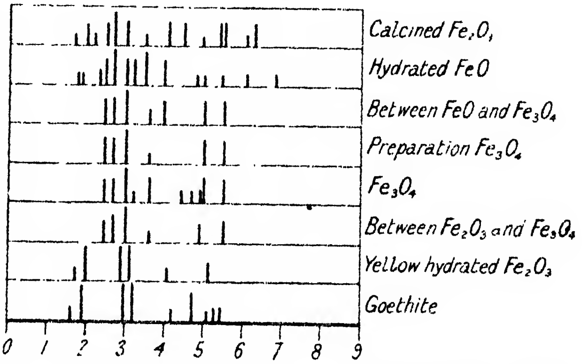
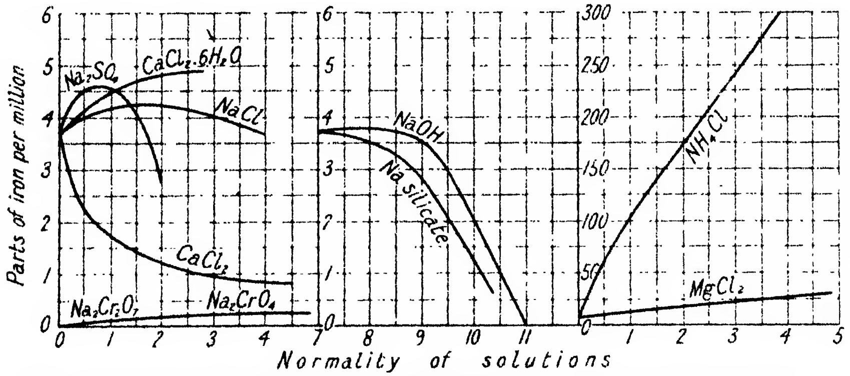


FIG. 507.—X-radiograms of some Hydrated Iron Oxides.

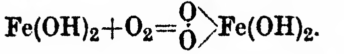


FIGS. 508 to 510.—The Solubility of Ferrous Hydroxide in Various Solutions.

dichromate, silicate, and hydroxide—are indicated in Figs. 508 to 510. The difference in the results for anhydrous calcium chloride and its hexahydrate is attributed to the presence of a small amount of calcium oxide in the former. It was found that the rates of corrosion of iron by these salt soln. are parallel with the solubilities of ferrous hydroxide in these soln., and this is taken to be in agreement with the colloidal theory of corrosion discussed by J. A. N. Friend. According to G. Pellini and D. Meneghini, ferrous hydroxide suspended in alcohol and treated at a low temp. with **hydrogen dioxide** furnishes a mixture of ferric hydroxide, and iron peroxide. A. S. Loevenhart and J. H. Kastle discussed the effect of inhibitors on the catalytic decomposition of hydrogen dioxide by ferrous hydroxide. G. Kassner observed that ferrous hydroxide is oxidized by **sodium dioxide.**

Ferrous hydroxide readily dissolves in **acids,** forming the respective ferrous salts ; and, according to G. Schmidt, much heat is evolved. E. Petersen observed that ferrous hydroxide is soluble in **hydrochloric acid;** and J. Lefort, that it is soluble in hydrochloric acid. W. van Wüllen Scholten found that ferrous hydroxide is oxidized by **alkali hypochlorites;** C. W. Hempel, that **iodic acid** is reduced ; and B. Sjollema, and E. Weitz and H. Müller, that in boiling soln. in the absence of free alkali, **potassium perchlorate** is reduced quantitatively by ferrous hydroxide to form potassium chloride. W. Feld observed that ferrous hydroxide suspended in water is converted to ferrous sulphide by **hydrogen sulphide.** J. Lefort observed that the hydroxide is soluble in conc. **sulphuric acid.**

M. Darso, J. L. Gay Lussac, and G. Schmidt considered that ferrous hydroxide is slightly soluble in aq. **ammonia,** but this is probably a case of peptization to form the hydrosol. H. Becquerel said that the hydroxide is soluble in aq. ammonia in the presence of ammonium salts, and this is attributed to the formation of complex ammines. The action was studied by O. Faust, E. Deiss and G. Schikorr, and V. Paissakowitsch. Ferrous hydroxide generally acts as a reducing agent. W. R. Dunstan and T. S. Dymond found that feebly alkaline soln. of **hydroxylamine** are decomposed by ferrous hydroxide to form ammonia and a little nitrogen ; and F. Haber, C. Kjellin, and A. Kurtenacker and R. Neusser showed that if an alkali-lye or ammonia emulsion of ferrous hydroxide is employed, the yield of ammonia is almost quantitative. On the other hand, E. Ebler and E. Schott found that with a conc. soln. of hydroxylamine, nitrogen and nitrous oxide are at first turbulently evolved, and only towards the end of the reaction is ammonia formed. C. Kjellin found that β-methyl hydroxylamine, β-ethyl hydroxylamine, and β-*iso*-propylhydroxylamine are reduced by ferrous hydroxide to the primary amines. F. Haber said that **hydrazine** is not attacked by ferrous hydroxide. W. R. Dunstan and T. S. Dymond found that **hyponitrous acid** is slowly decomposed by ferrous hydroxide with the formation of nitrogen, but neither ammonia nor hydroxylamine is produced. According to E. Divers and T. Haga, if **nitric oxide** be passed into a soln. of potassium hydroxide mixed with some ferrous hydroxide, ferric oxide is formed, and the nitric oxide is largely converted into ammonia, but neither hydroxylamine nor alkali hyponitrite could be detected among the products of the reaction. On the other hand, W. R. Dunstan and T. S. Dymond observed that in this reaction a little ammonia and no hydroxylamine are formed, but some hyponitrite, nitrogen, and a little nitrous oxide are produced. In the absence of alkali, hyponitrite, ammonia, and hydroxylamine are not formed, but nitrogen and nitrous oxide appear. In the presence of a conc. soln. of potassium hydroxide, ammonia, nitrogen, and nitrous oxide are formed, but no hyponitrite. A. Klemenc, H. Reihlen and A. von Friedolsheim, and O. Baudisch and L. A. Welo also studied the reduction of nitric oxide by ferrous hydroxide, and the formation of hydrated ferrosic oxide. J. Gay, and E. Péligot found that **nitrogen peroxide** is reduced to nitrogen and nitrous oxide by ferrous hydroxide. W. von Zorn showed that freshly precipitated ferrous hydroxide energetically reduces **sodium nitrite** in aq. soln. ; heat is evolved, and hyponitrite, ammonia, nitrogen, and nitrous oxide are formed. E. Divers and T. Haga observed no hyponitrites in the products of the reaction ;

but W. R. Dunstan and T. S. Dymond said that the gas which is evolved is a mixture of nitrogen and nitrous oxide, and in the soln. hyponitrites, but not hydroxylamine, are formed ; if an excess of ferrous oxide is employed, nitrogen and ammonia are produced. O. Baudisch and co-workers found that alkali nitrites are quantitatively reduced in the presence of an excess of ferrous hydroxide, *in statu nascendi*, in neutral or alkaline soln., and in the absence of oxygen. With boiling soln. of alkali hydroxide, ammonia is the sole product ; and with boiling soln. of alkali carbonate, ammonia and nitrous oxide are formed. According to E. Divers and T. Haga, alkali nitrites yield much ammonia when treated with ferrous hydroxide in the presence of a soln. of potassium hydroxide—but no hydroxylamine, or hyponitrite, or any gaseous product is formed. The reducing action was also studied by W. von Zorn, and G. Schikorr. By this reaction S. Miyamoto determined the nitrites in soln. as ammonia. The velocity of reaction between potassium nitrite and ferrous hydroxide in alkaline soln. was measured at 25°, 35°, and 45°. When the initial concentration of the nitrite is very small compared with that of the alkali hydroxide, the velocity curve is linear. The velocity constant increases with the concentration of the alkali hydroxide, and is expressed by the formula : $k=e^{20\cdot609\quad 8098\cdot2/}p(1+0\cdot79C_{\mathrm{KOH}})$. The velocity constant is increased 2·35 times for each rise in temp. of 10°. The presence of potassium sulphate in the system has no effect on the reaction velocity. The speed of the reaction is too great for measurement at the b.p., 108°. A. Thum said that the ferrous hydroxide is rapidly converted to hydrated ferrosic oxide, and then slowly to hydrated ferric oxide. F. Kuhlmann, and W. von Zorn observed that a warm, dil. soln. of **potassium nitrate** is reduced by ferrous hydroxide and ammonia is formed—*vide supra*. S. H. Carsley observed that the reduction of the nitrate to ammonia is quantitative and the hydroxide forms the black magnetic ferrosic oxide ; and instead of $8\mathrm{Fe(OH)_2}+\mathrm{NaNO_3}=4\mathrm{Fe_2O_3}+6\mathrm{H_2O}+\mathrm{NaOH}+\mathrm{NH_3}$, with the intermediate formation of $\mathrm{Na[Fe(OH)_3]}$, S. H. Carsley, and C. Sandonnini and S. Bezzi prefer the equation : $12\mathrm{Fe(OH)_2}+\mathrm{NaNO_3}=4\mathrm{Fe_3O_4}+10\mathrm{H_2O}+\mathrm{NaOH}+\mathrm{NH_3}$. In dil., neutral soln., previously boiled ferrous hydroxide reduces the nitrate more slowly than does the freshly precipitated oxide owing to the dehydration and agglomeration of the hydrated ferrous oxide. E. Divers and T. Haga found that alkali nitrates were not reduced ; but W. R. Dunstan and T. S. Dymond said that a little ammonia, and a small quantity of a gas are produced ; and with small proportions of potassium nitrate, the conversion to ammonia is complete. The reaction was also studied by E. Deiss and G. Schikorr. S. Miyamoto found that the reduction of the nitrates does not proceed so easily as is the case with the nitrites, but that the reduction does occur in boiling soln., and it is quantitative, so that it can be employed for the determination of nitrates in soln. The velocity of reaction between potassium nitrate and ferrous hydroxide in alkaline soln. was measured at 108° and 112·2°, the velocity constant being approximately $7\cdot577\times10^{-3}$ (calc. $7\cdot726\times10^{-3}$; C_{KOH} : 5·5394 mol. per litre) and $2\cdot331\times10^{-2}$ (calc. $2\cdot326\times10^{-2}$; C_{KOH} : 6·9541 mol. per litre respectively). According to O. Baudisch and co-workers, ferrous hydroxide in neutral or faintly alkaline soln. is unable to reduce nitrates to nitrites ; but the reduction takes place with the co-operation of atm. oxygen. Nascent ferrous hydroxide is far more powerful as a reducing agent than the freshly precipitated ferrous hydroxide towards nitrites. It is assumed that ferrous hydroxide absorbs oxygen, forming *ferrous peroxyhydroxide* : $[\mathrm{Fe(H_2O)_6}](\mathrm{OH})_2+\mathrm{O_2}=[\mathrm{FeO_2(H_2O)_5}](\mathrm{OH})_2+\mathrm{H_2O}$, otherwise expressed :  $\mathrm{Fe(OH)_2}+\mathrm{O_2}=\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\!>\!\mathrm{Fe(OH)_2}$. The peroxide so formed, in virtue of its iron nucleus, has the power of activating the oxygen subsidiary valencies of other substances and forming unstable compounds with them. S. H. Carsley said that O. Baudisch and co-workers prepared their hydrated ferrous oxide at different temp., so that their results are complicated by differences in the degrees of agglomeration of the hydrated oxide. The effect of oxygen on hyrdated ferrous oxide is to form an unstable higher oxide—$\mathrm{Fe_2O_4}$ or $\mathrm{FeO_3}$—as O. Baudisch assumed.

O. Baudisch and co-workers showed that ferrous peroxyhydroxide can act as an oxidizing agent, as is shown by the conversion of alcohol to aldehyde and by its behaviour towards starch and sugar. It acts in this respect in the same manner as light energy alone or in the presence of traces of iron. It can effect the reduction of alkali nitrate to ammonia. The first action is supposed to involve a reaction with the peroxyhydroxide and the nitrate: $FeO_2(OH)_2+2NaNO_3=Fe(OH)_2+2NaNO_2+2O_2$, and the nitrite is then reduced by the hydrated ferrous oxide to ammonia. Both types of reaction can take place in one and the same soln. Formaldoxime and traces of nitromethane are formed when a methyl alcohol soln. of nitrite is treated with ferrous sulphate and an excess of sodium hydrocarbonate and shaken with air. The nitric acid is reduced to hyponitrous acid, which reacts with the formaldehyde produced by the oxidation of methyl alcohol, yielding formhydroxamic acid, which is in part converted into formaldoxime. Both iron and ferrous peroxyhydroxide are ferromagnetic, but ferrous hydroxide is not so. According to O. Baudisch and L. A. Welo, when the precipitate of hydrated ferrous oxide is stored in the absence of air—although apparently stable even when boiled—it gradually loses its power of reducing nitrates to nitrites, and of catalysing the oxidation of organic compounds such as uracil and lactic acid, although on exposure to air they still absorb oxygen. The loss of therapeutic efficacy undergone by certain mineral waters through keeping has been correlated with a precipitation and consequent inactivation of ferrous salts analogous to the ageing process described above; it was found that the ageing of the mineral water was accelerated by exposure to light. The ageing process is attributed to the gradual passage of the hydrate from the amorphous to the crystalline state.

G. Schmidt found that dried ferrous hydroxide rapidly absorbs **carbon dioxide,** becoming at the same time hot and black. According to E. Deiss and G. Schikorr, the oxidizing action attributed to carbon dioxide is really due to the oxygen dissolved in the water. P. N. Raikow found that ferrous hydroxide reacts with carbon dioxide to form ferrous carbonate and hydrocarbonate. F. K. Cameron and W. O. Robinson also studied this reaction. H. C. Allen, and S. Miyamoto observed that ferrous hydroxide in a soln. of alkali hydroxide also reduces **nitrobenzene** to aniline at ordinary temp. E. J. Morgan and J. H. Quastel found that **methylene blue** is decolorized; and F. Feigl, that **benzidine** is not coloured blue by ferrous hydroxide. L. Cramer noted that **gelatin** is coagulated by ferrous hydroxide. C. C. Palit and N. R. Dhar studied the action of the hydroxide as a catalyst in the oxidation of **glycerol;** and N. R. Dhar, in the induced oxidation of fats, proteins, sugar, starch, formic acid, etc. C. H. Herty and co-workers studied the reaction between **silicon** and ferrous oxide, and found for the equilibrium constant, K, in the reaction $Si+2FeO\rightleftharpoons 2Fe+SiO_2$, $K=0{\cdot}000165$. W. A. Roth and co-workers determined thermochemically that in the reaction with **silica,** $2FeO+SiO_{2\,quartz}=Fe_2SiO_4+8{\cdot}1$ Cals. O. von Keil and A. Dammann, J. H. Whiteley and A. F. Hallimond studied the reaction with **silica.**

G. Grube and H. Gmelin found that by anodically polarizing iron in a 40 per cent. soln. of **sodium hydroxide,** and a low current density, in the absence of air, the iron goes into soln. as **sodium hypoferrite,** Na_2FeO_2. At higher temp. this forms ferrites and ferrate—*vide infra.* W. Biltz and co-workers prepared spinels with ferrous oxide and **alumina, ferric oxide,** or **chromic oxide.** J. H. Andrew and co-workers found that mixtures of **manganese oxide** and ferrous oxide form a complete series of solid soln. with a m.p. rising almost linearly from that of ferrous oxide at 1410° to that of manganese oxide at 1585°. The liquidus is within 20° of the solidus throughout the whole range.

According to A. Levol, **cupric hydroxide** and **cupric salts** are reduced by ferrous hydroxide. The reaction was studied by H. R. Ellis and W. H. Collier, F. Förster and V. Herold, H. Frischer, F. Herrmann, and T. S. Hunt. According to E. Müller and F. Kapeller, the reducing power of a soln. containing ferrous and ferric ions increases with the ratio $Fe^{\cdot\cdot}/Fe^{\cdot\cdot\cdot}$. For example, (i) Atmospheric oxygen does not oxidize an acid soln. of ferrous sulphate, but is quickly absorbed if an alkali is added. In the former, the ratio cannot much exceed 10^3, whereas in presence of normal alkali it is $1{\cdot}5\times10^{22}$, owing to the greater solubility of ferrous hydroxide. (ii) Soln. of ferrous sulphate and **cupric sulphate** do not react, but cuprous oxide is precipitated if potassium fluoride is added to the neutral mixture, and metallic copper if it is added to the acidic soln. In this case, the ratio is increased by the conversion of ferric ions into complex ions containing iron and fluorine. In neutral soln. the cuprous ions produced by the reduction separate as hydroxide, whilst in acidic soln., owing to the higher conc. reached, they yield metallic copper and cupric ions. (iii) The oxidation of hydriodic acid to iodine by ferric ions, $2\mathrm{I}'+2\mathrm{Fe}^{\cdot\cdot\cdot}=\mathrm{I}_2+2\mathrm{Fe}^{\cdot\cdot}$, is also reversed by the addition of potassium fluoride. R. C. Wells represented the main reaction between ferrous hydroxide and **cuprous salts** by $3\mathrm{FeO}+2\mathrm{CuCl}=2\mathrm{Cu}+\mathrm{Fe}_2\mathrm{O}_3+\mathrm{FeCl}_2$, especially when the cuprous salt is in excess; with a decrease in the latter, the reaction is $4\mathrm{FeO}+2\mathrm{CuCl}=2\mathrm{Cu}+\mathrm{Fe}_3\mathrm{O}_4+\mathrm{FeCl}_2$. The reaction $\mathrm{Cu}^{\cdot}+\mathrm{Fe}^{\cdot\cdot}\rightleftharpoons\mathrm{Cu}+\mathrm{Fe}^{\cdot\cdot\cdot}$ results in the separation of copper when the $\mathrm{H}^{\cdot}$-ion concentration $p_{\mathrm{H}}>5{\cdot}0$. H. Ost observed that ferrous hydroxide reacts with **magnesium chloride** to form ferrous chloride and magnesium hydroxide; and similarly with **magnesium sulphate;** but E. Deiss and G. Schikorr observed no reaction with magnesium sulphate. C. A. Graumann observed that a mixture of **zinc sulphide** and ferrous oxide, when heated, does not give off zinc vapour. C. W. Hempel found that ferrous hydroxide reduced **mercuric chloride** to mercurous chloride; H. Ost, that it forms aluminium hydroxide when added to neutral soln. of **alum**; E. Deiss and G. Schikorr, that **chromic hydroxide** is not reduced by ferrous hydroxide; and C. W. Hempel, that **platinum tetrachloride** is reduced to the metal.

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§ 29. Ferrosic Oxide ; or Magnetic Oxide of Iron

The Chinese have been credited with knowing something about the magnetic needle so far back as 1100 B.C. In his *Περί λίθων*, written about 325 B.C., Theophrastus referred to the power of attraction which some stones—*e.g.* the *λίθος σιδηροναγοῦσα*—have for iron—*vide* the history of manganese ; and the subject was discussed by O. Lenz.[1] At the beginning of our era, Pliny, in his *Historia naturalis* (**36**. 25), discusses the mineral *magnes* which has the power of attracting iron ; and added that in Æthiopia, there is a mountain in which the stone *theamedes* is found ; this mineral repels and rejects iron. This report may be founded on the repulsive action of the like poles of two magnets. The property of polarity which distinguishes the *lodestone* (or *lòadstone*) is exceptional. Pliny also mentions the magnetic properties of the *siderites* or *herachion*. This mineral is also the *μαγνῆς λίθος*, mentioned by Dioscorides in his first-century work *Περί ὕλης ἰατρικῆς*. According to E. Wiedemann, the Arabian Abû Mûsa Gâbir ben Hajjan mentioned that a sample of magnetic iron ore lifted 100 dirhems of iron, but after it had stood for some time it could not lift 80 dirhems of iron. The Arabian, Al Dimaschque, also wrote on the subject about 1320. Magnetic iron ore was described by A. Aphrodisiensis, and the subject was discussed by M. Steinschneider, and V. Rose. It was called *Siegelstein* by G. Agricola ; the *minera ferri nigricans magneti amica*, or *magnet* of J. G. Wallerius ; the *minera ferri attractoria* of A. Cronstedt ; the *magnetischer Eisenstein* of A. G. Werner ; and the **magnetite** of W. Haidinger.

Analyses were reported by H. Arsandaux,[2] J. J. Berzelius, W. Bornhardt, A. Breithaupt, A. Cathrein, A. H. Chester, F. W. Clarke, E. Classen, C. Despretz, E. Dittler and H. Hueber, J. N. von Fuchs, J. L. Gay-Lussac, F. F. Grout and T. M. Broderick, B. J. Harrington, M. F. Heddle, T. H. Holland, E. Hugel, C. J. B. Karsten, A. Knop, F. von Kobell, G. A. Koenig, A. Lacroix, S. M. Losanitsch, D. Lovisato, G. W. Maynard, J. A. Michaelson, W. G. Miller, T. Nordström, G. Nyiredy, T. Petersen, W. B. Phillips, F. J. Pope, C. F. Rammelsberg, L. Ricciardi, F. Scafile, B. Schwalbe, E. Sochting, J. del Pan, A. Stanojevic, J. Thiel, G. P. Tschernik, J. H. L. Vogt, T. L. Walker and A. L. Parsons, C. H. Warren, M. Weibull, and F. Zambonini. The results are, in the main, in agreement with the formula of *iron tritatetroxide*, or **ferrosic oxide,** Fe_3O_4, or $FeO.Fe_2O_3$, for the idealized mineral. The *ferropicotite* of A. Lacroix, found in Madagascar, has the composition $(Fe,Mg)O.(Al,Fe)_2O_3$. F. von Sandberger reported either stannous or stannic oxide in the magnetites of Hirschberg. Manganous oxide may be present, and M. Weibull writes the formula $(Fe,Mn)O.Fe_2O_3$; some magnesia and alumina were found by A. Knop to be associated with the mineral thus making the formula $(Fe,Mg)O.(Al,Fe)_2O_3$; and for the chromiferous varieties described by A. Cathrein, $FeO.(Fe,Cr)_2O_3$; while the titaniferous varieties may have $FeTiO_3$ or $MgTiO_3$ in solid soln. with Fe_2O_3; but, as shown by W. B. Phillips, magnetite exhibits a wide variation in composition, for the extremes in 30 analyses were:

	Fe as FeO	Fe as Fe_2O_3	$FeO : Fe_2O_3$
Magnetite (ideal) . . .	24·11	48·29	1 : 2·00
Octahedra from Vogelsberg . .	39·85	15·22	1 : 0·38
Sheperd Mt., Missouri . . .	1·36	63·95	1 : 47·02

T. L. Walker found the dominant mineral in loadstone from Bon Accord, Transvaal, to be $(Fe,Ti)_2O_3$. J. D. Dana classed the magnetites as (1) ordinary massive, crystalline or sandy magnetites; (2) magnesian magnetites; (3) niccoliferous magnetites; (4) titaniferous magnetites; (5) manganesian magnetites; and (6) ochreous magnetites. W. N. Hartley and H. Ramage observed the presence of sodium, potassium, rubidium, silver, copper, gallium, manganese, lead, and nickel.

The existence of ferrosic oxide as a chemical individual was demonstrated by J. L. Gay Lussac, and J. J. Berzelius. J. L. Gay Lussac regarded it as a particular stage in the oxidation of iron, but J. Dalton, and J. J. Berzelius considered it to be a compound of ferrous and ferric oxides. The graphic formula is usually based on the assumption that the oxide contains both ferric and ferrous iron, as is exemplified by the presence of both salts of iron when ferrosic oxide is dissolved in acids. The graphic formula is $O{=}Fe{-}O{-}Fe{-}O{-}Fe{=}O$, or $Fe(FeO_2)_2$. S. H. Emmens, and W. G. Brown preferred formulæ in which the iron atoms were supposed to be quadrivalent. The formula $Fe(FeO_2)_2$ agrees with the spinel structure deduced by M. L. Huggins from the space-lattice.

According to S. Hilpert, the formation of the magnetic ferrosic oxide from non-magnetic, hydrated ferrous and ferric oxides shows that the magnetic property lies primarily in the combination of the two—where ferric oxide acts as an acid anhydride, and ferrous oxide as a base. This makes magnetic ferrosic oxide a **ferrous ferrite,** $Fe(FeO_2)_2$, *i.e.* a member of the family of spinels. That the magnetic property depends on the acidic property of the ferric oxide is shown by the fact that the ferrous oxide can be replaced by cupric, cobaltous, calcium, barium, and potassium oxide to form magnetic ferrites—*vide infra.* Indeed, cupric ferrite, $(CuO)^+(Fe_2O_3)^-$, is as strongly magnetic as $(FeO)^+(Fe_2O_3)^-$. It is possible to oxidize magnetite to magnetic ferric oxide; but in the compound $FeO.Fe_2O_3$, only the ferrous iron can be oxidized to furnish $(Fe_2O_3)^+(2Fe_2O_3)^-$, or *ferric orthoferrite,* $Fe^{\cdots}(FeO_3)^{\cdots}$, and this red powder is the true magnetic ferric oxide (*q.v.*). The cobalt ferrite, $(CoO)^+(Fe_2O_3)^-$, can be similarly oxidized to $(Co_2O_3)^+(2Fe_2O_3)^-$. O. Mügge's study of the reduction products of hæmatite and the oxidation products of magnetite led him to suggest that magnetite is a solid soln. of ferric oxide in the cubic form of ferrous oxide; and this view is favoured by A. Gawalowsky, and K. Hofmann. A. Krause and J. Tulecki obtained magnetic ferrous ferrite, at 18°, (i) by adding ammonia to an acid soln. of ferrous chloride containing meta ferric hydroxide in suspension; and (ii) by adding ammonia to a mixed soln. of ferrous and ferric chlorides. The latter varied in composition owing to oxidation, and contained more water than the former; the former approximated closely to $Fe(FeO_2)_2-\frac{1}{2}H_2O$.

S. Breislak,[3] J. J. Ferber, C. W. C. Fuchs, F. Galiani, G. Gioeni, P. Groth, A. Johnsen, A. Lacroix, T. Monticelli and N. Covelli, L. Pilla, S. C. Ponte, J. S. Presl, C. F. Rammelsberg, A. Scacchi, G. Strüver, D. F. Wiser, and F. Zambonini found that magnetite occurs as a sublimation product in the lava of Vesuvius and Etna. J. H. L. Vogt regarded magnetite as a product of magmatic differentiation; thus, J. Morozewicz observed that in artificial magmas, magnetite is easily formed when the proportion of silica is low, for any iron in excess of that needed to combine with silica is liable to be deposited as magnetite. The order of its separation with respect to other minerals is not invariable. Magnetite, like other spinels, may be formed by the breaking down of other minerals, or by reactions between them; *i.e.* magnetite may be a product of contact metamorphism. Thus, C. Doelter obtained it by fusing various rocks with limestone; the fusion of acmite furnishes magnetite and a glass; and glaucophane gave a mixture in which magnetite occurred. The fusion of biotite, and microcline gave F. Fouqué and A. Michel-Lévy magnetite, leucite, and olivine; J. Lenarcic found magnetite in the mass produced by fusing a mixture of leucite and augite, but when magnetite is dissolved by fused labradorite, augite is formed. C. F. W. A. Oetling found it in the products of the fusion of felspathic basalt. M. Vucnik, and B. Vukits found magnetite among the products of mixtures of anorthite and hedenbergite, albite and hedenbergite, olivine and augite, elæolite and augite, and elæolite and diopside. This subject was discussed by H. L. Alling, A. Bauer, R. Beck, G. Berg, K. Bogdanovich, K. Busz, R. A. Daly, O. A. Derby, S. Foslie, P. Geiger, V. M. Goldschmidt, V. Hämmerle, A. G. Högbohm, E. Hussak, E. P. Jennings, H. E. Johannson, J. F. Kemp, T. Kjerulf, L. de Launay, W. Lindgren, G. Medanich, K. Petrasch, H. Sjögren, R. B. Sosman, A. C. Spencer, O. Stutzer, A. E. Törnebohm, H. S. Washington and E. S. Larsen, and G. H. Willams, etc. According to F. W. Clarke, magnetite occurs as an accessory mineral in rocks of all classes, and it sometimes forms the principal constituent. It is most abundant in rocks rich in ferromagnesian minerals—*e.g.* the norites, diabases, gabbros, or peridotites; but it may be also associated with nepheline rocks and anorthites. In many cases it forms large ore masses which are highly titaniferous; indeed, some ores shade by imperceptible graduations into ilmenite with over 40 per cent. of titanic oxide; they frequently contain spinel, and corundum. The magnetite-ilmenite ores were studied by S. Brunton, F. F. Osborne, P. Ramdohr, G. M. Schwartz, M. Kamiyama, J. T. Singewald, and C. Warren.

In many cases, magnetite is not of direct igneous origin. H. Rösler observed it in clay deposits from rivers and seas. C. R. van Hise found it associated with grünerite and actinolite in the slates and cherts in the great iron deposits of Lake Superior region, and the adjacent parts of Michigan, Wisconsin, and Minnesota. The magnetite of the Mesabi district is, according to C. K. Leith, derived from the leaching of a hydrated iron silicate which he called *greenalite*. C. W. von Gümbel, and L. W. Collet and G. W. Lee observed magnetite in the freshly formed sediments at the bottom of the sea. The mineral *itabirite* (*vide* ferric oxide) is thought by E. Hussak to have been formed as a chemical sediment. Observations on the formation of magnetite in this way were made by K. Bogdanovich, F. F. Osborne, P. Krusch, R. Brauns, J. Ahlburg, G. Rose, etc. The formation of magnetite in colloidal soln. has been discussed by G. Berg, K. C. Berz, S. Hilpert, and H. Stremme. C. R. van Hise also added that magnetite may be formed from marcasite and pyrite, and from the oxidation of siderite, and by further oxidation, it may pass into hæmatite and limonite, and through the agency of carbonated waters, transformed back into siderite. L. de Launay discussed the reduction of hæmatite to magnetite by the reducing action of bituminous substances associated with quartz veins at Grängesberg, Sweden. A. J. Moses described magnetite pseudomorphs after hæmatite; and E. Döll, after breunnerite; E. L. Perry, after chrysotile; and A. Liversidge found magnetite present in many minerals and rocks.

The occurrence of magnetite as an inclusion in meteorites was reported by J. Antipoff,[4] J. J. Berzelius, A. Brezina, S. Cloez, E. Cohen, A. Damour, A. Daubrée, J. M. Davison, C. G. Ehrenberg, E. E. Howell, A. Krantz, S. Meunier, C. F. Mohr, J. Murray and A. F. Renard, F. Pisani, G. vom Rath, C. von Reichenbach, G. Rose, C. U. Shepard, G. Tschermak, and G. H. F. Ulrich. Magnetite also occurs in some atmospheric dusts.

Magnetite, ferrosic oxide, or *pierre d'aimant*, may be formed as an accidental product in industrial processes or products. Thus, it forms a large proportion of the *smithy scale* or *iron scale* of the blacksmith. G. E. Allan and J. Brown [5] assume that the seat of the magnetization in the case of the created ore, etc., is ferrosic oxide. E. L. Perry observed fibrous magnetite formed after chrysotile on Casper Mountain, Wyoming. J. F. L. Hausmann observed magnetite formed in the masonry of a lead furnace at Goslar; A. Laurent, in an iron furnace at Châtillon-sur-Seine; H. Wieser, in a blast-furnace at Plons; G. M. Schwartz, in iron ores that had been sintered; J. B. J. D. Boussingault, in a roasting furnace for iron ores at Rio (Pyrenées-Orientales); J. F. L. Hausmann, F. Sandberger, and T. Scheerer, in the sole of a puddling furnace; and A. Krantz, A. Lacroix, and H. von Dechen, in the *débris* from fires at Hamburg, etc. W. G. Müller, and J. Spiller observed it in crystals among the iron residues obtained in the reduction of nitrobenzene to aniline; R. Kattwinkel, in steam-pipes 20 years old; C. F. Rammelsberg, in the sulphate pan of a Leblanc soda works; E. Svalander and J. Landin, in an iron pan used for heating a mixture of sodium chloride and hydrosulphate; J. H. L. Vogt, at the bottom of a converter smelting copper ore; F. K. L. Koch found that iron plates laid beneath the hearths of iron-smelting furnaces and exposed to a red-heat are in the course of 6 or 10 years completely converted by the moisture of the soil into magnetic oxide, partly crystalline and partly amorphous. The same compound is said to be formed on the under-side of refining hearths where the iron comes in contact with water vapour—*vide supra*, the composition of rust. A. Laurent and C. Holms observed that on the hearths of puddling furnaces there is formed a mixture of ferrous silicate and magnetic oxide; and the latter crystallizes in geodes in regular tetrahedra, truncated octahedra, and rhomboidal dodecahedra. J. H. L. Vogt observed that magnetite occurs in furnace slags; E. Keller, in blast-furnace and reverberatory furnace mattes; M. Faraday, in pottery; P. P. Sustchinsky, in porcelain from Carlsbad; J. W. Mellor, in bone-china; and A. Hopwood, in fired clay-ware. R. Boyle observed that fired bricks are magnetic, and if the red-hot brick be allowed to cool in the same position it becomes magnetized in the same direction as the earth's magnetic field; and J. B. Beccaria also observed that bricks or ferruginous stones struck by lightning become permanently magnetized in the same direction as the earth's magnetic field. G. Gherardi also established the existence of a permanent magnetism in all kinds of ancient and modern clay-wares, and showed that edifices made from magnetic bricks must have an influence on measurements of terrestrial magnetism, a subject studied by J. Lamont, F. Kohlrausch, R. W. Wilson, and C. C. Marsh. G. Folgheraiter said that the various clay-wares found in excavations and ancient tombs afford an indelible record of the state of the earth's magnetism at the epoch and place of manufacture, and thereby furnish an indirect means of measuring the secular variation of the magnetic inclination of the earth since the clay-wares were manufactured. Observations on this subject were made by O. A. Gage and H. E. Lawrence, F. Pockels, B. Brunhes and P. David, and P. L. Mercanton.

The preparation of ferrosic oxide.—According to E. Mitscherlich,[6] in the rapid combustion of iron, either in oxygen or air, ferrosic oxide is formed. When iron is heated to dull redness in air it acquires a thin film which has successive shades of yellow, red, blue, and grey; and the analyses of R. Akermann and C. G. Sarnström, A. Laurent, and J. F. L. Hausmann gave for the product $FeO.Fe_2O_3$. R. Ruer and M. Nakamoto found that when ferric oxide is heated in nitrogen for a long time at 1150°, the product is ferrosic oxide with 2 per cent. of dissolved ferrous oxide; and when the ferric oxide is melted at 1550°, the product is ferrosic oxide with 4 per cent. of dissolved ferrous oxide. P. Ramdohr discussed this reaction. According to C. G. Mosander, the outermost layer of the scale formed when iron is heated in air, is ferrosic oxide, but within, the composition approximates $Fe_3O_4.nFeO$. The skin of oxide which is formed may be detached by bending or hammering the cold metal, or by plunging the hot metal into cold water. The product is called *hammer-slag*, *iron scale*, or *scaly iron*. The scale formed in the steel-rolling mills is called *roll scale*. C. G. Mosander found the external layer in one case approximated to $FeO.Fe_2O_3$, and the inner layer to $6FeO.Fe_2O_3$. If the oxidation be allowed to continue, the ferrosic oxide forms ferric oxide. Thus, J. Percy found the outermost layer in one case approximated Fe_2O_3; in the middle layer, $7FeO.3Fe_2O_4$; and the inner layer, $5FeO.Fe_3O_4$. F. S. Barff applied rust-protective coatings to iron by exposing the surface of iron at about 730° to the action of steam for several successive 1-hour treatments with intermediate cooling in air. R. M. Bozorth obtained X-radiograms of the products. He found three layers containing three oxides in the following sequence and thickness: Fe_2O_3, $0{\cdot}2\mu$; Fe_3O_4, $2{\cdot}0\mu$; and FeO, $97{\cdot}8\mu$. P. P. Fedotéeff examined the structure of the same protective coating produced at 1000° to 1100°. Octahedral crystals with deep, etched pits were observed, but no layer formation could be detected. The layer of oxide was optically homogeneous, though chemically it was richer in ferrous oxide next to the metal. L. B. Pfeil observed that when iron and steels are oxidized at a red-heat in air, the scale which is formed normally contains three layers: (i) an outer layer mainly ferric oxide—about 70 per cent. ferrosic oxide and 30 per cent. of ferric oxide; (ii) a middle layer with ferrous and ferric oxides in the proportion 3 : 1; and (iii) an innermost layer mainly ferrous oxide—*vide supra*, the corrosion of iron.

The oxide coatings produced by F. S. Barff, and G. Bower for the protection of iron and steel from rusting, were discussed by J. Percy, G. W. Maynard, S. Cornell, P. Askenasy, Simson and Co., R. Kattwinkel, R. Stumper, B. H. Thwaite, C. Platt, G. Weigelin, W. E. Ruder, A. H. Sang, P. S. Brown, and M. Matwéeff. Other ways of producing the oxide coating have been suggested—*e.g.* by the action of carbon dioxide at an elevated temp. (G. and A. S. Bower, Western Electric Co., and G. R. Tweedie); by treating the metal with a bath of fused alkali (M. Honigmann); immersion in a bath of fused alkali nitrate with or without manganese dioxide (W. B. Greenleaf, C. S. A. Tatlock, and E. Blassett); and by anodic oxidation in alkali-lye (A. de Méritens, and L. Revillon).

According to K. A. Hofmann, in the oxidation of iron, a layer of ferric oxide is first formed on the surface; the adjacent iron then acts as a reducing agent, causing a graduation from ferric oxide through a zone of magnetic iron oxide and ferrous oxide to an underlying layer of metallic iron. The finer the grain-size, and therefore the greater the free surface area, the higher the proportion of ferric oxide in the product. Iron containing finely disseminated ferric oxide gave a pyrophoric product after a short reduction in hydrogen below 600°. Exothermic absorption of oxygen on the surface of this material in air causes a rise of temp. proportional to the ratio surface : mass. Spontaneous combustion takes place if this ratio is sufficiently large. The pyrophoric property is removed by heating for a long time, or at a high temp. in an inert atmosphere. P. Oberhoffer and K. d'Huart regarded hammer-slag as a mixture of ferrous and ferric oxides which approximated Fe_3O_4; but P. Oberhoffer also suggested that it might be a solid soln. of ferrous and ferric oxides.

Observations *sur les battitures de fer* were also made by P. F. G. Boullay, G. Bower, and P. Berthier, who gave for its composition $4FeO.Fe_2O_3$; J. W. Döbereiner, who gave $3FeO.Fe_2O_3$; and M. Beaujeu and C. Méne, who gave Fe_8O_9 and $Fe_{11}O_{12}$. E. J. Maumené gave $20FeO.9Fe_2O_3$, *i.e.* $Fe_{38}O_{47}$, which is very near Fe_3O_4. H. Chandra, A. Kaufmann and F. Haber described a bluish-black oxide of the composition $2FeO.3Fe_2O_3$, or Fe_8O_{11}, obtained by the action of potassium nitrate on a boiling soln. of ferrous sulphate rendered alkaline with ammonia; and H. Chandra, and O. Hauser obtained a $4FeO.Fe_2O_3$ by dehydrating the hydrate (*q.v.*). E. J. Kohlmeyer also obtained indications of the formation of $FeO.3Fe_2O_3$; $3FeO.5Fe_2O_3$; and $3FeO.4Fe_2O_3$; and complex products were obtained by H. Wicht—*vide infra*, solid soln. of ferric oxide and ferrous oxide—but R. Ruer and M. Nakamoto, and A. Simon and T. Schmidt could not confirm this. H. St. C. Deville considered that the oxide $FeO.Fe_3O_4$, or rather Fe_4O_5, is formed when steam acts on iron at an elevated temp.; but P. P. Fedotéeff and T. N. Petrenko showed that at 1000° to 1100°, the oxidation with steam or carbon dioxide proceeds $Fe \rightarrow FeO \rightarrow Fe_3O_4$; and with mixtures of steam and air, $Fe \rightarrow FeO \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$. F. Wüst obtained $2FeO.Fe_2O_3$ by heating ferric oxide in vacuo at 1100°; and $3FeO.Fe_2O_3$, at 1200°. J. W. Döbereiner heated ferrous carbonate and obtained $3FeO.Fe_2O_3$; E. Glasson, $4FeO.Fe_2O_3$; and J. N. von Fuchs, A. Knop, and C. F. Rammelsberg, $5FeO.2Fe_2O_3$; whilst from the oxalate, C. F. Rammelsberg obtained $4FeO.Fe_2O_3$. The physical properties of these mixtures or solid soln. were examined by G. K. Burgess and P. D. Foote, E. Greulich, S. Hilpert and J. Beyer, R. B. Sosman and J. C. Hostetter, and H. Wicht. Analyses of mill scale were reported by A. Ledebur.

What was formerly called anhydrous *æthiops martialis*, or *l'oxyde de fer noir*, or *black oxide of iron*, approximates to ferrosic oxide, and was prepared by the incomplete oxidation of iron by air or steam. F. Küspert described a demonstration experiment for the combustion of iron in oxygen. Near the beginning of last century, ferrosic oxide was prepared by oxidizing iron in air by J. L. Gay Lussac, F. Stromeyer, and H. Davy. J. J. Berzelius showed that ferric oxide dissociates forming ferrosic oxide when it is heated, so that ferrosic oxide is formed when iron is heated in air at a high enough temp. even if ferric oxide were first produced. O. Bauer and E. Deiss, and A. Kropf said that the principal product obtained by burning iron in oxygen is ferric oxide; most others say ferrosic oxide. E. Mitscherlich obtained ferrosic oxide in octahedral crystals by burning iron in a blast-flame. W. G. Mixter, and W. A. Roth observed that the conversion of iron into ferrosic oxide is not complete when iron burns in oxygen, even at 12 to 15 atm. press. When the non-oxidized iron is removed by a magnet, W. G. Mixter obtained a product approximating Fe_3O_4. H. Wicht found that the fused product obtained by burning iron in oxygen has 2·5 to 10 FeO, Fe_2O_3; A. Mittasch's product with oxidizing gases under press. was Fe_3O_4; R. W. G. Wyckoff and E. D. Crittenden's product approximated Fe_3O_4; and E. Deiss and H. Leysaht added that with the slow combustion of iron in oxygen, ferric oxide is formed, and with rapid combustion, ferrosic oxide.

F. Bergius found that the reaction between iron and liquid water under press. furnishes ferrosic oxide in a form which is easily reduced; and E. V. Shannon regarded magnetite as a transient intermediate and unstable stage in the atmospheric oxidation of meteoric iron to limonite; and A. Payen, H. Ost, N. J. B. G. Guibourt, A. Ackermann, E. Deiss and G. Schikorr, and J. Huggett observed its formation in the earlier stages of the rusting of iron in aerated water. According to J. L. Gay Lussac, and C. Despretz, red-hot iron in contact with steam forms hydrogen and ferrosic oxide. Red-hot iron filings repeatedly sprinkled with water also yield the black oxide. Unlike C. N. A. de Haldat du Lys, H. V. Regnault found that the oxidation of heated iron by steam does not progress farther than ferrosic oxide. J. A. N. Friend and co-workers found that when iron is heated in steam to 820° to 950°, it acquires a film of magnetic oxide, and the layers underneath contain various proportions of ferrous oxide associated with the magnetic oxide in solid soln. If the iron is in thin sheets, the product, with a prolonged heating in steam, is all ferrosic oxide. S. Hilpert and J. Beyer observed that the composition of the oxide so obtained is variable; thus, if ferric oxide be heated to 700°, in a current of hydrogen, sat. with water vapour at 30°, contains 85 per cent., and at 800°, 92 per cent. of ferrous oxide. P. P. Fedotéeff and T. N. Petrenko added that ferrous oxide is first formed and that a continuous series of solid soln. is formed; and that the end-product of the reaction at 1000° to 1100° is ferrosic oxide. G. Chaudron observed that below 570° the reaction is $3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2$; and above 570°, ferrous oxide is first formed: $Fe+H_2O \rightleftharpoons FeO+H_2$, and then ferrosic oxide: $3FeO+H_2O \rightleftharpoons H_2+Fe_3O_4$. H. Moissan found that when iron is heated to dull redness in a current of hydrogen, saturated with steam at 90°, ferrosic oxide is formed.

The equilibria between ferrosic oxide in the presence of carbon monoxide and carbon dioxide, and in the presence of hydrogen and water vapour, have been discussed previously in connection with ferrous oxide and with the reactions in the blast-furnace; likewise also the range of stability has been discussed in connection with ferric oxides. H. Moissan showed that if reduced iron is heated to 440° in a current of carbon dioxide, ferrosic oxide is produced. J. Donau observed that if iron wire be heated to 1200° in a current of carbon dioxide, crystals of ferrosic oxide exhibiting magnetic polarity are formed; the presence of moisture facilitates the formation of large crystals. P. P. Fedotéeff and T. N. Petrenko obtained similar results with carbon dioxide as were obtained with steam at 1000° to 1100°. G. Chaudron represented the reaction below 570° by $3Fe+4CO_2 \rightleftharpoons Fe_3O_4+4CO$; and above that temp. ferrous oxide is first formed: $Fe+CO_2 \rightleftharpoons FeO+CO$, and this product is subsequently oxidized to ferrosic oxide: $3FeO+CO_2 \rightleftharpoons Fe_3O_4+CO$. The range of stability of the phases FeO, and Fe_3O_4 in the system: C–O–Fe has been previously discussed. G. Lepetit obtained ferrosic oxide by the action of a 3 : 1 mixture of carbon dioxide and carbon monoxide on iron at 700° and 720° at a press. of one to one-third atm.

Iron can be oxidized to ferrosic oxide by other oxidizing agents. L. N. Vauquelin, E. J. Kohlmeyer, and C. F. Bucholz prepared ferrosic oxide by heating to a high temp. an intimate mixture of powdered iron and ferric oxide tightly packed in a closed crucible. According to J. Percy, the magnetic oxide is formed by boiling an excess of iron filings with water and freshly precipitated, undried, hydrated ferric oxide. The water is decomposed with the evolution of some hydrogen, and the boiling is continued until sufficient ferrous oxide has been formed to convert the ferric oxide into the magnetic oxide. W. Spring exposed a mixture of iron and ferric hydroxide to a press. of 1000 to 1200 atm. and obtained evidence of the formation of ferrosic oxide. W. Bruhns heated a mixture of finely powdered iron and amorphous titanic oxide with hydrofluoric acid at 270° to 300° for 24 hrs. Numerous plates of ilmenite and octahedra of magnetite were formed. C. Doelter obtained the crystals without the fluoride. E. Weinschenk added iron to an ammoniacal soln. of copper oxide, and heated the mixture to 151°, in a sealed tube, for 6 hrs. S. Laszczynsky oxidized iron by heating it in a bath of chlorates or perchlorates; and W. B. Greenleaf, C. S. A. Tatlock, and E. Blassett, by heating it in a bath of alkali nitrate- -W. Vaubel found that ammonium nitrate also converts iron into ferrosic oxide—*vide supra*, the production of an oxide coating to protect iron from rusting. A. Gorgeu prepared magnetite by adding iron to molten iron sulphate; it is said that the sulphate acts catalytically, being alternately reduced to sulphite by the iron and oxidized to sulphate by the oxygen of the atmosphere. Instead of iron, iron sulphide can be used, and instead of iron sulphate, alkali sulphate or sulphide, or sulphur can be used. F. Martin and O. Fuchs obtained ferrosic oxide by heating iron with sulphates of the alkaline earths; and K. A. Hofmann and K. Höschele by heating iron with magnesium chloride in a weakly reducing atmosphere.

The formation of ferrosic oxide in the reaction: $4FeO=Fe+Fe_3O_4$ observed by G. Chaudron to occur below 570° has been discussed in connection with ferrous oxide. It is also formed by treating ferrous oxide by processes employed for converting iron into ferrosic oxide. H. V. Regnault, and C. R. A. Wright and A. P. Luff obtained ferrosic oxide by the oxidation of hammer-slag, and roll-scale. It was also obtained by F. Wöhler by heating the hydrate, $Fe_3O_4.H_2O$, in a closed vessel, and by H. Moissan at a temp. of 300° in an indifferent gas. T. Sidot observed that octahedral crystals of ferrosic oxide are produced when ferric oxide is heated for a long time at a high temp., but not sufficient to fuse the oxide, and he added that the product exhibits magnetic polarity if the tube containing the oxide be placed in the earth's magnetic meridian. According to A. Simon and T. Schmidt, in the decomposition of ferric oxide at a constant press. of 10 mm., the isobar for the decomposition has a sharp break at 1300°, corresponding with the complete conversion of ferric to ferrosic oxide, without the formation of any solid soln., or intermediate oxide. The X-radiograms of ferric oxide were of an unknown type; those of ferrosic oxide, of the spinel type; and those of partially decomposed ferric oxide corresponded with a mixture of ferric and ferrosic oxides, and included no other lines. G. Rose obtained ferrosic oxide by heating ferric oxide with borax in a reducing flame; H. V. Thompson, by heating ferric oxide with an excess of sodium chloride for several hours; K. A. Hofmann and K. Höschele, by heating ferric oxide with magnesium chloride in a weak reducing atmosphere; F. Knapp, by heating 40 per cent. of ferric oxide with glass as a flux, and subsequently removing the glass by treatment with hydrofluoric acid; and E. Weinschenk, by strongly heating a mixture of ferric oxide, ammonium chloride and sulphur—if the temp. be not high enough, iron disulphide is produced. According to O. Mügge, and A. A. Read, when ferric oxide is maintained at 1500° in nitrogen, or, according to H. Moissan, if it be heated in the electric furnace, in air, it is converted into magnetite. H. Wicht said that the product obtained by fusion varies in composition between FeO and Fe_2O_3. H. Moissan thought that ferrosic oxide represents a definite stage in the reduction of ferric oxide or its hydrate at 350° to 400° in hydrogen, but, as shown in connection with ferrous oxide, the reduction is a continuous process. H. Moissan stated that if ferric oxide is heated to dull redness in hydrogen, saturated with water vapour at 90°, ferrosic oxide is formed. S. Hilpert and J. Beyer recommended heating the ferric oxide at 400° in hydrogen, saturated with water vapour at 50°, and so arranged that the gas and vapour passes over a heated copper spiral before it passes over the ferric oxide. H. Moissan heated, at 420°, ferric oxide in carbon monoxide and obtained ferrosic oxide; G. Lepetit preferred a 1 : 3-mixture of carbon monoxide and dioxide at 700° to 720° and at one to one-third atm. press. R. Schenck, and A. Laurent obtained ferrosic or ferrous oxide by a similar process. H. R. Gregory and G. MacDonald used producer gas; and K. Elbe, and S. Lilja, organic residues from distillation processes. L. de Launay obtained impure ferrosic oxide by heating in a sealed tube, at 250°, a mixture of ferric oxide and petroleum.

J. Durocher prepared ferrosic oxide by heating to redness a mixture of ammonium carbonate and ferrous chloride—some hæmatite is also formed; H. St. C. Deville and H. Caron, by melting iron fluoride and boric acid in a platinum crucible suspended above the fluoride, and all contained in a hermetically sealed carbon crucible; H. St. C. Deville, by passing hydrogen chloride over ferrous oxide heated at a high temp.; J. L. Gay Lussac, F. Stromeyer, A. Gautier, and E. A. Parnell, by passing steam over ferrous chloride at a dull red-heat; and A. Gorgeu, by heating molten ferrous chloride to bright redness in an incompletely closed crucible; J. von Liebig and F. Wöhler obtained the magnetic oxide as a heavy, black powder by fusing in air a mixture of ferrous chloride at a low red-heat with dry sodium carbonate and extracting the sodium carbonate with water. C. von Hauer obtained ferrosic oxide by heating to redness ammonium ferrous chloride, and also by passing a mixture of air and steam over heated ferrous chloride; E. Stirnemann, by the action of the vapour of ferric chloride and water on heated china clay, or a mixture of silica, sodium aluminate, and calcium carbonate; or, by heating in a bomb for 12 hrs., at 570° to 580°, a mixture of ferrous and ferric chlorides and water (5 : 8 : 2); and M. Kuhara, by boiling a soln. of ferrous chloride, in the absence of air, for many hours along with finely powdered calcspar, siderite, pyrites, or iron silicate—if some ferric chloride be also present, some hæmatite is formed. R. Klemm could not verify this.

J. S. C. Wells found that at 200°, precipitated iron sulphide forms a mixture of ferrosic and ferric oxides. H. V. Regnault found that when steam is passed over red-hot iron sulphide, ferrosic oxide is formed, and A. Gautier showed that the reaction in a closed vessel is reversible : $3FeS+4H_2O \rightleftharpoons Fe_3O_4+3H_2S+H_2$. According to W. S. Millar, iron sulphides are oxidized to ferrosic oxide when heated in sulphur dioxide. According to A. Gorgeu, iron sulphides act energetically on fused alkaline sulphates, with evolution of a large quantity of sulphur dioxide, and ultimate formation of magnetite and an alkaline sulphate. The alteration in weight is due to the loss of the sulphur originally present in the sulphide, and the absorption of 1·33 times its weight of oxygen by the iron in the sulphide. The yield is better the greater the intermediate formation of a double alkaline ferrous sulphide, and is best of all when a mixture of sodium sulphide and sulphite is used instead of the sulphate. F. Kuhlmann obtained ferrosic oxide by heating calcium chloride and ferrous sulphate in a closed crucible.

H. Moissan obtained ferrosic oxide by heating ferrous carbonate slowly in a current of nitrogen, or carbon dioxide at dull redness—if heated rapidly some ferrous oxide is produced. F. Duffschmid added that the composition of the product varies from $3{\cdot}2FeO.Fe_2O_3$ to $3{\cdot}5FeO.Fe_2O_3$. A. Gautier obtained ferrosic oxide by heating siderite to dull redness in a current of steam ; and H. Krämer, by heating the siderite in a mixture of 2 vols. of carbon dioxide and 1 vol. of carbon monoxide. L. H. Twenhofel observed that when ferric oxalate is heated to 550° in a current of carbon dioxide, ferrosic oxide is formed ; and K. A. Hofmann and K. Schumpelt, likewise obtained it by heating ferric formate at 150° in a rapid current of moist carbon dioxide. T. Ishiwara observed the formation of magnetite in the oxidation of iron carbide, Fe_3C. W. Ipatéeff and N. Kondyreff obtained crystals of ferrosic oxide by the action of hydrogen at 250° and 135 atm. press. on a soln. of ferrous cyanide—if ferrous formate or acetate is used, much ferric oxide is also formed ; W. Ipatéeff and A. Kisseleff also obtained ferrosic oxide with soln. of potassium ferrocyanide or ferricyanide at 350°, and 200 atm. press. ; and with ferrous sulphate soln. at 330°, and 200 atm. press. ; but with soln. of ferrous nitrate, ferrosic and ferric oxide were produced in proportions dependent on the temp., press., and time of action. Water gas at 330 atm. press. forms magnetite when its acts on a soln. of ferrous acetate at 350° to 360°.

H. Debray obtained crystals of magnetite by heating to redness a mixture of ferric phosphate with 3 to 4 parts of potassium or sodium sulphate. H. Grandeau added that a temp. of 1400° to 1500° is necessary for the development of the crystals ; if the temp. is too low, a complex alkali ferric phosphate is formed. M. Schläpfer obtained magnetite in his experiments on the hydrothermal decomposition of the calcium carbonate with iron silicate, and slowly cooling the mass ; and A. Gautier, and A. Brun, by heating iron silicates at 750° to 800° in a current of steam. F. Fouqué and A. Michel-Lévy, H. Andesner, F. Angel, K. Bauer, C. Doelter, W. Hämmerle, G. Medanich, J. Morozewicz, K. Petrasch, H. H. Reiter, J. H. L. Vogt, and M. Vucnik obtained magnetite by melting ferruginous silicates—*vide supra.*

R. Phillips found that if a mixture of ferrous sulphate and sodium carbonate be treated with sufficient potassium chlorate added all at once, hydrated ferric oxide is formed, but if added in small portions at a time, the black ferrosic oxide is formed and is not affected by subsequent addition of the chlorate. W. Gregory found that when a soln. of ferrous sulphate is divided into two equal parts, and one part is oxidized and mixed with the other, and both precipitated from the boiling soln. by ammonia, a black, highly magnetic oxide is formed—*vide infra,* hydrated ferrosic oxide. J. Attfield described a similar process. In C. F. Wülfing's process, as described by F. J. R. Carulla, some ammonia is added to a ferrous liquor

– say, waste liquor used for pickling iron—and air is blown into the mixture to oxidize the lower oxide. More ammonia is added to decompose completely the ferrous salt in soln., and the combination of the two oxides is brought about by means of heat and steam, or air press. The product is used as a magnetic oxide paint for protecting iron from corrosion. According to F. A. Abel and C. L. Bloxam, when ammonia is added to a soln. of a ferrous salt, a white precipitate is formed if air be excluded; in contact with air, the precipitate becomes bluish-green, dark green, and finally black. In this state the precipitate is insoluble in water. If a mixture of ferrous and ferric salts be similarly treated, two distinct precipitates are formed, namely, the bluish-white ferrous hydroxide, and the brown ferric hydroxide. On standing for a short time, or on boiling, a reaction takes place between the two hydroxides, and one of the magnetic oxides results. S. Hilpert said that it is impossible for the two precipitates in such a mechanical state of division to react with one another. For a reaction to take place, one of them must be dissolved. Ferric hydroxide is insoluble in water and in soln. of ammonium salts, but ferrous hydroxide is easily soluble in an excess of ammonium salt. The combination of the two hydroxides is therefore brought about by the precipitated ferrous hydroxide dissolving, and in this state penetrating and diffusing through the ferric hydroxide. The combination occurs slowly if there is no great excess of the ammonium salt, but with much greater rapidity in the presence of a considerable excess. If the precipitation is made in a conc. soln. of ammonium chloride, only ferric hydroxide is precipitated, but this immediately combines with the dissolved ferrous hydroxide with such violence and rapidity that the soln. becomes quite hot. Hence it is easy to produce the magnetic oxide by adding the mixed salt soln. to an excess of aq. ammonia. If the precipitation is carried out without excluding air, or with an insufficient excess of ammonia, the product is never homogeneous, but consists of ferric hydroxide which has combined with some of the ferrous hydroxide, and of ferrous hydroxide which has been partly oxidized, and thus rendered insoluble. If the salts in soln. are compounded so as to furnish Fe_3O_4, the composition of the precipitate will approximate to this formula. If a soln. of ammonium chloride, containing ferrous and ferric salts in the proportions required for Fe_3O_4, be boiled for several hours, the combination is never complete and some ferrous hydroxide remains dissolved so that the precipitate contains some unchanged ferric hydroxide. It is thus difficult to prepare the definite compound $FeO.Fe_2O_3$ by this method, and much more so with respect to other complexes $(FeO)_m(Fe_2O_3)_n$. O. Baudisch and L. A. Welo found that nitric oxide is a good reagent for oxidizing precipitated ferrous oxide to hydrated ferrosic oxide when the gas is bubbled through the freshly prepared pulp. The subject was studied by E. Deiss and G. Schikorr.

The manufacture and use of ferrosic oxide has been described by the Aciéries de Gennevilliers, G. Bredig and co-workers, W. Eminger, P. Fireman, T. Goldschmidt, A. T. Larson and C. N. Richardson, J. Laux, A. Lucas, Metall-Gesellschaft A.-G., E. Müller, E. A. C. Smith, and H. Wicht; and the preparation of *magnetite electrodes*, by P. Askenasy, P. Askenasy and J. Neustadt, H. Blackman, Chemische Fabrik Buckau, Chemische Fabrik Griesheim-Elektron, Consortium für Elektrochemische Industrie, P. P. Fedotéeff and T. N. Petrenko, F. A. J. Fitzgerald, J. F. Ginsberg, H. C. Hubbell, S. Laszczynsky, B. Lepsius, W. Seeger, and M. de Kay Thompson and T. C. Atchison.

The physical properties of ferrosic oxide.—Magnetite occurs in iron-black crystals, or massive with a laminated, coarse or fine, granular structure. It may also occur as an impalpable powder. The mineral is opaque, but thin dendrites in, say, mica are nearly transparent, and their **colour** is pale brown to black. According to A. W. Wright,[7] thin films are greyish-brown in transmitted light. According to F. E. E. Germann, the black pigment employed by the prehistoric North American Indians was magnetite. F. J. R. Carulla found that the mixed oxides, prepared by C. F. Wülfing's process, containing Fe_3O_4 associated with Fe_2O_3, varied over the range black, bluish-black, brownish-black, greenish-black, to green. J. B. L. Romé de l'Isle, and R. J. Haüy showed that magnetite forms octahedral **crystals**

belonging to the cubic system; and H. St. C. Deville showed that the crystals are characteristic of those belonging to the spinel family. Magnetite crystallizes in the holohedral cubic system; but cubic crystals are rare. The habit is more commonly octahedral or dodecahedral, with the faces striated parallel to the (110) : (111)-edge. The crystals are sometimes considerably modified. L. Brugnatelli, R. Scheibe, G. Kalb, and H. P. Whitlock have described various forms of crystals. The crystals are rarely rhombohedral. J. del Pan, and J. Morozewicz said that rhombododecahedral forms separate from magmas rich in ferrous and ferric oxides. Magmas rich in iron may give skeleton forms, grains, and rods. C. Doelter found the number of nuclei developed in unit volume in unit time is relatively large, but the **velocity of crystallization** is small. F. Sauerwald and G. Elsner found that the mechanical strength of ferrosic oxide increases with the temp. of calcination, and this is attributed to an increase in the adhesive force between the surface of the crystallites. **Twinning** occurs about the (111)-plane, and, according to A. Cathrein, O. Mügge, K. Chudoba, and H. Sjögren, sometimes polysynthetic twinning furnishes laminæ which produce striations on an octahedral face, and often a pseudo-cleavage. The **cleavage** is not distinct; but, according to A. Grühn, A. Cathrein, O. Mügge, and J. Strüver, an octahedral parting is often highly developed. According to F. Becke, J. Beckenkamp, F. Rinne and H. Mielke, F. F. Osborne, G. Kalb, O. Mügge, and L. Brugnatelli, the **corrosion figures** developed by hydrochloric, nitric, and sulphuric acids and potassium hydrosulphate on an octahedral face are inverted triangular pits often having truncated edges; rectangular pits appear on the dodecahedral faces; while on a cubic face, quadrilateral elevations are produced by dodecahedral planes, or planes nearly coinciding with them. The chief etching zone, in which the planes forming the corrosion figures lie, is that of the trigonal trisoctahedra, and a secondary zone of the tetragonal trisoctahedra. K. Veit studied the gliding planes.

Observations on the crystals were also made by E. Artini, F. Becke, J. Beckenkamp, J. Blumrich, G. Boeris, A. Breithaupt, W. C. Brögger, S. Brunton, H. Bücking, A. des Cloizeaux, H. Credner, J. D. Dana, H. von Dechen, C. Doelter, G. Flink, J. H. Gladstone, B. Granigg, A. Gorgeu, P. Groth, W. Haidinger, B. J. Harrington, C. Hartmann, E. Hatle, J. A. Hedvall, F. Hessenberg, F. R. van Horn, E. Hussak, L. Jaczowsky, P. von Jeremejeff, M. Jerofejeff, K. Jimbo, G. Kalb, J. F. Kemp, G. A. Kenngott, F. von Kobell, N. von Kokscharoff, A. Lacroix and C. Baret, J. Lehmann, C. C. von Leonhard, G. Leonhard, A. Lévy, L. Liebener and J. Vorhauser, A. Michel-Lévy, W. H. Miller, J. Millosock, T. Monticelli and N. Covelli, J. Morozewicz, O. Mügge, P. Niggli, S. Nishikawa, A. E. Nordenskjöld, T. Petersen, M. Pictorsky, F. A. Quenstedt, G. von Rath, C. F. Rammelsberg, F. Rinne and H. Mielke, H. Rosenbusch, G. Roster, A. Sadebeck, F. Sandberger, A. Scacchi, R. Scheibe, M. Schläpfer and P. Niggli, A. Schmidt, H. Schneiderhöhn, G. M. Schwartz, J. B. Scrivenor, G. Seligmann, G. Silberstein, S. T. Singewald, H. Sjögren, F. S. Starrabba, J. Strüver, E. Tacconi, T. Wada, C. H. Warren, E. Wildschrey, G. Woitschach, T. L. Walker and A. L. Parsons, H. P. Whitlock, J. F. Williams, F. Zambonini, V. R. von Zepharovich, etc.

According to W. H. Bragg, the **X-radiograms** correspond with a space-lattice of the diamond type—**5.**·39, 8—in which if *a* represents the length of the side of a cube containing one molecule, $a=4{\cdot}18$ A.; the face diagonal has a length 5·92 A., and the cube diagonal, a length 7·25 A. A cube containing eight molecules of $Fe''(Fe'''_2O_4)$ has twice these dimensions. In order to maintain the trigonal symmetry, the four oxygen atoms, ○, Fig. 511, are arranged at the corners of a regular tetrahedron, and the tetrahedron is so oriented that the lines drawn from the centre to the four corners of the tetrahedron are parallel to the four diagonals of the crystal cube. The oxygen tetrahedra take the place of the carbon atoms of the diamond, and are arranged so that the four perpendiculars from the corners on the faces are parallel to the four cube diagonals. The bivalent atoms of iron, ●, Fig. 511, are placed one at the centre of each oxygen tetrahedron. In order to satisfy the conditions of symmetry, the tervalent atoms of iron, ⊙, Fig. 511, are arranged so that each of four atoms of iron, *D*, *E*, *F*, *G*, Fig. 511, is placed on one of the four perpendiculars from the tetrahedron on opposite faces, and half-way

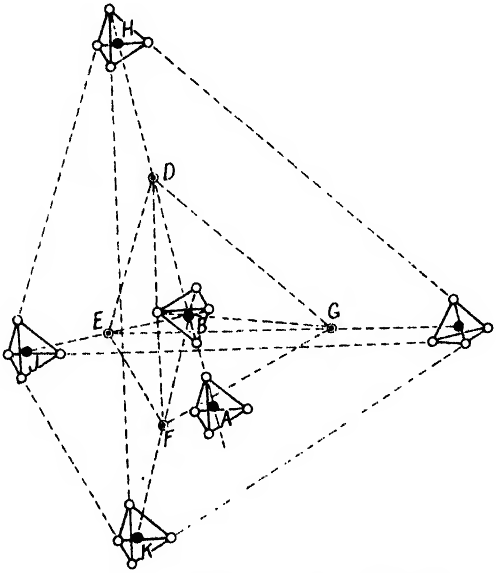


Fig. 511.—Illustration of the Trigonal Symmetry of Magnetite.

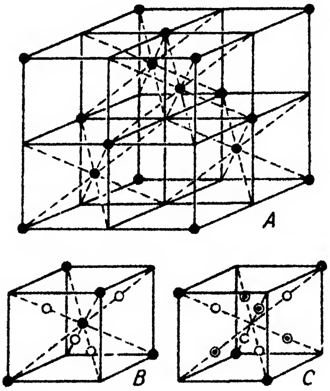


Fig. 512.—The Space-Lattice of Ferrosic Oxide.

between two tetrahedra so as to be shared equally by them. In the diagram, Fig. 511, illustrating the trigonal symmetry, *BH*, *BJ*, *BK*, and *BG* are trigonal axes; $BD=DH=BE=EJ=BF=FK=BG=5{\cdot}4$ A.; and $AB=3{\cdot}60$ A. The structure was depicted another way by S. Nishikawa who represented the lattice of ferrosic oxide by Fig. 512. The eight Fe''-atoms of the eight $\mathrm{Fe}''(\mathrm{Fe}'''_2\mathrm{O}_4)$ molecules are arranged like the carbon atoms in the diamond, *A*, Fig. 512; two cubes of the unit cell are represented by *B* and *C*, Fig. 512. Four of the cubes, *B*, Fig. 512, contain a Fe''-atom in the middle, and each of the four cubes, *C*, Fig. 512, has Fe'''-atoms on the diagonals at the corners of tetrahedra. The oxygen atoms are also situated on the diagonals of the small cubes at the corners of tetrahedra. Observations on this subject were made by J. A. Hedvall, P. Niggli, H. Groebler and P. Oberhoffer, P. F. Kerr, H. Forestier, G. Frebold and J. Hesemann, A. Simon and T. Schmidt, J. Cates, and M. L. Huggins—see Fig. 512. According to R. W. G. Wyckoff and E. D. Crittenden, the unit cube of magnetite has an edge of 8·37 A.; W. H. Bragg gave 8·30 A.; A. A. Claassen, 8·40 A.; G. L. Clark and co-workers, $a=8{\cdot}374$ A.; J. Thewlis, 8·4 A.; T. Gebhardt, 8·367 A.; and S. Holgersson, 8·40 to 8·417 A., or 8·412 A. for natural and 8·417 A. for artificial magnetite. J. A. Hedvall, G. Frebold and J. Hesemann, and S. Holgersson obtained identical values for natural and synthetic ferrosic oxide. According to J. Thewlis, there are two kinds of iron atoms in the $\mathrm{Fe}_3\mathrm{O}_4$ lattice, namely $\mathrm{Fe}^{\cdot\cdot}$ and $\mathrm{Fe}^{\cdot\cdot\cdot}$, and one kind of oxygen atom. Each $\mathrm{Fe}^{\cdot\cdot}$-atom is in the middle of a tetrahedron of oxygen atoms; and each $\mathrm{Fe}^{\cdot\cdot\cdot}$-atom is in the middle of an octahedron of oxygen atoms. Each oxygen atom is at the corner of three octahedra and one tetrahedron of oxygen atoms—*cf.* Fig. 514 in connection with ferric oxide. According to L. A. Welo and O. Baudisch, J. Thewlis, and R. B. Sosman and E. Posnjak, the lattice of ferrosic oxide can accommodate oxygen atoms up to $\mathrm{Fe}_2\mathrm{O}_3$ without change—*vide infra.* K. T. Compton and E. A. Trousdale, A. H. Compton and O. Rognley, S. Holgersson, and M. de Broglie observed no change in the relative intensities or positions of the X-ray spectral lines when ferrosic oxide is placed in a magnetic field. According to R. W. G. Wyckoff and E. D. Crittenden, if an excess of ferrous iron is associated with the ferrosic oxide, it appears as a separate phase, which disappears when an equivalent amount of alumina, silica, or zirconia is added, as promoter for the ferrosic oxide used as a catalyst. With alumina, ferrous aluminate is formed and enters into solid soln., whilst the composition of the oxide tends towards that of ferrosic oxide. The unit cube of magnetite containing potassium aluminate differs but little in size from the unit cube of ferrosic oxide, and it is impossible to say whether or not solid soln. occurs. Promoters maintain a large surface of iron in catalysis by inhibiting sintering of the reduced metal, so that the crystals of the latter grow only very slowly. M. L. Huggins discussed the electronic structure; and J. Forrest, the magnetic lattice.

The **microstructure** of magnetite was examined by A. Lacroix, P. Ramdohr, O. Mügge, C. H. Warren, S. Brunton, S. T. Singewald, G. M. Schwartz, and H. Schneiderhöhn; **inclusions** of ilmenite, etc., by B. Granigg, L. Thiébaut, and E. Hussak. O. Mügge studied the **corrosion figures** of magnetite and other spinels. W. Haidinger, A. Scacchi, C. F. Rammelsberg, J. W. Gruner, G. Seligmann, and H. Bücking discussed **overgrowths** or **parallel growths** of magnetite with hæmatite; J. W. Gruner, with spinel; J. D. Dana, and A. Lacroix, with mica; J. F. Williams, with hypersthene; A. Breithaupt, with chlorite; T. Nordström, with bronzite; F. J. Pope, F. Becke, A. Cathrein, J. W. Gruner, and M. Kamiyama, with ilmenite; and G. Seligmann, A. Cathrein, and O. Mügge, with rutile; and P. von Jeremejeff, with perowskite. J. H. L. Vogt regarded the Norwegian titanomagnetite as a mixture of magnetite and ilmenite. The miscibility of magnetite with $FeTiO_3$, $FeTi_2O_4$, in basaltic slags was studied by V. M. Goldschmidt. B. J. Harrington considered that the titanium in many titaniferous magnetites can be regarded as being present as Ti_2O_3, or as $FeTiO_3$, in which tervalent iron replaces tervalent titanium. E. Hussak considered that the titanium in the *titanomagnetites*—of A. Vendl, J. Szabo, W. G. Miller, A. Knop, T. Nordström, A. Cathrein, F. Schaearzik, and P. Rozlozsnik and E. Emszt—is present rather as inclusions, and that titanomagnetite *kein selbständiges Mineral ist.* R. Ramdohr found that in the slow cooling of titanomagnetite, ilmenite separates in plates; spinel also separates out, as $MgO.Al_2O_3$, or $FeO.Al_2O_3$. The subject was also discussed by M. K. Palmunen. L. W. Fisher studied the isomorphism of the mineral with kreittonite, dysluite, gahnite, magnesioferrite, and spinel. C. U. Shepard described slender, rhombic prisms of magnetite occurring on the cubic octahedra and dodecahedra of magnetite of Monroe, New York; and he called the mineral **dimagnetite,** since its composition is the same as that of magnetite. J. D. Dana regarded dimagnetite as a **pseudomorph** of magnetite possibly after ilvaite.

As indicated above, S. Hilpert [8] and co-workers believe that ferrous and ferrosic oxides form a series of solid soln., perhaps with limited miscibility, and perhaps with the formation of intermediate compounds. The analyses of substances equivalent to hammer-slag—*vide supra*—indicate that various mixtures may be formed. Such mixtures were also obtained by A. Matsubara, E. Terres and A. Pongracź, R. Ruer and M. Nakamoto, L. Wöhler and O. Balz, and others. E. D. Eastman found that up to 1100° ferrosic and ferrous oxides do not form a continuous series of solid soln. though they do dissolve in one another to a limited extent. Iron can dissolve 20 to 25 molar per cent., *i.e.* 6 to 8 per cent., oxygen, although metallic iron is not appreciably soluble in the oxide—*vide supra*, ferrous oxide. O. Mügge concluded from his study of the reduction products of hæmatite, and the oxidation products of magnetite, that magnetite itself is a solid soln. of ferrosic oxide in cubic ferrous oxide. R. W. G. Wyckoff and E. D. Crittenden examined a mixture containing 75·24 per cent. total iron; 3·34 per cent. free iron, 40·49 per cent. ferrous iron, and 31·41 per cent. ferric iron. This showed under the microscope crystals of ferrosic oxide embedded in a fine-grained eutectic mixture of magnetite and ferrous oxide. If magnetite can dissolve ferrous oxide, and if the latter can dissolve magnetite, at ordinary temp., there should be a shift in the lines of one or other or both of the structures. A comparison of the results with those with ferrosic oxide gives no evidence of solid soln., at ordinary temp., of ferrous oxide in ferrosic oxide. H. Groebler and P. Oberhoffer, however, obtained the X-radiograms indicated in Fig. 507—*cf.* Fig. 513, ferrous oxide—with mixtures containing the proportions of ferrous, and ferrosic oxide indicated. The lines with Nos. 1 to 3 with up to about

5 per cent. ferrous oxide have the shift characteristic of solid soln. In No. 4, new lines appear along with the lines of the solid soln., and these are the lines of ferrous oxide; they persist with samples up to No. 9, and they can be recognized in samples Nos. 10 to 12 along with the lines of metallic iron. At a reduction temp. of 800°, therefore, 5 per cent. of ferrous oxide can form a solid soln. with ferrosic oxide; with higher proportions, the ferrous oxide occurs as a second solid phase, and with about 31·9 per cent. Fe_3O_4, the ferrosic oxide lattice disappears, and the lines due to that of ferrous oxide alone appear. The iron dissolved in ferrous oxide, Nos. 10 to 12, causes no shift of the lines, thus indicating the absence of a solid soln. The vanishing of the X-ray spectrum of magnetite when the composition approaches 61 per cent. of FeO, and 31·9 per cent. of magnetite is explained by assuming that magnetite begins to take on the cubic lattice of ferrous oxide at this dilution, and that the extra oxygen atoms are distributed haphazard in the interstices between the other iron and oxygen atoms. They call the oxygen atoms that fail to take part in the X-ray spectrum "vagabond atoms"—*der überschüssige Sauerstoff frei im Gitter vagabundiert.* R. M. Bozorth, in his examination of the ferrosic oxide protective coatings on iron, observed no evidence of the formation of solid soln. of ferrous and ferrosic oxide, because he found no evidence of a variation in atomic spacing greater than 0·5 per cent. Negative evidence in the application of the X-ray method does sometimes occur—*e.g.* it fails to show iron tritacarbide in steel specimens where the Fe_3C areas and crystals are plainly visible under the microscope. A. Simon and T. Schmidt could detect no solid soln. in the conversion of ferric to ferrosic oxide by heat.

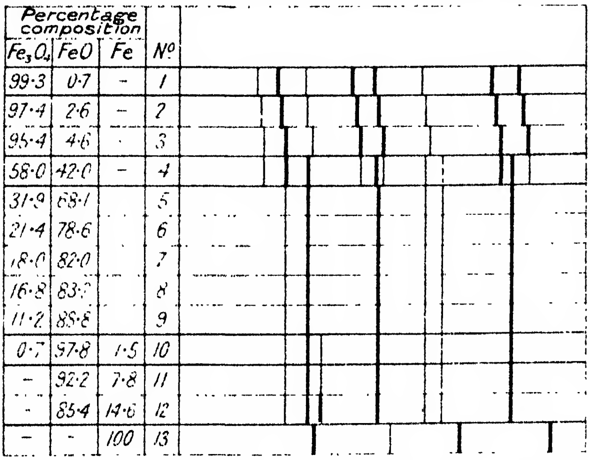


FIG. 513.—Diagrammatic X-ray Spectra of Iron Oxides Lower than Fe_3O_4.

According to H. Moissan,[9] and M. Berthelot, there are two **allotropic forms** of ferrosic oxide. Ferrosic oxide prepared by heating ferric oxide or metallic iron, reduced by hydrogen, in a current of hydrogen sat. with aq. vapour at 90°; or by heating ferrous carbonate to dull redness in a current of carbon dioxide; or by heating reduced iron in a current of carbon dioxide at 440°, is a black, magnetic powder of sp. gr. 4·86; it is readily attacked by conc. nitric acid; and when heated, becomes incandescent, forming ferric oxide. The other modification of ferrosic oxide is produced when ferric oxide, obtained by oxidizing the first modification, is heated above 1500°, when oxygen is given off leaving a black magnetic oxide of sp. gr. 5·00 to 5·09; it is almost unattacked by boiling conc. nitric acid, and does not form ferric oxide when heated. Indeed, it is one of the most stable oxides of iron. When the low temp. form of ferrosic oxide is heated to whiteness in a current of nitrogen, it agglomerates, increases in density, no longer forms ferric oxide when heated in air, and is, indeed, identical with the second, inert form of ferrosic oxide. The fact that the high temp. form does not give ferric oxide when heated is explained by assuming that when the lower temp. form of ferrosic oxide is converted into ferric oxide, the heat evolved is less than that evolved when the low temp. form is converted into the high temp. form, and therefore the formation of ferric oxide from the high temp. form of ferrosic oxide would be an endothermic reaction—*vide infra,* the thermal expansion (P. Chévenard), the sp. ht. (G. S. Parks and

K. K. Kelley, R. W. Millar, and A. Piccard and co-workers). electrical conductivity (C. C. Bidwell, J. Königsberger, and J. Königsberger and K. Schilling), the thermoelectric force (C. C. Bidwell), and magnetic properties (P. Weiss and co-workers, J. Königsberger, G. E. Allan, F. Rinne, J. Huggett and G. Chaudron, and P. Chévenard) of this oxide; and also the calorescence of ferric oxide. J. A. Hedvall observed no difference in the crystalline structure, for the X-radiograms of the alleged allotropic forms are the same. According to L. A. Welo and O. Baudisch, the catalytic activity of different samples of magnetite varies with the mode of preparation, those made by precipitation of a mixture of ferrous and ferric sulphate being much more active than those made by precipitation of ferrous sulphate and subsequent partial oxidation. The activity of active magnetite is not destroyed by oxidation, but both activity and magnetic properties are lost on heating at 550°. Comparison of the water absorption and X-ray diffraction spectra of active and inactive oxides indicates that the crystals of the former are smaller than those of the latter. It is thought that both magnetic properties and catalytic activity are related to the spatial arrangement of the atoms within the molecule. In addition to the change which occurs at the Curie point, C. C. Bidwell reported breaks in the curves of electrical conductivity and thermoelectric force between 600° and 800°; and H. H. Reiter, a transformation point at 1260°.

The **specific gravity** of magnetite, or ferrosoferric oxide, ranges from 4·96 to 5·40—average, 5·16. R. Böttger[10] gave 4·960 to 5·094; G. A. Kenngott, 4·90 to 5·20 for compact magnetite, 5·168 to 5·180 for crystalline magnetite, and 5·27 after heating for a long time; H. Kopp gave 5·12 at 0°; C. F. Rammelsberg, 5·106 to 5·185; H. Arsandaux, 5·065; W. Herapath, 5·300 at 16·5°; P. F. G. Boullay, 5·400 to 5·480; E. Madelung and R. Fuchs, 5·1718; V. Quittner, 5·252; S. Holgersson, 5·194; H. Nathorst tabulated the sp. gr. of the Swedish magnetites and found that they ranged from 4·24 to 5·11. The presence of impurities in the mineral must make the sp. gr. vary. E. Wilson and E. F. Herroun obtained a low value—4·10 to 5·06—and E. Madelung and R. Fuchs a high one—5·5471. F. Sauerwald and G. Elsner, and P. Chévenard examined the effect of heat on the sp. gr.; and J. J. Saslawsky the observed and calculated mol. vol. L. Playfair and J. P. Joule, 5·453 at 3·9°. H. Moissan gave 4·86 for ferrosic oxide prepared at a low temp., and 5·00 to 5·09 for that prepared at a high temp.; and for the artificial crystals, A. Gorgeu gave 5·21 to 5·25. W. Biltz studied the mol. vol. The **hardness** of magnetite is 5·5 to 6·5; and A. Gorgeu gave for the artificial crystals, 6·0 to 6·5; J. Donau gave 6·0 for a sample prepared at 1100° to 1200°; and for a sample obtained from the sulphide, 6·0 to 6·5. P. Pfaff found that the scratching hardness of magnetite on an octahedral face is 22 when the hardness of talc is unity. P. J. Holmquist compared the hardness offered in the slitting machine; J. L. C. Schröder van der Kolk, the cleavage and hardness; E. Friederich, the hardness, at. mol., and valency; G. A. Kenngott, and J. L. C. Schröder van der Kolk, the hardness and at. vol.; and A. Reis and L. Zimmermann, and S. Holgersson, the hardness and the lattice structure. A. Grühn studied the **gliding planes** of the crystals under press. up to 30,000 atm. F. D. Adams tried the effect of **compression,** up to 43,000 lbs. applied in 17 mins., on a crystal of magnetite, and found that the mineral broke to pieces, and that the fragments had the form of little plates which separated from the crystal parallel to the octahedral faces. There were no signs of plastic deformation. P. W. Bridgman gave for the compressibility, $\beta=0\cdot0_{6}59$ or $dv/v_0=5\cdot397p-2\cdot01p^2$ at 30°, and $dv/v_0=5\cdot376p+2\cdot01p^2$ at 70°, where dv denotes the decrease in vol. with a rise of press. of p kgrms. per sq. cm. for values of p below 12,000 kgrms. per sq. cm. L. H. Adams gave $\beta=-0\cdot0_{6}55$, and $d\beta/dp=0\cdot0_{11}4$; and E. Madelung and R. Fuchs gave $0\cdot0_{6}54$ to $0\cdot0_{6}57$ megabars per sq. cm. when the value for mercury is $3\cdot86\times10^{-6}$. F. Sauerwald and G. Elsner made some observations on the mechanical strength of samples heated to different temp. F. B. Hofmann made some observations on the accumulation of the powder at the boundary surface of water and organic liquids.

H. Kopp[11] observed that the cubic coeff. of the **thermal expansion** of magnetite is 0·000029 between 17° and 50°; and F. Pfaff gave for the mean linear coeff. 0·00009540. H. Forestier observed a break in the dilation curve between about 570° and 965°. G. Chaudron and H. Forestier observed that the dilation increases continuously up to 570° and then decreases. There is a sudden fall at 695°. With artificial magnetite, a contraction was observed; and at 550° the expansion was normal. P. Weiss and G. Foëx observed an anomaly at 570°; at 0°, $\alpha=0{\cdot}0_58$, and at 570°, $\alpha=0{\cdot}0_424$; above 570° there is a decrease in the value of α; and at 680°, there is a break in the curve attributed to the effects of the Curie transformation, although P. Chévenard observed that the change in Curie's constant between 625° to 765° did not influence the expansion perceptibly. T. Okamura studied the subject. H. de Sénarmont found that the **thermal conductivity** of magnetite in different directions is the same, and the isothermal lines are circular. J. Kruckenberg gave $k=0{\cdot}003$ to 0·006 cal. per cm. per degree per second for the thermal conductivity of magnetite. F. E. Naumann gave 0·1641 for the **specific heat** of magnetite; H. V. Regnault, 0·16023 between 10° and 99°; H. Kopp, 0·153 to 0·159; R. Ulrich, 0·1687 between 20° and 98°; and A. Abt, 0·16505 to 0·16582 between 15° and 96°. W. Bertram gave:

	96·5°	219°	448°	586°	678°	738°	783°
c .	0·1592	0·1766	0·1982	0·2095	0·2137	0·2176	0 2188

and $c=0{\cdot}1487+0{\cdot}000148(\theta-20)-0{\cdot}0_7725(\theta-20)^2$. P. N. Beck gave:

	101°	198°	301°	395°	496°	540°	580°
Sp. ht. .	0·16791	0·17572	0·18509	0·19341	0·20346	0·20788	0·21235

for which $c=0{\cdot}161178+0{\cdot}0_3111114\theta+0{\cdot}0_61551\theta^2$. There is a transition point at 585°, after which:

	593°	620°	648°	704°	726°	748°	791°
Sp. ht. .	0·21336	0·21437	0·21519	0·21735	0·21835	0·21952	0·22259

for which $c=0{\cdot}161699-0{\cdot}002969610\theta+0{\cdot}0_523718\theta^2$. There are striking peaks in the sp. ht. curve at −156° and at 593°. The latter is approached the more gradually as the temp. is raised, but falls off precipitately after the peak is passed. This type of peak is characteristic of ferromagnetic materials as they pass their Curie points and become paramagnetic. P. Weiss and P. N. Beck showed that as magnetite passes from the ferromagnetic to the paramagnetic state at the critical temp., heat is rapidly absorbed, so that the sp. ht. rises to a maximum, then decreases, and again increases. The mean values of the sp. ht., $dQ/d\theta$, at different temp. are indicated in Fig. 514. K. Honda and J. Okubo consider that the discontinuity near the Curie point is not an effect of magnetic energy, but rather an effect of the heat of the transformation of iron from one form to another. O. C. Ralston added that it is doubtful if the peak in the curve, Fig. 514, is a discontinuity in the sp. ht., but the tip of the peak rather represents the point on a magnetization-temperature curve, where the ferromagnetism is being lost more rapidly before the point is reached where only paramagnetism remains. H. A. Lorentz calculated $\delta c=0{\cdot}0644$ for the differential of the sp. ht. on the assumption that the magnetic molecule is $\frac{1}{3}Fe_3O_4$. P. Weiss and co-workers showed that at the Curie point $d/(\delta c)/d\theta$ will be zero. J. R. Ashworth, and A. Dumas discussed the relation between δc and the Curie point. I. Maydell studied the mol. ht. J. R. Ashworth studied the relations between the thermal and magnetic constants.

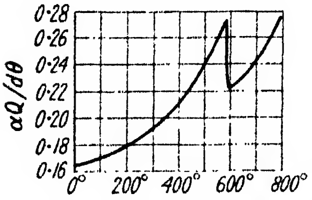


FIG. 514.—The Effect of Temperature on the Specific Heat of Magnetite.

P. Weiss and co-workers gave for the sp. ht. of artificial magnetite and of the natural mineral from Traversella, Piedmont:

	300°	400°	500°	550°	585°	585°	593·5	593·5	625°	670°
Natural .	—	-	0·259	0·281	0·299	0·2255	0·226	0·226	0·229	0·232
Artificial .	0·199	0·222	0·255	0·277	0·295	0·295	0·300	0·221	0·223	0·226

They also observed a difference in the results between 18° and 175° for samples that had and had not been previously heated to 300°. M. Tigerschiöld calculated a mol. ht. of 36·08 at 17°, from A. Matsubara's observations on gaseous equilibria. G. S. Parks and K. K. Kelley gave for the sp. ht. per gram:

°K .	90·0°	96·9°	153·2°	193·5°	197·2°
C_p .	0·0488	0·0550	0·0968	0·1186	0·1205
°K .	276·3°	278·7°	292·1°	295·0°	—
C_p .	0·1513	0·1525	0·1558	0·1570	- -

and R. W. Millar, for the mol. ht.:

°K .	60·5°	87·6°	100·7°	110·4°	114·7°	124·8°	153·7°	206·2°	261·1°
C_p .	5·495	10·36	13·67	19·25	36·27	18·95	22·63	28·59	32·68

The results are plotted, along with those for ferrous oxide, in Fig. 504. W. A. Roth and W. Bertram gave for the sp. ht., c, between $\theta°$ and 20°, $c=0{\cdot}1487+0{\cdot}0_3148(\theta-20)-0{\cdot}0_7725(\theta-20)^2$; and for the mol. ht., at $\theta°$:

	100°	200°	300°	400°	500°	600°	700°
C .	39·59	45·12	49·66	53·20	55·73	57·23	57·74

J. Lehmann found that when magnetite is heated, and suddenly cooled by cold water, irregular cracks appear on the octahedral and dodecahedral faces. F. Sauerwald and G. Elsner studied the sintering of powdered ferrosic oxide. According to S. Hilpert and E. J. Kohlmeyer, purified ferrosic oxide has a **melting-point,** or rather the f.p., 1527°; and there is a break in the cooling curve between 1250° and 1350°. E. J. Kohlmeyer later gave 1600°; O. Ruff and O. Goecke, 1538°; B. Garre, 1527°; J. Kleffner and E. J. Kohlmeyer, 1580° in an atm. of nitrogen; J. C. Hostetter and H. S. Roberts, 1590°; and R. B. Sosman, 1580°. P. Curie's value, 1377°, is too low. A. Brun gave 1260° for the m.p. of magnetite from Zermatt; and C. Doelter found that the mineral begins to soften at 1195°, and is fluid at 1210°, and that its m.p. is approximately the same as that of orthoclase; C. Schubert gave 1080° to 1090°. Observations were also made by H. H. Reiter. The low values obtained with the natural mineral are usually attributed to the presence of impurities. R. Ruer and M. Nakamoto found that a mixture of ferrous and ferrosic oxides (4 : 96) begins to melt slightly over 1550°.

J. A. Hedvall said that the oxide is stable at a red-heat. R. Ruer and M. Nakamoto found that in a current of nitrogen ferrosic oxide begins to decompose over 1300°, and that the composition of the oxide heated to 1500° is Fe : O=1 : 1·32. P. T. Walden found that ferrosic oxide does not show an appreciable **dissociation pressure** at 1350°; but A. Simon and T. Schmidt said that it amounts to about 1 mm. at 1350°. H. von Jüptner calculated for the reaction: $2Fe_3O_4=6FeO+O_2$, $\log [O_2]=\log p=32254T^{-1}+1{\cdot}75 \log T^{+2{\cdot}8}$; and for the reaction: $Fe_3O_4=3Fe+2O_2$, $\log [O_2]=\log p=-29628T^{-1}+1{\cdot}75 \log T^{+2{\cdot}8}$. The dissociation press., in atm., are:

	600°	1000°	1400°	1800°	2000°	2400°
p .	$0{\cdot}0_{46}8038$	$0{\cdot}0_{24}6252$	$0{\cdot}0_{14}1850$	$0{\cdot}0_{9}3783$	$0{\cdot}0_{7}2817$	$0{\cdot}0_{4}1889$
$p1$.	$0{\cdot}0_{41}1914$	$0{\cdot}0_{21}2642$	$0{\cdot}0_{12}1389$	$0{\cdot}0_{7}1088$	$0{\cdot}0_{6}5792$	$0{\cdot}0_{3}2346$

No determinations of the dissociation press. have been made; but estimates have been made by L. Wöhler and co-workers, A. Matsubara, K. Hofmann, W. Biltz, A. McCance, and F. Wüst and P. Rütten. The reduction of magnetite by platinum shows that some dissociation of magnetite occurs; and the gain of 3 per cent. excess ferrous oxide when ferrosic oxide is heated to 1550° shows that the oxygen press. at this temp. is appreciable. This explains a possible difficulty in determining the m.p., since the m.p. will be lowered by the contamination of the ferrosic oxide with ferrous oxide.

H. Dulong, and T. Andrews made some observations on the **heat of formation** of ferrosic oxide. According to M. Berthelot, this amounts to $(FeO,Fe_2O_3)=4\cdot4$ Cals.; but W. G. Mixter found 9·2 Cals. for the thermal value of this reaction. H. le Chatelier gave for $3Fe_2O_3$(calcined)$=2Fe_3O_4+O-45\cdot18$ Cals.; and H. von Jüptner, 52·4 Cals. O. Ruff and E. Gersten gave $(3Fe,2O_2)=265\cdot2$ to 267·1 Cals.; E. D. Eastman and R. M. Evans, 258·0 to 266·98 Cals.; L. Wöhler and R. Günther, 264·8 Cals.; M. Berthelot, 267·4 to 270·8 Cals.; W. A. Roth and co-workers, 265·7 Cals.; J. Jermiloff, 274·6 Cals.; A. C. Halferdahl, 267·28 Cals.; W. D. Treadwell, 247·2 Cals. at 1000°; W. G. Mixter, 265·7 Cals.; O. Doepke, and W. A. Roth, 265·4 Cals.; M. Tigerschiöld, 217·0 Cals.; and H. von Jüptner, 270·8 Cals. W. A. Roth and co-workers gave $FeO+Fe_2O_3=Fe_3O_4+7\cdot0$ Cals. G. Preuner calculated for the heat of oxidation of iron to ferrosic oxide at 960°, 237,740 cals., and E. Baur and A. Glässner, 236,240 cals. at 960°, and 267·38 Cals. at 490°. The best representative value is 265·7 Cals. E. D. Eastman and R. M. Evans gave for the heat of formation $Q=-2{,}643{,}630+11\cdot00T+0\cdot0112T^2-0\cdot00000248T^3$, from the carbon monoxide reduction equilibrium; and $Q=-256{,}377-3\cdot76T-0\cdot006594T^2+0\cdot0000296T^3$, from the hydrogen reduction equilibrium. A negative heat of formation, of course, means an evolution of heat. H. le Chatelier gave for the $(3FeO,O)=76\cdot6$ Cals.; O. Ruff and E. Gersten, 85·8 Cals.; and H. von Jüptner, 73·7 Cals. H. von Jüptner gave $3Fe_2O_3=2Fe_3O_4+O+52\cdot4$ Cals., and H. le Chatelier, $3FeCO_3+O=Fe_3O_4+3CO_2+0$ Cals. W. G. Mixter found the heat of formation of fused magnetite to be 265·2 Cals., and ordinary magnetite 265·7 Cals., leaving 0·5 Cal. for what he called the heat of polymerization, assuming, of course, that the error of experiment is zero. U. Hofmann and E. Groll calculated for the reaction $3Fe+4CO_2=Fe_3O_4+4CO-5380$ cals., when $[p_{CO_2}]^4=K[p_{CO}]^4$, at 1 atm. press.:

	550°	500°	450°	400°	350°	300°	250°
K .	0·927	—	2·22	—	6·25	—	22·1
p_{CO} .	0·5048	—	0·451	—	0·388	—	0·316
Q .	—	10,295	—	9273	—	8148	— cals.

and for $Fe_3O_4+6CO=Fe_3C+5CO_2+41{,}850$ cals., when $[p_{CO}]^6=K[p_{CO_2}]^5$:

	550°	500°	450°	400°	350°	300°	250°
$\log K$	−1·13	—	−2·82	—	−5·01	—	−7·96
p_{CO} .	0·415	—	0·260	—	0·130	—	0·046
Q .	—	46,023	—	45,097	—	44,000	— cals.

M. Berthelot gave 46·8 cals. for the **heat of solution** of ferrosic oxide in hydrochloric acid. E. D. Eastman calculated the **free energy** of ferrosic oxide to be:

	600°	700°	800°	900°	1000°
Free energy .	−198,320	−190,425	−182,550	−174,735	−166,980 cals.

Observations on the subject were made by F. Wüst and P. Rütten, and A. McCance. R. Dallwitz-Wegener discussed the subject. G. S. Parks and K. K. Kelley gave 81·0 for the **entropy**, 27·10 Cals. for the heat of formation, and −246·8 for the free energy at 25°; whilst R. W. Millar gave 34·69 for the entropy at 25°. A. C. Halferdahl gave −83·1 units for the change of entropy in the formation of magnetite at 25°. O. C. Ralston calculated from the sp. ht. data, values for the change in entropy, δS, which occurs when a mol. of Fe_3O_4 is formed from its elements:

	25°	100°	200°	300°	400°	500°	585°	700°	800°
δS .	−81·5	−78·9	−76·3	−71·7	−71·1	−68·1	−65·4	−63·9	−63·7

The calculations of E. D. Eastman and R. M. Evans, and G. N. Lewis and M. Randall furnish for the free energy $-264{,}630-11T\log T-0\cdot112T^{-2}+0\cdot00000124T^3=11\cdot34T$, from the carbon monoxide equilibrium; and from the hydrogen equilibrium, $-256\cdot320-3\cdot76T\log T+0\cdot0066T^2-0\cdot00000T^3+40\cdot56T$. O. C. Ralston gives as the best representative value $-269{\cdot}246-8{\cdot}1425T\log T+0{\cdot}000341T^2+136{\cdot}332T$. The free energy of magnetite is

	25°	100°	200°	400°	585°
cals. .	−241,500	−235,415	−227,800	−212,980	−199,278

	700°	900°	1100°	1300°
cals. .	−19,960	−176,995	−162,195	−148,163

S. Loria[12] found for artificial magnetite, with light of wave-length λ=439, 589·6, and 665·5$\mu\mu$, the **indices of refraction** respectively 2·46, 2·42, and 2·45; and the **extinction coefficients** respectively 0·69, 0·55, and 0·50; and S. Loria and C. Zahrzewsky obtained similar results for natural ferrosic oxide, viz.:

λ . .	4390	4660	5030	5330	5896	6330	6655	7040
μ . .	2·46	2·43	2·42	2·41	2·42	2·44	2·45	2·42
k . .	0·69	0·66	0·60	0·57	0·55	0·53	0·50	0·45

W. W. Coblentz found the **ultra-red reflecting power** rises uniformly from about 4 per cent. at 1μ to 38 per cent. at 13μ. S. Holgersson calculated 27·55 for the **molecular refraction** with the μ^2 formula. Observations on the **emissivity** of ferrosic oxide were made by H. le Chatelier and co-workers, B. Monasch, and E. Domek. G. K. Burgess and R. G. Waltenberg gave for light of wave-length $0{\cdot}65\mu$, 0·63 when the value for platinum is 0·33; they also gave for the molten oxide 0·53. G. K. Burgess and P. D. Foote found the monochromatic emissivity, E', at different temp. to be:

	800°	900°	1000°	1100°	1200°
E' . .	0·98	0·97	0·95	0·93	0·92

and the total emissivity, E:

	500°	600°	700°	800°	900°	1000°	1100°	1200°
E . .	0·85	0·85	0·87	0·87	0·87	0·88	0·88	0·89

Surfaces of molten iron and steel quickly acquire a coating of oxide whose outer surface is essentially magnetite. The above results furnish a table of corrections for optical and radiation pyrometers sighted on surfaces of iron oxide consisting mostly of magnetite. The temp. drops through the layer of oxide, so that the true temp. of the metal beneath the oxide layer is higher than it is at the outside of the oxide layer. Thus, for observations with optical and radiation pyrometers:

Observed temp. .		500°	600°	700°	800°	900°	1000°	1100°	1200°
True temp.	Optical .	—	600°	700°	801°	902°	1004°	1106°	1210°
	Radiation	530°	630°	735°	835°	940°	1040°	1145°	—

P. D. Foote studied the Kerr effect; there is a maximum in the curve for the Kerr effect at which the **electromagnetic rotation** changes; and there is probably also a minimum. P. Dziewulky made observations on the magneto-optic rotation. S. Loria, and H. E. J. G. du Bois studied the effect of magnetic fields of different strength; S. Loria, H. E. J. G. du Bois, and L. R. Ingersoll, the effect of light of different wave-lengths; and P. Martin, the effect of temp. J. Kerr observed that a suspension of finely powdered ferrosic oxide is doubly refracting in a magnetic field. J. L. Glasson studied the X-ray spectrum. C. Doelter observed that magnetite, like the spinels generally, is fairly opaque to the **X-rays,** standing in this respect between quartz and rock salt. A. Dima found the **photoelectric effect** with magnetite to be very small; and F. Krüger and E. Taege observed that if some hydrogen sulphide is present the effect is more marked. C. H. Kunsman found that a fused mixture of iron oxide with 1 per cent. of an alkali or alkaline earth oxide, with or without alumina, when used as a hot anode, or employed as a coating for platinum anode, gave, after partial reduction, steady **positive ion currents** up to 10^{-4} amp. per sq. cm. in a vacuum of 10^{-6} mm. A. J. Dempster observed no reflection of positive ions by crystals of magnetite. E. Rupp and E. Schmid studied the reflection of electrons from films of ferrosic oxide. A. W. Wright obtained by cathodic spluttering in vacuo a thin mirror of magnetite which was greyish-brown in transmitted light. E. T. Wherry found magnetite to be a poor radio-detector.

R. J. Haüy[13] found that magnetite acquires a negative charge of **frictional electricity** when rubbed with a handkerchief; and H. F. Vieweg studied the subject. F. Crook noted that it is attracted by a rubbed stick of shellac. P. Weiss studied the **electrostatic moment** of magnetite. The observations of J. F. L. Hausmann and F. C. Henrici, F. von Kobell, G. Cesaro, E. Wartmann, F. Beijerinck, and W. Skey showed that the **electrical conductivity** of ferrosic oxide is less than that of copper. E. Weintraub found the conductivity of magnetite to be $0{\cdot}0116\times10^4$ mhos per cm. cube when that of copper is 64×10^4 mhos per cm. cube. The conductivity increases with rise of temp. H. Bäckström found that at 40° the **electrical resistance** of rods cut parallel to the cubic and the dodecahedral normals are the same. The electrical resistance decreases slowly with a rise of temp. A. Abt found that the resistance of a cm. cube of magnetite from Moravitza ranged from 7·06 to 4900 ohms; the variation is attributed to the variation in the proportion of contained quartz as impurity. R. D. Harvey, and H. Löwy studied the subject. The effect of variations of temp. were measured by S. P. Thompson, H. Bäckström, C. C. Bidwell, and C. Fery. S. L. Brown gave 562·5 ohms per cm. cube for the sp. resistance, R, of fused magnetite at 20° and for the resistance at $\theta°$ between $-3°$ and 365°, $R=562{\cdot}5(1{\cdot}82-0{\cdot}0524\theta-0{\cdot}00057\theta^2)$. C. Doelter found that the electrical resistance is 1·198 ohm at 15°, it is 0·614 ohm at 115°; and between 500° and 600° the results were irregular. J. Königsberger and K. Schilling measured the electrical resistance, R_E ohms, of artificial ferrosic oxide, at different temp., Fig. 515. The results show a break at about 530°, and a minimum at 220°. A number of samples broke on passing 530°. For α-ferrosic oxide:

	15°	82°	192°	221°	240°	280°	410°	485°
R . .	0·00794	0·00582	0·00446	0·00434	0·00435	0·00446	0·00770	0·0112

and for β-ferrosic oxide, there is a minimum at 815°:

	550°	605°	660°	710°	755°	815°	840°	905°
R . .	0·0069	0·0068	0·0064	0·0059	0·0056	0·0054	0·0055	0·0060

S. Veil also noted a discontinuity in the conductivity curve between 500° and 600° at the Curie point; C. C. Bidwell attributed the effect at 600° to 800° to a partial oxidation of the ferrosic oxide. Observations were also made by B. Young, R. von Haslinger, E. Renschler, T. Okamura, and J. Königsberger. E. Wilson and E. F. Herroun found that the resistance of magnetite varies with the impressed voltage, the resistance decreasing as the potential difference was increased. The effect of heating and subsequently cooling to the ordinary temp., was to diminish both the resistance and the temp. coeff., whilst the application of magnetic force or compressive stress also caused a decrease in resistance. A press. of 887 kgrms. per sq. cm. decreased the resistance 1·1 to 3·9 per cent. In one case a sample with high magnetic retentivity behaved exceptionally, its resistance being scarcely affected by variation in the applied potential difference or by alternating changes of temp.; furthermore, the application of a magnetic field made relatively little difference in the resistance, although this was diminished by compressive stress. C. W. Heaps found that for a magnetic field of strength 4000 to 5000 gauss, the ratio dR/R attains a maximum. T. W. Case observed no change in the electrical resistance on exposure to light. The electrical resistance of compressed powders was

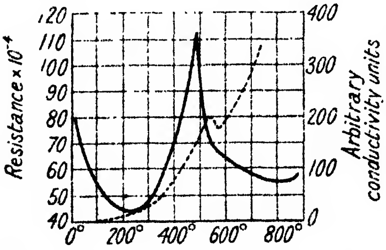


FIG. 515.—The Effect of Temperature on the Electrical Resistance of Magnetite.

measured by J. Königsberger and K. Reichenheim, F. Streintz, S. Veil, R. von Hasslinger, J. Königsberger, B. Young, E. Renschler, and C. C. Bidwell. R. von Hasslinger inferred that with artificial ferrosic oxide, the conductivity at high temp. is electrolytic; but C. Doelter said that the conductivity is electronic, *i.e.* metallic, both at ordinary and at elevated temp. The subject was discussed by O. Lehmann, J. Königsberger and co-workers, R. von Hasslinger, W. Nernst, and S. Veil.

Some observations on the **thermoelectric force** of magnetite were made by T. J. Seebeck, and W. G. Hankel. J. Weiss and J. Königsberger found that the thermoelectric force of magnetite against copper is 6×10^{-5} volt per degree, so that the current flows through the warm junction to the copper. S. L. Brown and L. O. Shuddemagen represented the results for the Fe : Fe_3O_4 couple by $E=0{\cdot}427(\theta-20)$; and they found the thermoelectric force of the couples of magnetite with iron, copper, and cuprous oxide to be:

	Fe			Cu			Cu_2O		
Hot junction .	90°	517°	639°	102°	315°	550°	92°	312°	650°
Voltage . .	0·030	0·211	0·300	0·035	0·125	0·225	0·112	0·405	0·770

C. Féry also measured the thermal e.m.f. of magnetite against iron; and C. C. Bidwell, against platinum—at 200°, the temp. coeff. of the e.m.f. was −0·00005 volt per degree; and in the curve representing the effect of temp., there is a transformation point between 700° and 800°.

P. Béchtereff found the **electromotive force** of the cell with molten sodium hydroxide $Fe_3O_4 \mid NaOH + KMnO_4 \mid C$ rises with temp. up to 0·9 volt, and then gradually falls as the mixture approaches its b.p. C. A. L. de Bruyn observed that the e.m.f. of the cell $Fe_3O_4 \mid 0{\cdot}1N\text{-}Fe^{\cdot\cdot}SO_4 + Fe^{\cdot\cdot\cdot}{}_2(SO_4)_3 \mid N\text{-}KCl,Hg_2Cl_2 \mid Hg$ is a little less than the observed value for platinum. The results are:

$Fe^{\cdot\cdot}$ . .	67·5	48·5	36	16	1 per cent.
$Fe^{\cdot\cdot\cdot}$ . .	32·5	51·5	64	84	99 ,, ,,
E . .	0·334	0·366	0·378	0·401	0·480 volt.

G. Tammann also made some observations with magnetite containing some hæmatite, and found for the cell $Fe_3O_4 \mid 4N\text{-}ZnSO_4 \mid Zn$, 1·20 volt; $Fe_3O_4 \mid PbCl_2$ sat. soln. $\mid Pb$, 0·60 volt; $Fe_3O_4 \mid 2N\text{-}CuSO_4 \mid Cu$, 0·14 volt; and $Fe_3O_4 \mid Ag_2SO_4$ sat. soln.$\mid Ag$, 0·03 volt. H. Bäckström observed that while the electrical conductivity of magnetite is isotropic, different **electrode potentials** are developed by the contact of different faces of a crystal with electrolytes, and consequently different faces of the crystal in the electrolyte set up a difference of potential and an electric current results. A. von Hansen also found that an octahedral face is negative towards a cubic face. Irregular results were obtained using different concentrations of hydrochloric or sulphuric acid. W. D. Treadwell found the potential, *E* volt, of ferrous oxide against ferrosic oxide from measurements of the cell $FeO,Fe_3O_4 \mid$ electrolyte $\mid O_2$, to be:

	875°	950°	970°	980°	1000°	1010°	1020°	1090°	1100°
E . .	0·967	0·898	0·915	0·927	0·897	0·880	0·890	0·856	0·838

E. Baur and co-workers, working with the cell $FeO,Fe_3O_4 \mid$ electrolyte $\mid CuO,Cu_2O$, obtained $E=0{\cdot}9$ volt at 900°. Calculations based on equilibrium data in an atm. of hydrogen and steam were made by E. Baur and A. Glässner, G. Chaudron, G. Preuner, W. D. Treadwell, and L. Wöhler and R. Günther. R. C. Wells measured the electrode potential of magnetite in *N*-soln. of sulphuric acid, and found 0·91 volt; potassium chloride, 0·40 volt; and sodium hydroxide, −0·22 volt; P. Béchtereff found the potential of magnetite against molten sodium hydroxide to be the same as that of iron, cobalt, nickel, platinum, gold, silver, copper, and constantan between 330° and 650°. This is taken to mean that the observed result is a gas potential and not the potential of ferrosic oxide. E. Renschler studied the behaviour of ferrosic oxide electrodes and found that as a cathode the oxide behaves similarly to iron, but as anode it is characterized by a lower potential. In the electrolysis of ammonium sulphate and sodium chlorate—for the preparation of persulphate or perchlorate—the yields with the ferrosic oxide anode are very small, and in this respect the behaviour resembles that of platinized platinum; and in the electrolysis of a soln. of ammonium sulphate, the electrode is attacked. In the electrolysis of iodide soln., the behaviour is very like that of platinum; with bromide soln., the yield is less than with platinum; and with chloride soln., without a diaphragm, the yield is smaller than with platinum, and falls below 66 per cent. If the electrodes are smooth, the yields are higher; and if rough, the electrode is strongly attacked and the current efficiency is reduced. The oxygen over-voltage measured by H. C. Howard is in normal sodium chlorate soln. 0·4 to 0·6 volt less than is the case with platinum. B. la Croix von Langenheim said that in a 16 per cent. soln. of sodium hydroxide, a magnetite cathode is slowly reduced. Observations were made by P. P. Fedotéeff, and K. Elbs.

Magnetite shows the property of ferromagnetism to a marked degree *vide supra*, iron. A. L. Hölz[14] stated that in a strong magnetic field, the ratio of the permanent **magnetism** of magnetite to that of glass-hard steel is as 1·5 : 1; and A. Abt gave 1·82 : 1 to 2·21 : 1. Observations were made by C. B. Greiss, F. F. Hornstein, and G. A. Kenngott. P. Weiss found the saturation intensity of magnetization ranges from 435 to 469 gauss. H. E. J. G. du Bois obtained a limit to the intensity of magnetization, I=350, showing that saturation is complete when the magnetizing force H=1·500. V. Quittner gave I_∞=482 gauss; P. D. Foote, 290 gauss; S. Loria, 360 gauss. For artificial ferrosic oxide, P. Weiss gave 476·5 gauss; S. Loria, 450 gauss; and A. Droz, 455 gauss. A. Droz, and P. Weiss obtained different values for the saturation value of the intensity of magnetization with crystals sectioned about different axes of symmetry. P. Weiss and H. K. Onnes found the saturation intensity at −257·2° to be 90·75 gauss; and at −253°, 95·9 gauss. The subject was investigated by P. Weiss, W. Kopp, W. Lenz, and W. H. Keesom. L. A. Welo found that the remanent magnetism increases under press., so that at 1200 atm. and a field-strength of 40 gauss, there is a 45 to 50 per cent. increase. H. E. J. G. du Bois also observed:

Magnetic force, H	500	1000	2000	1200
Intensity of magnetization, I . .	325	345	350	350
Induction, B	8361	9041	10,084	20,084
Permeability μ	16·7	9·0	5·0	1·7

E. Wilson and E. F. Herroun observed that with a field-strength of H=55 gauss, the maximum permeability, μ=35; the coercive force, H_c=20·7 gauss; and the remanent induction, B_r=1168 gauss; for compressed powder, the permeability, μ, attains a maximum of 9·16 with H=103. C. W. Heaps found the permeability of a magnetite crystal ranged between 1·2 to 1·38 as the field-strength was raised to 5000 gauss. Magnetite with a high maximum susceptibility may give a smaller remanence than samples with a smaller maximum susceptibility. Observations were made by A. Abt, E. Becquerel, J. C. Stearns, G. R. Wait, L. F. Bley, J. Donau, P. Elias, C. B. Greiss, and A. L. Holz. For the hysteresis loops of magnetite, by R. B. Sosman and E. Posnjak, *vide* Fig. 526. The relation between the remanence of remanent magnetism, B, and the field strength, H, is illustrated by Fig. 516, with that for nickel for comparison. C. W. Heaps studied the Barhausen effect; and T. D. Yensen, the magnetization of thin films.

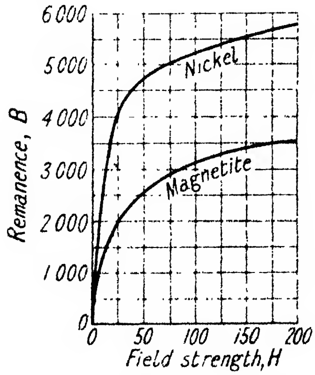


FIG. 516.—Field-strength—Remanence Curve for Magnetite.

M. C. Bandy supposed that loadstone has been formed by lightning striking outcrops of magnetite ore. H. Forestier observed that the remanence of natural and artificial magnetite is increased after heating and cooling. P. Erman, M. Faraday, W. M. Mordey, and E. Colardeau made some observations on this subject. J. Kunz discussed the magnetic moment of the elementary magnets. G. R. Wait studied the permeability of magnetite in alternating fields of high frequency; V. Quittner, the magnetic hysteresis, and A. Perrier, the effect of temp. on the hysteresis. The relation between the magnetization and the strength of the field was measured by C. Benedicks, G. G. Bring, and H. Nathorst. R. Chevallier observed that with artificial ferrosic oxide, the intensity of magnetization, *I* gauss:

Field-strength, *H*		0	60	120	180	195	gauss
I	increasing, *H*	0	3	7·7	12·6	13·8	,,
	decreasing, *H*	2·3	6·2	9·9	13·2	13·8	,,

F. Stutzer and co-workers gave $75\cdot00\times10^{-6}$ to $97\cdot35\times10^{-6}$ for the coeff. of magnetization of magnetite; E. Wilson and E. F. Herroun found the susceptibility to be 300×10^{-6} to 615×10^{-6}; and W. R. Crane, 37×10^{-6}. H. Wilde attributed the apparent increase in magnetism on raising the temp., to a surface resistance which disappears on raising the temp., on increasing the magnetizing force, or on diminishing the mass of the substance. The magnetic susceptibility of magnetite is dependent on the field-strength, *H*, and E. Wilson and E. F. Herroun observed that the change is greater the larger the susceptibility. E. Holm investigated this subject; and W. Sucksmith, and J. W. Fisher studied the gyromagnetic effect obtained when the magnetization of magnetite is conducted in a rotary field. M. Faraday, P. Erman, and E. Becquerel observed that at a red-heat, the magnetism of magnetite is lost, but is restored again on cooling. F. Rinne showed that the magnetizability of magnetite gradually rises with increasing temp. and then suddenly falls; whilst on cooling, the phenomena are reversed. P. Curie found that there is an inversion in the magnetic susceptibility of magnetite at about 535°; E. H. Barton and W. Williams said 557°; F. Rinne, 575°; H. E. J. G. du Bois, 555°; J. Huggett and G. Chaudron, 570°; S. Veil, 550°; P. Weiss and P. N. Beck, 580° and 588°; P. Weiss, A. Piccard and A. Carrard, 593·5°; P. Weiss, A. Piccard and A. Carrard, 593°; Chemische Fabrik Griesheim-Elektron, 585°; P. Weiss and G. Foëx, 581°; S. Wologdine, 525°; G. E. Allan, 550°; T. Ishiwara 580° for the natural and 510° for artificial magnetite; and H. Takagi, 515° for natural material. R. Forrer studied the subject. K. Honda and T. Sone's value, 690°, refers to an artificial sample with much ferric oxide; for natural magnetite they gave 580°. The actual temp. is influenced by the magnitude of the induction or of the magnetizing force. Attempts have been made to detect discontinuities in other physical properties at the Curie point. P. Chévenard observed a break in the thermal expansion curve of magnetite at about 570°, and G. Chaudron and H. Forestier, a similar one with ferrosic oxide; G. E. Allan observed a thermal effect accompanying the magnetic transformation; and J. Königsberger and K. Schilling found a break in the electrical conductivity curve of magnetite near 530°. S. Veil also made observations on this subject; L. F. Bates, J. R. Ashworth, and L. A. Welo and O. Baudisch studied the relation between the Curie point and the intensity of magnetization; and G. R. Wait, the permeability in oscillating fields.

The reciprocal of the magnetic susceptibility, χ, when plotted against the absolute temp., T, usually gives a straight line, $C=\chi(T-\theta)$, where θ denotes the *Curie point*, or the temp. of magnetic inversion; C is called the *Curie constant*. P. Curie found that between 850° and 1360°, the magnetic susceptibility, χ, decreases regularly with a rise of temp., $T°$, so that $\chi\times10^6=28,000T^{-1}$. According to P. Weiss and G. Foëx, when the results are plotted, the curve consists of a series of four straight lines:

	581° to 622°	622° to 680°	680° to 710°	710° to 770°	770° to 900°	900° to 1360°
Curie point .	581	558	—	433	194	0
Curie constant .	0·00445	0·00682	—	0·0105	0·0180	0·028

P. Weiss argued that wherever the line changed direction, a new form of magnetite is responsible for some other physical change. No other investigator has noticed changes in other physical properties corresponding with those for the magnetic change reported by P. Weiss. P. Curie's curve shows no sharp change in direction. The following is a selection from the data :

	−138°	−21·5°	19°	215°	610°	627°	656°	913°	1332°
$\chi \times 10^6$	22·1	36·8	37·6	37·0	50·2	45·0	31·0	13·8	10·6

By the method of treatment, the samples must have been converted into ferric oxide before the measurement was made. The critical temp. of inversion is not sharply defined. Observations were also made by H. Takagi. L. H. Adams and J. W. Green found that pressure has no perceptible influence on the critical temp. The passage from the ferromagnetic to the paramagnetic state was formerly thought to be accompanied by a sharp discontinuity. The results of P. Weiss and P. N. Beck show that the change is not abrupt. Actually, the intensity does not fall to zero, but rather to a low, nearly constant value. The susceptibility is reversible ; but between 920° and 680°, the susceptibility on the cooling curve is rather less than on the heating curve. C. H. Li found that the magnetic properties changed abruptly at −160°, the temp. at which R. W. Miller observed that the thermal capacity suddenly increases to a maximum.

J. Hugget and G. Chaudron found the transformation point on the temperature-magnetization curve of magnetite occurs at 570°, there are anomalies when the magnetite is heated in air owing to superficial oxidation. There is the irreversible Curie point at 570°. If magnetite be heated in air at 330° it forms an unstable, strongly magnetic compound with a composition between Fe_2O_3 and Fe_3O_4. Martite and oligist are unstable at 570° and 675°. K. Renger observed that the effect of a magnetic field of H gauss on the transformation temp. θ, is $\theta = 563 + 0{\cdot}08H$, and P. Weiss gave

H . . .	0	1438	2903	5094	8144	10,430	11,930
θ . . .	563°	566°	567·5°	569°	570·4°	571°	572°

R. Forrer observed that, at −153°, magnetite has a singular change of state which manifests itself by a discontinuous variation in magnetization due to an abrupt decrease in the coeff. of magnetic hardness. It does not affect the magnetic moment, or the law of thermal variation of saturation. T. Okamura studied the phenomenon at low temp. W. Sucksmith and H. H. Potter discussed the P. Weiss relation between the sp. ht. and the magnetization of magnetite ; and J. R. Ashworth, the application of an equation of state—*vide* iron. K. T. Compton and E. A. Trousdale, and A. H. Compton and O. Rognley showed that no change in the structure of single crystals occurs in a strong magnetic field. E. Wedekind, and E. Wilson and E. F. Herroun studied this subject ; and P. Weiss the residual magnetism. Y. Kato and T. Takei made magnets of iron oxide.

S. Hilpert and J. Beyer prepared mixtures of ferrosic and ferrous oxides, which were non-magnetic, by reducing ferric oxide in a stream of hydrogen and steam at 400° to 1100°. No crystalline structure was observed in the black masses. The higher the proportion of contained ferrous oxide, the more rapid the dissolution in acids. The magnetic susceptibility fell to zero with proportions of ferrous oxide approximating 74 per cent. of ferrous oxide. It is considered that when all the ferrosic oxide is in solid soln. in the ferrous oxide, it loses its ferromagnetism. This is in agreement with the failure of the X-radiograms to detect ferrosic oxide in the mixture. The bend in the curve with between 20 and 25 per cent., say 21·5 per cent., of ferrous oxide probably represents a sat. solid soln. of ferrous in ferrosic oxide. The complex $2FeO.Fe_2O_3$ occurs at 23·6 per cent. of ferrous oxide. W. Borchers found that the ferrous and cuprous sulphides in copper mattes reduces the ferric oxide as far as $2FeO.Fe_2O_3$. A solid soln. with 74 per cent. of ferrous oxide is hence taken to represent a sat. soln. of Fe_3O_4 in FeO at about 1000°. The kink in the curve with 61 per cent. of FeO, corresponding with $6FeO.Fe_2O_3$, may have no significance. J. Huggett and G. Chaudron partially reduced ferric oxide in hydrogen, and homogenized the samples by heating them for 30 hrs. at 650°. The products containing ferrous oxide split up with ferrosic oxide and iron near 300° ; at 575°, a magnetic anomaly occurred owing to the Curie point of magnetite ; at about 600°, the decomposition components of the ferrous oxide recombined so that another magnetic anomaly occurred. P. Weiss and G. Foëx observed a faint trace of magnetism in artificial ferrosic oxide up to 678°, but R. B. Sosman attributed this to the presence of a little magnetic ferric oxide produced by the oxidation of the magnetite. H. Takagi did not obtain a discontinuity in some samples of magnetite when heated between 600° and 900°. H. Sachse studied the magnetizability of ferrosic oxide dispersed in alumina, silica, or strontium sulphate.

Lord Kelvin (W. Thomson) found that crystals belonging to the cubic system are magnetically isotropic, but this is not the case with magnetite, for the crystals are magnetically anisotropic. According to P. Weiss, the magnetic permeability of magnetization varies with the inclination of the magnetizing field to the crystallographic axis ; thus, the results with rods cut parallel to the axes (111), (110), and (100), or parallel to the cube, octahedron, and rhombic dodecahedron faces, expressed in c.g.s. units, for an external field *H*, a total magnetism *I*, and a remanence B_r, are :

(111)	*H* . .	22·9	43·3	79·1	146·2	239·3	326·8	436·0
	I . .	172·4	263·8	347·0	399·0	414·3	418·2	422·2
	B . .	49·6	61·0	70·5	75·9	75·6	75·6	75·2
(110)	*H* . .	19·7	38·4	75·0	144·5	238·1	316·5	499·6
	I . .	162·2	249·3	323·0	376·6	392·1	403·8	410·1
	B . .	40·5	50·8	58·6	63·4	63·7	64·6	65·6
(100)	*H* . .	18·1	39·8	78·4	151·9	251·7	342·4	435·6
	I . .	174·1	233·4	271·3	307·5	340·6	365·2	387·0
	B . .	61·6	74·0	83·6	89·3	89·7	90·6	89·3

These results show that magnetite is magnetically anisotropic. The ælotropic magnetic properties of magnetite show that the theories which regard magnetization as resulting from the orientation of particles of fixed magnetic moment are not sufficient to explain the magnetization of crystalline bodies. The subject was discussed by V. Quittner, J. Beckenkamp, W. Voigt, J. Kunz, S. Sano, C. H. Li, W. Peddie, F. Wallerant, K. Honda and J. Okubo, G. R. Wait, A. Droz, and B. Bavink. J. C. Stearns tried unsuccessfully to detect a change in the intensity of the X-ray beam reflected from a crystal of magnetite when under the influence of a magnetic field. He concluded that electrons revolving in orbits within the atom cannot account for ferromagnetism.

C. W. Heaps and J. Taylor observed the Barkhausen effect with dark-coloured magnetite showing well-developed cleavage planes, but not with specimens showing rounded corners, and uneven faces. The subject was discussed by J. Beckenkamp, and W. Voigt. Observations were also made by B. Bavink, F. Rinne, A. Droz, V. Quittner, E. Wilson and E. F. Herroun, and E. Wilson—*vide supra*, the formation of magnetite in bricks, etc. For the hysteresis loop, see Fig. 291.

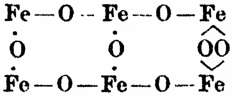
E. Wilson observed that with tensile stresses up to 130 kgrms. per sq. mm. in a given field, the susceptibility of magnetite at first increases with stress, decreases, and then it exhibits a reversal as in the case of iron. The magnetic force at which the percentage increase in permeability has a maximum value is less than the force for which the maximum susceptibility occurs. I. Kruckenberg observed no proportionality between the change in length, *dl*/*l*, of magnetite and the permeability. According to K. Yamada, the coercive force of magnetite is greater than that of soft iron ; and the intensity of magnetization is about half that of nickel. The hysteresis resembles that of iron in weak fields. The energy dissipated during a cycle for $H=+288$ is about 54,400 ergs. The change of length in weak fields is slow, but goes on increasing at a steady rate, so that the maximum elongation was not attained with several hundred gauss.

C. W. Heaps found that the magnetostriction of an octahedral crystal of magnetite along the three axes, with field-strengths, H, up to 5000 gauss, gave curves which were all similar in form—first convex towards the H-axis, and then concave, tending towards a maximum near 5000 gauss. With a longitudinal field of 5000 gauss, the diagonal axis expands 30×10^{-4} per cent., the trigonal axis, 12×10^{-4} per cent.; and the tetragonal axis contracts 4×10^{-4} per cent. With an equal transverse field, the percentage changes are a contraction of the diagonal axis of 44×10^{-4} per cent., a contraction of the trigonal axis of 28×10^{-4} per cent., and an expansion of the tetragonal axis of 4×10^{-4} per cent. respectively. The effect perpendicular to a plane is independent of the direction of the field in that plane. No departure from cubic symmetry was established. The magnetostriction curve is supposed to be the resultant of two superposed effects, and the Villari reversal probably a consequence of the heterogeneous crystal arrangement in the iron. F. Gross said that since ferrosic oxide is the only magnetic oxide of iron, it is not improbable that the magnetic properties of iron in general are due to the presence of the atomic group:

A. Krause and J. Tulecki attributed the magnetic properties to the presence of the group:

$$--\mathrm{Fe}{<}{}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Fe}--$$

and represented the constitution (*vide* γ—Fe_2O_3):



Magnetite crystals are sometimes magnetically polarized, and they form strong permanent magnets; indeed, the history of magnetism is closely associated with the discovery of the lodestone by the ancients. On the other hand, most natural magnetite is not polarized; and the cause is unknown. The natural magnetite which possesses polarity like a magnetic needle, or magnet, is called *loadstone*. There are all gradations between ordinary magnetite with little or no polarity, and that in which a fragment will pick up large iron nails. W. H. Newhouse and W. H. Callahan, and W. H. Newhouse suggested the loadstone is generally formed from oxidized magnetite—ferromagnetic ferric oxide—which possesses a higher remanence than ordinary magnetite—ferro-ferric oxide. The polarity is further supposed to have been induced by a concentration of the earth's field chiefly at the ends of an ore body, but occasionally at points within magnetite ore bodies due to irregularities of mineralization or the faulting. J. W. Gruner does not agree with this conclusion, and added that no brownish oxidized ore was observed by himself, or by P. Ramdohr, or F. F. Osborne. The polar magnetism of magnetite was studied by T. L. Walker, and F. Hornstein. W. Sucksmith found the ratio for the gyromagnetic effect to be about 0·495—*vide supra*, the magnetism of iron.

As previously indicated, S. Hilpert assumed that the magnetic qualities of magnetite, regarded as ferrous ferrite, $FeO.Fe_2O_3$, and of other ferrites are dependent on the presence of the acid anhydride, Fe_2O_3. E. Take assumed that the magnetic properties of Heusler's non-ferrous alloys depend on the spacing and arrangement of the atoms; J. Forrest, and R. B. Sosman also assumed that with magnetite, ferromagnetic ferric oxide, and iron, the magnetic properties are bound up with the spacing and arrangement of the iron atoms without regard to the other atoms present. The argument is mainly based on the inversion temp. at which the magnetism in all these substances is lost. A. H. Compton and O. Rognley observed that magnetization and demagnetization have no effect on the crystal structure of magnetite. J. R. Ashworth studied the relations between the thermal and magnetic constants; and K. Gosh, the relation between the electrical conductivity and magnetism.

The chemical properties of ferrosic oxide.—The transformation of magnetite in nature into hæmatite, martite, etc., has been discussed by J. Roth,[15] W. L. Uglow and F. F. Osborne, K. C. Berz, P. Jeremeieff, A. Lacroix, B. Stälhare and T. Malmberg, J. F. Williams, W. H. Newhouse, W. H. Newhouse and W. H. Callahan, L. H. Twenhofel, A. Reuss, and C. R. van Hise. The general characteristic of ferrosic oxide prepared at high temp. is its resistance to many chemical agents, and accordingly, W. G. Günther [16] proposed using it in chemical plants for resisting chemical reagents. According to J. L. Gay Lussac, magnetite is reduced to metal by **hydrogen** at all temp. above 400°, and generally at the same temp. as water is decomposed by iron, a reaction studied by H. V. Regnault, H. Fleissner and F. Duftschmid, W. Müller, and G. Gallo. According to F. Gläser, the reduction by hydrogen begins at about 305°. P. H. Emmett and J. F. Shultz gave for the equilibrium constant, K, of the reaction: $Fe_3O_4+H_2 \rightleftharpoons 3FeO+H_2O$, $K=p_{H_2O}/p_{H_2}=1{\cdot}18$ at 700°, and 2·37 at 800°. For W. Biltz and H. Müller's observations on the ratios $Fe_3O_4 : FeO$, and Fe_3O_4/Fe, *vide supra*, ferrous oxide. The reversible reaction with hydrogen has been previously discussed—and *vide infra*, ferric oxide. M. Tigerschiöld stated that above 800°, ferrosic oxide is more readily reduced by hydrogen, and below 800°, by carbon monoxide. A. de Hemptinne found that ferrosic oxide is reduced in an atm. of dry hydrogen in an electric discharge when the oxide is in contact with one of the electrodes. K. Hofmann emphasized the importance of surface phenomena in the reduction. The reduction of molten iron oxide by hydrogen was studied by J. Reese, M. Boistel, C. Adams, C. Kröger, and S. L. Madorsky; and P. H. Emmett and J. F. Shultz studied the system: $Fe_3O_4-H_2-Fe-H_2O$.

According to H. Moissan, ferrosic oxide prepared below 500° oxidizes to ferric oxide when heated to redness in **air**, but the oxide prepared at a high temp. is not so readily changed to ferric oxide. R. Ruer and M. Nakamoto found that ferrosic oxide at 1370° is completely converted to ferric oxide, but at 1400°, the ferric oxide begins to decompose. E. Greulich said that the upper limit is 1380°. K. Honda and T. Sone found that at 1100°, magnetite in air is converted into ferric oxide; and the change is completed at 1300°. They added that below 1300°, hæmatite is more stable than magnetite. The peculiar ferromagnetic properties of ferric oxide prepared by the oxidation of magnetite have been discussed by R. B. Sosman and E. Posnjek—*vide infra*, ferric oxide. G. Friedel found that if heated in air, magnetite can be converted into martite without losing its form. The temp. at which oxidation begins depends on the grain-size of the powder, and, as shown by F. Gläser, and H. Abraham and R. Planiol, the powder prepared at a low temp. may be pyrophoric. O. Mügge found that both the natural and artificial oxide are oxidized when heated for a long time. E. Greulich observed that when magnetite is heated in air, oxidation begins at about 400°, but the ferric oxide acts as a protective skin which retards the progress of the reaction, so that even at 1000°, only 95·6 per cent. was oxidized in 100 hrs. Above that, the rate of oxidation increases more rapidly, so that it is nearly complete in 2 hrs. at 1100°, and in 1 hr. at 1200°. Above 1380° no further reaction can occur, and at 1450° the product is no more oxidized than the original magnetite. This shows that ferric oxide breaks down into ferrosic oxide at these elevated temp. At 1500° to 1550°, the product had an excess of ferrous oxide, showing that the magnetite decomposes into ferrous oxide. W. Eitel discussed the reaction $2Fe_3O_4+\frac{1}{2}O_2 \rightleftharpoons 3Fe_2O_3$. J. W. Gruner observed that oxidation begins at 150° on the octahedral faces of the crystals. G. Gilbert supposed that magnetite may form ferric oxide by surface oxidation in hot, dry climates, but more usually, hydrated ferric oxide is formed. The subject was discussed by T. M. Broderick, J. W. Gruner, R. B. Sosman and J. C. Hostetter, L. H. Twenhofel, and P. A. Wagner. L. H. Twenhofel found that in the first oxidation of magnetite, the oxygen atoms are irregularly spaced within the magnetite lattice. A. Bickel and C. van Eweyk observed that a sample of magnetic oxide of iron retained its power to give the benzidine reaction after keeping in conductivity water for 5 months, another sample (ferrosic carbonate) which was originally non-magnetic but gave a powerful benzidine reaction, with similar treatment became unable to give the reaction.

A. Gorgeu found that boiling **water** does not attack ferrosic oxide, nor was any attack observed by steam at a bright red-heat—*vide supra*, reactions in the blast-furnace. R. Müller found that water, sat. with carbon dioxide at 3·5 atm. press., dissolved from two samples of magnetite respectively 0·307 per cent. and 2·428 per cent. of ferrous oxide in 50 days. J. W. Gruner found that in 77 days, peat-water dissolved 31 parts of iron per million from powdered magnetite; and in 182 days, 41 parts. H. D. Rankin converted magnetite into a soluble form by heating it to redness, and afterwards treating it under press. with alkali-lye.

H. Moissan found that **fluorine** does not act on magnetite in the cold, but at a dull red-heat, a white fluoride is formed. H. Davy observed that **chlorine** reacts on magnetite very much more quickly than it does on ferric oxide (*q.v.*) at a red-heat; but W. Kangro and R. Flügge did not agree. They observed that at 1000°, 99·4 per cent. of iron was removed as ferric chloride in 270 hrs. L. Mathesius found that an aq. soln. of **bromine** does not act on magnetite; and H. Moissan said that the oxide prepared by the reduction process does not decolorize an aq. soln. of **iodine** provided metallic iron is absent. E. Zalinsky found that an excess of **hydrofluoric acid**, acting for 20 hrs., dissolved magnetite completely; and K. F. Stahl added that magnetite is more readily dissolved by hydrofluoric acid than it is by any other acid. E. Deussen said that it requires 5 to 10 hrs. to dissolve hammer-slag, and if a longer time be allowed, less iron is dissolved owing to the formation of a sparingly-soluble oxyfluoride. The powdered mineral is also completely soluble in **hydrochloric acid**, and J. J. Berzelius said that if the mineral be in excess, and the acid dilute, ferrous oxide passes into soln., and red ferric oxide remains undissolved. According to A. Gorgeu, magnetite is not attacked by the dil. acid (1 : 10), but it is slowly attacked by the conc. acid; when some of the solid soln. approximating Fe_3O_4 are treated with hydrochloric acid, some ferrous oxide dissolves and ferric oxide remains. J. Liebig and F. Wöhler, and V. Neuwirth noted that magnetite does dissolve in hydrochloric acid; according to G. Gilbert, it dissolves more readily in a hot hydrochloric acid soln. of stannous chloride; and A. Damour noted that the presence of potassium iodide accelerates the rate of dissolution. According to K. A. Hofmann and K. Ritter, magnetite is not attacked by a soln. of **calcium hypochlorite.** E. Müller discussed the use of magnetite electrodes in preparing bleaching liquor by electrolysis. F. Leteur showed that magnetite is readily dissolved by heating it with conc. hydrochloric acid, sp. gr. 1·18, in a closed vessel at 65° to 70°. F. Becke studied the etching of magnetite with this acid.

J. J. Berzelius, and H. Rose observed that when the mineral is heated with **sulphur**, sulphur dioxide, and ferrous sulphide are formed. A. Gautier found that at a white-heat in a current of **hydrogen sulphide**, ferrous sulphide, hydrogen, sulphur dioxide, and a little sulphur trioxide are formed; and C. Doelter found that when magnetite is heated with an aq. soln. of hydrogen sulphide at 80° to 90°, some pyrite is formed. D. L. Hammick observed that there is no appreciable reaction with **sulphur dioxide** at a red-heat. According to H. Lotz, when a plate of magnetite is exposed to the action of moist air charged with 1 per cent. of sulphur dioxide and 19 per cent. of carbon dioxide, and the plate washed with water, the ferrous oxide was most vigorously attacked:

	MgO	CuO	MnO	FeO	Al_2O_3	Fe_2O_3
Magnetite contained .	2·47	1·64	9·32	24·24	8·47	53·93 per cent.
Water contained .	0·0728	0·0208	0·0008	0·3395	0·0232	0·0052

F. Becke studied the etching of magnetite with **sulphuric acid.** O. Mügge found that a crystal of magnetite is only slightly attacked by fused **potassium hydrosulphate,** near its m.p., but at a higher temp., the mineral is vigorously attacked. F. Becke studied the etching of the crystals with this salt.

U. Sborgi and E. Gagliardo found that **boron nitride** reacts with ferrosic oxide at 750°, forming nitric oxide. J. J. Berzelius noted the formation of nitrogenized iron when ferrosic oxide is heated in dry **ammonia;** and he also observed no change occurs when hammer-slag is located with an aq. soln. of ammonium chloride. A. T. Larson and A. P. Brooks observed that ferrosic oxide is a good catalyst for the synthesis of ammonia; and A. K. Brewer showed that photochemically, the catalyst has the same photoelectric threshold as electrolytic iron. F. Emich found that **nitric oxide** converts heated ferrosic oxide to ferric oxide.

G. Tammann and G. Bätz observed that precipitated **silica** begins to react with ferrosic oxide at 800°, and with quartz at 950°. As indicated in connection with the allotropism of ferrosic oxide, H. Moissan showed that the high temp. form of this oxide is almost insoluble in boiling, conc. **nitric acid,** while the low temp. form is soluble in the conc. acid but not in dil. acid. A. Gorgeu also found that the dil. acid (1 : 10) scarcely attacks ferrosic oxide until its temp. has been raised nearly to the b.p. The conc. acid attacks the oxide slowly. H. L. Heathcote said that ferrosic oxide is more soluble in conc. than in dil. nitric acid, for acid of sp. gr. 1·4, 1·3, and 1·15 dissolved respectively 0·02332, 0·01752, and 0·00124 grm. of ferrosic oxide per 10 c.c. of acid. F. Becke studied the etching of magnetite with this acid. A. Gorgeu found that ferrosic oxide is slowly attacked by **aqua regia.** G. Hawley found that only a little magnetite is dissolved by a boiling mixture of equal vols. of conc. nitric acid and a 15 per cent. aq. soln. of sodium chlorate.

According to P. Berthier, when magnetite is heated with **carbon** it is reduced to the metal—*vide supra,* the reactions in the blast-furnace. G. Tammann and A. Sworykin discussed the reaction with carbon. H. H. Meyer found that the reduction of ferrosic oxide by sugar charcoal begins at 760°; with wood charcoal, 900°. Ferrous oxide is formed at 860° with sugar charcoal; at 880° to 920°, with coke; at 690°, with wood charcoal, or at 900° if the wood charcoal has been first heated to 1000° in nitrogen. The reaction was studied by W. Baukloh and R. Durrer. J. Bökmann studied the reaction with **iron carbide:** $Fe_3O_4+3Fe_3C \rightleftharpoons 12Fe+2CO+CO_2$. O. Meyer and W. Eilender studied the reduction of magnetite with **methane.** C. Despretz, B. Stälhane and T. Malmberg, W. Müller, F. Göbel, H. Fleissner and F. Duftschmid, and F. Leplay and A. Laurent noted that **carbon monoxide** reduces red-hot ferrosic oxide to the metallic state, and carbon dioxide is formed, and conversely that red-hot iron is oxidized to ferrosic oxide by carbon dioxide and carbon monoxide is formed. The mean of A. C. Halferdahl's values for the free energy of the reaction $Fe_3O_4+CO=3FeO+CO_2$ is $-265113+79{,}383T$, and the triple point $4FeO=Fe_3O_4+Fe$ is near 572°. The free energy of magnetite at 25° is −241,950 cals. A. Laurent observed that a mixture of equal vols. of **carbon dioxide** and monoxide converts red-hot iron into ferrosic oxide. These balanced reactions have been previously discussed—*vide supra,* ferric oxide. E. K. Riedel studied the reduction of the oxide with water-gas. A. Gorgeu found that ferrosic oxide at a bright red-heat is not attacked by carbon dioxide. C. M. Bouton discussed the reaction with methane. H. Moissan observed that ferrosic oxide is not attacked by **acetic acid** at 8°; and H. C. Bolton found that it is not attacked in a short time by boiling conc. soln. of **citric acid** or **tartaric acid;** but conc. citric acid shows signs of attacking the oxide during 8 days' exposure. F. W. O. de Coninck and A. Raynaud found that at a dull red-heat, ferrosic oxide reacts with **calcium oxalate** to form ferrous oxide, calcium carbonate, and carbon dioxide

L. Kahlenberg and J. W. J. Trautmann studied the reaction with **silicon.** J. Lenarcic found that 1 part of magnetite dissolves in 20 parts by weight of molten **labradorite** at 1220°; and C. Doelter, that fused magnetite magma at 1200° to 1230° did not attack **corundum** and **quartz,** but **olivine, leucite,** and **orthoclase** were corroded. G. Tammann and G. Bätz said that ferrosic oxide does not react with silica until oxygen is given off to form ferrous oxide. J. H. L. Vogt said that continuous series of solid soln. are formed with **spinel** and magnetite with a eutectic on the f.p. curve with 3 per cent. of spinel. P. Ramdohr studied the action of ferrosic oxide on **ilmenite,** $FeTiO_3$.

J. L. Gay Lussac and L. J. Thénard, and J. J. Berzelius found that magnetite is reduced by **sodium** or **potassium** at about 300°, and iron is formed. B. Garre said that the reaction between ferrosic oxide and magnesium begins at 575°, and evolves 710·2 Cals. of heat. R. B. Sosman and J. C. Hostetter found that in contact with **platinum** at 1200°, iron is formed and oxygen is evolved—the iron forms a solid soln. with the platinum. P. Curie did not observe any attack on platinum by ferrosic oxide at a high temp. C. T. Anderson studied the reduction of ferrosic oxide by **iron** at 1350° to 1550°; and V. Shuleikin and X. Solovova, the radiation of heat in the thermite reaction with **aluminium.**

H. Moissan observed that **calcium oxide** at a high temp. converts ferrosic oxide into calcium ferrite; A. Gorgeu, that ferrosic oxide is oxidized by molten **sodium sulphate** without changing its crystalline form; and J. W. Gruner, that 4 months' exposure to molar soln. of **sodium chloride, sodium carbonate,** or **magnesium sulphate** does not change magnetite. For the action on **ferrous sulphide,** *vide infra;* for the action on **manganous sulphide,** *vide* **12.** 64, 21. W. O. Hickok studied the action of **stannous chloride;** H. von Wartenberg and E. Prophet, the action of the oxide on **magnesia;** and H. von Wartenberg and H. J. Reusch, the action of **alumina.**

The solubility relations between **ferrous oxide** and ferrosic oxide have been previously discussed. S. Hilpert and J. Beyer[17] first pointed out the existence of solid soln. of the two oxides. P. P. Fedotéeff and T. N. Petrenko assumed that a continuous series of solid soln. of the two oxides is formed when iron is oxidized by steam between 1000° and 1100°. R. W. G. Wyckoff and E. D. Crittenden observed no evidence in the X-radiograms of the formation of solid soln. of ferrous oxide in ferrosic oxide at ordinary temp.; the elementary cells of ferrous oxide appear to be enlarged a little in the presence of much ferrosic oxide. Under the microscope, the crystals of ferrosic oxide appear to be embedded in a eutectic mixture of ferrosic and probably ferrous oxide. H. Groebler and co-workers observed that the ferrous oxide obtained by reducing ferric oxide in a mixture of equal vols. of carbon monoxide and dioxide at 800° contains 39 per cent. of ferrosic oxide and the lattice dimensions of the ferrous oxide are not altered. This phenomenon is explained in terms of the hypothesis of G. F. Hüttig that the extra oxygen exists as vagabond atoms in the spaces in the lattice. The diagram, Fig. 517, based on the observations of E. D. Eastman and R. M. Evans, R. B. Sosman and J. C. Hostetter, R. Schenck, G. Chaudron, P. van Groningen, L. Wöhler and R. Günther, A. McCance, and A. Matsubara, enables the solubilities of ferrous oxide in ferrosic oxide, and of ferrosic oxide in ferrous oxide, to be tabulated. O. C. Ralston compiled the results of these and various other observers. J. Huggett and G. Chaudron gave 31 for the percentage proportion of Fe_3O_4 in FeO; R. Schenck gave for Fe_3O_4 and FeO, and FeO in Fe_3O_4, respectively 35 and 0 at 700°; E. D. Eastman and R. M. Evans, 32 and 6·35 at 772°; R. Schenck, 32 and 0·75 at 800°; and H. Groebler and P. Oberhoffer, 39 and 5 at 800°; A. Matsubara, 38 and 6·35 at 863°; R. Schenck, 28 and 19 at 950°; S. Hilpert and J. Beyer, 26 and 21·5 at 1000°; A. Matsubara, (51) and 15·7 at 1070°, and 26 and 6·35 at 1175°. The agreement is poor. The relations between ferrous and ferrosic oxides have been summarized in Figs. 20 to 31. The curves for the solubilities of ferrous oxide in ferrosic oxide, and conversely, should approach one another so that in the molten state the two oxides should have unlimited miscibility. The constitutional diagram of C. Benedicks and H. Löfquist, Fig. 486, shows the existence of an invariant point where iron and ferrous and ferrosic oxides can coexist; below that temp., iron and ferrosic oxide are present, and above it, on one side, ferrous oxide and iron are stable, whilst on the other side, ferrous and ferrosic oxides are stable. G. Chaudron, L. Wöhler and R. Günther, and E. D. Eastman and R. M. Evans gave 570° for the temp. of the univariant point; P. van Groningen gave 571°; and J. B. Ferguson, between 526° and 577°. G. Chaudron's magnetic measurements gave between 550° and 580°; G. Chaudron and H. Forestier's dilation measurements, 570°; and M. Tigerschiöld's calculations, based on A. Matsubara's observations, gave 534°.

R. Vogel and E. Martin studied the system: $FeO-Fe_3O_4$. L. B. Pfeil's study of the system: $FeO-Fe_2O_3$ is summarized in Fig. 517. The boundaries of the Fe_2O_3-phase have not been determined, and, as shown by R. B. Sosman and J. C. Hostetter, it is probable that dissociation occurs at high temp. to form magnetite. The solubility of iron in ferric oxide is represented by the *EO*, Fig. 517; *F* occurs near 72·2 per cent. of iron, and 1590°; *G*, at 72·6 per cent. of iron, and 1430°; and *GM* and *FN* indicate a decreasing solubility as far as about 1000°; *H*, at 75 per cent. of iron, and 1430°, represents the maximum solubility of oxygen; *D*, the eutectic of iron and ferrous oxide, at 77·28 per cent. of iron, and 1370°, is in accord with the observations of F. S. Tritton and D. Hanson, and the subject was studied by R. W. G. Wyckoff and E. D. Crittenden, A. McCance, and P. Oberhoffer and K. d'Huart; *I* represents the maximum solubility of iron, in ferrous oxide, and occurs at 76·9 per cent. of iron; *IL*, the solubility curve of iron in ferrous oxide, is vertical because no decrease in solubility could be detected between 1370° and 575°; *HL* represents the solubility of magnetite in ferrous oxide; and *ML*, at 575°, represents the transition curve for all specimens containing the ferrous phase. Specimens cooled rapidly from above 575° are very slowly attacked by conc. hydrochloric acid, and specimens cooled slowly are rapidly attacked by 0·1 per cent. hydrochloric acid. In both cases the ferrous phase is preferentially attacked. In agreement with G. Chaudron, A. Matsubara, and E. D. Eastman, the ferrous phase, in all cases, is unstable at about 575°, and below that temp. decomposes into a eutectoid of iron and ferrosic oxide. P. P. Fedotéeff and T. N. Petrenko made observations on solid soln. of ferric and ferrosic oxides. Unlike R. B. Sosman and J. C. Hostetter, G. Gilbert does not consider that a solid soln. is formed under geological conditions—*vide infra,* ferric oxide.

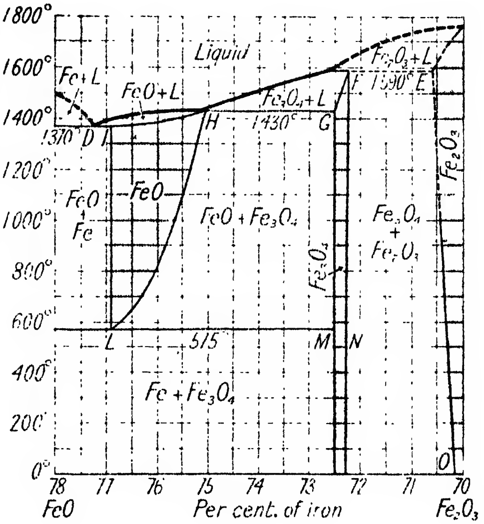
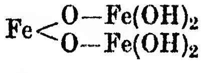


FIG. 517.—The System $FeO-Fe_2O_3$.

H. Wada found that active magnetic oxide administered to rabbits caused the urinary C : N ratio to increase considerably, the administration of the inactive oxide had only a slightly delayed effect.

As indicated above in connection with the preparation of ferrosic oxide, if white hydrated ferrous oxide be exposed to air, for a short time, or if a mixture of soln. of a ferrous and ferric salt be treated with alkali-lye, green **hydrated ferrosic oxide** is formed which, on exposure to air, ultimately passes into rusty brown hydrated ferric oxide. A. Ackermann,[18] E. Deiss and G. Schikorr, H. Ost, A. Payen, and N. J. B. G. Guibourt observed the formation of this hydrate by the action of aerated water on iron, when the hydrated ferrosic oxide appears as an intermediate stage of rusting. E. Ramann said that it is formed as a black film on iron when the metal is dipped in nitric acid or a soln. of some other oxidizing agent—*vide supra,* passivity. J. von Liebig and F. Wöhler, A. Krause, V. Paissakowitsch, O. Faust, and H. Chandra observed its formation in the oxidation of hydrated ferrous oxide, or of a lower oxide than Fe_3O_4, as indicated in connection with the action of air on ferrous hydroxide. M. Roloff, O. Faust, and V. Paissakowitsch noted its formation in the anodic oxidation of iron or ferrous hydroxide, in the presence of alkali-lye, or ammonia. According to J. von Liebig and F. Wöhler, F. Wöhler, H. Abich, J. Mercer, F. J. R. Carulla, C. F. Wülfing, W. Gregory, L. A. Welo and O. Baudisch, and S. Hilpert, if a hydrochloric acid soln. of magnetite, or a mixed soln. of ferrous and ferric salts in the molar proportion 1 : 1, be treated with alkali-lye, and washed, a black hydrated ferrosic oxide is formed. The mixed soln. of ferrous and ferric salts was obtained by mixing suitable proportions of soln. of the two salts; by mixing a certain proportion of nitric acid to the soln. of a ferrous salt—R. Phillips used potassium chlorate as the oxidizing agent, and L. A. Welo and O. Baudisch, potassium nitrate. J. Lefort recommended pouring the soln. of the mixed iron salts into an excess of boiling potash-lye. T. C. Estelle observed that ferrosic oxide can be hydrated by heating it with soda-lye as in the case of ferric oxide (*q.v.*). R. Böttger, and J. Noel recommended treating a soln. of ferrous sulphate with sodium carbonate, washing the precipitate once by decantation, and boiling it with conc. potash-lye. E. Soubeiran obtained by this process a precipitate which gave off carbon dioxide when treated with acids. According to E. Deiss and G. Schikorr, the brown liquid obtained by mixing ferrous and ferric hydroxide soln., rapidly changes to a green colour, and finally turns black with complete precipitation of the colloid. The green substance probably results from the combination of one molecule of ferrous hydroxide with one of ferric hydroxide, but attempts to isolate the compound have been unsuccessful. J. Preuss boiled a mixture of 4 parts of powdered iron and 5 parts of ferric oxide in water. Hydrogen is evolved, and the mixture becomes dark brown and finally black. The product is washed, wrapped in bibulous paper, and dried in hot air. The so-called *Eisenmohr*, *iron-black*, hydrated *æthiops martialis*, or *æthiops martialis Lemeryi*, was produced as a black powder, by L. Lémery, by exposing a mixture of iron filings and an excess of water for a long time in air, and frequently stirring the mixture. The light, black powder is collected from time to time. G. Cavezzali kept the iron filings moist for about 5 days, and obtained the black powder—*l'oxyde de fer noir*—by levigation. P. Sabatier and J. B. Senderens obtained the highly magnetic hydrate by the action of nitric oxide and moist air on iron; and H. Bollenbach and E. Luchmann, by boiling a strongly alkaline soln. of potassium ferricyanide and an excess of ferrous sulphate.

The composition of these products is variable, but in some cases approximates to hydrated ferrosic oxide, $Fe_3O_4.nH_2O$, where n may be 1 to 1·5. According to J. Lefort, when the precipitate is dried over calcium oxide and sulphuric acid, it approximates $Fe_3O_4.H_2O$; J. von Liebig and F. Wöhler gave $3Fe_3O_4.2H_2O$. The composition was discussed by L. A. Welo and O. Baudisch, and the constitution by O. Baudisch and P. Mayer, and E. Deiss and G. Schikorr. They represented the hydroxide formed by the simultaneous precipitation of a mixed soln. of equimolar parts of ferrous and ferrosic hydroxides as a hydrated ferrous hydroferrite: $Fe(OH)_2+Fe(OH)_3=H_2O+HO.Fe.O.Fe(OH)_2$, and in the presence of another molecular proportion of ferric hydroxide: $HO.Fe.O.Fe(OH)_2+Fe(OH)_3=H_2O+(HO)_2Fe.O.Fe.O.Fe(OH)_2$. Consequently, hydrated ferrosic oxide is considered to be a hydrated ferrous ferrite:



$$Fe\begin{matrix}\diagup O-Fe(OH)_2\\ \diagdown O-Fe(OH)_2\end{matrix}$$

According to F. Wöhler, the black hydrate forms, when dried, a brownish-black, brittle, strongly magnetic mass. J. Woost, and O. Faust measured the electrode potential of hydrated ferrosic oxide. J. von Liebig and F. Wöhler, J. Lefort, H. Abich, and N. J. B. G. Guibourt observed that the dry as well as the hydrated ferrosic oxide are equally magnetic; and A. Quartaroli added that the magnetic susceptibility of ferrosic oxide is a hundred times greater than that of the hydrated ferric oxide. L. A. Welo and O. Baudisch found that the magnetic permeability of the powder of sp. gr. 1·32, lies between 2·6 and 3·4; the remanent magnetism is about 8 per cent.; and the coercive force 14 gauss. Other preparations gave 34 per cent. remanent magnetism, and a coercive force of 149 gauss. Hydrated ferrosic oxide contains about 7 per cent. of water, which, according to J. Lefort, is given off at about 90°—*cf.* hydrated ferrous oxide.

J. von Liebig and F. Wöhler observed that hydrated ferrosic oxide is stable in air; whilst J. Lefort found that the moist oxide is slowly oxidized, but the dried oxide is stable. O. Faust, and L. A. Welo and O. Baudisch found that the hydrated oxide is apt to oxidize when it is being washed and dried. S. Hilpert said that it can be almost wholly dehydrated in vacuo over conc. sulphuric acid; and J. Lefort, F. Wöhler, S. Hilpert, and H. Abich added that when it is heated in the absence of air, all the water can be expelled. The precipitated hydrate cannot be dried by heat, because it readily oxidizes in air to form ferric oxide. F. Wöhler added that in the preparation of the hydrate, the iron does not reduce the ferric oxide directly, .but the reduction is effected by the nascent hydrogen produced by the action of the iron on the water. In the words of F. Wöhler, "the ferric oxide does not give up oxygen to the iron, but induces the decomposition of the water by its predisposing affinity for ferrous oxide"; and he added that zinc is not oxidized by boiling it with water and hydrated ferric oxide. The hydrates of alumina and chromic oxide do not oxidize the iron. F. Wöhler, J. Preuss, and J. Lefort observed that hydrated ferrosic oxide forms a yellow soln. when treated with hydrochloric acid; J. Lefort found that it is soluble in hydriodic acid; and in conc. sulphuric acid. S. Hilpert observed that the freshly precipitated hydrate is oxidized under water by persulphates. O. Faust said that the hydrate is not soluble in aq. ammonia in the presence of ammonium salts; E. Ramann, that it is readily soluble in dil. nitric acid, and but sparingly soluble in the conc. acid; and J. Lefort, that it is sparingly soluble in phosphoric acid, in arsenic acid, and in hydrocyanic acid, and soluble in acetic, oxalic, and tartaric acids. Some salts of ferrosic oxide regarded as a base have been reported—*vide infra.*

J. Lefort obtained a precipitate $6FeO.Fe_2O_3.4H_2O$ from a soln. of 6 eq. of ferrous sulphate and 1 eq. of ferric sulphate. O. Hauser, and H. Chandra obtained a hydrated ferrosic oxide by the action of a hot, conc. soln. of potassium hydroxide on ferrosic ammonium carbonate; when the product is dried at 100° its composition is $4FeO.Fe_2O_3.5H_2O$, or $Fe_6O_7.5H_2O$. It is readily acted on by air, yielding hydrated ferric oxide. A. Kaufmann, L. A. Welo and O. Baudisch, F. Haber, and H. Chandra also prepared the hydrated oxide $Fe_8O_{11}.nH_2O$, or $2FeO.3Fe_2O_3.nH_2O$, by adding 22 grms. of a 20 per cent. soln. of ammonia with 21 grms. of crystalline ferrous sulphate dissolved in 200 grms. of water, to the boiling soln. of 2·55 grms. of nitric acid, and boiling for 15 mins.—*vide supra* for the anhydrous oxide. J. Woost measured the potentials of the precipitated hydrates; and P. Fireman, F. J. R. Carulla, C. F. Wülfflng, A. Kaufmann, and F. Haber discussed the application of the hydrated oxide as a black pigment.

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§ 30. Ferric Oxide

> Il fait dans un plus grand nombre de substances terreuses encore la fonction de principe colorant. On pourroit dire, du moins par rapport au règne minéral, que quand la nature prend le pinceau, c'est très-souvent le fer oxydé qui est sur la palette.—R. J. Haüy.

In his *Περί λίθων*, written 325 B.C., Theophrastus referred to **hæmatite,** or rather *αἱματίτης*—from *αἷμα*, blood—a mineral so named because it had the appearance of having been formed of concreted blood ; although, according to A. H. Baumgärtner,[1] and K. C. Schmieder, it is not certain if Theophrastus really referred to that mineral now known as hæmatite. The ancient Greek also described a second kind of hæmatite—*αἱματίτης ξανθή*—which had a yellowish-white colour, and which was probably a yellow ochre or limonite known for a long time as brown hæmatite. In the first century, Dioscorides, in his *Περί ὕλης ἰατρικῆς* (**5**. 143, *c.* 40), also mentioned the same mineral ; and Pliny, in his *Historia naturalis* (**36**. 25, 37, 38, *c.* 77), said that *hæmatites* is a stone of a blood-red colour which, when powdered, yields a tint like that of blood or of saffron. Pliny also said that *schistos* and *hæmatites* have a certain affinity. These varieties were discussed by A. Nies. Virgil, in his Æneid (**10**. 174), thus referred to the deposits of the mineral on the island of Elba—*Ilva . . . insula inexhaustis chalybum generosa metallis.* (Elba, an island distinguished by inexhaustible iron-mines.) Allusions to *hæmatites*, or *Blutstein* and *schistos*, or *Glasköpfe*, were described by G. Agricola, J. L. Bausch, and A. B. de Boodt.

J. G. Wallerius[2] described three varieties of this mineral : (i) *Minera ferri specularis* ; (ii) *Hæmatites ruber* ; and (iii) *Ochra tritura rubra—Speglande Eisen-*

glimmer ; R. J. Haüy, described (i) *Fer oxydé rouge ;* and (ii) *Fer oligiste ;* and J. B. L. Romé de l'Isle, (i) *hématite*, or *terre martiale en stalactites ;* and (ii) *Mine de fer grise* or *fer spéculaire.* Among the older mineralogists, the term hæmatite included fibrous, stalactitic, and other solid, massive varieties as well as limonite and turgite—*vide infra.* J. D. Dana gives the following classification of the main varieties of hæmatite: (i) *Specular hæmatite—specularite*—has a metallic lustre, and the crystals are often glossy or shining—hence the term *specular iron,* or *Eisenglanz,* or *oligiste.* When the structure is foliated, the mineral is called *micaceous hæmatite,* or *Eisenglimmer ;* and if the micaceous hæmatite is soft and unctuous, it is called *Eisenrahm.* The term *hæmatite* is also used for some of the less hydrated natural ferric oxides. W. L. von Eschwege, E. Hussak, F. Zirkel, W. Haidinger, and A. Pelikan called the mineral *specular schist,* or *itabiryte*—or *itabirite*—from Itabira, Brazil—is a schist—*Eisenglimmer-schiefer*—containing much specular hæmatite in grains or scales, or in the micaceous form. (ii) *Compact columnar hæmatite,* or *fibrous hæmatite,* occurs in radiating masses with a submetallic or metallic lustre, and coloured brownish-red to iron-black. It is also called *red hæmatite.* When it occurs in reniform masses with a smooth fracture, it is called *kidney ore, bloodstone, Glaskopf,* and *Eisenniere.* (iii) *Red ochre*—the *Rotheisenocker* of A. G. Werner—is a red, earthy variety. The so-called *reddle* or *ruddle, Röthel* or *Rothstein,* and *red chalk,* are varieties of red ochre mixed with more or less clay. (iv) *Clay ironstone—Thoneisenstein* or *argillaceous hæmatite* is brownish-black, reddish-brown or deep red, and hard; with a submetallic lustre or no lustre. It is mixed with more or less clay or sand. The reddish variety with a jasper-like texture is called *jaspery clay ironstone ;* and the variety occurring in minute, flattened concretions, *lenticular iron ore,* or *fossil ore*—according to A. F. Foerste, the *oolitic ore* from the Clinton group, Ohio—has the remains of bryozoan corals. According to A. Frenzel, A. Breithaupt called a variety of jaspery clay ironstone *jaspohämatite.*

The mineral is very widely diffused in nature ; it was analyzed by C. F. Bucholz,[3] and J. H. Hassenfratz. At first, the proportion of oxygen was regarded as variable —*e.g.*, by A. Breithaupt, R. Kirwan, and A. G. Werner. Analyses were reported by A. Schmidt, J. Loczka, A. Koch, J. Königsberger and O. Reichenheim, A. F. Brainerd, J. Königsberger, F. von Kobell, G. B. Hogenraad, C. F. Rammelsberg, M. Dittrich, R. Rohrer, A. Bergeat, M. F. Heddle, A. J. Moses, F. Zambonini, etc. Artificial preparations were analyzed by C. F. Bucholz, J. L. Gay Lussac, F. Stromeyer, J. J. Berzelius, T. Thomson, J. W. Döbereiner, J. Samsonowicz, and H. St. C. Deville. The results are in agreement with the formula for **ferric oxide,** or *iron sesquioxide,* Fe_2O_3. C. F. Rammelsberg, M. Dittrich, R. Rohrer, A. Schmidt, J. Loczka, and A. Koch found some crystals free from titanic oxide, but several others reported the presence of titanic oxide—J. J. Berzelius, H. Rose, F. von Kobell, L. J. Igelström found in some Swedish samples molybdenum, and thallium ; W. N. Hartley and H. Ramage observed spectroscopically in various samples, Rb, Na, Mn, Cu, Ag, Ca, Pb, Ga, In, Tl, and Ni.

The formation of ferric oxide from the colloidal or hydrated oxide, etc., has been discussed by J. M. van Bemmelen,[4] O. Ruff, H. Wölbling, H. W. Fischer, H. Stremme, L. Hugounenq and J. Loiseleur, F. F. Osborne, A. N. Zavaritsky, M. Godlewicz, G. W. Stose, E. C. Harder and T. C. Chamberlin, J. Johnston and E. D. Williamson, R. B. Sosman, and O. Mügge ; and its formation in nature by the oxidation of siderite, by H. Wölbling.

What might be called the accidental formation of ferric oxide has been noticed under various conditions in chemical and metallurgical processes. E. Mitscherlich [5] observed ferric oxide crystals in the masonry of a pottery oven where salt was used for the glazing; J. Knett, in salt-glazed stoneware—*vide infra, aventurine glazes ;* J. J. Nöggerath, in some clay of the Wieliczka salt-mine after some timber in the vicinity had been burned; F. Kuhlmann, and A. des Cloizeaux, ferric chlorides ; J. F. L. Hausmann, in the masonry of a blast-furnace in the Harz ;

J. B. J. D. Boussingault, in cavities in a furnace at Ria, Pyrénées-Orientales; F. von Hochstetter, A. Arzruni, H. Vater, C. F. Rammelsberg, and K. B. Doss, in the masonry of the sulphate-furnaces of soda-works of Hruschau, Silesia, and of Schönebeck, Magdeburg; and A. Krantz, in the remains of a fire in Hamburg. J. Knett observed that crystals of ferric oxide are formed in salt glazes; and W. G. Fearnsides, when the vapours from salty coals meet atmospheric air in the firebricks, and when damp iron-stone is calcined in the open by salty coal in the interior of the heap: and M. Bellière found the crystals on pottery in a salt-glazing kiln. A deposit of crystalline hæmatite is formed as a sublimate, covering all the surfaces fairly thickly, and cementing together the neighbouring iron-stone blocks just where the vapours from the interior meet the air. H. E. Merwin and J. C. Hostetter observed the formation of hæmatite crystals in the attempt to reduce the amount of iron in glass pots by passing chlorine into the covered pot for several hours at 1100°; where the effluent chlorine and ferric chloride vapour meets the air, crystals of hæmatite are formed. C. E. Munroe observed the formation of hæmatite in the iron pipes alternately carrying hydrogen chloride and air in Deacon's process for chlorine; W. Müller found hæmatite crystals in the residues obtained in the reduction of nitrobenzene to aniline. A. Payen found crystals of specular ferric oxide in the iron-rust of a building reputed to be 700 to 800 years old. The deposit of ferric oxide which appears on glass globes and reflectors of gas lamps is attributed by H. E. Roscoe and L. T. Thorne, H. Morton, and A. Guntz to the decomposition of traces of iron carbonyl in the gas which was formed from the iron used as desulphurizing agent.

The preparation of ferric oxide.—Ferric oxide is the end-product of the oxidation of iron, of its lower oxides or hydroxides, and of many of its salts. In some cases the product is well crystallized, and in other cases it appears as an amorphous powder, although J. A. Hedvall [6] pointed out that the oxide is always crystalline even when it appears as an impalpable powder. A. Arzruni has compiled a bibliography of the modes of preparing artificial crystals of hæmatite. As pointed out by E. L. Schubarth, the early chemists knew that when iron is roasted in air, it forms ferric oxide—*vide supra*. W. Günther, and D. Tassara described technical applications of the process of oxidation: and R. O. Snellenberger found that the presence of ferrous or cupric sulphate accelerates the oxidation of iron by air. P. Sabatier and J. B. Senderens observed that iron reduced by hydrogen at a low temp., when heated to 200°, burns with incandescence, forming ferric oxide; L. W. Winkler, P. P. Budnikoff, and W. Müller made analogous observations. Burnt, pyrophoric iron was found by J. A. Hedvall to yield ferric oxide when it is heated to 1000° in air. According to P. P. Fedotéeff and T. N. Petrenko, the end-product of the oxidation of iron in air at 1000° to 1100° is ferric oxide, and ferrous and ferrosic oxides are formed as intermediate products. C. N. A. de Haldat du Lys stated that steam acts on iron turnings at a red-heat, forming rhombohedral crystals of ferric oxide, but H. V. Regnault obtained ferrosic oxide, not ferric oxide, by this procedure. H. Arctowsky obtained crystals by the action of the vapour of ammonium chloride and air on red-hot iron. J. L. Gay Lussac passed the vapour of nitric acid over red-hot iron and obtained ferric oxide; P. Sabatier and J. B. Senderens found that iron, reduced by hydrogen below 400°, burns vigorously in contact with nitrogen peroxide, forming ferric oxide; and iron reduced at a dull red-heat requires heating to 340° for complete oxidation. F. Emich said that finely-divided iron heated in a current of nitric oxide forms ferric oxide, but at 200°, P. Sabatier and J. B. Senderens said that the product approximates to ferrous oxide. According to L. Hackspill and R. Grandadam, if iron is heated with alkali hydroxide, carbonate, nitrate, or sulphate in vacuo, it is oxidized to ferric oxide. S. Meunier found that large, glistening plates of ferric oxide are produced when an intimate mixture of potassium dichromate, ferrous carbonate, and iron (148; 58 : 56 grms.) is covered with a layer of cryolite and strongly heated in a crucible. L. Ott likewise obtained crystals by cooling a soln. of iron in molten sodium heptamolybdate. A. C. Becquerel covered an iron plate with a paste of lead chromate, then cemented thereon a glass plate so as to prevent the evaporation of water, and found that crystals of both ferric and ferrous oxides are formed as well as iron chromate and lead oxide. C. Monnett, and R. Lorenz obtained the hydrated oxide by using an iron anode in the electrolysis of a soln. of alkali chloride.

The lower oxides, and the hydrated oxides generally furnish ferric oxide when roasted in air. T. W. Richards and G. P. Baxter obtained the oxide of a high degree of purity for their at. wt. determinations by roasting the hydrate precipitated by ammonia from a soln. of the nitrate. Analogous processes were employed by A. F. Benton and P. H. Emmett, A. Simon and T. Schmidt, and C. R. A. Wright and A. P. Luff. C. Monnett also oxidized hydrated ferrous oxide. G. Friedel obtained ferric oxide pseudomorphous with magnetite by heating magnetite for several hours in the oxidizing blowpipe flame. J. Gill, and J. Laux oxidized magnetite. W. C. Hansen and L. T. Brownmiller observed that precipitated ferric oxide changes to hæmatite at 300°. The natural hæmatites contain a deficiency of oxygen eq. to 0·4 to 5·0 per cent. of ferrous oxide. Such a product requires heating in air for a long time before it takes up enough oxygen to approach ferric oxide in composition. E. Greulich found 1 hour's heating at 1200° will suffice, but at 1000°, 100 hrs. are necessary. O. Baudisch dissolved iron, derived from the carbonyl, in hydrochloric acid, and obtained γ-$Fe_2O_3.OH$, by autoxidation in the presence of pyridine. This on dehydration gave what he called *active iron*, γ-Fe_2O_3. C. M. Loane made the active oxide by the low temp. oxidation of pyrophoric iron.

A. Frenzel also heated in a covered crucible the hydrated oxide contaminated with much ammonium chloride and obtained rhombohedral crystals; and E. Millosevich observed the formation of the crystals around furmaroles emitting vapours of iron chloride. T. L. Phipson prepared crystals similar to those found on Vesuvius, by the action of the vapour of ammonium chloride on ferric oxide at a high temp. H. Arctowsky also obtained hæmatite crystals *de la plus grande beauté* in a similar way. W. Bruhns obtained red hexagonal plates by heating in a sealed tube a mixture of water, hydrated ferric oxide mixed with a little ammonium fluoride; C. Doelter, and G. Friedel obtained a similar crystal by working without the ammonium fluoride at 450° to 500°—at about 280°, powdered ferric oxide is formed. P. P. Budnikoff and K. E. Krause found that all the water is expelled from the hydrate at 650°. The preparation of ferric oxide by heating the hydrated oxide in various ways was described by H. and W. Pataky, J. Laux, H. F. Saunders, A. R. Davis, O. S. Neil, W. H. Giles and H. A. Wilson, R. and C. Steinau, G. Lunge and F. M. Lyte, J. Gill, P. Fireman, and J. F. N. Macay; and by heating the hydroxide with water, by N. M. Culloch, and T. Storer and C. J. A. Taylor. R. Willstätter and co-workers prepared ferric hydroxide from ferric ammonium alum, ammonia, and ammonium sulphate in weakly alkaline soln., and dried it by acetone. H. de Sénarmont heated hydrated ferric oxide suspended in water or in a sat. soln. of sodium or calcium chloride for 48 hrs. at 200°, or 8 days at 160° to 180°, and obtained ferric oxide as a red powder, by working at 300°; some tabular crystals were formed. Similar results were obtained by heating a soln. of ferric chloride with sodium or calcium carbonate; and H. N. Stokes, likewise, by heating pyrite or marcasite with alkali-lye. A. Vesterberg obtained pseudomorphs of ferric oxide after ferric sulphate by heating hydrated ferric oxide, prepared as a pseudomorph after ferric sulphate.

J. D. Hedvall prepared ferric oxide of different colours by roasting ferrous sulphide for 4 hrs. at 600°; pyrohotite for 10 hrs. at 700°; and marcasite for 6 hrs. at 700°. Likewise, also, by roasting ferrous sulphate for 9 hrs. at 700°; and ammonium ferrous sulphate for 5 hrs. at 700° and then 3 hrs. at 1000°. A. Gorgeu obtained ferric oxide crystals by heating ferrous or ferric sulphate or a mixture of the two in fused sodium sulphate. J. A. Reavell, and O. S. Neill obtained the oxide for use as a pigment in this way; and E. Mitscherlich, M. Lachaud and

C. Lepierre, and H. O. Hofman and W. Mostowitsch obtained crystals of hæmatite by roasting ferric sulphate, or ammonium ferrous sulphate. V. Rodt found that the hydroxide obtained by oxidizing hydrated ferrous or ferric sulphide is FeO(OH) and free sulphur, no FeS_2 is formed. If the product is heated to 210°, the oxide is ferromagnetic. A. Matthiessen and S. P. Szczepanowsky mixed purified ferrous sulphate and dried sodium sulphate in nearly equal proportions, and introduced it gradually into a red-hot platinum crucible. The mass was kept in fusion until the evolution of sulphur dioxide ceased. The crucible was then allowed to cool, and the fused mass extracted with water. If the temp. be properly regulated, the whole of the iron was left as a very fine crystalline oxide. This oxide was thoroughly washed by decantation in order to remove every trace of the sodium sulphate. C. F. Rammelsberg, and A. Ditte used sodium chloride in place of sodium sulphate. Processes involving the production of iron sulphates and the conversion of the sulphate to ferric oxide, so as, in some cases, to recover the sulphur, were described by R. Phillips, J. C. Heckman, E. A. Parnell, K. Shibata and T. Kohno, O. S. Neill, J. Leech and J. Neale, T. Terreil, C. V. Bacon, R. Vidal, C. A. Weeks, A. J. Moxham, J. McFetridge, M. N. d'Andria, E. F. J. Duclos, and A. Crossley and H. A. Allport. F. Wibel found that a soln. of copper and ferric sulphates, heated to 210° for 10 hrs., furnished scaly crystals of ferric oxide.

The various halides of iron furnish ferric oxide when heated in air or oxygen. J. L. Gay-Lussac heated molten ferrous chloride in a stream of oxygen and found that chlorine was evolved and ferric oxide formed ; with moist air in place of oxygen, some hydrogen chloride was also evolved. J. A. Hedvall found that 4 hrs. at 600°, or 1 hr. at 1000°, sufficed. A. Gorgeu heated ferrous chloride in a partially closed crucible, and obtained ferric oxide at a dull red-heat and ferrosic oxide at a bright red-heat. H. Schulze studied the reaction. A. Duboin prepared red plates of ferric oxide from a molten mixture of ferrous chloride, and potassium hydrofluoride and fluoride. J. A. Hedvall roasted ammonium ferrous chloride 4 hrs. at 600°, and obtained ferric oxide; and E. Stirnemann obtained microscopic, hexagonal plates by heating ferric oxychloride, FeOCl, at 450° in a sealed tube. J. L. Gay Lussac, and H. Schulze also obtained ferric oxide by heating ferric chloride in a current of oxygen; G. F Hüttig and H. Garside washed out any unchanged chloride with alcohol. T. Katsurai and T. Watanabe obtained crystals with the structure of hæmatite by heating a soln. of ferric chloride in an autoclave at 150°. J. L. Gay Lussac prepared crystals of ferric oxide resembling the so-called *sublimed hæmatite* found on the walls of the crater of Vesuvius, by decomposing heated ferric chloride by steam ; he assumed that the mineral is formed in nature by the action of steam on a mixture of sodium chloride and iron sulphate ; and that silicates in the presence of sodium chloride are decomposed by steam. R. Bunsen discussed the products; and E. Stirnemann, the process. M. Coppola, E. A. Parnell, E. W. Wescott, S. J. Levy and G. W. Gray, D. Tyrer, and P. Tschirwinsky also prepared the crystals by J. L. Gay Lussac's process. H. E. Merwin and J. C. Hostetter observed the formation of crystals of hæmatite in the removal of iron from fireclay pots at 1000° to 1100°. H. St. C. Deville found that amorphous ferric oxide becomes crystalline if it is heated to redness in a current of hydrogen chloride ; this is supposed to explain how crystals of ferric oxide have been formed in the cavities of volcanic lava. The habit of the crystals varies with the temp., and W. Bruhns obtained rhombohedral prisms of ferric oxide along with some ferrosic oxide by working at about 960°. P. Hautefeuille and A. Perrey passed a mixture of hydrogen chloride and steam over amorphous ferric oxide and obtained crystals resembling hæmatite. As indicated above, T. L. Phipson, A. Frenzel, G. A. Kenngott, and H. Arctowsky obtained crystals of the oxide by the action of the vapours of ammonium chloride on ferric oxide at a high temp. E. Weinschenk observed some ferric oxide crystals are formed in the synthesis of pyrites from a mixture of ferric oxide, sulphur, and ammonium chloride. A. Daubrée also obtained the crystals by the action of the vapour of ferric chloride on heated quicklime. J. M. van

Bemmelen and E. A. Klobbie thought that calcium ferrite is more likely to be produced. J. Durocher prepared the oxide by heating to redness a mixture of ferrous chloride and ammonium carbonate—some ferrosic oxide is formed at the same time; and M. Kuhara, by the action of soln. of iron chlorides or sulphates on carbonates or silicates at 100°—R. Klemm could not verify this. A. J. Evans, and E. Mitscherlich obtained ferric oxide by heating the nitrate; and A. F. Benton and P. H. Emmett recommended 135 hrs. at 525°; whilst J. A. Hedvall said the reaction is completed in 4 hrs. at 700°, and in 1½ hrs. at 1000°. T. W. Richards and G. P. Baxter said that the product is practically free from gas after being heated many hours at 900°. Dark red, finely powdered ferric oxide was obtained by F. K. Bell and W. A. Patrick by heating the basic nitrate 2 hrs. at 900°, and 1 hr. more at 900° after powdering the product. B. Lambert and J. C. Thomson heated the nitrate in iridium in preference to platinum vessels.

L. Brandt recommended the following process for preparing ferric oxide of a high degree of purity, and for use in the standardization of the soln. used in the volumetric determination of iron. H. Kinder said that the process does not remove phosphorus if it be present in the initial products.

Iron, as free as possible from phosphorus and cobalt, is dissolved in hydrochloric acid, and after dilution and precipitation with hydrogen sulphide, the filtrate is evaporated to a small vol., oxidized with nitric acid, evaporated to dryness with hydrochloric acid, dissolved in water, and extracted with ether, whereby an ethereal soln. of ferric and ferrous chlorides is obtained. The ether is distilled off and the residue, dissolved in a little dil. hydrochloric acid, is completely reduced with sulphur dioxide with the addition of a trace of iodine, and the clear ferrous chloride soln. precipitated with an excess of ammonium oxalate. The ferrous oxalate, after thorough washing, is finally ignited in quartz-glass vessels to constant weight.

G. Schmidt, J. Pelouze and E. Frémy, and F. Duftschmidt produced ferric oxide by roasting ferrous carbonate; and J. A. Hedvall added that 4 hrs. at about 700°, or 2 hrs. at 1000°, may suffice. O. L. Erdmann and R. F. Marchand, and O. Pattenhausen obtained finely divided ferric oxide by heating ferrous oxalate to redness in air or oxygen; A. Vogel recommended 200°; and H. Moissan, a dull red-heat. J. A. Hedvall discussed the effect of time and temp. on the colour of the product—*vide infra*. The process was also examined by T. W. Richards and G. P. Baxter, G. Frebold, H. Kinder, and L. Brandt—*vide supra*. J. M. Eder and E. Valenta recommended roasting ammonium ferric oxalate at 160° to 170°; J. A. Hedvall, ferric acetate for 6 hrs. at 700°, or 2 hrs. at 1000°. V. N. Ipatieff and W. Werchowsky precipitated ferric oxide from soln. of ferric acetate at 350° by hydrogen at 230 atm. press.; and at 400°, by hydrogen at 420 atm. press. L. Brandt, and A. Terreil obtained ferric oxide by roasting potassium ferrocyanide; V. N. Ipatieff and I. N. Kondyreff, by the action of hydrogen under press. on a soln. of ferric thiocyanate; and A. Mittasch and co-workers, by oxidizing iron carbonyl.

G. Rose, C. Doelter, and W. Florence observed that some six-sided plates of ferric oxide were formed when ferric oxide is heated with borax in the oxidizing flame of a blowpipe. C. von Hauer obtained crystals of hæmatite by heating a mixture of powdered ferric oxide and borax, and washing the product with hydrochloric acid. F. Fouqué and A. Michel-Lévy observed that ferric oxide crystals are often formed when ferruginous silicates are melted, but J. H. L. Vogt observed that crystals of ferric oxide are rarely, if ever, found in ordinary furnace slags. According to J. H. L. Vogt, and F. W. Clarke, ferric oxide can separate from silicate magmas only when ferrous compounds are either absent, or present only in subordinate proportions, because ferrous oxide unites with ferric oxide to form magnetite. Hence, magnetite is characteristic of rocks rich in ferromagnesian minerals, while hæmatite occurs chiefly in the more siliceous and felspathic granites, syenites, trachytes, rhyolites, andesites, and phonolites; and it is also found in the crystalline schists; magnetite, however, is the more common pyrogenic mineral. In igneous rocks, as F. W. Clarke has shown, ferrous oxide generally exceeds the ferric oxide—the proportions being roughly as 1·3 : 1·0, and this excess seems to determine the more frequent formation of magnetite. Ferric pyrite, and ferrous pyrrhotite appear to follow the same rule of association. J. Morozewicz also observed that ferric oxide is formed only in silicates with a low proportion of ferrous iron, and is produced by melting acidic rather than basic silicates.

Spangles of what is possibly ferric oxide are frequently developed in pottery glazes highly charged with ferric oxide; and when deliberately produced, the products are called *aventurine glazes*, *sunstone glazes*, etc., though aventurine effects are produced in glazes and glasses in other ways. In the case of glazes highly charged with ferric oxide, the firing temp. and rate of cooling are important factors in producing the effects. The subject was discussed by H. Mäckler, P. Ebell, L. Petrik, etc. The formation of ferric oxide in molten silicates was also examined by F. Angel, C. Doelter, V. Hämmerle, G. Medanich, J. Morozewicz, K. Petrasch, H. H. Reiter, and J. H. L. Vogt. F. Kuhlmann crystallized the oxide from molten calcium chloride; and F. Parmentier, from molten potassium molybdate. H. B. Kosmann described a deposit of strongly magnetic limonite at Harteberg, Silesia; the hydrated ferric oxide contained no ferrous oxide, and he ascribed the ferromagnetic property to a "peculiar molecular grouping." Ferromagnetic hæmatite occurs as a light chocolate-brown powder in the gossan deposit at the Iron Mountain, California, and M. Sarzeau, and J. L. Smith described minerals which may have been ferromagnetic ferric oxide, but the evidence is not clear. P. A. Wagner observed it near Johannesberg, South Africa, and the deposit was described by G. Gilbert. P. A. Wagner proposed to call it **maghemite.** The term *oxymagnite* was suggested by A. N. Winchell. G. Frebold and J. Hesemann believe that the ferromagnetic hæmatite is formed in nature only under a restricted supply of oxygen up to the temp. of 320°, whilst ordinary hæmatite is produced at a lower temp. J. Huggett observed that natural hæmatite and martites always contained some magnetic oxide.

J. Robbins described the preparation of a **ferromagnetic ferric oxide,** Fe_2O_3, by the oxidation of magnetite by heating it in air, or by fusing it with potassium nitrate. He showed that the product was free from ferrous iron, and that it could not in consequence owe its magnetic properties to the presence of ferrosic oxide, as is the case with ordinary magnetic hæmatite. The magnetic variety was also prepared by F. J. Malaguti by the oxidation with potassium chlorate of ferrous hydroxide and other hydrated iron oxide, and subsequent ignition. W. L. Dudley, O. Hauser, and A. Frenzel also obtained it by heating hydrated ferric oxide. A. Liversidge observed that some specimens of iron rust are ferromagnetic even when free from ferrous iron. This product was also obtained by E. F. Herroun and E. Wilson. R. Chevallier heated in air, at 350°, commercial, powdered, black magnetic oxide containing some free iron. H. Abraham and R. Planiol reduced ferric oxide with hydrogen or carbon monoxide at 500°, and obtained magnetite which on rapid re-oxidation at high temp. gives red, paramagnetic ferric oxide, but on slow oxidation in air at 200° to 250° gives yellowish-brown, strongly magnetic ferric oxide. R. B. Sosman and E. Posnjak prepared the ferromagnetic oxide by oxidizing precipitated ferrosic oxide, and also by dehydrating lepidocrocite, $Fe_2O_3.H_2O$, whilst they found that dehydrating goethite, Fe_2O_3,H_2O, gives only paramagnetic ferric oxide. J. Huggett obtained analogous results.

E. Wedekind and W. Albrecht concluded that the hydrated oxides are always more magnetic than the corresponding oxides; that in the range of 22 to 43 per cent. of water, the magnetic susceptibility decreases as the water of hydration increases; and that oxyhydrates, like artificial goethite, precipitated in the usual manner and heated in an autoclave, at various press., are ferromagnetic—*vide infra*, hydrated ferric oxide. This subject was discussed by E. F. Herroun and E. Wilson, G. Chaudron and A. Girard, G. Gilbert, W. H. Newhouse and W. H. Callahan, P. A. Wagner, W. H. Newhouse, and L. H. Twenhofel. L. A. Welo and O. Baudisch obtained the ferromagnetic oxide by precipitating hydrated ferric oxide from a soln.

of eq. proportions of ferrous and ferric sulphates, by means of an excess of a hot, conc. soln. of sodium hydroxide. The black precipitate is then washed, dried, and oxidized at 220° to 230° in air. O. Hauser, A. Kaufmann and F. Haber, and S. Hilpert prepared the ferromagnetic oxide by oxidizing magnetite, or ferrous hydroxide, with soluble, oxidizing agents. R. Chevallier treated conc. soln. of ferrous sulphate with an excess of sodium hydroxide, and oxidized the resulting ferrous hydroxide by hydrogen dioxide. The precipitated oxide was dried several weeks in vacuo. The more conc. the soln. of sodium hydroxide, and the greater the excess, the more highly magnetic was the resulting ferric oxide. The optimum temp. of precipitation was 45° to 50°; when the precipitation was made at a higher temp., the product was less magnetic. R. Chevallier added that these products lost their ferromagnetic qualities if heated to 100° for an hour, or to 200° for a few minutes, whereas the ordinary forms of ferromagnetic ferric oxide retain their magnetic qualities up to about 600°. O. C. Ralston considers that R. Chevallier produced some sodium ferrite, or ferrate, which contaminated his ferric oxide, and that the observed magnetism was due either to these products directly, or to their decomposition products. S. Veil obtained ferromagnetic ferric oxide by oxidizing ferrous sulphide suspended in water, and afterwards dehydrating the resulting hydrated ferric oxide; C. L. Jackson and J. H. Derby, by roasting ferrous iodide; L. V. Pratis, by heating a mush of ferrous sulphate obtained by the action of iron on dil. sulphuric acid; M. Sarzeau, by boiling a soln. of ferrous hydrocarbonate; F. Frankenburger and co-workers, by the action of water on lithium ferric nitride, Li_3FeN_2; F. J. Malaguti, and E. F. Herroun and E. Wilson, by roasting ferrous oxalate, citrate, or tartrate, or ferric acetate.

U. R. Evans [7] obtained **films of ferric oxide** on strips of iron by anodic oxidation in $0{\cdot}1N$-NaOH; or by dipping the iron in a soln. of iodine in a 10 per cent. soln. of potassium iodide. A. Krause obtained films on glass and porcelain from hydrosols peptized by acids. A. Kundt obtained films by cathodic spluttering of iron in a tube not completely freed from oxygen. W. N. Hartley obtained films in an analogous manner; F. H. Constable, by heating a layer of a paste made of ferrous oxalate or ferric oxide with oleic acid, and subsequently oxidizing the film of grey iron; and H. Zocher and K. Jacobsohn by the slow hydrolysis of ferric chloride soln. V. Kohlschütter and J. L. Tüscher, G. Jander and A. Winkel, and S. S. Kistler prepared an **aerosol** by vaporizing the metal in an electric arc, and carrying the vapour by a current of air, or other gas, into a chamber where it is suddenly chilled. A. Mittasch obtained the finely-divided oxide by burning iron carbonyl alone or mixed with other combustible or inert gases. J. Y. Johnson sprayed the carbonyl mixed with a combustible vapour, say alcohol, into a spray of air or oxygen, and ignited the mixture with platinized asbestos. W. E. Gibbs, and S. S. Kistler studied the aerosol.

Ferric oxide is produced as a by-product in the roasting of pyrites to obtain sulphur dioxide for the manufacture of sulphuric acid: $4FeS_2+11O_2=2Fe_2O_3+8SO_2$. Ferric oxide is also formed when iron, or ferrosic oxide, or hydrated ferric or ferrous oxide is heated for a considerable time in contact with air, and the product was once called *crocus martis adstringens;* while the ferric oxide obtained by deflagrating a mixture of iron filings with three times its weight of nitre, and removing the soluble alkali by washing with water, was called *crocus martis zwelferi;* and the ferric oxide obtained by igniting ferrous or ferric sulphate was called *colcothar*, and also *caput mortuum vitrioli.* Yellow or yellowish-red ferric oxide was generally called *crocus martis*, a term which appears in the Latin version of Gebert: [8] "Mars is filed and calcined until it is well rubified and become an impalpable powder which is called *crocus martis.*" L. Lémery called the black oxide of iron *æthiops martis;* Basil Valentine, and A. Libavius describe the preparation of these red oxides in various ways. J. Zwelfier, in 1652, obtained what he called *crocus martis* by heating iron with nitre and afterwards washing out the soluble matters. In the sixteenth century the *caput mortvum vitriolis* of the alchemists was also a by-product in the preparation of fuming sulphuric acid (*q.v.*). Basil Valentine called it *colcothar* or *colchotar*. E. O. von Lippmann discussed the origin of the terms.

According to F. E. E. Germann, the red pigment employed by the prehistoric North American Indians was hæmatite. The roasting of ferrous sulphate, obtained in the weathering of iron pyrites, furnishes ferric oxide for use as a pigment; and the pigment is also obtained from waste acidic liquors in the pickling of iron, etc. The ferrous salt is oxidized to the ferric state by nitric acid or bleaching powder, and the ferric hydroxide precipitated by lime. Ferric oxide is produced by roasting ferrous oxide, carbonate, or other salt of a volatile acid—*e.g.* T. L. Phipson, and A. Vogel recommended the oxalate.

The physical properties of ferric oxide.—The **colour** of the ferric oxide is determined by the time and temp. of the roasting of the ferrous salt. J. A. Hedvall said that the possible colours range from bright yellow to bluish-black. He said that when ferric oxide is heated at 650° to 1000° all the varieties become brown or dark violet, and above 1000°, they become black or bluish-black. This statement does not cover the facts. A. Salvetat found that the orange-red ferric oxide, or *rouge orange*, can be obtained only when some zinc or aluminium salt is associated with the ferrous sulphate, and the mixture is calcined at a dull red-heat—*rouge sombre*. L. A. Keane, J. H. Yoe, and F. H. Scheetz attributed the yellow colour of some pigments and of bricks to the very finely divided ferric oxide being prevented by alumina from agglomerating to red ferric oxide. Free alumina, however, is rarely present in the brick clays, which burn buff-yellow. According to A. Salvetat, a nasturtium-red, or *rouge capucine*, is produced by calcining the ferrous sulphate at the lowest possible temp., dull redness; a blood-red, or *rouge sanguine*, is produced if the temp. be rather higher than dull redness; flesh-red, or *rouge de chair*, is obtained at a still higher temp.; and by working at progressively higher and higher temperatures, the colours pass from carmine-red, or *rouge carmine*, to red-lake or *rouge laquex*, to pale violet-red, or *rouge violatre pale*, to violet-red, or *rouge violatre*, which is obtained at a very high temp. Darker tints are produced by associating more and more manganese salt with the ferrous sulphate, and calcining the mixture at a very high temp. In this way were obtained deep violet-red, or *rouge violatre foncé*; very deep violet-red, or *rouge violatre très foncé*; and iron-grey, or *gris de fer*. Certain manufacturers have specialized in producing particular tints, and the products have received special names—*e.g.* Pannetier's reds, etc. The varying colours of the ferric oxide are, according to L. Wöhler and C. Condrea, determined by the average grain-size of the particles rather than by variations in the mol. structure. Thus, brown and violet samples can be changed to yellowish-red by alternate grinding and washing; and G. Meir obtained low-temp. tints by separating the finest particles from deep reds prepared at a high temp. W. Ostwald suggested a similar hypothesis. J. A. Hedvall assumed that there are several stable, crystalline modifications of ferric oxide, and that the difference in the reflection of light from crystals of different shapes accounts for most of the differences in colour. The bright yellow variety consists of thin plates, and the others, of small grains or prisms. All varieties give the same X-radiogram, and belong to the same crystal system. The subject was studied by H. Wagner. When the light-yellow form darkens at 600°, the leaflets lose their forms and become granular. The subject was discussed by J. W. Mellor.

A range of various shades of red is produced by roasting hydrated iron oxides, *e.g.* the ochres, to furnish *burnt ochre*; sienna-earths, to furnish *burnt sienna*; and umbers, to furnish *burnt umber*. The colours have also received various trade-names—*e.g. Chinese red, Naples red, terra rosa, Indian red, Venetian red, Japanese red, Turkey red,* and scores of other terms are indicated in the trade catalogues. The so-called sequence of colours, *mars yellow, mars orange, mars red, mars violet,* and *mars brown,* were obtained in a similar way. Each dealer has more or less his own names for the different tints, and these are not necessarily the same as those of another dealer's. Thus one dealer's *caput mortuum* may be another dealer's *colcothar*, and *vice versa*. The Japanese red obtained by roasting *grès de Thiviers*, a ferruginous hydrated silica, is famed for its relatively great permanence of tint at a high temp. The dominant colouring oxide in all these cases is ferric oxide associated with more or less ferrosic oxide. W. H. Bruckner obtained Turkey-red tinted ferric oxide by anodic oxidation in a soln. of sodium sulphate.

According to R. B. Sosman and J. C. Hostetter, these two oxides form a continuous series of solid soln. A. Bouchonnet found similar relations between the different tints of a given ochre and the roasting temp., as those obtained by calcining ferrous sulphates. The colour of the ochres gradually deepens on heating from 100° to 250°, and between 230° and 260° changes sharply from yellow to red. The transition temp. depends on the particular ochre employed. Above this temp. the colour deepens up to 700° to 800°; and at about 900°, there is a marked contraction. Between 1000° and 1100°, the colour usually changes to black as ferric oxide is changed to magnetic or ferrosic oxide. The duration of the heating influences the colour only below 700° and above 1000°, and the rate of cooling has no influence on the tint. The sp. gr. gradually increases from the natural yellow ochre upwards with temp. to 1600°. The plasticity also decreases with rise of temp., and disappears completely at 800° to 850°. The yellow and red ochres are soluble in acids, but the varieties obtained above 950° are insoluble in cold or hot acids—excepting the hydrofluoric acid. The ochre from Vaucluse becomes magnetic even while still yellow, and this is assumed to show that an a-variety of ochre exists. The magnetic property disappears on prolonged heating, but reappears at 1600°. In general, the colour changes are attributed to differences in the average grain-size, rather than to differences in the degree of dehydration. According to T. Carnelley and J. Walker, the dehydration of the hydrated ferric oxides is complete at 500°, so that only below that roasting temp. can the tint of the pigment have any relation to the state of hydration of the product.

According to G. R. MacCarthy, the natural yellows, browns, and reds in rocks are due to the presence of ferric compounds. Hydrous ferrosic minerals are blue in colour, and are responsible for the blues frequently exhibited by clays and shales. These tints are not produced by disseminated organic matter. The greens are produced by mixture of iron-blues and iron-yellows, for no evidence of the existence of any single green compound has been found. The chocolate-red of hæmatite sometimes approaches purple, but the true purple colours of shales and slates are produced by mixtures of iron-reds and iron-blues. Anhydrous ferrosic compounds produce only greys and blacks, like the carbonaceous matter that is generally present in black, argillaceous rocks. The subject was discussed by D. S. Hager, P. Fireman, and H. Wagner. A. Veneuil said that the sapphire owes its colour to ferric and titanic oxides.

The *green colour* of the old Chinese, and Japanese celadon (or seladon) glazes can be imitated by firing suitable ferruginous glazes in the reducing atmosphere. A *blue colour* sometimes appears in glasses, glazes, and slags when they are partially devitrified. I must say that the blue opalescence effects on red Chinese glazes, and hundreds of glazes and slags which have come under my notice, do not require any hypothesis other than incipient devitrification, suggested by J. Fournet, to account for the results. However, others have seen differently. B. Silliman said that ferrous oxide can impart a blue colour to vitreous bodies; and R. Zsigmondy prepared blue glasses coloured with iron oxide under reducing conditions. J. Beckmann described blue glasses which he supposed were produced by iron oxide as tinctorial agent, and he quoted the analyses of J. F. Gmelin to show that blue colours can be produced on glasses, and enamels, and that the blue pigment on Chinese porcelain contains iron, but not cobalt. He also obtained similar results with some old Roman, blue tiles, and with some blue paint on an Egyptian mummy. J. J. Ferber also described blue volcanic slags and scoriæ which U. F. B. Brückmann said were probably used by ancient glass makers to produce blue colours.

C. J. B. Karsten, and J. J. Berzelius considered the blue colour of the slags was produced by titanic acid; C. J. B. Karsten also referred the blue colour in some cases to vanadium, and in others to a kind of artificial ultramarine. J. Fournet, M. Dartigues, and J. Percy attributed the colour to the presence of iron oxide. G. Bontempts also showed that iron oxide can impart a blue coloration to glass; and C. Mène observed that the blue colour may be developed in slags containing no tartaric acid. M. E. Chevreul favoured L. C. A. Barreswil's assumption that there is a blue coloured oxide of iron intermediate between ferrous and ferric oxide. G. R. MacCarthy argued that the green colours produced by iron oxide are derived from the blue and yellow component oxides. K. A. Hofmann and F. Resenscheck, W. Spring, and G. R. MacCarthy considered that "all iron salts which are of a decided blue colour contain both ferrous and ferric iron in the same molecule." This agrees with the observations of M. E. Chevreul, J. F. Persoz, and J. Napier. W. D. Bancroft and co-workers have prepared borate glasses coloured blue by iron oxide, and they attribute the coloration to the existence of an unstable blue modification of ferric oxide which is stabilized chiefly by ferrous oxide, and also by other substances. They report that in alkali borate glasses, ferrous oxide is colourless, ferric oxide is yellow, and mixtures of the two may be blue or green. If the ratio of ferrous to ferric oxide reaches 3 in borate glasses, the blue glass is almost free from a green tinge, and when the ratio reaches 4, the blue is well developed.

A. Nabl, and E. F. Holden referred the colour of citrene to the presence of submicroscopic hydrated ferric oxide; and a pink variety of quartz contained inclusions of red hæmatite of microscopic dimensions. W. Spring attributed the yellow colours of sedimentary rocks to hydrated ferric oxides; the reds to anhydrous ferric oxide; and the greens to ferrosic silicates. Colours obtained with special mixtures have also been described. Thus, T. Terreil obtained a red colour from a mixture of ferrous sulphate and sulphur, and the sulphur dioxide produced: $4FeSO_4+S=2Fe_2O_3+5SO_2$, was used in the manufacture of sulphuric acid. M. N. d'Andria obtained a colour by roasting a mixture of magnesium and ferrous sulphates; and others were described by N. McCulloch, A. Bunterock, H. Stein, etc.; and the manufacture of these colours is indicated in books, etc., by F. Rose, J. G. Gentele, G. Zerr and R. Rübencamp, H. Wagner, G. H. Hurst, S. Mierzinsky, and J. A. Reavell.

The colour of the ditrigonal scalenohedral and rhombohedral crystals of hæmatite is dark steel-grey or iron-black, and in thin layers it is blood-red by transmitted light; when earthy, the mineral is red. In layers of about 0·02 mm. it is transparent for red light, but in thinner layers it becomes transparent to most of the spectral rays of visible light. When warmed, the transparency decreases, but is recovered on cooling. C. F. Schönbein,[9] F. Muck, and E. J. Houston noticed that the colour of ferric oxide deepens as its temp. is raised. The reversible colour change which occurs at 650° was discussed by J. A. Hedvall. The streak of powdered mineral is cherry-red or reddish-brown. J. L. C. Schroeder van der Kolk said that the red streak becomes black when hot, and on cooling, red. The crystals of hæmatite are opaque except in thin layers. M. Lachaud and C. Lepièrre obtained ferric oxide in yellow hexagonal plates by heating ammonium ferric sulphate. According to E. A. Wülfing, the mineral is opaque down to a thickness of 0·1 mm., and then the colour passes from deep red to yellowish-red, and yellowish-grey. O. Anderson obtained plates of hæmatite 0·1μ thick, and found them to be yellow by transmitted light; with plates of increasing thickness, the colour passes from reddish-brown, to deep brownish-red, to blood-red. As indicated above, L. Wöhler and C. Condrea also found that if the grain-size of the particles is small the colour is yellow; if larger, red. W. R. Mott prepared anhydrous red and yellow ferric oxide by volatilization and found the grain-size of the yellow particles to be the smaller. According to J. Böhm, an X-ray study of ferric oxide shows that the calorescence or glow which may occur accompanies the transition of the material from the amorphous to the crystalline state. G. Chaudron and H. Forestier found that the glow which occurs between 400° and 600° is also attended by the change from the amorphous to the crystalline state. The variation in tint of preparations of pulverulent ferric oxide has just been discussed.

The observations of H. Abraham and R. Planiol, R. Chevallier, R. B. Sosman and E. Posnjak, and E. Wilson and E. F. Herroun agree that ferromagnetic ferric oxide—*vide infra*—is inclined to be yellower, and darker in colour than is the case with the ordinary paramagnetic oxide. E. Wilson and E. F. Herroun prepared samples ranging in colour from deep red to yellowish-brown; L. A. Welo and O. Baudisch, dark red; C. Frebold and J. Hesemann, reddish-brown; whilst that obtained by F. Frankenburger and co-workers by the action of water on lithium nitride is almost black.

The mineral occurs in columnar, botryoidal, lamellar—*e.g. flaky specularite*—granular, friable, or compact masses. The compact forms are brittle, the thin lamellæ are elastic; and some scaly varieties feel soft and unctuous. The fracture is subconchoidal, uneven, or earthy. N. H. Winchell, and W. S. Gresley described a form of *fibrous hæmatite*. The **crystals** may occur in thick or thin plates parallel to the (0001)-face, and they may be grouped in parallel positions or they may form rosettes. There may be other combinations. The crystals also occur in cube-like rhombohedra, with the rhombohedral (1014)-face striated, and often rounded over in convex forms. The (0001)-faces may also be striated. Hæmatite may also form columnar, botryoidal, or stalactitic shapes, or it may form lamellar masses with the thick or thin laminæ joined parallel to (0001), and bent in various ways. Some observations on the rhombohedral crystals were made by R. J. Haüy, A. Girard and G. Chaudron, and L. A. Emmerling. The trigonal-hexagonal-rhombohedral crystals were found by N. von Kokscharoff to have the axial ratio $a : c = 1 : 1{\cdot}36557$; G. Melczer gave 1 : 13654; E. Kleinfeldt, 1 : 1·3651 to 1 : 13656; and S. di Franco, 1 : 13668. **Twinning** occurs; there are penetration twins about the (0001)-plane, and the composition face may be perpendicular to the (0001)-face; twinning also occurs less commonly about the (1011)-plane producing polysynthetic twinning lamellæ showing a fine striation on the (0001)-face, and giving rise to a distinct or pseudo-cleavage parallel to (1011). This twinning was studied by F. Mohs, W. Haidinger, M. Bauer, O. Mügge, and O. V. Jereméeff. There is no definite **cleavage**, but there are partings about (0001) due to the lamellar structure, and about (1011) due to twinning. F. F. Osborne, G. Kalb, and G. Melczer studied the **corrosion figures** obtained with hydrochloric acid. Ferric oxide is dimorphous; in addition to the rhombohedral crystals just described there is a cubic form—*vide infra*, ferromagnetic ferric oxide. Numerous measurements have been made on the crystals of the rhombohedral form:

Observations on the crystals of hæmatite have been reported by A. d'Achiardi, G. d'Achiardi, G. Aminoff, A. Arzruni, M. Berek, A. Bergeat, H. Biäsch, J. R. Blum, O. B. Bøggild, A. Breithaupt, A. Brezina, T. M. Broderick, W. C. Brøgger, L. Bucca, H. Bücking, L. Busatti, K. Busz, H. Buttgenbach, M. Carrère, E. J. Chapman, J. H. Collins, L. Colomba, F. Cornu, E. Döll, H. Dufet, P. A. Dufrénoy, G. Fink, S. di Franco, W. F. Foshay, A. Frenzel, V. Goldschmidt, F. Gonnard, J. P. Graffenauer, R. P. Greg and W. G. Lettsom, P. Groth, W. Haidinger, R. W. Harre, R. J. Haüy, M. F. Heddle, F. Hessenberg, T. S. Hunt, P. V. Jereméeff, W. P. Jervis, G. Kalb, G. A. Kenngott, E. Kleinfeldt, F. von Kobell, A. Koch, A. Krantz, A. Lacroix, A. Lacroix and P. Gautier, F. von Lasaulx, E. Laval, I. Lea, C. C. von Leonhard, A. Lévy, O. M. Lieber, J. Loczka, O. Luedecke, E. Manasse, J. S. Martin, G. W. McKee, F. Mohs, A. J. Moses, F. Millosevich, O. Mügge, C. F. Naumann, J. J. Nöggerath, W. Nowacki, F. Papp, A. Pelikan, F. Pfaff, L. V. Pirsson, G. von Rath, J. B. L. Romé de l'Isle, G. Rose, P. A. de Saxe-Cobourg-Gotha, A. Sadebeck, A. Scacchi, A. and E. Scacchi, T. Scheerer, A. Schmidt, A. Schwantke, J. Schweitzer, G. Sillem, B. Silliman, L. J. Spencer, A. de Stefani, J. Strüver, P. von Sustschinsky, V. V. Syedeltschikoff, H. Tertsch, H. Traube, P. Tschirwinsky, G. Uzielli, T. Wada, E. Weinschenk, D. F. Wiser, V. von Zepharovich, K. Zimanyi, and F. Zirkel, etc. A bibliography was compiled by H. Biäsch. Observations on the artificial crystals were made by H. Arctowsky, A. Arzruni, K. B. Doss, W. Florence, G. Friedel, F. von Hochstetter, H. E. Merwin and J. C. Hostetter, W. Müller, C. F. Rammelsberg, H. Vater, etc.

L. Pauling and S. B. Hendricks, W. H. and W. L. Bragg, H. Sachse, J. A. Hedvall,

V. M. Goldschmidt, W. H. Zachariasen, W. C. Hansen and L. T. Brownmiller, P. E. Wretblad, J. Böhm and F. Ganter, and J. Topping studied the **X-radiograms** of hæmatite and corundum, and found them similar. L. Pauling and S. B. Hendricks found that the rhombohedral space-lattice of hæmatite has α-55° 17′, and the side of unit triangle, a=5·420 A.; he said that the hexahedral mol. of ferric oxide can be assumed to consist of an equilateral triangle of oxygen with a metal atom immediately above and below the centre of the triangle; and that the lattice has 3 mols. per unit prism. The side of unit triangle is a=5·035 A.; the axial ratio $a:c$=1 : 1·363, and the calculated density, 5·243. T. Katsurai and T. Watanabe gave a=5·42 A., and α=55° 17′; V. M. Goldschmidt and co-workers, a=5·42 A., and α=53° 14′; R. Brill, a=5·429 A., and α=54° 58′; S. Katzoff, a=5·4135 A., and α=55° 17·5′; L. Passerini, a=5·020 A., and c=6·860 A., $a:c$=1 : 1·366, and $v=148·6\times10^{-24}$ c.c. for the hexagonal cell, and a=5·43 A., and α=55° 6′ for the rhombohedral cell; and W. H. Zachariasen, α=58° 14′; a=5·42 A.: and $a:c$ =1 : 1·367, and the calculated density, 5·25. E. A. Harrington gave α=55° 17′, and a=5·406 A.; and P. E. Wretblad, edge of lattice=5·419 A.; α=55·28°; a=5·027 A., c=13·73 A.; and $a:c$=1 : 2·7306. A hexahedral molecule is assumed consisting of an equilateral triangle of oxygen with a metal atom immediately above and below the centre of the triangle. W. Jansen studied the fibrous varieties, and found that the crystals are hexagonal with a=5·035 A., and c=13·726 A. L. Pauling and S. B. Hendricks inferred that the arrangement of the atoms in the lattice is such that each metal atom is surrounded by 6 oxygen atoms which are not at the corners of a regular octahedron. Three of these atoms are a few per cent. nearer the metal than the others. This indicates that the location of the electrons in the outer shells of an ion causes it to have different effective radii in different directions. Each oxygen atom is surrounded by 4 metal atoms, 3 of which are nearer than the other two. The interionic distances of hæmatite are: the smallest oxygen-oxygen distance, 2·545 A.; and the metal-oxygen distances, 2·060 A. and 1·985 A. L. A. Welo and O. Baudisch, and J. Thewlis found that the lattices of ferrosic and γ-ferric oxides are analogous, and of similar dimensions. The unit cube of ferrosic oxide contains 8 molecules and is represented by $Fe_{24}O_{32}$, and the unit cube of γ-ferric oxide has 12 molecules and is represented by $Fe_{24}O_{36}$. Consequently, room for 4 additional oxygen atoms has to be found in the unit cube of Fe_3O_4. J. Thewlis' representation of the structure of ferrosic oxide has been previously discussed, and is illustrated in Fig. 518, and the structure of γ-ferric oxide with its four additional oxygen atoms is illustrated

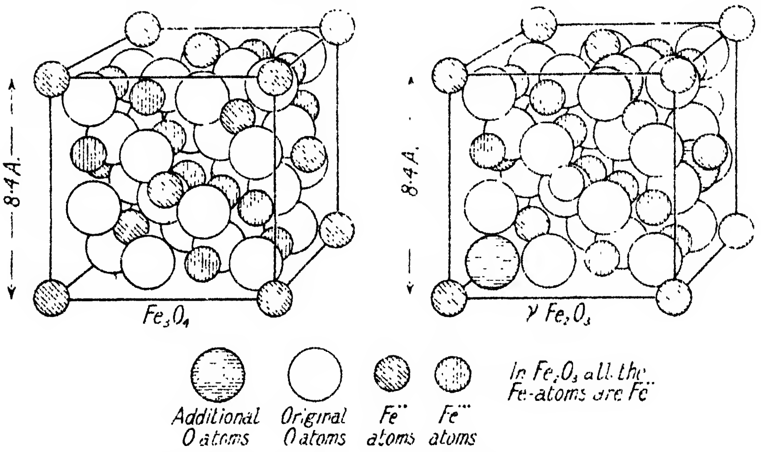


FIG. 518.—Lattice Structure of Fe_3O_4.

FIG. 519.—Lattice Structure of γ-Fe_2O_3.

in Fig. 519. One of the conditions necessary for ferromagnetism, on W. Heisenberg's theory is that each atom must have 8 nearest neighbours; H. Sachse applied this test to Fe_3O_4, α-Fe_2O_3, and γ-Fe_2O_3, and found the condition satisfied by Fe_3O_4 and γ-Fe_2O_3, but not by α-Fe_2O_3. This condition is also satisfied by J. Thewlis' representations, Figs. 518 and 519. J. Topping studied the potential energy of the crystals; and N. Akuloff and M. Degtiar, the slip-lines.

Observations on the crystals were made by A. Simon and T. Schmidt, J. Böhm, G. Kalb, P. F. Kerr, W. P. Davey, V. Schmaeling, C. Mauguin, J. Wasastjerna, and H. Groebler and P. Oberhoffer—*vide supra*, ferrous and ferrosic oxides, Fig. 512. Observations on kidney ore, by J. A. Hedvall, J. Böhm, and F. Rinne, show that it is a form of hæmatite. J. A. Hedvall, E. A. Harrington, G. Frebold, and G. Frebold and J. Hesemann found that the space-lattices of natural and artificial ferric oxides are the same. K. Honda and T. Sone observed a structural change at 1300°; whilst K. T. Compton and E. A. Trousdale could detect no change in the space-lattice under the influence of a magnetic field. R. D. Williams and J. Thewlis noted that the crystals of the α-oxide or trigonal oxide, formed from γ-lepidocrocite, are of the order of 10^{-4} cm. across, and those of the γ-oxide or cubic oxide are of the order 10^{-7} cm. across when first formed, but their final size, just before they are transformed into the trigonal form, is of the order 10^{-6} cm. The transformation occurs over the range 500° to 600°.

L. A. Welo and O. Baudisch observed a loss in catalytic power in passing from the cubic to the trigonal form, but S. Roginsky and E. Schulz found no difference in the catalytic decomposition of potassium permanganate. F. Pfaff, and J. Strüver have noticed the similarity between the crystal forms of hæmatite and corundum; and A. Hamberg, the resemblance between the crystals of ilmenite and pyrophanite. It was inferred that these minerals have a similar constituent:

$Fe(FeO_3)$	$A(AlO_3)$	$Fe(TiO_3)$	$Mn(TiO_3)$
Hæmatite	Corundum	Ilmenite	Pyrophanite

P. J. Holmquist stated that there are two crystalline forms: α-ferric oxide, stable at a low temp.; and β-ferric oxide, stable at a high temp. H. Forestier and G. Chaudron observed a break in the thermal expansion curve at 680°; R. B. Sosman and J. C. Hostetter, a sharp reversible endothermal break in the heating curve at 678°, and a small irregularity between 775° and 785°; E. J. Kohlmeyer, breaks at 1035°, and between 1250° and 1350°; and C. C. Bidwell, a break at 1320°—but these have not been established as definite transformation points. K. Honda and T. Sone observed a break in the thermomagnetic curve at 1300°; G. G. Brown and C. C. Furnas observed what they regarded as breaks in the sp. ht., and thermal conductivity curves at 360°, and calculated the thermal value of the change at 360° to 4·85 cals. per gram, or 775 cals. per mol. H. le Chatelier noted a change in the heat of formation curve at about 900°; J. d'Ans, and G. Keppeler and J. d'Ans stated that a polymorphic transformation occurs at 640°, and that is the optimum temp. for the activity of ferric oxide as a catalyst for the oxidation of sulphur dioxide; and C. C. Bidwell, a break at about 720° in the curves for the electrical conductivity, and thermoelectric force. R. B. Sosman and co-workers noted a drop in the magnetic susceptibility at 678°; L. Blanc, and G. Chaudron, at 600°; and J. Huggett and G. Chaudron observed that the Curie point occurs at 675°. C. C. Furnas found the thermal value of the change between 650° and 825°, assuming that it is all one change, to be 41·8 cals. per gram, or 6692 cals. per mol. W. G. Mixter could detect no polymerization when the ferric oxide is heated, and J. A. Hedvall observed no change in the X-radiograms. The subject was also discussed by S. Hilpert. N. Parravano and G. Malquori observed that the oxides formed by heating the hydrogel, or by roasting the chloride or nitrate, have the same X-ray spectrum, and show no evidence of polymeric forms. L. A. Welo and O. Baudisch, and R. B. Sosman and E. Posnjak found that the X-radiograms of magnetite and of ferromagnetic ferric oxide, natural or artificial, are identical. The ferromagnetic form was called by F. Haber, and J. Hesemann, γ-Fe_2O_3. There is an irreversible transformation, γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$, between 400° and 700°; and the Curie point is between 500° and 700°. At about 700°, ferromagnetic ferric oxide with the cubic lattice of magnetite or martite is transformed into paramagnetic hæmatite with rhombohedral crystals. The unit cube of magnetite may be symbolized $Fe_{24}O_{32}$, and after oxidation $Fe_{24}O_{36}$. The unit cube of magnetite thus has room enough to accommodate 4 extra oxygen atoms. A. Simon discussed the structure of ferric oxide; L. Passerini, the solubility; and O. Hahn and O. Müller, the surface by the adsorption of radium emanations.

There are thus two forms of ferric oxide— one cubic, one trigonal or rhombohedral. The observations of H. Abraham and R. Planiol, R. Chevallier, J. Huggett and G. Chaudron, S. B. Hendricks and W. Albrecht, O. Hauser, R. B. Sosman and co-workers, L. A. Welo and O. Baudisch, and E. Wedekind and W. Albrecht show that (i) the X-radiograms of the two forms are indistinguishable one from the other; (ii) the magnetic permeability of cubic ferromagnetic oxide is not distinguishable from that of ferrosic oxide; (iii) the cubic form can be changed to the more stable rhombohedral form by heating it to various temp. between 550° and 1000°; and the catalytic activity of the cubic form is greater than is the case with the rhombohedral variety. The transition temp. appears to depend on the mode of preparation. To convert ferrosic oxide to the isomorphous cubic ferric oxide, 4 oxygen atoms must be crowded into the unit lattice of the ferrosic oxide. L. A. Welo and O. Baudisch considered that the extra oxygen required for the change $2Fe_3O_4 \rightarrow 3Fe_2O_3$ can be inserted in the crystal-lattice, without undue strain, so as to leave the structure essentially unchanged. J. W. Gruner, L. H. Twenhofel, G. Frebold and J. Hesemann, J. Böhm, and P. M. Wolf and H. Zeglin discussed changes in the X-radiograms in the oxidation of magnetite to ferromagnetic ferric oxide.

J. Beyer[10] observed that the chemical reactions of iron, and ferric oxide with hydrogen and steam, and the magnetic properties of the products, agree with the assumption that solid soln. are formed between ferrous and ferrosic oxides; R. Ruer and M. Nakamoto also noted the formation of solid soln. S. Hilpert called the complexes of FeO and Fe_2O_3, other than Fe_3O_4, indefinite mixtures—*vide infra,* ferrous ferrites. R. B. Sosman and J. C. Hostetter added that ferric oxide forms a continuous series of solid soln. with ferrosic oxide (*vide infra*), and they called them **martites.** E. D. Eastman showed that at 1100° and upwards ferric and ferrosic oxides form a continuous series of solid soln., but probably the soln. is limited below 1000°. J. Beyer found a similar state of things with ferrous and ferric oxides. E. D. Eastman also said that at and above 1100°, the two oxides form a continuous series of solid soln., although there are indications that below 1000° they may not be soluble in one another in all proportions. Hæmatite is hexagonal and magnetite cubic, at ordinary temp., and hence it may appear to be a *circuluo in probando* to assume that there is a hexagonal variety of magnetite which forms a solid soln., *i.e.* an isomorphous mixture with hæmatite. According to R. B. Sosman, a consideration of the point systems from which the crystal classes can be made up, shows that there is in reality a continuous transition from cubic to hexagonal. Suppose a cubical portion of some cubic lattice to be standing on one of its corners; then if it be compressed along the vertical diagonal axis it changes into a rhombohedron which becomes flatter with increasing compression, and the rhombohedron is a hexagonal form This transition requires, of course, that the lattice of the isometric and hexagonal forms be thus transformable. The subject was discussed by T. M. Broderick, P. Geijer, G. Gilbert, A. Lavenir, C. Friedel, J. W. Gruner, and P. Ramdohr. H. Forestier and G. Chaudron discussed the formation of solid soln. with ferric oxide and chromic oxide, and alumina—*vide* aluminium and chromium ferrites. W. Biltz and co-workers found that in the spinels, $MO.Fe_2O_3$, the mol. vol. of the Fe_2O_3 in $ZnO.Fe_2O_3$ is 30·4; and in the CuO, MgO, CdO, MnO, FeO, CoO, and NiO spinels, the mol. vol. of the Fe_2O_3 is round about 33·4. Hence they infer that there are two forms of ferric oxide: α-Fe_2O_3 with mol. vol. 30·4, and γ-Fe_2O_3 with a mol. vol. 33·4.

A. Johnsen discussed carnallite and hæmatite. G. Friedel discussed **pseudomorphs** of ferric oxide after magnetite. A. Breithaupt described a cubic variety of ferric oxide occurring in octahedra or dodecahedra, like magnetite. The pseudomorph is not ferromagnetic and it was called **martite.** This mineral was examined by F. von Kobell, C. F. Rammelsberg, J. F. L. Hausmann, R. van Aubel, J. R. Blum, H. Rosenbusch, G. vom Rath, A. Lavenir, and H. Gorceix. The general conclusion is that martite is a pseudomorph after magnetite. A. Scacchi obtained a variety of ferric oxide in acicular needles, thought to be *rhombic*. It occurs in the tufa of Pianura and Fiano, Campania, and was named *raphisiderite* — from ῥαφίς, needle; and σιδήρεος, iron. Pseudomorphs of ferric oxide after *iron pyrites* were reported by H. Traube, A. Schwantke, W. F. Petterd, H. Rosenbusch, J. R. Blum, A. Krantz, E. Döll, R. P. Greg and W. G. Lettsom, G. vom Rath, H. Gorceix, and A. Lavenir; after *lievrite*, by J. R. Blum; after *siderite*, by J. R. Blum; after *cerussite*, by A. Hofmann; after *pyromorphite*, by J. R. Blum, and D. F. Wiser; after *calcite*, by A. Breithaupt, J. J. Nöggerath, J. R. Blum, G. Sillem, H. A. Miers, O. Mügge, G. Rose, A. Frenzel, and W. Haidinger; after *dolomite*, by J. R. Blum; after *fluorite*, by J. R. Blum, G. Sillem, and A. Breithaupt; after *baryta*, by A. Breithaupt, M. F. Heddle, J. R. Blum, and R. P. Greg and W. G. Lettsom; after *anhydrite*, by P. Groth, and J. R. Blum; after *olivine*, by G. Tschermak; after *bronzite*, by J. R. Blum; after *garnet*, by J. R. Blum; after *felspar*, by J. R. Blum: and after *ferric sulphate*, by A. Vesterberg. J. W. Gruner, P. Ramdohr, and G. M. Schwartz discussed **intergrowths** with ilmenite and hæmatite (*q.v.*); and H. Baumhauer, intergrowths of rutile and hæmatite.

A. Frenzel[11] gave 4·914 to 4·917 for the **specific gravity** of hæmatite; C. F. Rammelsberg, 5·075 to 5·283; G. Rose, 5·191 to 5·230; F. E. Neumann, 5·079; J. Loczka, 5·289; M. Lachand and C. Lepierre, 4·95 at 14°; A. Bergeat, 4·998 and, after separating impurities, 5·247; G. Dewalque, 4·35; M. F. Heddle, 4·8; J. Joly, 4·644 to 4·923; J. Maillard, 4·90; A. Vesterberg, 5·06; A. Breithaupt, 5·261; P. V. Jereméeff, 5·02; E. Madelung and R. Fuchs, 4·8986 to 5·1568; E. F. Herroun and E. Wilson, 4·75 to 4·91; A. Lavenir, 5·194 to 5·205; and P. F. G. Boullay, 5·225. For the artificial oxide, W. Herapath gave 5·059 for the sp. gr. at 16·5°; H. Kopp, 5·121 at 12·5°; L. Playfair and J. P. Joule, 4·679 at 3·9° for the precipitated and 5·135 for the ignited oxide. P. P. Budnikoff and K. E. Krause found the sp. gr. of the oxide calcined at different temp. to be:

	450°	650°	850°	1000°
Sp. gr.	5·102	5·183	5·190	5·195

D. Tommasi gave 5·11 for the sp. gr. of the brown oxide obtained by dehydrating the precipitate from a ferric salt by alkali-lye, and 4·95 for that of the red or yellowish-red oxide obtained by oxidizing hydrated ferrous or ferrosic oxide or ferrous carbonate; and H. Rose gave 5·169 for the precipitated and 5·037 for the ignited oxide. Heating the oxide was found by H. Rose, G. Weymann, and F. Sauerwald and G. Elsner to increase the sp. gr. Thus, L. Blanc observed that the sp. gr. of the oxide heated to 500° to 600° is 4·910; to 650° to 700°, 5·040; to 750°, 5·110; and to 850°, 5·175; R. Ruer and J. Kuschmann, 5·200 at 15°/4° for a sample heated to 700°, and 5·1597 at 15°/4° after being heated to 1000°. A. Duboin gave 5·16; B. Aarnio, 5·09; and S. Hilpert and J. Beyer, 5·1. Observations were also made by F. Muck, and O. Hauser. H. P. Walmsley found the sp. gr. of the hexahedral particles of dispersed ferric oxide to 5·274, and of the cubic form, 5·400. F. J. Malaguti and A. Lallemand found for the non-magnetic oxide dried at 300°, 4·784; for the non-magnetic oxide which has been heated to *rouge vif*, 5·144; and for the strongly magnetic oxide, 4·686. E. J. Kohlmeyer and S. Hilpert found the sp. gr. of a sample that had been fused to be 5·190; and E. J. Kohlmeyer gave 5·187 to 5·193 for samples of highly purified oxide which had been heated high enough to convert some of the ferric oxide into ferrosic oxide. L. Blanc and G. Chaudron prepared the oxide by calcining the nitrate or sulphate at different temp., and found that when made at 500° to 600°, the large grains had a sp. gr. 4·910; at 620° to 700°, the fine grains had a sp. gr. of 5·040; at 750°, the grains of increasing size had a sp. gr. of 5·110; and at 850°, the grains of increasing size had a sp. gr. of 5·175. They attributed the decrease in the grain-size between 600° and 700° to an effect of the evolution of gas accompanying disintegration, but there is a polymeric transformation at about 678°. N. Parravano and G. Malquori found that the apparent sp. gr. of small cylinders of compressed ferric oxide is scarcely changed by calcination up to 700°; but above 800°, the apparent sp. gr. increased and the cylinders were less friable. X-radiograms show that the difference between the aggregated and non-aggregated oxide is solely one of grain-size. The general results of the sp. gr. determinations show that the best representative value of ferrosic oxide is 5·12 with the sp. vol. 0·1954, and mol. vol. 31·2, whilst for natural hæmatite the sp. gr. is 5·24; the sp. vol. 0·1910; and the mol. vol. 30·5. The densities 5·25 by W. Zachariasen; 5·355 by L. Passerini; and 5·243 by W. P. Davey, were calculated from the X-radiogram data. W. Biltz, and J. J. Saslawsky compared the observed mol. vol. with that calculated by the additive law. W. Ostwald and W. Haller observed that when the produced oxide is suspended in hexane, and other organic liquids, and then separated, the sp. vol. decreases in the order CCl_4, C_6H_{14}, C_6H_6, CH_3Cl, $(C_2H_5)_2O$, $CH_3.COOH$, C_2H_5OH, and $(CH_3)_2CO$. The effect is attributed to the adsorption of solvent films—*lyoadsorption*.

The **hardness** of the crystals is over 5 and may attain a value from 5·5 to 6·5. J. A. von Deurs and P. E. Raaschou[12] studied the fluidity of slip—water and ferric oxide. A. Reis and L. Zimmermann studied the hardness and mol. vol. W. Voigt gave for the **elastic modulus,** E, in kilograms per sq. mm., $E_0=23{,}000$; $E_{45}=21{,}800$; $E_{45}=18{,}700$; and $E_{90}=23{,}100$; while the cubical coeff. of **compressibility** is $1{\cdot}04\times10^{-6}$. E. Madelung and R. Fuchs found the compressibility between 50 and 200 kgrms. per sq. cm. to be between $0{\cdot}0_658$ and $0{\cdot}0_5106$. According to F. Sauerwald and G. Elsner, briquettes made from the compressed and calcined oxide have a compressive strength dependent on the temp. of calcination. M. C. Lea was unable to detect any signs of the dissociation of ferric into ferrous oxide by mechanical press.

H. Fizeau found the coeff. of **thermal expansion** to be, $a=0{\cdot}0_5829$ and $0{\cdot}0_5836$, respectively parallel and vertical to the principal axis; this gives for the coeff. of cubical expansion, 0·00002501, at 40°. H. Kopp gave 0·00004 for the coeff. of cubical expansion; and 0·000007 for the coeff. of linear expansion. H. Bäckström obtained for the length, l, at $\theta°$, between 4° and 82°, in a direction parallel to the principal axis, $l=l_0(1+0{\cdot}0_576109\theta+0{\cdot}0_84901\theta^2)$, and in a direction perpendicular to the principal axis, $l=l_0(1+0{\cdot}0_5576918\theta+0{\cdot}0_712000\theta^2)$, where l_0 denotes the length at 0°. It follows that the coefficient of expansion in a direction perpendicular to the principal axis is the greater; but the coefficients of expansions in both directions are the same at −5·7°, namely, $0{\cdot}0_57555$; and below that temp., the coeff. of expansion parallel to the principal axis is the greater. H. Forestier and G. Chaudron observed a break in the dilation curve at about 675°.

C. C. Bidwell found the **thermal conductivity** of the compressed powder to be 0·00141 cal. per sec. per sq. cm. per degree at 200°; 0·00189, at 400°; 0·00235, at 600°; 0·00262, at 720°; 0·00294, at 800°; and 0·00390, at 1050°. C. H. Lees gave $k=-0{\cdot}003$ cal. per cm. per sec. per degree; J. Königsberger and J. Weiss gave $k=0{\cdot}035$; and J. Kruckenberg, $k=0{\cdot}006$. C. C. Bidwell gave the following results:

	159°	258°	415°	658°	854°	1047°
k .	0·00130	0·00154	0·00189	0·00251	0·00317	0·00390

G. G. Brown and C. C. Furnas gave for the thermal conductivity, k cals. per sec. per sq. cm. per degree, of powdered ferric oxide:

	125°	150°	300°	400°	500°	600°	700°	750°
k .	$0{\cdot}0_3918$	$0{\cdot}0_3925$	$0{\cdot}0_3940$	0·00108	0·00113	0·00122	0·00133	0·00138

The results of C. C. Furnas on rods of powder, and those of C. C. Bidwell on prepared rods are summarized in Fig. 520. H. de Sénarmont made some observations on the thermal conductivity of the crystals; and E. Jannetaz observed that the ratio for the conductivities in the direction of the principal axis and at right angles thereto is 1·232; N. Botez and H. Hertenstein gave 1·198; and H. Bäckström, 1·064 to 1·12 at 50°. According to F. M. Jäger, the quotient of the electrical and thermal conductivities of all metals is a constant, independent of their chemical nature, but directly proportional to the absolute temp. This ratio is not constant for the conductivities of hæmatite measured in the directions of the crystal axes.

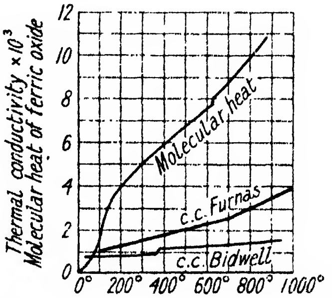


Fig. 520.—The Thermal Conductivity and Molecular Heat of Ferric Oxide.

J. Joly gave 0·1683 for the **specific heat** of hæmatite between 7·8° and 100°; P. E. W. Oeberg, 0·1645 to 0·1647 between 15° and 99°; A. Abt, 0·17425 between 16° and 95°; H. Kopp, 0·154 to 0·159 for the sp. ht. of hæmatite; R. Ulrich, 0·1627 between 19° and 98°; F. E. Neumann, 0·16695 to 0·1692. H. V. Regnault gave 0·16695 for the sp. ht. of hæmatite between 15° and 98°; while for calcined colcothar he gave 0·17167; for strongly calcined colcothar, 0·16921; and for yet more strongly calcined colcothar, 0·16814. G. G. Brown and C. C. Furnas gave for the sp. ht., in cals., of ferric oxide:

	0	40°	80°	120°	200°	300°	400°	500°	650°
Sp. ht. .	0·1550	0·1640	0·1750	0·1845	0·2025	0·2250	0·2645	0·2955	0·3420

The results for the **molecular heats,** C_p, from 298° K to 633° K, can be summarized by $C_p=14{\cdot}13+0{\cdot}0378T$; and between 633° K and 951° K, by $C_p=9{\cdot}16+0{\cdot}0491T$. W. Bertram gave:

	95°	225°	350°	461°	526°	569°	685°	764°	824°
c .	0·1598	0·1746	0·1854	0·1952	0·1995	0·2027	0·2084	0·2106	0·2110

and $c=0{\cdot}1514+0{\cdot}0001239(\theta-20)-0{\cdot}0_7577(\theta-20)^2$. Decomposition sets in at temp. exceeding 700°. G. S. Parks and K. K. Kelley found the sp. ht. at −184·0°, −123·7°, and 17·5° to be respectively 0·0408, 0·0842, and 0·1550, and the mol. ht. respectively 6·5, 13·4, and 24·8. The results of A. S. Russell, G. S. Parks and K. K. Kelley, P. E. W. Oeberg, A. Abt, J. Joly, C. C. Furnas, and H. V. Regnault fall about the mol. ht. curve, Fig. 520. A. S. Russell gave 0·0726 between 191·9° and −81·0°; 0·1318 between −73·7° and 0°; and 0·1600 between 3·5° and 44·0°. The corresponding mol. ht. are respectively 11·59, 21·05, and 25·53. W. A. Roth and W. Bertram gave for the sp. ht., c, between $\theta°$ and 20°, $c=0{\cdot}151+0{\cdot}0_31239(\theta-20)-0{\cdot}0_7577(\theta-20)^2$; and for true mol. heat:

	100°	200°	300°	400°	500°	600°	700°
C .	27·08	30·32	33·01	35·15	36·73	37·75	38·23

I. Maydel studied the mol. ht. F. J. Malaguti and A. Lallemand found the sp. ht. of non-magnetic ferric oxide dried at 300° to be 0·1863, and heated to redness, 0·1743; while the sp. ht. of the magnetic oxide heated to redness is 0·1730; and the sp. ht. of strongly magnetic ferric oxide is 0·1794.

J. J. Berzelius observed that precipitated, hydrated ferric oxide when heated loses water, and when passing from dull redness to bright redness it shows a **calorescence** similar to that described in connection with alumina, chromic oxide, and zirconia. The oxide thus becomes denser, less attacked by acids, and generally less sensitive chemically. L. Wöhler found that ferric oxide is calorescent only when precipitated from boiling soln.; that precipitated from cold soln. becomes calorescent only when well washed with hot water. J. Böhm said that the hydrated oxide caloresces as well when precipitated from cold soln. as it does from hot soln. L. P. de St. Gilles observed no calorescence with aged gels heated with water. F. Muck, and D. Tommasi observed no calorescence with the hydrogel obtained by oxidizing ferrous hydroxide or carbonate. J. J. Berzelius, and L. Wöhler observed no change in weight occurs during the calorescence, although H. Forestier and G. Chaudron obtained a marked shrinkage; J. J. Berzelius found the rate of solution in acids is decreased during the calorescence. The heating curves, obtained by K. Endell and R. Rieke, R. Wallach, and L. Blanc, show a sharp hump during the recalorescence period. K. Endell and R. Rieke observed that the material which showed the phenomenon had 0·5 per cent. of water. The calorescence temp. is 538°. L. Blanc observed the calorescence temp. to be 400° with the oxide precipitated cold, and it is feebler with the oxide precipitated from boiling soln. The temp. depends on the previous history of the hydrated oxide. N. S. Kurnakoff and E. J. Rode gave 325°–400° for the calorescence temp. of bog iron ore. A. A. Baykoff gave 380° for the beginning and 550° for the end; R. Wallach gave 400°; K. Endell and R. Rieke, 450°; H. le Chatelier, 950°; L. Wöhler, 540°; and at first it was assumed that two allotropic modifications exist. L. Wöhler regarded the phenomenon as due to an increase in the grain-size of the oxide. K. Endell and R. Rieke, and R. Ruer, to a change from the amorphous to the crystalline state; and this hypothesis is in agreement with the X-radiograms of J. Böhm of samples before and after calorescence. J. A. Hedvall, however, said that no oxide is amorphous, they are all crystalline or cryptocrystalline, and give identical X-ray spectra before and after heating to 1150°, showing that the calorescence is not caused by a change in structure. W. G. Mixter found that the thermal values of ferric oxide before and after the glow differ by 9·0 Cals. per mol. He calls this difference, the **heat of polymerization.**

E. J. Kohlmeyer said that finely powdered ferric oxide sinters and shrinks in volume on passing through 920° to 950°, and there is a kink in the heating curve in this region. C. C. Furnas observed that just before sintering, powdered ferric oxide becomes very active, and tends to flow like water, assuming an almost zero angle of repose although no liquid is present. The phenomenon may be caused by an evolution of gas, or by an accumulation of electric charges on the particles—*e.g.* the "boiling" of plaster of Paris, and other powders when heated, and the allied phenomenon which occurs in the roasting of some sulphide ores. H. Rose, C. Zenghelis, and L. Elsner observed that there is an appreciable **volatility** of ferric oxide in the porcelain oven $<1600°$; and H. Moissan added that at 2000° ferric oxide can be sublimed in a crystalline form. A. A. Read, and H. Rose, however, showed that at these temp. the ferric oxide is more or less dissociated, forming a magnetic or ferrosic oxide, consequently, not ferric oxide but rather ferrosic oxide would volatilize at these temp. Even magnetite has a dissociation press. approximating an atm. at 2500°. H. von Wartenberg and W. Gurr found that the mixture of oxides formed by the fusion of ferric oxide volatilizes rapidly at 1800°.

In 1848, H. Rose noticed that when ferric oxide is heated in a porcelain oven, at about 1400°, and the cold product dissolved in acid, a blue precipitate is formed when potassium ferricyanide is added to the soln. This was taken to mean that some ferric oxide is transformed by heat into ferrous oxide. C. F. Bucholz, J. J. Berzelius, and E. Mitscherlich showed by weighing that ferric oxide is dissociated at a white-heat, but J. L. Proust, C. L. Berthollet, and J. H. Hassenfratz did not agree. J. A. Hedvall said that the oxide is stable at a red-heat; H. Moissan, that oxygen is lost when ferric oxide is heated in the electric arc furnace; H. Rose, in the porcelain oven; H. Tholander, at a white-heat; and W. Suida, at a bright red-heat. H. Warth added that the association of alumina with the ferric oxide makes it less liable to decompose. E. D. Clarke said that the oxide on charcoal is reduced to metal in the oxyhydrogen flame, and that the metal then burns as a brilliant scintillation.

W. Suida found that at the temp. of a Bunsen burner, ferric oxide is not reduced provided reducing agents be excluded; but at a bright red-heat or white-heat, ferric oxide and ferric silicates do suffer an appreciable reduction in air, or in an atm. of nitrogen. If heated with molten borax, ferric oxide and ferric silicates suffer a little reduction in air, or in an atm. of nitrogen or carbon monoxide, but in an atm. of oxygen, the reduction is *sehr gering*. The observations of C. F. Rammelsberg, C. Bodewig, R. Hermann, and F. L. Hahn and M. Hertrich, N. A. Tananaeff, E. Selch, A. A. Read, and H. Rose also show that very little loss occurs at the temp. of the blast gas-flame. According to E. J. Rode, there is a terrace in the heating curve of ferric oxide at 745°, and this is attributed to the formation of an allotropic oxide; the fluctuations in the curve at 1280° are attributed to the elimination of oxygen. If hydrated ferric oxide is similarly treated, there is an endothermic reaction corresponding with an unstable modification of ferric oxide which is converted into the stable, crystalline oxide at 320° to 340°, with the evolution of heat; the crystalline oxide undergoes another transformation at 450°. J. C. Hostetter and H. S. Roberts stated that the dissociation of ferric oxide into ferrous oxide and oxygen when it is dissolved in molten glasses occurs above 1300°, the exact temp. is dependent on the composition of the glass. The colour of pottery glazes, admixed with ferric oxide, is very markedly altered by variations of temp. much below this. F. Wüst reported that the evolution of oxygen commences at 600°, and at 1050° the residue is $Fe_2O_3.FeO$; at 1100°, $Fe_2O_3.2FeO$; and at 1200°, $Fe_2O_3.3FeO$. W. Biltz found that with the partial press. of oxygen the same as it is in the atmosphere, the equilibrium **dissociation temperature** for the $Fe_2O_3 \rightarrow Fe_3O_4$ is 1970°, and for the dissociation $Fe_2O_3 \rightarrow Fe$, 3025°; while W. D. Treadwell observed that at 1322°, the **dissociation pressure** of the oxygen from ferric oxide is 0·21 atm., and 1 atm. at 1405°. G. P. Baxter and C. R. Hoover observed a constant difference in weight of about 0·004 per cent. in ferric oxide heated in the neighbourhood of 1100° in a current of air, and in a current of oxygen. The oxygen value was higher, and they gave for the dissociation press., p mm.:

	1150°	1200°	1260°	1280°	1290°
p . . .	0·5	1·0	2·0	4·0	10·0 mm.

G. Charpy and S. Bonnerot gave 0·18 mm. at 800°, and 0·36 mm. at 900°. R. B. Sosman and J. C. Hostetter showed that there is a measurable dissociation of ferric oxide heated in air at all temp. between 100° and 1300°, and that the amount of dissociation increases with temp. P. T. Walden reported for the dissociation press., p mm., of ferric oxide:

	1100°	1150°	1200°	1250°	1300°	1350°	1400°
p . .	5·0	7·0	9·0	20·0	59·5	166·0	454·0

so that the press. at 1350° is approximately equal to the partial press. of the oxygen of the atmosphere. W. Hempel and C. Schubert, and C. Schubert said that the reaction: $6Fe_2O_3=4Fe_3O_4+O_2$ sets in slowly at 1250°, and is complete at 1500°. R. Ruer and M. Nakamoto found that ferric oxide in dry nitrogen loses no weight when heated up to 1125°; at 1150°, oxygen is lost until ferrosic oxide with 2 per cent. of dissolved ferric oxide is formed; and above 1200° up to 1550°, oxygen is lost continuously when the substance melts, and when cold, the product is ferrosic oxide with 4 per cent. ferrous oxide in solid soln. They found the dissociation press. of ferric oxide in oxygen at 1150° is scarcely measurable; at 1383° it is 0·20 atm.; and at 1455°, it is 1 atm. This agrees with the observations of E. Greulich, H. O. Hofman and W. Mostowitsch, A. Girard and G. Chaudron, and E. J. Kohlmeyer. With a constant press. of 10 mm., the isobar of ferric oxide was found, by A. Simon and T. Schmidt, to show a sharp break at 1300° corresponding with complete conversion of ferric to ferrosic oxide without the formation of any solid soln., or intermediate oxide—*vide supra*, ferrosic oxide. H. von Jüptner calculated for the dissociation press. at equilibrium for $2Fe_2O_3=4Fe+3O_2$, $\log p=28884T^{-1}+1·75 \log T+2·8$; for $2Fe_2O_3=4FeO+O_2$, $\log p=-29146T^{-1}+1·75 \log T+2·8$;

and for $3Fe_2O_3=2F_3O_4+O$, $\log p=-11466T^{-1}+1{\cdot}75 \log T+2{\cdot}8$. The values of p atm., calculated from these equations, are respectively:

Products	600°	1000°	1400°
Fe	$0{\cdot}0_{40}3326$	$0{\cdot}0_{20}1466$	$0{\cdot}0_{12}4724$
FeO	$0{\cdot}0_{20}1217$	$0{\cdot}0_{21}8017$	$0{\cdot}0_{12}3070$
Fe_3O_4	$0{\cdot}0_{11}3564$	$0{\cdot}0_{3}3837$	1·394

Products	1600°	2000°	2400°
Fe	$0{\cdot}0_{9}2263$	$0{\cdot}0_{5}1364$	$0{\cdot}0_{3}3791$
FeO	$0{\cdot}0_{9}1552$	$0{\cdot}0_{5}1009$	$0{\cdot}0_{3}3726$
Fe_3O_4	17·41	617·9	8668·0

Calculations were also made by G. G. Brown and C. C. Furnas, L. Wöhler and O. Balz, W. Biltz, H. O. Hofman and W. Mostowitsch, and F. Wüst and P. Rütten. S. Hilpert could not verify P. T. Walden's observations because the results varied considerably with the method of preparation, and the previous treatment of the ferric oxide, for the velocity at which equilibrium is attained, is extremely slow. The amount of ferrous oxide formed in air at 1300° did not exceed 5 per cent. He also said that the application of the thermodynamic formula to calculate the dissociation is untrustworthy. According to R. B. Sosman and J. C. Hostetter, the solid phase produced by the dissociation, $3Fe_2O_3=2Fe_3O_4+O$, is a series of solid soln. ranging from Fe_2O_3 to a point very near, if not at, Fe_3O_4. This hypothesis is confirmed by the optical properties of the residues with over 18 per cent. FeO, and by the pressure-composition isotherms at 1100° and 1200°. If FeO denotes the percentage of ferrous oxide in the solid soln., and p mm., the press. of the oxygen in the solid soln., Fig. 522:

Fe_3O_4	2·90	5·80	8·73	14·57	29·30	44·15	59·2	74·4	89·7	100·00
FeO	0·90	1·80	2·71	4·52	9·09	13·70	18·37	23·07	27·83	31·03
p 1100°	0·37	0·22	0·17	0·13	0·10	0·092	0·085	0·069	0·052	$<0{\cdot}005$
p 1200°	5·0	3·6	3·0	2·6	2·15	1·80	1·55	1·27	0·85	$<0{\cdot}04$

Magnetite dissolved in ferric oxide lowers the dissociation press. The results are plotted in Fig. 521. Since the composition of the solid phase depends on the relation between the weight of the charge and the vol. of the space in which the oxygen collects, the results in which these facts have not been taken into consideration are untrustworthy. M. Tigerschiöld wrote the dissociation equation: $6Fe_2O_3=4Fe_3O_4+O_2$, and using R. B. Sosman and J. C. Hostetter's data, gave for the equilibrium constant, K, which is here also the oxygen press., $\log K=\log p=-20{,}946T^{-1}+3{\cdot}5\log T+0{\cdot}0011577T-0{\cdot}6332$. O. C. Ralston, combining these data, and also those of P. T. Walden, gave $\log p=-23{,}550T^{-1}+13{\cdot}83$. Ferric oxide at 1348° has an oxygen press. of 0·207 atm., so that it is stable in air up to this temp., and beyond that temp. it will lose oxygen. Ferric oxide would exert 1 atm. press. at 1430°, and it could be heated in an atm. of oxygen up to this temp. without losing oxygen. Magnetite dissolved in ferric oxide would lower the dissociation press. No evidence was obtained of the existence of compounds of the two oxides above 1000°. The shapes of the curves are taken to show that there is a continuous series of solid soln. from Fe_2O_3 to 90 per cent. Fe_3O_4. The steeper ends of the curves, and the flatness of the central portion of the curve at 1100° when compared with that of the central portion of the 1200° curve, indicated that it is possible that at a lower temp. the central portion will be horizontal. In that case, two immiscible solid soln. will be in equilibrium with one another—one soln. will

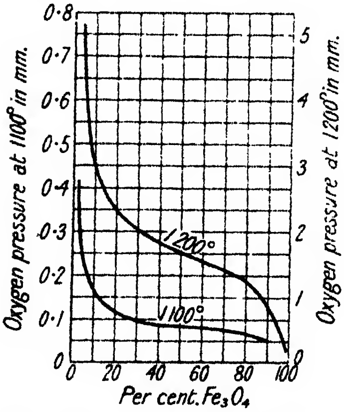


FIG. 521.—Dissociation Pressures in the System: Fe_2O_3–Fe_3O_4.

be Fe_2O_3 with some dissolved Fe_3O_4, and the other conjugate soln., Fe_3O_4 with some dissolved Fe_2O_3. The sloping ends of the curves would apply to unsaturated soln. M. Tigerschiöld deduced for the oxygen press., p, of solid soln. with 97·1 per cent. of Fe_2O_3, $\log p = -20{,}946T^{-1} + 3{\cdot}5 \log T + 0{\cdot}001157(T-600) + 0{\cdot}061$; and for solid soln. with 10·31 per cent. of Fe_2O_3, $\log p = -22{,}080T^{-1} + 3{\cdot}5 \log T + 0{\cdot}001157 (T-600) + 0{\cdot}061$. These are the approximate boundaries of the solid soln. of the system with ferric and ferrosic oxides. The results, plotted in Fig. 522, show the fields of stability of these two oxides—*vide infra*, ferric oxide. E. R. Wagner discussed the decomposition of the oxide in vacuum tubes.

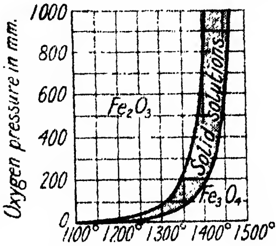


Fig. 522.—Oxygen Pressures in the System Fe_2O_3–Fe_3O_4 at Different Temperatures.

A. Smits and J. M. Bijvoet said that the two oxides are not isomorphous, and that it is very improbable that there is a continuous series of solid soln. of ferric and ferrosic oxides; and A. Simon and T. Schmidt explained the limited solubility of ferrosic in ferric oxide as an example of G. F. Hüttig's theory of vagabond atoms within the crystal lattice. P. P. Fedotéeff and T. N. Petrenko obtained solid soln. of the two oxides by oxidizing iron with a mixture of steam and air between 100° and 1100°, but not in the oxidation of iron by air alone. J. Huggett and co-workers said that their magnetic measurements indicate that 20 per cent. of ferrosic oxide can be dissolved in ferric oxide at 650°. The subject was also discussed by S. Hilpert and J. Beyer, H. S. Roberts and H. E. Merwin, P. Ramdohr, C. Benedicks and H. Löfquist, and E. D. Eastman. R. Ruer and M. Nakamoto obtained the composition curve of ferric oxide after heating it in nitrogen at different temp. No appreciable loss in weight occurred until about 1150°, when an abrupt loss occurred and the product contained about 98 per cent. of ferrosic oxide and 2 per cent. of ferric oxide. Further losses occurred as the temp. was raised. It is assumed that no solid soln. are formed until the product with 98 per cent. Fe_3O_4 is attained. The results contradict those of previous observers, unless some other interpretation is possible. The equilibrium conditions of ferric oxide in the presence of carbon monoxide and hydrogen were studied by A. Matsubara, and others—*vide supra*, Figs. 500 and 501. W. von W. Scholten titrated electrometrically a soln. of ferrous sulphate with a soln. of hypochlorite, and observed that in an acidic soln., the values of the potential furnished a smooth curve from ferrous to ferric sulphate, but in alkaline soln., there was an irregularity corresponding with the presence of a solid soln. of ferrous and ferric hydroxides.

E. J. Kohlmeyer observed that ferric oxide begins to sinter at about 950°, and it is very marked at 1360°; F. Sauerwald and G. Elsner studied the subject; H. O. Hofman and W. Mostowitsch observed a marked sintering after heating for half an hour at 1460°. The subject was also examined by J. A. Hedvall, and J. A. Hedvall and E. Helin. A. Brun gave 1300° for the **melting-point**; C. Schubert, 1500°; H. von Wartenberg and W. Gurr, 1570°; B. Garre, 1560°; and C. Doelter, 1350° to 1400°. These data do not represent true m.p., because R. Ruer and M. Nakamoto found that the product which melts in nitrogen at 1550° is ferrosic oxide with about 4 per cent. of dissolved ferrous oxide in solid soln. The m.p. of ferric oxide in the presence of enough oxygen to prevent dissociation has not been determined. W. Wicht observed that when ferric oxide is fused in the electric furnace, below 2000°, the product has the mol. proportion $FeO : Fe_2O_3 = 10 : 1$; H. Rose also noticed the partial reduction of ferric oxide during fusion —*vide supra*. S. Hilpert and E. Kohlmeyer found 1565° for a sample which, after melting, contained 10 per cent. of Fe_3O_4. C. G. Fink and C. L. Mantell observed that a sample at 1492° showed signs of softening, and it became fluid at 1503°. Observations were also made by O. Ruff and O. Goecke. The possible **allotropic changes** have been discussed elsewhere. There is a definite transformation point at about 700°, and the best representative value of this **transformation point** is taken to be 678°. H. Forestier and G. Chaudron found that mixtures of ferric oxide with ferrosic oxide, alumina, or chromic oxide, lower the transition temp.; and H. Warth found that alumina makes ferric oxide more stable at high temp.

E. J. Kohlmeyer found that red ferric oxide becomes black at 920° to 950°; it sinters strongly at 1370° and the evolution of oxygen begins; the product (solid soln.) melts at 1470°, and becomes quite liquid between 1525°, and 1600°. The m.p. of ferric oxide in oxygen gas is 1562° to 1565°. There is a break in the cooling curve between 1250° and 1350°, and a second between 1028° and 1035°. E. J. Kohlmeyer interprets his observations by assuming that near 1525°, when re-melting occurs, the material has the composition $3FeO.4Fe_2O_3$; that the melt which gave the longest pause at 1470° had the composition $3FeO.5Fe_2O_3$; and that which gave the longest pause at 1370° had the composition $FeO.3Fe_2O_3$. From these results, he set up a temperature-constitution ferric oxide. R. B. Sosman and J. C. Hostetter regard the alleged compounds as solid soln.—*vide supra*.

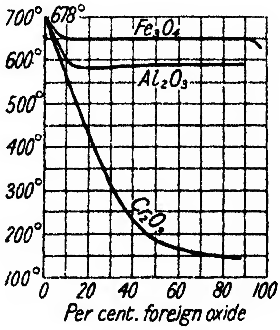


FIG. 523.—The Effect of Foreign Oxides on the Transition Temperature of Ferric Oxide.

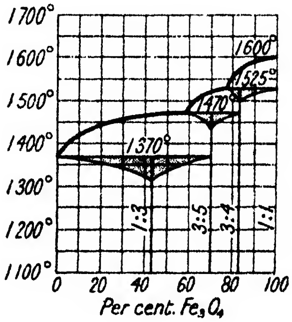


FIG. 524.—Equilibrium Diagram of the Binary System: Fe_2O_3–Fe_3O_4.

H. le Chatelier gave for the **heat of formation** (2Fe,3O)=194·4 Cals., and (2FeO,O)=65·2 Cals.; and for the conversion of ordinary to calcined ferric oxide, he gave 2·14 Cals. G. H. Brodie and co-workers gave (2Fe,3O)=267·4 Cals. per mol.; W. A. Roth, 198·5 Cals; W. G. Mixter gave (2Fe,3O)=192·2 Cals., (2FeO,O)=63·7 Cals., and $2Fe_3O_4+O=3Fe_2O_3+54{\cdot}5$ Cals.; and A. Simon and T. Schmidt calculated for $2Fe_3O_4 \rightarrow 3Fe_2O_3+36{\cdot}815$ Cals. W. A. Roth and co-workers gave $Fe_2O_3+3Cl_2=2FeCl_3+3O+7{\cdot}4$ Cals.; and $FeO+Fe_2O_3=Fe_3O_4+7{\cdot}0$ Cals. M. Tigerschiöld gave (2Fe,3O)=197·1 Cals. W. D. Treadwell gave $2Fe_3O_4+\frac{1}{2}O_2=3Fe_2O_3+49{\cdot}5$ Cals. O. Döpke gave (2Fe,3O)=197·4 Cals. H. von Jüptner estimated $4Fe+3O_2=2Fe_2O_3+132$ Cals.; $4FeO+O_2=2Fe_2O_3+133{\cdot}2$ Cals.; and $2Fe_3O_4+O=3Fe_2O_3+52{\cdot}4$ Cals. Observations were made by T. Andrews. G. S. Parks and K. K. Kelley calculated 197·5 Cals. for the heat of formation, —63·9 for the **entropy,** and —178·4 for the **free energy** at 25°. A. C. Halferstein gave $-107{,}748+63{\cdot}551T$ cals. for the free energy of the reaction $6Fe_2O_3=4Fe_3O_4+O_2$, and for the free energy of ferric oxide, $-194{\cdot}666+63{\cdot}514T$, so that the free energy at 25° is —175,780 cals. J. Chipman and D. W. Murphy studied the subject. R. Dallwitz-Wegener discussed the free energy of the compound, and K. K. Kelley, the entropy.

E. A. Wülfing observed that the **indices of refraction** of hæmatite for the *A*-, *a*-, *B*-, and *C*-lines are respectively $\omega=2{\cdot}904$, 2·949, 2·988, and 3·042, and $\epsilon=2{\cdot}690$, 2·725, 2·759, and 2·797; while C. Försterling gave for red, yellow, green, and blue light respectively $\omega=3{\cdot}05$, 3·11, 3·17. and 2·7; and $\epsilon=2{\cdot}87$, 2·88, 2·92, and 2·84. U. R. Evans, and F. H. Constable studied the optical properties of thin films of the oxide. Observations were also made by A. Kundt. G. Kalb, and L. Michel observed that the **birefringence** is strong; and the **optical character** is negative. According to R. B. Sosman and J. C. Hostetter, the observable optical properties of crystals of completely oxidized magnetite, and of hæmatite are not distinguished; they are uniaxial, and negative; $\epsilon=2\cdot74$ for $\lambda=700\mu\mu$; the birefringence is greater than 0·21; and the ω-absorption is greater than the ϵ-absorption. For samples of ferric oxide heated at 1200°, and containing FeO per cent. of ferrous oxide:

FeO .	0·58	5·60	12·99	16·11	17·79
ϵ . .	2·74	2·73	2·72	2·71	2·71

and $\omega-\epsilon$ in the first case exceeds 0·21, and in the penultimate case exceeds 0·16. The refractive index of magnetite is 2·42 for $\lambda=700\mu\mu$, and that of hæmatite is 2·74, so that the refractive index is lowered by dissolved magnetite, but the lowering is not proportional to the amount of ferrosic oxide in soln. All this agrees with the assumption that solid soln. of ferric and ferrosic oxides are formed when ferric oxide is heated to the temp. at which oxygen is given off. T. M. Broderick stated that some of the specimens of hæmatite assumed by R. B. Sosman and J. C. Hostetter to be solid soln., contained residual free magnetite which was visible on polished surfaces under the microscope. He added that before assuming the presence of solid soln. in natural hæmatite, the effect of free magnetite must be accounted for, and optical homogeneity must be shown in materials containing both Fe_2O_3 and Fe_3O_4. The variation in the colour of reflected light from adjacent grains similarly oriented; the apparent lack of enough magnetite to account for the magnetic properties; and the differences in the behaviour of the grains on etching, all support the hypothesis that solid soln. are present.

C. Försterling found the **absorption coefficients** for red, yellow, green, and blue light to be respectively 0·0875, 0·135, 0·173, and 0·377 for the ordinary ray, and 0·0670, 0·111, 0·126, and 0·305 for the extraordinary ray. M. Kimura and M. Takewaki studied the subject. Ferric oxide colours glass a yellowish-brown, and ferrous oxide a bluish-green. The tinctorial effect of the latter is greater than that of the former. S. English and co-workers investigated the effect of these oxide on the transmission of light of short wave-length by glass. The limits of transmission with the smaller proportions of oxide are:

Oxide . .	0·005	0·010	0·030	0·060 per cent.
Fe_2O_3-glass .	2600	2670	2840	2960 A.
FeO-glass . .	2600	2600	2780	2870 A.

Observations were also made by G. Jaeckel, and D. Starkie and W. E. S. Turner. The effect changes on exposure to light, owing to the transformation of ferrous into ferric oxide. The converse effect was noticed by W. W. Coblentz and R. Stair when the glass is heated in a gas-flame, owing to the presumed reduction of some ferric to ferrous oxide. The subject was studied by A. Rüttenauer, and A. Salmony. The scattering of light by suspended particles was measured by G. I. Pokrowsky. W. W. Coblentz observed that the ultra-red **reflecting power** was about 12 per cent. from 1μ to 13μ; whilst J. Königsberger found for light vibrating perpendicular to the principal axis, 25·71 per cent., or for light vibrating parallel to the chief axis, 22·86 per cent. J. Hofmann found the emission spectrum in the blue is greater than in the red. R. Eisenschitz and A. Reis, and E. Domek made observations on this subject. M. Kahanowicz found that the energy, E, emitted between 300° and 1100° follows the fourth power law, $E=1\cdot30\times10^{-10}T^4e^{-380\cdot5/T}$. The radiation energy was also discussed by E. Schmidt, V. Polak, C. P. Randolph and M. J. Overholser, I. Langmuir, F. Wamsler, M. Kahanowicz, and F. Paschen. According to J. Königsberger, the absorption coeff., a, for the long heat waves are $a=26$ for $\lambda=0\cdot5$ to $4\cdot0\mu$; $a=24$ for $\lambda=1\cdot6$ to $4\cdot0\mu$; $a=17$ for $\lambda=4\cdot0$ to 40μ; and $a=47$ for $\lambda=15$ to 40μ. F. Rinne found that the **pleochroism** of samples from Tvedestrand and Strassfurt is ω brownish-red, and ϵ yellowish-red; and H. Tertsch, with a sample from Vesuvian ash, ω=dark blood-red, and ϵ yellowish-red. The **spark spectrum** of hæmatite was observed by A. de Gramont, and W. N. Hartley and H. Ramage. M. Kimura and M. Takewaki found that the oxide is opaque for ultra-violet light. G. K. Burgess and P. D. Foote found that the **ultra-red emissivity** of ferric oxide for radiation of wave-length $\lambda=0{\cdot}65\mu$ varies from 0·98 to 0·92 over the interval 800° to 1200°; and the total emissivity increases from 0·85 at 500° to 0·89 at 1200°. K. Hild studied the total radiation of the oxide at 800° to 1400°. H. A. Barton and co-workers studied the emission of **positive ions** by the ferric oxide catalyst for ammonia. J. Ewles, and A. Pochettino found that the mineral exhibits a green **cathodoluminescence,** but W. Crookes observed none. M. Ishibashi studied the effect of **cathode rays.** C. B. Thwing found the **dielectric constant** of ferric oxide to be 14·20. According to J. A. Fleming and J. Dewar, the dielectric constant of water at −185° is very greatly increased in the presence of ferric oxide, but, from the slope of the curve, at lower temp., the effect would probably become less. A. Dufour showed that the spectral line 5789·7 A. shows the Zeeman effect when in a magnetic field of 28,000 gauss parallel to the lines of force. C. Doelter, and W. Ackroyd and H. B. Knowles measured the **absorption of X-rays** by ferric oxide; and C. H. Kunsman, the emission of **positive ions.** P. Martin observed the **Kerr effect** parallel to the chief axis evidenced by a positive rotation of 0·2″ and it increases towards the violet; and H. E. J. G. du Bois observed no Kerr effect vertical to the chief axis of hæmatite. S. Loria observed a smaller rotation than 0·2″ when taken parallel to the base. G. A. Dima found that the **photoelectric effect** of ferric oxide is smaller than that of ferrous oxide. H. A. Barton and co-workers, and E. Badareu observed the liberation of positive ions by heated ferric oxide. A. Wehnelt observed no emission of electrons at 1600°, but F. Jentzsch observed the effect. The thermionic emission of electrons between 2000° and 2500° was studied by G. P. Thomson, G. W. C. Kaye and W. F. Higgins, and A. K. Brewer; the surface electrons, by J. E. Nyrop; and the reflection of electrons from a film of ferric oxide, by E. Rupp and E. Schmidt. R. Whytlaw-Gray and co-workers, and E. Thomson found that the particles which exhibit the Brownian movement form straight chains under the influence of an electrostatic field.

R. J. Haüy observed that hæmatite is electrified like glass when it is rubbed with a handkerchief. The **electrical conductivity** of ferric oxide is good compared with that of many other metal oxides. G. Cesaro reported that the electrical conductivity of hæmatite is negligibly small; and F. Beijerinck obtained a similar result, but added that martite is a good conductor, and that the conductivity increases with rise of temp. Observations were made by P. J. Pelletier, S. P. Thompson, J. F. L. Hausmann and F. C. Henrici, E. Wartmann, W. Skey, F. von Kobell, and T. du Moncel. A. Abt found the **electrical resistance** of hæmatite to vary from 1430·52 to 6500 ohms. R. D. Harvey studied the subject. H. Bäckström found that the mineral is a good conductor, and that the conductivity of the crystal is different in different directions. Thus, the conductivity in the direction of the principal axis (0001) is nearly double what it is when perpendicular to that axis. If R_c denotes the electrical resistance in the direction of the principal axis, and R_a, the electrical resistance in a direction inclined to that axis, then, at 0°, R_c=80·8, and R_a=40·8; at 17°, R_c=68·7, and R_a=35·1; and at 100°, R_c=33·1 reduced to a length of 1 sq. mm. section; and R_a=18·3. The ratios R_c/R_a are respectively 1·98, 1·96, and 1·81, while at 236·7°, the ratio is 1·55. For a temp. θ°,

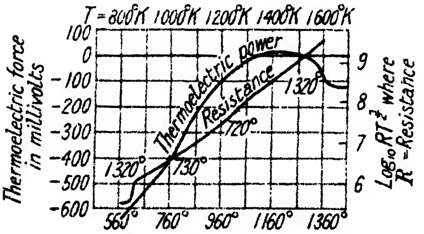


FIG. 525.—Electrical Resistance and Thermoelectric Power of Ferrous Oxide.

between 0° and 80°, the resistance, R, in a direction parallel to the chief axis, is $R=R_0(1+0{\cdot}014178\theta+0{\cdot}0_312533\theta^2-0{\cdot}0_651621\theta^3)$; and the resistance in a direction perpendicular to the chief axis, $R=R_0(1-0{\cdot}012796\theta+0{\cdot}0_31108\theta^2-0{\cdot}0_646464\theta^3)$. The resistance of hæmatite was 38·4 ohms at 19·9° when 3·01 per cent. of moisture was present. Heating a specimen to 1000° and cooling rapidly gave a specimen which was a poor conductor, but with slow cooling the conductivity was greater. J. Königsberger and co-workers, O. Reichenheim, and K. Baedeker obtained results in agreement with these values. J. Rosenthal observed that the conductivity of compressed ferric oxide is perceptible at 300°, and increases as the temp. rises. A. A. Somerville found the resistance of a rod at 252° was 10^7 ohms, and only 80 ohms at 1100°. Observations were made by S. Hilpert and E. Kohlmeyer, J. A. Osteen, J. Königsberger, S. Veil, C. C. Bidwell, G. Reboul and E. Bodin, G. Reboul, and E. Bodin. C. C. Bidwell's results for ferric oxide are summarized in Fig. 525. The electrical resistance is represented in terms of $\log_{10} R/T^{3/2}$, where T denotes the absolute temp., and R the resistance. There are breaks in the curve at 1320° and at 730°. T. W. Case observed no change in the electrical resistance of hæmatite on exposure to light. E. Diepschlag and F. Wulfestieg studied the high temp. electrical conductivity of ferrosic oxide mixed with silica, magnesia, or alumina. T. Frey observed no unipolarity in the compressed powder of ferric oxide.

Observations on the **thermoelectric force** of ferric oxide were made by T. J. Seebeck, and W. G. Hankel. According to H. Bäckström, the thermoelectric force between copper and hæmatite is such that a current flows from the base of the crystal through the hot junction to the copper with an e.m.f. of 0·0002879 volt per degree rise of temp., but if the hot junction is parallel to the chief axis, the e.m.f. is 0·0003138 volt per degree. J. Königsberger and J. Weiss obtained 0·0005 volt per degree at about 50°. C. C. Bidwell's results for ferric oxide against platinum are summarized in Fig. 525. There is a transformation point between 710° and 730°, and one at 1320°. There is a reversal in sign at 1125°. J. Königsberger discussed the theory of the thermoelectric force of ferric oxide against the metals.

W. D. Treadwell measured the press. of the oxygen in the transformation $Fe_2O_3 \rightarrow Fe_3O_4$ from the **electromotive force** of the oxide against an electrode of molten silver sat. with oxygen in the cell Fe_3O_4,Fe_2O | molten borax or glass | O_2,Ag between 800° and 1193°. The result is 0·262 volt, from which it is calculated that $2Fe_3O_4+\frac{1}{2}O_2=3Fe_2O_3+61{\cdot}3$ Cals. ; 0·897 volt was obtained for the cell Fe,FeO | electrolyte | O_2,Ag, from which it follows that $3FeO+\frac{1}{2}O_2=Fe_3O_4+74{\cdot}2$ Cals. ; and 1·040 volt for the cell Fe,FeO | electrolyte | O_2,Ag, from which it follows : $Fe+\frac{1}{2}O_2=FeO+66{\cdot}6$ Cals. W. D. Treadwell gave for the e.m.f. of the cell Fe_3O_4,Fe_2O_3 | electrolyte | O_2, in volts :

	980°	1000°	1010°	1018°	1050°	1080°	1080°	1100°
E.m.f. .	0·285	0·262	0·285	0·251	0·229	0·213	0·225	0·200

and the value at 1100° is in good agreement with the value calculated from the dissociation press. E. Liebreich, and E. Liebreich and F. Spitzer gave for the e.m.f., E volt, at 20°, of the cell Fe_2O_3 | KCl,H_2SO_4 | Fe, $E=0{\cdot}090$; Fe_2O_3|KCl,H_2SO_4|KCl,$HgCl_2$|Hg, $E=-0{\cdot}526$; and Fe_2O_3|KCl,NaOH|KCl,$HgCl_2$| Hg, $E=-0{\cdot}520$. For single crystals in the cell : $Fe_2O_{3\,\text{natural}}$ | Conc. feebly acidified soln. $ZnSO_4$ | Zn, G. Szivessy gave $E=1{\cdot}3335$ volt at 18°. V. H. Gottschalk and H. A. Buehler found that the electromotive force of hæmatite against copper in distilled water is 0·08 to 0·26 volt. S. B. Christy, and A. von Oettingen measured the potential of ferric oxide in soln. of potassium cyanide. K. Fischbeck and E. Einecke observed only 1 per cent. reduction of ferric oxide used as cathode, and this was attributed to the effect of impurities, or of occluded hydrogen. F. Peters, when comparing the capacities of accumulators with negative plates of natural and artificial ferric oxide, obtained no evidence of the electrolytic inactivity of ferric oxide indicated by T. A. Edison, and P. de Beaux. The subject was discussed by O. Pattenhausen. K. Fischbeck and E. Einecke studied the electrolytic reduction of solid ferric oxide; K. R. Dixit, the potential; and S. Borowik, the electrolytic valve action of ferric oxide.

Ferric oxide is usually paramagnetic, but it also exists in a ferromagnetic form both in nature and as a synthetic product; and this even in the absence of magnetite. Hæmatite may not only have a feeble **magnetic power,** but it may also exhibit polar magnetism. J. Plücker said that the relative magnetic powers of iron and hæmatite are as 100,000 : 759. The magnetic power of hæmatite was also noted by M. Faraday, L. F. Nilson and O. Pettersson, T. J. Seebeck, A. C. Becquerel, E. Colardeau, C. B. Greiss, C. F. Rammelsberg, A. Streng, H. A. J. Wilkens and H. B. C. Nitze, F. Bitter, R. Forrer, and T. L. Phipson. W. M. Mordey said that an alternating current magnet with hæmatite powder does not form radical lines of force about the poles as with ordinary ferromagnetic substances, but the powder arranges itself in rings. According to J. L. Smith, ferric oxide is magnetic when it contains small proportions of cobalt or nickel oxide. The magnetic properties of ferric oxide have been attributed by F. J. Malaguti, S. de Luca, J. L. Smith, S. H. Emmens, G. Gilbert, A. Collon, O. Mügge, T. T. Smith, W. H. Newhouse and W. H. Callahan, L. Duparc and co-workers, S. Hilpert and co-workers, R. Chevallier, R. B. Sosman and J. C. Hostetter, P. A. Wagner, G. Frebold and J. Hesemann, D. P. R. Chaudhuri, V. Daniloff and co-workers, O. Baudisch, A. Quartaroli, G. Jouravsky and co-workers, H. Sachse, G. E. Allan, and G. E. Allan and J. Brown to the presence of ferrous oxide, ferrosic oxide, or a ferrite. H. A. J. Wilkens and H. B. C. Nitze, and S. Veil discussed the magnetic separation of hæmatite.

According to S. Hilpert, since ferrosic oxide (*q.v.*) is constituted $FeO.Fe_2O_3$, *i.e.* ferrous ferrite, $Fe(FeO_2)_2$, or $(FeO)^{+}(Fe_2O_3)^{\cdot\cdot}$, the magnetic property is attributed to the acidic radicle. When ferrosic oxide is oxidized to red, ferromagnetic oxide, only the base ferrous oxide is oxidized to form ferromagnetic ferric oxide constituted $(Fe_2O_3)^{+}(2Fe_2O_3)^{-}$. Consequently, S. Hilpert assumes that metastable, magnetic ferric oxide is constituted $Fe^{\cdot\cdot\cdot}(FeO_3)'''$, ferric orthoferrite, whilst the non-magnetic ferric oxide is constituted $Fe_2^{\cdot\cdot\cdot}O_3''$. R. B. Sosman referred the magnetic qualities to the spacing and orientation of the iron atoms, without reference to the other atoms of the molecule. E. V. Shannon said that terrestrial ferromagnetic ferric oxide is not the same as the product of the oxidation of meteorites.

G. E. Allan and J. Brown found that both hæmatite and artificial ferric oxide become magnetic when heated in a magnetic field, and on cooling from 1000°, both oxides become permanently magnetized, presumably owing to the formation of ferrosic oxide. In hydrogen, the temp. at which the magnetic power is acquired is higher (300°), and is more sharply defined than it is in air. The curve showing the relation between the magnetic power and temp., in hydrogen, has maxima at 425°, 575°, and 750°, and these breaks are supposed to indicate the optimum temp. for the various stages in the reduction of ferric oxide by hydrogen. H. Moissan observed that ferric oxide becomes magnetic when heated in the electric furnace, and A. A. Read, when it is heated in the oxyhydrogen flame. The phenomenon is here attributed to the formation of magnetic ferrosic oxide, and not to the formation of ferromagnetic ferric oxide. V. Rodt obtained the ferromagnetic oxide by heating the product of the oxidation of hydrated ferrous or ferric oxide to 210°. W. H. Albrecht and E. Wedekind found that the magnetic susceptibility, χ mass units, of the hydroxide prepared by R. Willstätter and co-workers' process had a susceptibility:

Age . . .	0	1	1·5	4	6	25	30
Mols. H_2O . .	2·01	1·6	1·31	1·27	1·22	1·08	1·0
$\chi \times 10^6$ . . .	116	191	192	192	155	99	60

When prepared by precipitation from ferric nitrate soln., by ammonia at different temp.:

	Hot-washed				Cold-washed			
Temp. .	0°	25°	50°	100°	0°	25°	50°	100°
Mols. H_2O	1·43	1·52	1·45	1·12	2·37	2·11	2·09	1·38
$\chi\times10^6$.	285	321	323	255	203	261	257	230

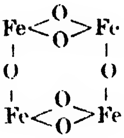
For the different hydrates:

H_2O . .	4·0	3·5	2·1	1·2	0·5
$\chi\times10^6$ . .	85	140	158	159	210

and for ferric oxide prepared, at different temp., from iron pentacarbonyl:

	815°	725°	575°	450°
$\chi\times10^6$ . .	2600	1100	1600	1200

According to E. Wilson, if the magnetic susceptibility of magnetite is 10, that of red hæmatite is 0·00020. P. Hausknecht, T. T. Smith, G. Dupouy, J. R. Ashworth, G. F. Hüttig and H. Kittel, L. Blanc and G. Chaudron, H. Sachse, A. Serres, M. Faraday, J. Königsberger, S. Meyer, E. Feytis, P. Weiss and R. Forrer, J. Plücker, G. Wiedmann, F. J. Malaguti, L. Külp, S. Henrichsen, A. Ditte, F. Rinne, C. F. Rammelsberg, A. Delesse, G. A. Kenngott, A. Liversidge, T. L. Phipson, G. B. Hogenraad, A. Abt, F. Schalch, F. Stutzer and co-workers, J. Kunz, B. Bavink, and E. Wilson and E. F. Herroun made comparative measurements of the magnetic susceptibility of ferric oxide. W. Hagen compared the susceptibilities of ferric oxide and chloride. R. Wallach measured the relative susceptibilities of ferric oxide prepared (i) by ammonia precipitation from a cold dil. soln. of ferric chloride; (ii) from hydrated ferric hydroxide obtained as just indicated, but heated in boiling water; and (iii) by the action of water on sodium ferrite. The first oxide gave a marked break in the heating curve at about 350°, and the third gave a break at about 750°. W. H. Albrecht found that ferric oxide obtained by calcining ferrosic oxide at 650°, 700°, and 1000°, in oxygen, had a magnetic susceptibility ranging from $3·4\times10^{-6}$ to 88×10^{-6} mass unit; and samples prepared by heating hydrated ferric oxide had values ranging from 22×10^{-6} to 34×10^{-6} mass unit. G. Wistrand gave $60·7\times10^{-6}$; E. Wedekind and W. H. Albrecht gave $\chi=220\times10^{-6}$ to 2600×10^{-6} for ferric oxide obtained by the combustion of iron pentacarbonyl; L. A. Welo and O. Baudisch, $144,000\times10^{-6}$ for the oxide obtained from ferrosic oxide at 300°, and 2700×10^{-6} for the oxide obtained from ferrosic oxide at 550°. E. F. Herroun and E. Wilson, $22,800\times10^{-6}$ to $55,000\times10^{-6}$ for the oxide obtained by dehydrating lepidocrocite, γ-$Fe_2O_3.H_2O$; $128,000\times10^{-6}$ for the oxide obtained from ferric oxide; $34,700\times10^{-6}$ for the oxide obtained from ferrous oxalate; 63×10^{-6} for the oxide obtained from basic ferric acetate; and 4400×10^{-6} for powdered iron-rust free from ferrous oxide; K. Honda and T. Sone obtained for commercial ferric oxide, $20·6\times10^{-6}$ at 10·5° to 17·5°; G. Berndt, 262×10^{-6} for $H=27$ gauss, and 354×10^{-6} for $H=201·7$ gauss; and R. Chevallier, $122,000\times10^{-6}$ for the oxide obtained from ferrosic oxide at 400°; and $12,700\times10^{-6}$ for the oxide obtained from ferrous sulphate soln., soda-lye, and hydrogen dioxide. The effect of impurities on the susceptibility was examined by E. F. Herroun and E. Wilson, J. Huggett and G. Chaudron, and S. Veil. J. Königsberger, S. Meyer, and G. Berndt found that the susceptibility, χ, decreases with an increase in the strength of the magnetic field; but L. A. Welo and O. Baudisch found that the susceptibility of ferric oxide obtained by oxidizing ferrosic oxide increases as the field-strength increases up to 65 gauss. G. F. Hüttig and H. Kittel found that the values varied with the mode of preparation; for a specimen of Fe_2O_3, the magnetic susceptibility was $22·8\times10^{-6}$ mass unit; and after heating in oxygen 4 hrs. at 600°, $57·6\times10^{-6}$ mass unit. The dissolved oxygen thus raises the susceptibility. The oxygen is adsorbed on the surface, or it is diffused in the lattice. A. Krause and co-workers attributed the magnetic properties to the $—Fe=O_2=Fe—$ group, and represented the constitution of ferromagnetic γ-Fe_2O_3, by



According to E. F. Herroun and E. Wilson, for a maximum field-strength, $H=180$ gauss, the permeability is a maximum, $\mu=3·68$; the coercive force, $H_c=64·7$ gauss: and the remanent induction, $B_r=252$ gauss. The remanence was studied by E. Holm, C. B. Greiss, A. Delesse, A. Abt, and R. B. Sosman and J. C. Hostetter. T. T. Smith observed that the normal magnetization curve of hæmatite has a sharp rise followed by a slow increase which is proportional to the field-strength. The loss of energy by hysteresis increases with an increase in the maximum field until it attains a constant value, about 150 gauss. H. Forestier and G. Chaudron found that the coeff. of magnetization of ferric oxide varies with the thermal and magnetic treatment to which the sample is subjected. Starting with an oxide devoid of all magnetization, the magnetization-temperature curve shows an increase in the coefficient of magnetization up to 600°; this is followed by a sharp decrease, which ends at 675°. The magnetization-temperature curve obtained on cooling is separated from that obtained on heating below 600°, and the coefficient of magnetization increases on cooling down to the ordinary temp. On repeating the experiment with the same sample, a curve is obtained which is rigorously reversible and superposable on the cooling curve of the first experiment: moreover, the sample is now polarized. Magnetization can be destroyed by heating beyond 675° and cooling in a non-magnetic field. Under the same conditions with magnetite and ferrites, a very sharp increase in the coefficient of magnetization is obtained. The subject was also discussed by J. Huggett and G. Chaudron, R. Chevallier, and G. Berndt. R. B. Sosman and E. Posnjak found that the hysteresis loops of magnetite, and ferromagnetic ferric oxide—natural and artificial—are different, Fig. 526. C. W. Heaps, and C. W. Heaps and J. Taylor observed the Barkhausen effect in the magnetization of crystals of hæmatite. J. Kruckenberg studied the magnetostriction of ferric oxide.

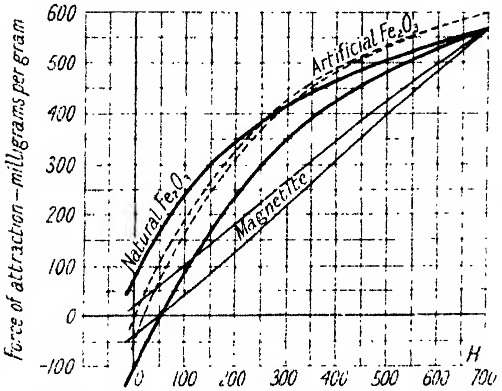


FIG. 526.—Hysteresis Loops of Magnetite and Ferromagnetic Ferric Oxide.

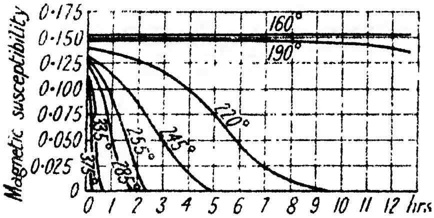


FIG. 527.—The Effect of Time and Temperature on the Magnetic Susceptibility of Ferromagnetic Ferric Oxide.

According to H. Sachse, and H. Sachse and R. Haase, the regular ferromagnetic ferric oxide is unstable at all temp. The susceptibility lost about 60 per cent. of its original value in 4 years, and at the same time, the faculty of transformation is greatly increased. The effect of temp. and time on the susceptibility is illustrated in Fig. 527. The curves show a period of induction. The unstable ferromagnetic oxide is a pseudomorph after magnetite, and this changes to that of ordinary, stable ferric oxide. H. Sachse studied the X-radiograms.

E. F. Herroun and E. Wilson found the magnetic susceptibility of hæmatite to range from $25\cdot0\times10^{-6}$ to $36\cdot8\times10^{-6}$ mass unit, and that of specular iron ore from 107×10^{-6} to 517×10^{-6}. G. Grenet obtained values ranging from 316×10^{-6} to 9×10^{-6} for the coeff. of magnetization. T. D. Yensen studied the magnetization of thin films. J. Tyndall and H. Knoblauch, J. Kunz, O. Mügge, A. Girard and G. Chaudron, B. Bavink, and T. T. Smith studied the relation of the magnetic field and the axes of the crystal on the magnetization. J. Westman found that a crystal of hæmatite is paramagnetic in all directions, but the magnetic susceptibility in the direction of the principal axis, (0001), is only a few hundredths of its value taken perpendicular to the chief axis. Thus, the magnetic susceptibilities in absolute units, with a field-strength, *H*, are :

H	48	60	72	Mean
Perpendicular to chief axis . .	1·780	1·840	1·900	1·840
Parallel to chief axis . . .	0·050	0·073	0·093	0·072

K. Honda and T. Sone found that the magnetic susceptibility, χ mass units, of paramagnetic ferric oxide increases as the temp. rises from −173° somewhat as follows :

	−173°	−52°	−4·5°	104°	371°	596°	696°	817°	1301
$\chi\times10^6$.	13·9	15·4	20·4	21·2	25·1	32·4	14·7	14·7	12·6

The rapid increase in the susceptibility in passing from about 0° to 596° is attributed to the presence of traces of magnetite. The rapid decrease in the susceptibility from about 596° represents the known magnetic transformation on magnetite at 690°. The curve Fig. 527, represents the susceptibility of hæmatite at elevated temp. Hence, it is inferred that the susceptibility of pure hæmatite would suffer a small decrease on raising the temp. from −190° to 1300°. When ordinary paramagnetic ferric oxide is cooled, the susceptibility falls rapidly down to −40°, and thereafter very slowly ; from −40° to −185°, the curve is reversible, but when warmed above −40°, if in a magnetic field, the hæmatite becomes ferromagnetic, so that at room temp., the susceptibility is nearly twice the value of the original sample. With further heating to about 600°, the susceptibility increases irreversibly in the magnetic field, and then rapidly falls to the original value at about 690°. Above this temp., no marked change occurs, and what there is, is reversible. On cooling below 690° in a magnetic field, the susceptibility increases as the temp. drops to room temp. The susceptibility induced by this heat-treatment is much below that of magnetite, but during the change of temp. from −40° to 600°, if carried out in a magnetic field, the material becomes ferromagnetic.

S. Hilpert gave 500° for the Curie point, he also found an irreversible transformation which occupies some days at 400°, a few hours at 500° ; and is almost instantaneous at 700°. J. Huggett and G. Chaudron gave 675° for the Curie point ; and there is an anomaly at 570° which is attributed to the presence of a little magnetite. R. B. Sosman and E. Posnjak found that natural ferromagnetic ferric oxide becomes paramagnetic at 750°. E. F. Herroun and E. Wilson observed that the effect of temp. on the susceptibility is greatly influenced by the mode of preparation of the samples ; and L. Blanc and G. Chaudron, by the grain-size of the material. R. B. Sosman and E. Posnjak also found that ferromagnetic ferric oxide undergoes two types of inversion at high temp. : (1) A reversible inversion, consisting in a relatively sudden change from ferromagnetic to paramagnetic at a temp. not far above 500°. On cooling, the ferromagnetic condition is again assumed. This inversion is similar to those in metallic iron and in magnetite, although at a different temp. (2) An irreversible inversion, consisting in a complete loss of the ferromagnetic property, the oxide becoming like ordinary paramagnetic Fe_2O_3 and perhaps identical with it. This change occurs at an increasing rate as the temp. rises, being slow at 500°, while it is complete in a few minutes at 650° and higher. L. A. Welo and O. Baudisch observed that when magnetite is oxidized to ferric oxide at 220°, there is an increase in the maximum magnetic permeability from 2·93 to 3·39, and when magnetic ferric oxide is heated to 550° in nitrogen, the permeability falls to 1·045, the value for non-magnetic hæmatite. Magnetite can be heated at 800° in an inert atm. without permanent loss of permeability. L. H. Twenhofel observed the transition from ferromagnetic to paramagnetic ferric oxide occurs at 500°, and by heating natural ferrosic oxide, ferromagnetic ferric oxide can be obtained at 800°. J. Huggett and G. Chaudron also found that ferromagnetic ferric oxide is irreversibly transformed, into the non-magnetic variety, when heated to a high enough temp., and heat is at the same time evolved. The reversibility with the ordinary, impure oxide is attributed to the elevation of this temp. above the point of magnetic transformation. The magnetite break occurs at 570° with specular ferric oxide, and martite. The Curie point occurs at 620°. There is a maximum in the curve with the purified oxide at 350°, and this is taken to represent the transformation temp. for the passage of ferromagnetic ferric oxide to the ordinary oxide. R. Yoshimura noted that the presence of chromic oxide lowers the transformation temp. H. Abraham and R. Planiol, L. Blanc, and L. Blanc and G. Chaudron observed that the magnetic form is converted into the non-magnetic from at 600° to 650° ; R. Chevallier said that there is a rapid decrease in the ferromagnetism at 600° to 700°, but is not completely gone at 745° ; R. B. Sosman and E. Posnjak said that the irreversible change is slow but noticeable at 500°, and that it is rapid at 650°. The change at approximately 678°, which may involve a re-crystallization of the oxide, is probably associated with the rearrangement of the atoms in the molecule where the metastable, ferromagnetic molecule forms the stable molecule of paramagnetic hæmatite. The Curie point where there is a reversible loss of ferromagnetism is probably not associated with any molecular rearrangement of the molecule of ferric oxide; at any rate, the X-radiograms of iron, and of magnetite show that no change occurs in the space-lattice of the crystals. The reversible loss of the ferromagnetism of ferric oxide occurs just over 500°, a temp. which is lower than 593·5°, the Curie point of magnetite. It is thought that the magnetic change is associated with the electrons in one of the first three shells of electrons of the atom of iron. K. T. Compton and E. A. Trousdale, and A. H. Compton and O. Rognley could not detect any change in structure when crystals of hæmatite are placed in a strong magnetic field.

J. Beyer found that in a series of solid soln. of ferric and ferrosic oxides, the magnetizability decreases as the proportion of ferric oxide increases, and with over 82 per cent., it becomes zero. J. Huggett and G. Chaudron examined the magnetic properties of mixtures of ferric and ferrosic oxides as they were raised quickly to 800°, and then cooled. The regular magnetic transformation of magnetite at 570° appears in all mixtures with up to 90 per cent. of ferric oxide; there is a magnetic anomaly at 670° with high proportions of ferric oxide, and at 650° with mixtures having from 10·35 to 80·54 per cent. of ferrosic oxide. The anomaly could be faintly traced with mixtures having a little more ferrosic oxide. It is assumed that mixtures with up to 10·35 per cent. of ferrosic oxide are solid soln. of ferrosic oxide in an excess of ferric oxide, and that the transformation point is lowered by increasing proportions of ferrosic oxide until, at 10·35 per cent., the solid soln. is saturated, and any further addition of ferrosic oxide will remain as a new solid soln. of ferric oxide in ferrosic oxide, and the new solid soln. does not mix with the sat. soln. of ferric oxide in ferrosic oxide. The solid soln. of ferrosic oxide in ferric oxide is sat. when 80·54 per cent. of ferric oxide has dissolved, and any further addition of ferrosic oxide produces soln. of magnetite that are not sat. with ferric oxide. The magnetic transformation of ferrosic oxide in the range tested is not altered by the ferrosic oxide being in solid soln. The temp. of the polymorphous change of the ferric oxide is definitely lowered by increasing proportions of ferrosic oxide. R. B. Sosman and J. C. Hostetter found the susceptibility to be proportional to the amount of ferrosic oxide present in soln. No indication of intermediate compounds was observed by R. B. Sosman and J. C. Hostetter or by J. Huggett and G. Chaudron. R. Becker and H. W. F. Freundlich studied the disposition of colloidal particles of ferric oxide on the surface of a magnetized iron plate.

The chemical properties of ferric oxide.—The transformations of hæmatite in nature have been discussed by J. R. Blum,[13] A. H. de Bonnard, E. von Federoff and S. N. Nikitin, A. Frenzel, T. Grandjean, G. Grattarola, R. C. van Hise, H. A. Miers, R. Pumpelly, and G. Tschermak. H. Wedding and T. Fischer found that hæmatite absorbs 0·0002 to 0·0008 mgrm. of **hydrogen** per gram—W. A. Lazier and H. Adkins said that none is absorbed. Ferric oxide is reduced to iron when heated in hydrogen. G. Magnus said that the lowest temp. at which reduction occurs is a little above the b.p. of mercury, namely, 357°. If reduced at the lowest possible temp., the metal is pyrophoric; H. Moissan obtained the pyrophoric metal by reducing the oxide at 440°; if, however, the oxide be reduced at higher temp.—*e.g.* 600°—the product is not pyrophoric. Observations on the action of hydrogen on ferric oxide were made by G. E. Allen and J. Brown, A. Brun, H. Fleissner and F. Duftschmid, A. C. Fieldner and A. L. Feild, C. G. Fink and C. L. Mantel, S. Hauser, P. Sabatier and J. B. Senderens, H. Nishimura, C. Kröger, M. O. Kharmadaryan and G. V. Marchenko, and F. Stromeyer. R. Yoshimura discussed the use of ferric oxide in oxidizing the hydrogen in water gas. W. A. Lazier and H. Adkins discussed the adsorption of hydrogen.

C. R. A. Wright and A. P. Luff said that the reduction occurs at 245°; and F. Gläser said that the reduction occurs at 245°; reduction was observed during 4 hrs.' heating at 283°. E. Vollgold said that hydrogen acts vigorously at 475°. M. Siewert reported that ferric oxide is not reduced at 270° to 280° by hydrogen; at 280° to 300°, ferrous oxide is formed; and above 300°, at about 357°, the metal is produced. H. S. Taylor and R. M. Burns found that even after 26 days, the reduction of ferric oxide by hydrogen is not completed at 450°. G. B. Taylor and H. W. Starkweather said that ferric oxide gel is reduced to ferrosic oxide at 350°, and to metallic iron at 450°; ignited ferric oxide is not appreciably reduced at 350°, but it passed to the metal at 450°; alumina and chromic oxide retard the reduction. The copper (or nickel) first produced during the reduction of copper (or nickel) oxide by hydrogen acts as a catalytic agent on the subsequent course of the reaction, but P. H. Emmett, and A. F. Benton and P. H. Emmett observed no autocatalysis during the reduction of ferric oxide by hydrogen. P. H. Emmett likewise observed no evidence of the autocatalysis of the reaction by the iron as it is reduced from the oxide. For the reduction of the molten oxide, *vide supra*, ferrosic oxide.

F. Wüst and P. Rütten showed that the temp. of the beginning of the reduction as well as the speed of the reduction depends on the previous history of the ferric oxide. Thus, according to W. Müller-Erzbach, moist ferric oxide, obtained by the roasting of iron, begins to be reduced at 293°, and if dry, at 305° to 330°; moist ferric oxide obtained by roasting the oxalate is reduced at 278°, that obtained from the hydrate, at 286°, and hæmatite, or very strongly calcined ferric oxide, at a red-heat. A. F. Benton and P. H. Emmett found that the oxide, obtained by calcining the nitrate at 525°, is reduced less readily at 300° than is the precipitated oxide, dried at 250°, and it is reduced at 285°. S. Hilpert found that ferric oxide obtained from the oxalate at 800°, 1000°, and 1200°, begins to be reduced by hydrogen respectively at 280° to 290°, at 290°, and at 330° to 350°; and ferric oxide obtained by heating the hydrated oxide to 400°, 850°, 950°, and 1200°, begins to be reduced respectively at 280°, 280° to 290°, 300°, and at 330° to 350°. P. H. Emmett and K. S. Love found that the rate of reduction of the cubic ferric oxide is rather quicker than is the case with the rhombohedral oxide. The rate of reduction of either oxide is reduced 50 to 90 per cent. if the oxide has been heated at 550° instead of at 300°. The presence of alumina does not affect appreciably the rate of reduction of Fe_2O_3 to Fe_3O_4, but it markedly retards the speed of reduction of Fe_3O_4 to Fe. K. Hofmann found the speed of reduction of ferric oxide is greatest when the grain-size is between 0·02 and 0·05 mm. diameter; with smaller grains, sintering retards the reactions. J. Percy said that in the reduction by hydrogen, ferrosic oxide appears to be first formed, and if the reduction occurs at a low temp. the product will sometimes be found to consist almost entirely of the magnetic ferrosic oxide and it is then coloured black, not grey. According to E. Berger, the curve representing the quantity of ferric oxide reduced in hydrogen at 209·5° after different intervals of time, has a break corresponding with Fe_3O_4, but not with FeO. A. F. Benton and P. H. Emmett found that at 285° to 300°, the speed of reduction is greatest at the beginning and decreases continuously until the composition has attained Fe_3O_4, or just a little beyond this stage, when it proceeds at a nearly constant rate. K. Hofmann observed that ferrosic oxide is reduced more slowly than ferrous oxide under similar conditions. The speed of reduction of powdered ferric oxide is a maximum at about 550°, and at about 100°; that there are minima in the curve at about 750°, and between 900° and 925°. These minima also occur with ferrosic oxide. K. Hofmann also said that it is unlikely that ferric oxide is reduced in stages: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$, because below 564°, ferrous oxide does not appear in the equilibrium diagram, Fig. 20, and ferrous oxide is formed more readily than ferrosic oxide or iron; whilst above 564°, ferrosic oxide is not formed. F. Gläser, and H. Moissan supposed that the reduction proceeds in the stages just indicated, but S. Hilpert also showed that this assumption is *nicht richtig*. According to E. J. Rode, the time-temp. curve of ferric oxide in hydrogen exhibits two breaks; one at 300° to 325° corresponds with the formation of ferrosic oxide, and the other, at 350° to 370°, corresponds with the reduction of ferrosic oxide to iron. There is no evidence of the intermediate formations of ferrous oxide.

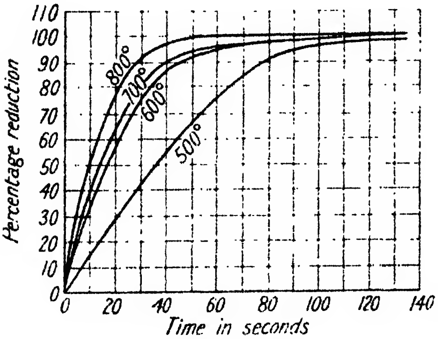


FIG. 528.—The Effect of Temperature on the Speed of Reduction of Hæmatite by Hydrogen.

H. Kamura measured the speed of reduction of hæmatite by hydrogen. Nearly perfect reduction can be effected in about 2 hrs. at 500°. As the temp. rises from 500° to 600°, the higher the temp., the faster the reduction, Fig. 528. Probably the reduction proceeds in stages: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. He also measured the relation between the temp. and the vol. of hydrogen passed over the heated hæmatite, and the results are in general agreement with the results for the equilibrium constant, $K=[H_2O]/[H_2]$, which increases as the temp. increases. At 600°, the speed of reduction increases rapidly, and the vol. of hydrogen employed decreases suddenly, presumably owing to the appearance of the new phase, FeO, which could not exist below 570°. Above 600°, the speed of the reduction does not increase as it does around this temp., and the vol. of hydrogen used does not make much difference. Hence, H. Kamura inferred that this would be the most economical temp. for the reduction of iron ores by hydrogen. The subject was studied by S. Mita, and H. Saito. G. E. Allan and J. Brown suggested that the breaks observed in the curve representing the magnetic properties of the products obtained by the action of hydrogen on ferric oxide represent various stages in the reduction of ferric oxide. S. Hilpert, and J. Beyer found that at 500°, there is a sharp break in the velocity of the reaction when the composition approximates Fe_3O_4; at higher temp., the products—solid soln.—contain more and more ferrous oxide, until at 1100°, 98·5 per cent. ferrous oxide is present. If water vapour be absent, and hydrogen alone be employed as reducing agent, definite intermediate reduction products cannot be isolated. M. Tigerschiöld said that the reactions $3Fe_2O_3+CO=CO_2+2Fe_3O_4$ and $3Fe_2O_3+H_2=H_2O+2Fe_3O_4$ are practically irreversible.

K. Hofmann emphasized the effects of surface phenomena during the reduction, and did not obtain ferrosic oxide as an intermediate product. A. F. Benton and P. H. Emmett concluded that the reduction of ferric to ferrosic oxide is a "non-interfacial" reaction—*vide* nickel oxide. H. Debray, H. St. C. Deville, E. Baur and A. Glässner, and G. Preuner made observations on the equilibrium conditions, a subject which has been previously discussed. L. Wöhler and O. Balz gave for $K=[H_2O]/[H_2]$, in converting Fe_2O_3 to Fe_3O_4, $K=7{\cdot}5$ at 350° and 17·9 at 950°. For W. Biltz and H. Müller's observations on the equilibrium $Fe_2O_3/Fe_3O_4=p_{H_2O}/p_{H_2}$, *vide supra*, ferrous oxide. The gas phase in the 3-phase equilibria: $FeO+Fe+G$, and $Fe_3O_4+FeO+G$ has been studied both as $[CO]/[CO_2]$ and $[H_2]/[H_2O]$. The systems are univariant at constant press., but the relations are independent of press., so that there is no need to keep the press. constant. F. E. C. Scheffer studied the subject from the point of view of the phase rule. According to A. Bornträger, ferric oxide is reduced by nascent hydrogen so that if ferric oxide be added to hydrochloric acid in which metallic iron is dissolving, it is quickly reduced and dissolved as ferrous chloride. A. F. Benton studied the adsorption of hydrogen by ferric oxide. W. A. Bone and R. V. Wheeler noticed that ferric oxide, like platinum, acts catalytically in the surface combustion of hydrogen in oxygen—*vide infra*.

R. Ruer and J. Kuschmann found that ferric oxide, which has been calcined at 700°, adsorbs **air** to the extent of 0·0025 per cent. at room temp. J. Milbauer observed that if ferric oxide be heated to 480° in **oxygen** under 12 atm. press., no chemical change occurs, and no higher oxide is formed. A. F. Benton studied the adsorption of oxygen by ferric oxide. Several oxides between ferric and ferrosic oxide have been reported. The irregularities in the dissociation press. of ferric oxide led S. Hilpert to suspect the formation of intermediate oxides. E. J. Kohlmeyer's observations on the cooling curves of ferric oxide, which had been heated rapidly to its m.p., showed breaks corresponding with the three oxides, *ferrous triferric oxide*, $FeO.3Fe_2O_3$, *triferrous pentaferric oxide*, $3FeO.5Fe_2O_3$, and *triferrous tetraferric oxide*, $3FeO.4Fe_2O_3$, as well as inversion points at 1028° to 1035° and at 1250° to 1350°; but R. B. Sosman and J. C. Hostetter were unable to detect any evidence of these compounds or these inversion points. They did find a sharp inversion on the cooling curve at 678°, and a barely detectable irregularity between 755° and 785°. O. Hauser, and H. Chandra obtained *tetraferrous ferric oxide*, $4FeO.Fe_2O_3$—*vide supra*; and F. Kaufmann, H. Chandra, and F. Haber also reported *diferrous triferric oxide*, $2FeO.3Fe_2O_3$, to be deposited on heating, in the absence of air, the golden-yellow soln. obtained by electrolyzing at 0° a soln. of ammonium nitrate using a carbon anode and an iron cathode, and a cathode current density of 0·00002 amp. per sq. cm. It is said to be obtained by boiling a soln. of 21 grms. of crystalline ferrous sulphate in 220 grms. of water and 22 grms. of 20 per cent. aqua ammonia; adding 2·5 grms. of potassium nitrate, in small quantities at a time, and continuing the boiling for 15 mins. The product is bluish-black while ferrosic oxide is brownish-black. H. Chandra said that although this product can be dried at 180°, it is unstable at higher temp.—*vide supra*, ferrosic oxide. R. B. Sosman and J. C. Hostetter were unable to find any indication of its existence between 1100° to 1200°, and, as indicated above, they showed that ferric and ferrosic oxides form a continuous series of solid soln. over the ranges represented by these products. A. Simon observed no solid soln. of ferric and ferrosic oxides. R. Ruer and J. Kuschmann found that ferric oxide which had been heated to 700° adsorbs air, but this property is almost completely lost when the oxide is heated to 1000°. E. Reichardt and E. Blumtritt observed that 100 grms. of ignited ferric oxide absorbed 39 grms. of gas from the atmosphere, and that gas contained 83 per cent. of nitrogen, 13 per cent. of oxygen, and 4 per cent. of carbon dioxide. P. H. Emmett and K. S. Love observed that the catalytic decomposition of **ozone** at −74° is equally rapid with the cubic and trigonal forms of oxide, but it is less rapid with varieties of either oxide which have been heated to 550° than those heated to

300°. A. Mailfert stated that ozone does not act on dry ferric oxide, but in the presence of potassium hydroxide, a ferrate is formed.

O. L. Erdmann, L. Brandt, and W. Müller-Erzbach discussed the adsorption of **water** vapour, or the hygroscopic properties of ferric oxide; S. S. Bhatnagar and S. L. Bhatia studied the rate of evaporation of adsorbed water from ferric oxide. B. Aarnio said that if ferric oxide has been completely dehydrated it is not hygroscopic. H. Freundlich and co-workers studied the absorption of water by the oxide; and L. V. Lyutin, suspensions of the oxide in water. P. H. Emmett and K. S. Love found that the adsorption of water is 10 to 60 per cent. less with cubic ferric oxide than it is with the rhombohedral form. In general, the adsorption with both forms of oxide is 75 to 80 per cent. less with oxides which have been heated to 550°, than with those which have been heated only to 300°. The catalytic activities of the two varieties of ferric oxide on the rate of combination of hydrogen and oxygen are approximately the same with samples of both which have been heated to 250°, or to 550°. O. Ruff and A. Riebeth prepared plastic mixtures of ferric oxide with water, *N*-HCl and *N*-KOH. A. Quartaroli, and E. Rosenkranz studied the catalytic action of the oxide on **hydrogen dioxide.**

G. Schikorr discussed the action of hydrated ferric oxide on water—*vide infra*, the corrosion of iron. Ferric oxide is generally considered to be insoluble in water, but C. Doelter found that if hæmatite be heated on a water-bath, at about 80°, with distilled water in a sealed tube, the water dissolves about 0·13 per cent.; a sat. soln. of sodium chloride under similar conditions dissolved 2·74 per cent. in 23 days; while a 10 per cent. soln. of sodium carbonate similarly dissolved 1·987 per cent. in 26 days. J. W. Gruner observed that peat-water dissolved from hæmatite 25 parts of iron per million in 77 days, and 27 parts in 182 days. R. Ruer and J. Kuschmann studied the adsorption of atm. moisture by ferric oxide. According to H. Wölbling, anhydrous hæmatite cannot be hydrated by mixing it with aq. soln. of acids, bases, and salts, for no sign of such a change was observed after two years' contact; but the hydrated forms of hæmatite may form higher hydrates in this way. O. Ruff studied the hydration of the oxide under press.—*vide infra*. P. H. Emmett and K. S. Love found that the catalytic activity of the two forms of ferric oxide on the oxidation of benzidine or guaiacum by **hydrogen dioxide** is nearly the same provided the oxides have been heated to 300°; if heated to 550°, the activities of both forms are almost annulled. For the action of **sodium dioxide,** *vide infra*, ferrates and perferrates.

H. Moissan found that **fluorine** does not act on ferric oxide in the cold, but when warmed ferric fluoride is formed. H. Davy said that at a red-heat, **chlorine** does not act on ferric oxide, but it decomposes ferrosic oxide at a lower temp. According to R. Weber, and H. Schulze, when ferric oxide is heated to a high temp. in a current of chlorine, a small proportion of ferric chloride is formed; but E. Mallet and P. A. Guye observed no action at ordinary temp. W. Kangro and R. Flügge observed that something is wrong with some of these statements, for, with hæmatite at 1000°, 100 per cent. of iron was volatilized as chloride in 210 mins., and at 800°, 88·1 per cent. in 420 mins. In another case, with an hour's heating:

	600°	700°	800°	900°	1000°
Loss in iron	0·9	14·2	29·6	60·2	75·8 per cent.

and at 900°:

Time in hours . . .	1·5	4·5	12·6	20·4
Loss in iron	14·0	29·6	60·2	70·0 per cent.

Hence, the action is quite perceptible at 700°, and it is rapid at 900°. W. A. Roth gave $Fe_2O_3+3Cl_2=2FeCl_3+3O+7{\cdot}4$ Cals. at 97°. R. Wasmuht observed that ferric oxide alone reacts with chlorine at about 525°; if carbon is present, at 500°; and if sulphide or phosphide is present, at 250°. V. Spitzin also observed that chlorine begins to act on ferric oxide at 400°. L. Mathesius observed that **bromine** water does not attack ferric oxide, but a warm soln. of bromine and ammonium acetate dissolves the oxide—a cold soln. does not do so. I. L. Bell found that an aq. soln. of **iodine** does not attack ferric oxide.

As shown by J. J. Berzelius, and H. Rose, ferric oxide is more or less soluble in acids; but H. le Chatelier observed that ferric oxide which has been calcined at 950° is insoluble in acids. G. Gore studied the action of liquid **hydrogen fluoride** on ferric oxide. C. W. Scheele noted that ferric oxide is soluble in **hydrofluoric acid**; and E. Zalinsky said that, unlike magnetite, hæmatite is but sparingly soluble in hydrofluoric acid. K. F. Stahl found that calcined ferric oxide dissolves more readily in hydrofluoric acid than it does in other acids. According to E. Deussen, the rate of solution of ferric oxide in acids is smaller, the higher the temp. at which it has been previously calcined. He found that the following quantities of ferric oxide were dissolved by 10 c.c. of hydrofluoric acid, and **hydrochloric acid,** at 25°:

	Calcined Fe_2O_3			Non-calcined Fe_2O_3		
Time .	4½	43½	139½	4½	21¾	45¾ hrs.
N-HF .	0·0880	0·2035	0·2194	0·1581	0·2235	0·2279 grm.
N-HCl .	0·0224	0·1000	0·1910	0·0409	0·1230	0·2125 grm.

With uncalcined ferric oxide and 10 c.c. of 0·5*N*-acid at 25° acting for 2¾, 23½, and 56½ hrs., the amounts of ferric oxide dissolved by ½*N*-HF were respectively 0·0579, 0·1045, and 0·1162 grm., and with ½*N*-HCl, respectively 0·0126, 0·0382, and 0·0672 grm. Similarly, with 10 c.c. of ¼*N*-acid acting for 2¾, 24¾, and 142½ hrs., the amounts of ferric oxide dissolved by ¼*N*-HF were respectively 0·0180, 0·0475, and 0·0534 grm., and by ¼*N*-HCl, respectively 0·0040, 0·0120, and 0·0306 grm. With a mixture of equal vols. of *N*-HCl and *N*-HF, the amounts of non-calcined ferric oxide dissolved in 2¾, 23¾, 96, and 264 hrs. were respectively 0·1011, 0·1976, 0·2223, and 0·2297 grm.; and by equal vols. of *N*-HCl and *N*-NaF in 2¾, 23¾, 72¼, and 215 hrs., respectively 0·0444, 0·0743, 0·0757, and 0·0766 grm. The subject was studied by P. P. Budnikoff and K. E. Krause, who showed that with 2*N*-HCl:

Calcined at .	450°	650°	750°	850°	950°	1000°
Solubility .	100·00	94·91	91·02	71·44	36·28	29·92 per cent

H. Debray observed that when ferric oxide is heated to redness in a current of **hydrogen chloride,** ferric chloride and water are formed. The reaction was studied by J. L. Gay Lussac, J. B. Moyer, F. A. Gooch and F. S. Havens, V. Spitzin, and F. W. Clarke and E. A. Schneider. Ferric oxide dissolves in conc. hydrochloric acid more quickly than magnetite, and more slowly than ilmenite. F. Leteur said that the oxide is readily dissolved by conc. hydrochloric acid, sat. with hydrogen chloride, when heated in a closed vessel at 65°. E. Weinschenk, and C. R. Fresenius said that the oxide prepared at a high temp. dissolves but slowly in the acid. G. Melczer observed that the basal faces of the rhombohedral crystals are more rapidly attacked than the prismatic faces. According to A. Classen, calcined ferric oxide dissolves quickly in hydrochloric acid if the finely powdered oxide has been digested or boiled with a dil. soln. of potassium oxide. H. Bornträger found that the presence of a little manganese dioxide with the hydrochloric acid enables ignited ferric oxide to be dissolved with great ease. The effect is attributed to the chlorine evolved, since all the halogens hasten the solution of ferric oxide in hydrochloric acid. H. Bornträger also observed that strongly calcined ferric oxide dissolves readily in hydrochloric acid containing a little free chlorine, bromine, iodine, or hydrogen dioxide; and F. P. Dunnington, and N. A. Tananaeff made a similar observation with respect to the hydrogen dioxide. According to H. Bornträger, the dissolution is also facilitated if nascent hydrogen, say from iron wire, is produced in the system; and N. A. Tananaeff found that the presence of a little stannous chloride accelerates the dissolution of calcined ferric oxide in hydrochloric acid. W. R. E. Hodgkinson and F. K. S. Lowndes, E. J. Mills and G. Donald, F. E. Brown and W. C. O. White, and G. J. Fowler and J. Grant observed that the presence of ferric oxide facilitates the decomposition of **potassium chlorate,** and more chlorine is given off when ferric oxide is used as catalytic agent than is the case with manganese dioxide. R. Chenevix found that ferric oxide dissolves in **chloric acid**; and A. J. Balard, that it dissolves in **hydrobromic acid.**

R. Weber observed that when ferric oxide mixed with **sulphur** is heated to redness, sulphur dioxide and iron sulphide are formed. A. C. Halferdahl found that ferric oxide is reduced to ferrosic oxide by sulphur, and that the free energy of the reaction $6Fe_2O_3+\frac{1}{2}S_2=4Fe_3O_4+SO_2$ is $-15,900$ cals. at 600°, and $-52,600$ cals. at 1400°. K. Hilgenstock studied the action of the vapour of sulphur on ferric oxide. A. Gautier found that with **hydrogen sulphide** at a white-heat, the reaction symbolized: $2Fe_2O_3+7H_2S=4FeS+3SO_2+7H_2$, occurs. G. Weyman found that the hydrated or anhydrous ferric oxide, prepared between 100° and 650°, is equally active as regards the absorption of hydrogen sulphide in the cold; this is taken to mean that the activity of the oxide is dependent primarily on the mol. structure, and not on the degree of hydration. P. Nicolardot also explained the behaviour of ferric oxide towards hydrogen sulphide by assuming differences in the mol. state. The reaction was studied by K. Hilgenstock. H. Diecke, R. Cox, and E. Brescius found that in the reaction at about 100°, the product contains more sulphur than corresponds with ferric sulphide, and L. T. Wright regarded the product as a mixture of ferrous and ferric sulphides with free sulphur. L. Gedel said that under alkaline conditions, the product is wholly ferric sulphide, and under acidic conditions, a mixture of mono- and di-sulphides and free sulphur; E. T. Allen and co-workers found it to be a mixture of ferrous sulphide and sulphur—the former being completely soluble in cold, dil. hydrochloric acid, after the free sulphur has been extracted with ammonium polysulphide. In the absence of air, and with the hydrated ferric oxide suspended in water, W. Mecklenberg and V. Rodt obtained ferric sulphide which was pyrophoric when dried; and V. Rodt added that the moist ferric sulphide is readily converted by air into oxide and free sulphur; the ferric sulphide changes into a mixture of ferrous sulphide and iron disulphide on standing, and the formation of colloidal sulphur when ferric sulphide is dissolved in dil. hydrochloric acid makes it appear as if a ferrous salt is a product of the original reaction. L. T. Wright concluded that the action between hydrogen sulphide and hydrated ferric oxide involves: (i) $Fe_2O_3.H_2O\rightarrow Fe_2S_3+4H_2O$, and $Fe_2O_3.H_2O\rightarrow 2FeS+S+4H_2O$—the second reaction applies to 17 to 30 per cent. of the hydrated oxide. T. G. Pearson and P. L. Robinson, and L. A. Sayce found that the reaction varies considerably with temp.; at and below 100°, the primary product is ferric sulphide: $Fe_2O_3+3H_2S=3H_2O+Fe_2S_3$, and the ferric sulphide partially decomposes to ferrous sulphide and iron disulphide: $Fe_2S_3=FeS+FeS_2$; above 100°, these reactions give place more and more to the direct production of ferric disulphide, until, in the region above 300°, the only reaction concerned is: $Fe_2O_3+4H_2S=2FeS_2+3H_2O+H_2$. Between 400° and 500°, the iron disulphide gives place to a product soluble in hydrochloric acid with the liberation of sulphur. This material can be regarded as a mixture of ferrous and ferric sulphides, though some ferrosic sulphide, Fe_3S_4, may be formed. W. A. Damon studied the subject. J. C. Witt found that when ferric oxide is treated with an excess of **sodium sulphide,** a black, amorphous substance is formed. On removing most of the remaining sodium sulphide and adding water, a brilliant green soln. is produced. The results obtained on studying the soln. indicate that the colour is due to a colloid and not to a pure soln. of some iron compound. The exact composition of the disperse phase has not been determined, but apparently it contains neither sulphur nor sodium in chemical combination. The colloid is reversible.

According to F. Wöhler and F. Mahla, when ferric oxide is heated in **sulphur dioxide,** it is reduced to ferrosic oxide, and sulphur trioxide is formed. G. Keppeler represented the reaction with sulphur dioxide, between 500° and 800°, by $3Fe_2O_3+SO_2=2Fe_3O_4+SO_3$. D. L. Hammick could not obtain ferrous oxide by the action of sulphur dioxide at 300°, but a black powder was formed which, at a higher temp., in sulphur dioxide forms sulphur, sulphur trioxide, iron sulphide, and ferric oxide. B. Neumann and E. Goebel studied the adsorption of the gas by ferric oxide. The catalytic activity of ferric oxide in facilitating the oxidation of sulphur dioxide begins at about 400°, and attains a maximum at about 625°. This subject was discussed by G. Lunge and co-workers, C. W. Johnson, K. Hilgenstock, B. Neumann, and G. Keppeler and co-workers *vide* sulphur trioxide, **10**. 57, 27. R. D. Hall noted that **sulphur monochloride** vapour passed over heated ferric oxide forms ferric chloride. According to H. B. North and A. M. Hagemann, **thionyl chloride** does not act on ferric oxide at ordinary temp., but at 150°, the reaction which occurs is symbolized: $Fe_2O_3+3SOCl_2=2FeCl_3+3SO_2$, and the ferric chloride crystallizes from the liquid in green hexagonal plates. The reaction with **sulphuryl chloride** was studied by W. Hesse, and by H. Danneel and W. Hesse. W. L. Ray also observed that whilst liquid **selenium oxydichloride** acts very slowly on ferric oxide at room temp., the vapour at 400° forms ferric chloride and selenium dioxide. J. J. Berzelius, and H. Rose stated that ferric oxide is slowly attacked by **sulphuric acid;** A. Mitscherlich found that dissolution occurs most rapidly in a mixture of 8 parts of the conc. acid, and 3 parts of water; and L. Storch said that the ignited oxide is readily dissolved when warmed with 40 per cent. sulphuric acid. A. and P. Buisine observed that sulphuric acid of sp. gr. 1·530 to 1·712 begins to dissolve calcined ferric oxide in the cold; the action is slow and incomplete; with warm acid, the action is completed in a few hours, and it progresses more rapidly, the higher the temp. It is not necessary to proceed above 300°. J. A. Hedvall attributed the tardy dissolution of the calcined oxide to coagulation of the grains reducing the surface area. The reaction was studied by M. M. P. Muir.

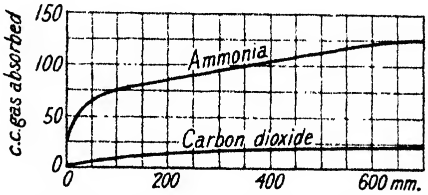


Fig. 529.—The Absorption of Ammonia, and Carbon Dioxide by Ferric Oxide.

E. J. B. Willey said that **nitrogen** is not absorbed when ferric oxide is heated in an atm. of that gas. A. Smits found that heated ferric oxide reacts vigorously with **magnesium nitride;** and likewise with **titanium nitride**—*vide supra*, ferrous oxide. F. Ephraim observed that when heated with an excess of **sodamide,** ferric oxide is reduced spontaneously to iron. Ferric oxide is not dissolved by aq. **ammonia;** but, according to A. W. F. Rogstadius, the Badische Anilin- und Soda-Fabrik, J. J. Berzelius, and H. L. Buff, when ammonia is passed over the red-hot oxide, water and iron nitride are reduced. N. Nikitin's measurements of the absorption of ammonia by ferric oxide at 11·8° and at different pressures are summarized in Fig 529. B. Dirks observed that ferric sulphate is formed when ferric oxide is heated with **ammonium sulphate** at 250°, and at a higher temp., sulphur trioxide is evolved; and H. Arctowsky, that with **ammonium chloride** at 350°, ferric chloride is formed. N Nikitin found that ferric oxide, obtained by igniting the fresh hydrogel at 350°, readily adsorbs ammonia; and by increasing the temp. of ignition of the ferric oxide, the capacity for adsorption is reduced. F. Ephraim observed that no iron nitride is formed when ferric oxide is heated with **sodamide.** For the action of **hydroxylamine,** *vide supra*, ferrous oxide. E. Briner and A. Rivier studied the formation of **nitric oxide** in the ferric oxide arc. P. Sabatier and J. B. Senderens observed that ferric oxide at 500° is not reduced by nitric oxide. C. F. Bucholz found that ferric oxide dissolves very slowly in **nitric acid,** but the ignited oxide is not attacked. U. R. Evans also noted the tardy dissolution of ferric oxide in conc. nitric acid, at room temp.; and H. de Sénarmont observed that the attack of the calcined oxide by nitric acid is slow. E. S. Hedges observed that freshly calcined ferric oxide dissolves perceptibly in conc. nitric acid at the temp., 74·5° to 75·5°, at which iron no longer becomes passive. M. Z. Jovitschitsch found that conc.

nitric acid does not dissolve strongly calcined ferric oxide when heated in a sealed tube at 170° for 10 hrs.; but when warmed on an asbestos plate, at ordinary press., it dissolves in the acid in 8 to 10 hrs. H. Bornträger noted that calcined ferric oxide does not dissolve completely in **aqua regia.** R. Weber found that when **phosphorus pentachloride** is heated with ferric oxide it reacts with incandescence; and H. Bassett and H. S. Taylor observed that **phosphoryl chloride** forms ferric oxide at ordinary temp.; and at 100°, E. Erlenmeyer and O. Heinrich found ferric oxide to be soluble in **phosphoric acid.**

C. J. B. Karsten and others stated that if ferric oxide mixed with **carbon** be gently heated, it is reduced to ferrosic oxide; and if heated strongly, metallic iron is formed. E. Vollgold said that carbon—coke—acts energetically at 875°; and H. Wedding found that the action begins about 700°, and G. Tammann and A. Sworykin, at 625° with sugar-charcoal. G. Charpy and S. Bonnerot added that ferric oxide is not reduced by solid carbon below 950° provided reducing gases are excluded. If no carbon monoxide be present, C. L. Mantell said that carbon does not reduce the oxide at 1000°. Observations were made by C. E. Williams and co-workers, F. Körber and H. H. Meyer, J. Parry, and H. H. Berger. R. Schenck observed that the reduction of ferric oxide by iron tritacarbide in vacuo, begins at about 400°, but with free carbon a reaction is perceptible at 680°. H. H. Meyer found that the reduction of ferric to ferrosic oxide by sugar-charcoal begins at 450°; by wood-charcoal, heated to 1000° in nitrogen, at 500°; and by coke, at 600°. E. J. Rode said that the time-temp. curve of a mixture of ferric oxide and charcoal shows three breaks—(i) at 400° to 650° due to the exothermic reduction of ferrosic oxide; (ii) at 750° to 830°, to the endothermic reduction of ferrosic to ferrous oxide; and (iii) at 875° to 995°, to the reduction of ferrous oxide to iron. W. Baukloh and R. Durrer showed that an intimate mixture of ferric oxide and carbon begins to evolve carbon dioxide in vacuo at 300° to form ferrosic oxide which is further reduced to ferrous oxide (*q.v.*) between 400° and 600°. P. Berthier, F. Margueritte, and J. Percy showed that it is not necessary for the oxide and the carbon to be in contact with one another. Lumps of ferric oxide a few inches in diameter, may be reduced to metallic iron by imbedding them in coarsely powdered charcoal, and heating the containing crucible to bright redness for several hours. At first, the mass is reduced to ferrosic oxide; iron is produced on the surface and then in the interior, and finally reaches the centre. A. F. E. Degen, and A. C. Becquerel assumed that the internal reduction is the result of an electrolysis, but according to F. Leplay and A. Laurent, the reduction in the interior is due to the penetration of carbon monoxide which is formed in the crucible—*vide supra*, hydrogen, and concentration. J. H. Jones and co-workers found that the reactivity of coke, $C+CO_2=2CO$, is increased by admixture with ferric oxide. J. N. Pring observed that at a high temp. ferric oxide is reduced by **aluminium carbide**; likewise with **silicon, chromium, and molybdenum carbides**—*vide supra*, ferrous oxide; R. Schenck showed that **iron tritacarbide** begins to reduce the oxide at 400°. J. Bökmann studied the reaction between iron carbide and oxide.

F. Göbel found that when ferric oxide is heated in **carbon monoxide,** it rapidly forms ferrous oxide, and at a higher temp. it is completely reduced to pyrophoric iron. H. Wedding observed the reduction of ferric to ferrous oxide occurs at about 700°. I. Braithwaite observed that at 700°, the reaction with carbon monoxide is symbolized by $3Fe_2O_3+CO=CO_2+2Fe_3O_4$, and at and below 850° some iron carbide is formed. K. Stammer also noted the formation of some iron carbide. O. Boudouard found that at temp. below 1000°, dry carbon monoxide is a more effective reducing agent than the moist gas, but at 1050°, moist and dry carbon monoxide behave alike. S. Hilpert showed that the temp. of reduction depends, as in the case of hydrogen, upon the previous history of the ferric oxide. The observations of O. Boudouard, R. Schenck and co-workers, and E. Baur and A. Glässner on the equilibrium conditions have been previously discussed—*vide* *supra*, hydrogen. F. Leplay and A. Laurent said that a mixture of equal vols. of carbon monoxide and dioxide merely reduces ferric to ferrosic oxide. The subject was discussed by J. L. Gay Lussac, H. Abraham and R. Planiol, O. Boudouard, F. Brinkmann, M. Decarrière and J. Antheaume, J. Eckell, H. A. Bahr and V. Jessen, A. Gautier and P. Clausmann, F. Hahn, H. Kamura, O. O. Laudig, L. Mathesius, R. Schenck and F. Zimmermann, F. Wüst and P. Rütten, and R. Yoshimura, F. Göbel observed that the formation of ferrosic oxide is an intermediate stage in the reduction of ferric oxide to iron—*vide supra*, hydrogen. J. L. Proust, and W. Naase found that ferric oxide is reduced to metal in a porcelain oven, doubtless by the action of the carbon monoxide. S. Hilpert found that the reduction with carbon monoxide begins at 240°. C. R. A. Wright and A. P. Luff found that the reduction begins at 202° to 220°, dependent on the physical state of the ferric oxide. J. A. Sokoloff said that the reduction of ferric oxide, prepared at 400°, begins at 200° to 230°, and if the ferric oxide has been prepared at a higher temp., a higher temp. is needed to inaugurate the reduction, and is independent of the proportion $CO : CO_2$ in the gaseous phase, but the temp. at which ferrous oxide is formed is lowered by raising the proportion of carbon monoxide. Carbon begins to appear when ferrous oxide is formed. S. Hilpert and T. Dieckmann observed that dry carbon monoxide reduces ferric oxide completely to iron at 950° and very little carbon is formed; iron tritacarbide appears at 850°. H. Tropsch and W. Krönig found that at 720°, the carbon which separates is nearly all free, only a little is combined as carbide. H. Saito showed that ferric oxide, which has been calcined at 800°, begins to be reduced by carbon monoxide at 320°; the separation of carbon begins at 320°, and attains a maximum at 500°. According to W. A. Bone and co-workers, carbon monoxide mixed with nitrogen, but free from hydrogen, begins to reduce hæmatite between 380° and 650°; carbon begins to separate when the oxide is partially reduced. The presence of 2 per cent. of hydrogen favours the reduction and lessens the tendency of carbon to separate. H. Willeke found that the reduction of ferric oxide by carbon monoxide is not influenced by the presence of beryllium oxide, but that the equilibrium is displaced by zinc or manganous oxide; and H. Franz observed that the presence of calcium oxide or alumina hinders the reduction. The reaction was studied by G. Charpy, H. Tropsch and A. von Philippovich, G. Chaudron, etc.—*vide supra*, reaction in the blast-furnace. H. Fleissner and F. Duftschmid studied the reduction of the oxide by water-gas, and by producer-gas. E. F. Armstrong and T. P. Hilditch, and K. Iwase and M. Fukushima found that the presence of ferric oxide favoured the oxidation of carbon monoxide by steam. W. A. Lazier and H. Adkins found 100 grms. of ferric oxide absorbed 65 c.c. of carbon monoxide at n.p.θ. C. J. Engelder and co-workers studied the catalytic activity of ferric oxide with titanic oxide or with cobaltic oxide on the oxidation of carbon monoxide; and R. Yoshimura, and N. A. Yajnik and F. C. Trehana, the catalytic activity of ferric oxide in the photochemical decomposition of carbon dioxide. A. F. Benton studied the adsorption of carbon monoxide, and of **carbon dioxide** by ferric oxide. N. Nikitin found that ferric oxide obtained by igniting the fresh hydrogel, at 350°, readily adsorbs carbon dioxide, and that the capacity for adsorption is reduced by calcining the hydrogel at a higher temp.—*vide supra*, Fig. 529. S. G. Lasky, B. S. Butler, and H. von Eckermann discussed the geological function of carbon dioxide on the $Fe_2O_3 : FeO$-ratio in limestone contact deposits. K. Hilgenstock studied the action of **carbon disulphide.** E. Vollgold said that the activities of carbon monoxide, **methane,** and hydrogen are relatively as 1 : 2 : 5. O. Meyer and W. Eilender studied the reaction. W. Müller-Erzbach found that methane, at the temp. of a Bunsen flame, reduces ferric oxide to ferrosic oxide, at a rather higher temp., to ferrous oxide, and finally, at a still higher temp., to metallic iron. The Gelsenkirchener Bergwerks found that the reduction of iron ores with methane occurs below 700° if a little powdered iron be present to start the reaction. W. P. Yant and C. O. Hawk studied the oxidation of methane with a ferric oxide catalyst. The reduction of ferric oxide earths by methane has been studied by C. E. Williams and co-workers, and by C. M. Bouton. H. W. Walker observed that **ethylene** at a high temp. reduces ferric oxide to ferrosic oxide, and ultimately to iron; the adsorption of ethylene and hydrocarbons, at lower temp., was studied by J. N. Pearce and A. M. Alvarado, H. Hollings and R. H. Griffith, and W. A. Lazier and H. Adkins, and they found 100 grms. absorbed 588 c.c. at n.p.θ. G. Charlot studied the oxidation of **toluene,** with ferric oxide as catalyst. C. M. McDowell and F. L. Usher studied the behaviour of suspensions in toluene, **amyl acetate,** and in chlorinated hydrocarbons.

J. Percy said that ferric oxide is reduced to the metal when heated in a current of **cyanogen.** J. von Liebig, F. Körber and H. H. Meyer, and L. Hackspill and R. Grandadam observed that molten **potassium cyanide** reduces ferric oxide to the metal; but at 570° to 750° with sodium cyanide in vacuo, iron and sodium in nearly equivalent proportions are formed as well as nitrogen, carbon monoxide and dioxide, and finely-divided carbon. It is supposed that sodium carbimide is first produced and that this decomposes to form sodium, nitrogen, carbon, and carbon oxides. J. Tscherniak found that **potassium thiocyanate** at 400° to 500° forms ferrous sulphide and potassium cyanate with the evolution of oxygen: and by a similar reaction, J. Milbauer obtained ferrous sulphide, potassium ferrous sulphide, $KFeS_2$, and potassium cyanide, and H. N. Warren, artificial pyrites, FeS_2. A. Kutzelnigg attributed the oxidizing action of powdered ferric oxide on a soln. of **potassium ferrocyanide** to adsorbed oxygen. J. Aloy and C. Rabaut found that hydrolysis of the benzolated **cyanohydrins** in the presence of acetic acid does not occur in the presence of ferric oxide. E. Deussen showed that 10 c.c. of a normal soln. of **oxalic acid,** at 25°, dissolves 0·0310, 0·0790, 0·1960, and 0·2320 grm. of ferric oxide respectively in 1¾, 6¾, 22, and 94 hrs. N. J. Harrar and co-workers found the solubility of ferric oxide, expressed in milligrams of Fe per 100 c.c. of soln., at 25°, in 40 and 60 days, to be for **formic acid**, respectively, 0·951 and 1·249; **acetic acid,** 0·327 and 0·439; **propionic acid,** 0·344 and 0·374; **oxalic acid,** 97·463 and 36·222; **malonic acid,** 4·159 and 6·260; **succinic acid,** 0·255 and 0·494; **lactic acid,** 2·025 and 2·054; **tartaric acid,** 3·175 and 4·386; **citric acid,** 2·961 and 3·372; **benzoic acid,** 0·428 and 0·428; **salicylic acid,** 4·891 and 5·124; and sulphuric acid, 20·320 and 27·813. N. J. Harrar and F. E. E. Germann studied the solubility of hydrated ferric oxide in various organic acids, and found for the solubilities, S grms. per 250 c.c. of soln., and colours; 1·008N-formic acid, S=1·040 (red to yellow); 1·054N-acetic acid, S=0·958 (red to yellow); 1·008N-propionic acid, S=0·702 (red to yellow); 0·782N-butyric acid, S=0·411 (red to yellow); 0·990N-oxalic acid, S=1·009 (vivid green); 0·991N-malonic acid, S=0·941 (green); 0·968N-succinic acid, S=0·498 (red to orange); 0·985N-glutaric acid, S=0·204 (orange); 0·315N-adipic acid, S=0·081 (orange); 1·020N-tricarballylic acid, S=0·156 (orange); 0·936N-maleïc acid, S=0·923 (red to green); 0·126N-fumaric acid, S=0·004 (colourless); 0·404N-mesaconic acid, S=0·014 (colourless); 1·094N-chloroacetic acid, S=0·985 (red to green); 1·062N-dichloroacetic acid (yellow to green); 1·049N-trichloroacetic acid (pale green); 0·026N-benzoic acid, S=0·006 (colourless): 0·129N-phenylacetic acid, S=0·003 (orange); 0·087N-phthalic acid, S=0·026 (colourless); 0·976N-hydrochloric acid, S=0·917 (green); and 0·962N-sulphuric acid, S=1·014 (pale green). If the acids be arranged in the order of their ionization constants, the strong acids furnish green coloured soln., and the weak acids, red coloured soln. D. Talmud and N. M. Lubman found the floatability of ferric oxide in **oleic acid** and in mixtures of oleic acid and ammonia to be a maximum when p_H=7. L. Kahlenberg and H. W. Hillyer observed no attack by a boiling soln. of **potassium tartrate.** F. W. O. de Coninck and A. Raynaud found that with **calcium oxalate** at a dull red-heat, it forms ferrous oxide, calcium carbonate, and carbon dioxide. W. Müller-Erzbach studied the adsorption of **ether** vapour by ferric oxide.

W. Haller studied the adsorption of ether, acetic acid, **alcohol,** and **acetone** by powdered ferric oxide: and N. A. Yajnik and F. C. Trehana, the photochemical reduction of **sugars.** M. Rakusin observed that egg **albumin** is not adsorbed from its aq. soln. by ferric oxide. E. Ullmann studied the diffusion of ferrum oxydatum saccharatum solubile; and F. H. Rhodes and co-workers, the effect of ferric oxide on the oxidation of **linseed oil.** N. R. Dhar discussed the oxidation of **insulin** with ferric oxide as catalyst.

H. Moissan found that **boron** acts as a reducing agent on ferric oxide at a red-heat. C. H. Burgess and A. Holt noted that ferric oxide is not soluble in molten **boric oxide,** and C. Mazzetti and F. de Carli said that there is a feeble reaction between the ferric and boric oxides at 820°; and the reaction was studied by J. A. Hedvall and N. von Zweigbergk. U. Sborgi and co-workers found that **boron nitride** reduces ferric oxide to ferrous oxide, forming boric oxide and nitric oxide. E. Vigouroux found ferric oxide is reduced when it is heated with **silicon;** and the reaction was studied by L. Kahlenberg and W. J. Trautmann. G. Rauter found **silicon tetrachloride** in a sealed tube with ferric oxide at 180° to 190° forms silica and ferric chloride; no reaction is perceptible at 140° to 150°. H. le Chatelier and B. Bogitsch, J. A. Hedvall and P. Sjöman, and A. Duboin noted that **silica** reacts with ferric oxide at an elevated temp. forming iron silicate. J. Kleffner and E. J. Kohlmeyer observed silica has no effect on the dissociation of ferric oxide. J. A. Hedvall and P. Sjöman observed evidence of reactions at 575° and 900°. G. Tammann and G. Bätz found that whilst quartz begins to react with ferric oxide at 950°, precipitated and calcined silica begins to react at 800°, but that the reaction is not really with ferric oxide but rather with ferrous oxide. When hornblende or basalt is mixed with wood charcoal and a small proportion of lime or sodium carbonate and heated first at 600° and then at 1400°, the iron is reduced almost quantitatively. In the absence of alkali, or when heated directly to 1400°, the reduction is less complete, and it is further diminished by the addition of quartz. When ferric oxide, magnetite, or ferrous oxide is heated with precipitated and ignited silica, each begins to react at 800°, but the reaction with quartz does not begin below 950°. More heat is evolved with the silica than with the quartz. When iron silicates, prepared by heating ferric oxide and silica, are reduced with hydrogen for 1 hr. at 850°, the proportion of the iron reduced falls from 24·4 per cent. when the molecular proportion of silica is 0·375 to 0·600. When the silica content is further increased the proportion of the iron reduced rapidly increases, and is 38·4 per cent. when the molecular proportion of the silica is 0·920. S. Hilpert and E. Kohlmeyer found that with **calcium metasilicate** at about 1220°, ferromagnetic calcium ferrite is formed. F. S. Tritton and D. Hanson found that mixtures with a low proportion of ferric oxide can be fused in **china clay** pots, without serious attack, but some ferric oxide is absorbed by the pot. S. English and co-workers, and V. Dimbleby and W. E. S. Turner studied the action of ferric oxide on **glass;** and J. H. Whiteley and A. F. Hallimond, A. H. Kuechler, and J. W. Mellor, on **firebricks,** and fireclays. P. Ramdohr studied the effect of **titanic oxide** in the system: $FeO–Fe_2O_3–TiO_2$. F. Halla, and G. Tammann and co-workers observed that ferric oxide reacts with titanic oxide at an elevated temp. T. L. Walker applied the term maghemite to the magnetic $(Fe,Ti)_2O_3$ from Bushveld, Transvaal. P. A. Wagner used the same term for magnetic ferric oxide other than martite. P. Ramdohr studied the action of ferric oxide on **ilmenite,**

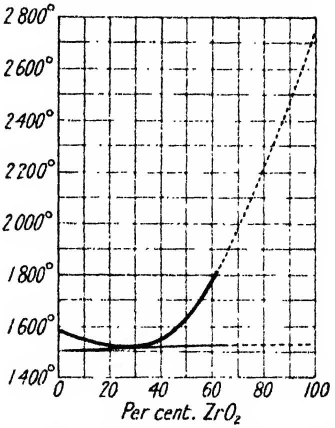


FIG. 530.—Melting-Point Curve for the Binary System: $ZrO_2–Fe_2O_3$.

$FeTiO_3$. H. von Wartenberg and W. Gurr obtained the m.p. curve, Fig. 530, for mixtures of **zirconia** and ferric oxide.

J. L. Gay Lussac and L. J. Thénard found that **potassium** reduces ferric oxide to iron; and similarly with **sodium.** M. Rosenfeld said that when sodium is triturated with ferric oxide, the mixture glows and iron is formed. Ferric oxide is reduced to metal when it is heated with **magnesium;** B. Garre said that the reaction begins at 575° and evolves 239·5 Cals. of heat. E. Donath observed that when the oxide is heated with **zinc** it is easily reduced to the metal. L. Franck observed that iron oxides are also reduced to metal when heated with **aluminium;** and T. W. and W. T. Richards tried to measure the cohesive force between aluminium and ferric oxide. According to J. Percy, when ferric oxide is "strongly" heated in contact with **iron,** it is reduced to ferrosic oxide. M. Billy obtained a similar result. R. B. Sosman and J. C. Hostetter found that when heated to 1200° with **platinum,** in air, ferric oxide is reduced to the metal which forms a solid soln. with the platinum. The loss in weight of platinum heated to 1000° to 1200° is much increased if it be in contact with ferric oxide.

For the reactions of ferric oxide with the **metal oxides,** *vide infra,* the ferrites; and for reactions with ferrous oxide, and ferrosic oxide, *vide supra.* L. Passerini studied the action of ferric oxide on **alumina**; and H. G. Fisk and W. J. McCaughey, on **magnesium oxide.** J. E. Adaduroff and G. K. Boreskoff precipitated a mixture of ferric oxide and **vanadium pentoxide** on broken firebrick for use as a catalyst. P. E. Wretblad found that mixtures of ferric oxide with **chromic oxide** form a continuous series of solid soln. in which the dimensions of the lattice change linearly from those of Fe_2O_3 to those of Cr_2O_3. The rhombohedral angle, α, shows a maximum:

$Fe_2O_3 : Cr_2O_3$	1 : 0	3 : 1	1 : 1	1 : 3	0 : 1
Length of edge	5·419	5·395	5·376	5·362	5·348
α	55·28°	55·37°	55·44°	55·28°	55·11°

L. Passerini, and H. Forestier and G. Chaudron also made observations on this subject, and R. Yoshimura discussed the action of chromic oxide on ferric oxide in the production of hydrogen by the water-gas reaction. Mixtures of ferric oxide and **manganic oxide** with 100 to 75 per cent. Mn_2O_3 give the same X-radiogram; a mixture with 45 per cent. of Mn_2O_3 shows a faint trace of ferric oxide lines; a mixture with 30 per cent. Mn_2O_3 shows the lines of Mn_2O_3 stronger than those of Fe_2O_3; and mixtures with less than 15 per cent. Mn_2O_3 show only the Fe_2O_3 lines. There is, therefore, a break in the series of solid soln. There is no evidence of an intermediate phase. S. L. Penfield and H. W. Foote's mineral *bixbyite,* discussed in connection with the permanganites, was shown by W. Zachariasen to belong to the isomorphous series of sesquioxides, Mn_2O_3, Fe_2O_3, Y_2O_3, etc. Its formula is, therefore, written $(Mn,Fe)_2O_3$, and not $Fe(MnO_3)$, or $FeO.MnO_2$. L. Pauling and M. D. Shappel observed that the body-centred lattice has $a=9·365$ A., and contains $16(Mn,Fe)_2O_3$. W. M. Bradley described a mineral which he called *skemmatite,* $3MnO_2.Fe_2O_3.6H_2O$, as an alteration product of pyroxmangite, $(Fe,Mn)SiO_3$. J. Percy said that ferric oxide is not attacked by soln. of the **alkali hydroxides.** P. Villard, J. d'Ans and J. Löffler, V. S. Yatloff, and S. Matsui and co-workers studied the conversion of **sodium carbonate** into sodium hydroxide by heating it with ferric oxide—*vide infra,* sodium ferrite. P. Rohland found a soln. of **calcium hydrocarbonate** slowly dissolves ferric oxide, and the dissolution is hastened by the presence of alkali or calcium sulphates. E. Mallet and P. A. Guye recommended ferric oxide for use as a diaphragm in the electrolysis of sodium salts in the production of **sodium hydroxide** which does not attack the ferric oxide. T. C. Estelle observed that ferric oxide can be hydrated by boiling it with a 70 per cent. soln. of soda-lye at 100° to 120°. This is of significance in connection with the electrolytic process for iron in which a conc. soln. of sodium hydroxide containing sodium ferrite is electrolyzed. Ferric hydroxide is dissolved from the ferric oxide anode by the conc. soda-lye, and iron is deposited on the cathode. The hydration of ferric oxide by hot conc. soda-lye involves the formation of a ferrite which is subsequently decomposed on cooling and diluting the liquor. During the action 20 parts of ferric oxide are taken up by 80 parts of sodium hydroxide when the heating is continued several hours. R. B. Sosman and J. C. Hostetter said that the best container for ferric oxide at 1100° to 1200° is fused **alumina** (alundum). The alundum vessel remains constant in weight at these temp., but loses weight at higher temp. H. Warth observed that alumina retards the reduction of ferric oxide to ferrosic oxide at elevated temp. L. Passerini observed that mixtures of alumina and ferric oxide form solid soln. and he measured their lattice constants. The subject was studied by H. Forestier and G. Chaudron, T. F. W. Barth and E. Posnjak, and H. von Wartenberg and H. J. Reusch. S. Izawa found that the presence of ferric oxide did not influence the luminescence of alumina in the cathode rays. D. Turner, and F. S. Tritton and D. Hanson found that crucibles of alumina or alundum, **chromite, zirconia,** and **lime,** crack and slag with fused mixtures of iron with a high proportion of oxide ; but bonded crucibles of **magnesia** can be used for the purpose ; magnesia pots absorb the oxide. H. Kittel and G. F. Hüttig studied the magnesia ferric oxide spinels. L. Jacqué observed that with lime, some ferrosic oxide is formed at 1220°—*vide infra,* ferrites. G. B. Taylor and G. A. Hulett found that the presence of ferric oxide favoured the thermal decomposition of **mercuric oxide.** G. Tammann and co-workers observed no reaction when ferric oxide is heated with **molybdenum trioxide;** a slight reaction with **tungsten trioxide ;** and about 15 per cent. reaction with **uranium trioxide.** For solid soln. of ferric oxide and **ferrous oxide** or **ferrosic oxide,** *vide supra.* H. S. Roberts and H. E. Merwin found that in the binary system FeO–Fe_2O_3, the stable phase at temp. below 1386° is a hæmatite solid soln. with less oxygen than Fe_2O_3 ; and just above 1386°, the stable phase is a magnetite solid soln. with considerably more oxygen than Fe_3O_4. E. Diepschlag and E. Horn studied the action of manganous, ferrous, and calcium sulphides on ferric oxide.

J. Krutwig showed that the presence of ferric oxide favours the formation of sodium sulphate from fused mixtures of sodium chloride and iron pyrites in air. G. Tammann studied the action of light on a 0·05*N*-soln. of **silver nitrate** in contact with ferric oxide. K. A. Hofmann and K. Höschele found that if ferric oxide is melted with dry **magnesium chloride,** the iron is almost all volatilized as ferric chloride. H. A. von Vogel observed that ferric oxide is not reduced by a boiling soln. of **stannous chloride,** and W. O. Hickok observed no action with stannous chloride as an etching liquid. C. A. Graumann, and V. Lepiarczyk observed only a slight reaction between **zinc sulphide** and ferric oxide at 1280° ; in a slow current of air at 1280°, sulphur dioxide and zinc vapour are given off, but the reaction soon comes to a standstill ; and in a current of carbon monoxide, iron is formed, and the iron liberates zinc with the production of iron sulphide. For the action on **ferrous sulphide,** *vide infra ;* and for the action on **manganous sulphide,** *vide* manganese sulphide, **12.** 64, 21. E. Diepschlag and E. Horn, and L. Wöhler and co-workers studied the action of **calcium sulphide.** W. H. MacIntyre and W. M. Shaw found that ignited ferric oxide shows no tendency to absorb appreciable amounts of **calcium sulphate** from soln. ; J. E. Adaduroff and V. P. Pligunoff showed that ferric oxide favours the thermal decomposition of calcium sulphate. C. A. Graumann found that with **zinc sulphide** in a reducing atmosphere, ferric oxide is converted into metallic iron and that acts on the sulphide.

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§ 31. Hydrated Ferric Oxide—Hydrosol

If a soln. of ferric chloride be treated with hydrated ferric oxide, added in small quantities at a time, or if ammonium carbonate be gradually added to ferric chloride, so long as the precipitated oxide continues to be re-dissolved on stirring, a brownish-red soln. of ferric hydroxide is produced. These soln. were investigated by J. M. Ordway,[1] J. Jeannel, A. Béchamp, and A. Scheurer-Kestner. The rate of dissolution of the hydrated oxide is slow ; and if the digestion in the cold is continued for a long time, the hydrated oxide dissolves until about 18 eq. have passed into soln. in 5 months. Ferric salts of the monobasic acids—*e.g.* hydrochloric and nitric acids—serve for preparing such soln., but salts of the polybasic acids—*e.g.* sulphuric acid—give insoluble basic salts.

According to T. Graham, the red liquid is a **colloidal solution** of hydrated ferric oxide ; and the **hydrosol** can be freed from the excess of the peptizing ferric chloride by dialysis. The dialyzed hydrosol is clear, and deep reddish-brown in colour ; and after 19 days' dialysis, contained 1·5 per cent. of hydrochloric acid, or 1 eq. of acid to 30·3 eq. of ferric oxide. The sol remained liquid for 20 days, and then spontaneously flocculated to form the **hydrogel.** A hydrosol prepared in this way is sometimes called *Graham's solution*, or *dialyzed iron*. There are various pharmaceutical preparations which are essentially hydrosols of hydrated ferric oxide—*e.g. liquor ferri oxychlorati dialysati*, *ferrum oxydatum dialysatum liquidum*, and *solutio ferri hydrati oxydati colloidalis*. E. Henrijean and W. Kopaczewsky discussed the presence of the hydrosol in mineral waters.

The hydrosol of hydrated ferric oxide was also prepared by T. Graham by the dialysis of cold soln. of ferric acetate ; and after 18 days' dialysis, about one half the iron was lost by diffusion and there remained a red liquid in which 1 part of acetic acid was associated with 15 to 16 parts of ferric oxide. R. Fabre and H. Penau found that the speed of hydrolysis is greatly increased by agitating the dialyzing liquid by a current of air or inert gas. L. P. de St. Gilles prepared a colloidal soln. of ferric oxide by the continued boiling of a soln. of ferric acetate ; the reddish-brown colour of the acetate becomes brick-red as the boiling continues, and the peculiar taste of ferric salts gives way to that of acetic acid. The colloid appears turbid or opalescent in reflected light, and clear in transmitted light. The brown ochreous precipitate obtained when the hydrosol is treated with a trace of sulphuric acid or of an alkaline salt, unlike ordinary hydrated ferric oxide, is relatively insoluble in the more conc. acids ; and when the soln. is poured into hydrochloric acid, the finely divided, granular, brick-red precipitate is in many respects unlike ordinary hydrated ferric oxide. It was accordingly called ***meta-ferric oxide***, by analogy with meta-alumina (**5**. 33, 11). To distinguish this colloidal soln. from those soln. with the properties of Graham's hydrosol, it is sometimes called ***St. Gilles' sol.*** The hydrosol was also prepared from soln. of ferric chloride by J. G. Ufer, E. Hatschek, J. M. van Bemmelen, F. W. C. Krecke, H. B. Weiser, and G. H. Ayres and C. H. Sorum. H. Neurath and W. Pauli discussed the conditions to obtain a product of a high degree of purity.

C. F. Schönbein, S. Hausmann, F. Beilstein and R. Luther, and E. A. Schneider observed that when an aq. soln. of ferric nitrate is boiled, a blood-red, colloidal soln. of ferric oxide is formed. A. Scheurer-Kestner obtained it by allowing an aq. soln. of the nitrate to stand for a long time, or by heating in a sealed tube, on a water-bath, a soln. of the basic nitrate. F. W. C. Krecke prepared Graham's sol by the hydrolysis of ferric nitrate soln. without dialysis; A. Scheurer-Kestner, and R. Wintgen obtained it by dialysis of the nitrate soln. T Cohen suggested introducing a metal like copper filings, or zinc dust, to take up the nitric acid liberated during the hydrolysis of the ferric nitrate. R. Wintgen estimated that the dialyzed soln. contains less than 0·002 per cent. of ferric oxide. G. Almkvist found that the solubility of ferric hydroxide is $1·4 \times 10^{-6}$ mol. per litre at 20°.

H. Debray obtained the hydrosol by warming an aq. soln. of ferric chloride to 70°, and then dialyzing the product. F. W. C. Krecke observed that the conc. of the sol so prepared depends on the temp. and duration of the heating, and he recommended slowly dropping one c.c. of a 32 per cent. soln. of ferric chloride into a litre of boiling water. C. H. Sorum dropped 40 c.c. of a molar soln. of ferric chloride into 5 litres of boiling water and dialyzed the hot liquid. The sol so prepared is clear, deep wine-red, almost free from chloride, and it contains 2·07 to 3·60 grms. of iron per litre; only very dil. soln. are stable. The hydrosol was also prepared by J. M. van Bemmelen, A. P. Buntin, E. Deiss and G. Schikorr, A. Janek and B. Jirgensons, B. Kuriloff, M. Neidle, A. W. Thomas and J. D. Garard, and J. G. Ufer. K. Ruegg recommended removing the acid from the aq. soln. of ferric chloride by the addition of hydrated alumina. J. Tribot and H. Chrétien said that the chloride which always persists in the hydrosol prepared by the dialysis of a soln. of hydrated ferric oxide in ferric chloride can be removed by electrodialysis in which the colloidal soln. containing the cathode is placed in the inner cell of the dialyzer, and the anode in the outer vessel containing the water which is frequently renewed.

H. Freundlich and S. Wosnessensky, and H. Freundlich and S. Loebmann obtained the hydrosol by the hydrolysis of iron carbonyl; E. Grimaux, P. A. Thiessen and O. Körner, and O. Körner, by pouring an alcoholic soln. of ferric ethylate, $Fe(OC_2H_5)_3$, in water—*Grimaux's sol;* P. A. Thiessen and O. Körner, by hydrolyzing ferric ethylate; and F. W. O. de Coninck, by adding salicylic acid to a soln. of ferric acetate, and keeping the mixture some months.

N. N. Gavriloff found that the oxidation of a soln. of ferrous hydrocarbonate by air, yields only a precipitate of hydrated ferric oxide which is not peptized by small amounts of hydrochloric acid or of ferric chloride; but with larger proportions of ferric chloride, the hydrosol of ferric oxide is formed solely from the added ferric chloride. Hydrogen dioxide gives a white precipitate with ferrous hydrocarbonate, but in the presence of ferric chloride or hydrochloric acid a colloidal soln. of ferric hydroxide is rapidly formed. G. Stadnikoff and co-workers, and V. Brünig also oxidized ferrous hydrocarbonate by hypochlorites, chlorine, or chlorine water. The minimum amount of ferric chloride necessary for peptization in the oxidation of ferrous hydrocarbonate is about 7 per cent. of the total iron. G. Stadnikoff and N. N. Gavriloff found that the hydrosol of ferric oxide for use as a coagulator in the drying of peat can be prepared by the oxidation of solutions of ferrous hydrocarbonate by means of chlorine water or hypochlorous acid. The necessary conc. (0·04 per cent. of ferrous iron) can be obtained on a commercial scale by the treatment of iron turnings with water and a current of flue gas.

M. Neidle and J. N. Crombie obtained the hydrosol by oxidizing ferrous chloride in the cold with potassium permanganate and dialyzing; M. Neidle, and F. L. Browne, by oxidizing ferrous chloride with hydrogen dioxide and dialyzing the hot soln. The dispersed soln. of iron spluttered from the electric arc with iron electrodes, under water, as indicated by T. Svedberg, A. Schmauss, E. F. Burton, and A. Wander, is probably a hydrosol of hydrated ferric oxide.

A. W. Dumansky and Z. P. Chescheva obtained a mixed ferrous and ferric hydrosol by the electrolysis of a soln. of ferric chloride, using a platinum cathode, and an anode of iron amalgam; and also by shaking iron amalgam with a soln. of potassium hydroxide containing some mannitol, and hydrogen dioxide.

As indicated above, freshly-precipitated and washed hydrated ferric oxide is peptized by a soln. of ferric chloride; and the hydrosol can, therefore, be obtained by (i) partial precipitation of a soln. of ferric chloride by ammonia, etc., and agitating the mixture; or (ii) adding the hydrated oxide directly to a soln. of ferric chloride, as was done by A. Béchamp, F. L. Browne, R. Fabre and H. Penau, B. Szilard, T. Graham, J. Jeannel, A. Müller, J. G. Oberhard, N. Pappada, H. Picton and E. Linder, A. Scheurer-Kestner, O. Schmatolla, and A. W. Thomas and A. Frieden. T. Graham obtained the hydrosol by a process equivalent to the peptization of the hydrogel, for he gradually added ammonium carbonate to a soln. of ferric chloride as long as the precipitate dissolved when the liquid was stirred. The liquid was then dialyzed. The process was also employed by F. L. Browne and J. H. Mathews, A. W. Dumansky, F. L. Browne, and J. G. Ufer. W. Wobbe, H. Schweikert, A. W. Thomas and co-workers, and T. L. Wright obtained the hydrosol by adding aq. ammonia to a soln. of ferric chloride so long as the precipitate re-dissolves on stirring. The clear, dark brown soln. so obtained scarcely tastes of iron. It is evaporated until it contains 3·5 per cent. of iron, and has a sp. gr. 1·05. The last traces of chlorine cannot be removed by dialysis, and the product still contains 0·75 per cent. of ferric chloride, but it is free from ammonium salts. G. D. Kratz added that this process does not give a conc. soln. of the colloid, but it avoids the necessity of washing and dialyzing a gelatinous precipitate. The process is best conducted by pouring a 10 per cent. soln. of ferric chloride into a large excess of conc. ammonia, the colloidal ferric oxide produced is coagulated by the ammonium chloride. On evaporating to dryness and washing with water, the ammonium chloride is first washed out, and then the ferric oxide deflocculates and passes through the filter-paper as a dark or bright red colloidal soln. If the original precipitate is left for some time in contact with its ammoniacal mother-liquor, spontaneous changes occur, so that after evaporation it is found to be insoluble. M. Neidle and J. Barab obtained the hydrosol by the hot dialysis of a soln. of ferric chloride to which was added enough aq. ammonia to react with 60 per cent. of the salt. R. Bradfield recommended removing the excess of precipitating agent by washing the precipitate in a centrifuge making 32,500 revs. per min. The main advantages are (i) the removal of the electrolytes formed on precipitation is more complete; (ii) the addition of a peptizing agent and its consequent incomplete removal by either prolonged boiling or dialysis is unnecessary; (iii) sols of a more uniform degree of dispersion can be prepared, since particles of similar size and of similar degrees of hydration are deposited in the same zone of the centrifuge bowl; (iv) sols of any desired conc., from a semi-gel to the merest trace, can be prepared by the addition of water to the more conc. form, and all conc. are very stable.

A. Müller made the hydrosol by using $0·5N$-KOH as precipitating agent in place of ammonia; and A. W. Dumansky and co-workers employed various carbonates, oxides, or hydroxides. According to H. Picton and E. Linder, when the hydrogel of hydrated ferric oxide is precipitated by univalent anions it is much more readily peptized by washing with water than is the case with polyvalent anions. P. Schmidt used 0·05 per cent. nitric acid, or 0·067 per cent. hydrochloric acid as peptizing agent. A. von Buzagh observed that the quantity of peptizing agent—ferric chloride, hydrochloric acid, or sodium oleate—required for the peptization of the hydrogel of ferric oxide is dependent on the quantity of gel, which is taken to mean that the peptization is dependent on an anterior adsorption. C. H. Sorum, Wo. Ostwald and W. Rödiger discussed the peptization with hydrochloric acid; and A. M. Belousoff and co-workers, by copper and silver salts. A. W. Thomas and A. Freiden, and A. J. Rabinowitsch and V. A. Kargin attributed the stability of the ordinary hydrosol to the presence of adsorbed ferric chloride. The subject was discussed by W. D. Bancroft, W. von Neuenstein, S. Liepatoff, and Wo. Ostwald. The peptization of the hydrogel by glycerol, sugar, and other hydroxylic organic compounds in alkaline soln. was studied by H. J. Babel, N. G. Chatterji and N. R. Dhar, H. W. Fischer, P. Goldschmidt and co-workers, T. Graham, E. Grimaux, C. Mannich and C. A. Rojahn, A. W. Dumansky and L. G. Krapiwina, M. R. Mehrotra and K. C. Sen, A. Müller, J. Puls, H. Rose, C. Gropengiesser, K. C. Sen and N. R. Dhar, and K. C. Sen. The peptization of the hydrogel by acetic acid was studied by A. F. G. Cadenhead and W. H. Vining, and H. B. Weiser; by arsenious acid, by A. Boutaric and G. Perreau, E. Grimaux, M. R. Mehrotra and K. C. Sen, and by K. C. Sen and co-workers; and A. Fodor and A. Reifenberg, by silicic acid. A. J. Rabinowitsch and V. A. Kargin studied the behaviour of the acid soln. on dilution.

Colloidal soln. can also be prepared by the use of **protective colloids.** O. Fisseler obtained colloidal soln. by mixing 3 grms. of sodium protalbinate or lysalbinate, dissolved in lukewarm water, with the calculated quantity of ferric chloride in aq. soln. The precipitated ferric protalbinate or lysalbinate was dissolved in soda-lye, and the dark red soln. dialyzed until salt no longer passed through. The residue on the dialyzer was filtered, and evaporated on a water-bath, and dried over sulphuric acid in vacuo. The dark red plates form a clear, colloidal soln. with water. The colloid is flocculated by adding dil. sulphuric acid; a soln. of sodium chloride in the cold has no visible action, but if heated, yellow flecks separate from the turbid soln. A 10 per cent. soln. of calcium chloride acts similarly; but a 10 per cent. soln. of sodium phosphate does not give a precipitate in hot or cold soln. C. Paal and W. Hartmann, and Kalle and Co. employed an analogous process. F. Sichel used starch xanthogenate as protective colloid; A. W. Dumansky and Z. P. Chescheva, mannitol; H. Freundlich and G. Lindau, hæmoglobin, and globin; W. Bachmann, glycol, glycerol, mannitol, dextrose, sucrose, dextrin, and starch; and J. Müller, cherry gum. J. N. Mukherjee attempted to find a relation between the stability and degree of dilution of the hydrosol. J. W. Bain and W. L. McClatchie studied the ultra-filtration of the hydrosol.

The general idea of H. Debray, L. P. de St. Gilles, T. Graham, and L. M. de la Source was that the hydrosol of hydrated ferric oxide is an allotropic, soluble modification which is associated with some impurities. Numerous observations by A. Béchamp, H. Debray, J. Duclaux, F. Giolitti, A. Hantzsch and C. H. Desch, E. Heymann, H. Picton and E. Linder, M. Neidle, P. Nicolardot, J. M. Ordway, R. Ruer, A. Scheurer-Kastner, L. M. de la Source, J. G. Ufer, H. P. Varma and S. Prakash, and G. N. Wyrouboff —show that some salt must be present, presumably adsorbed, in order that the colloidal soln. be stable. The hydrosol has not the inky or ferruginous taste characteristic of ferric salts, rather does the hydrosol produce a rough sensation on the tongue. H. W. Fischer and E. Kuznitzky also found that in well-dialyzed hydrosols, a ferro-cyanide soln. does not give the prussian blue colour produced by ferric salts. E. Grimaux, and E. A. Schneider found that hydrogen sulphide acts on the cold hydrosol to form ferric and ferrous sulphides. K. Haerting found that the hydrosol reacts with cellulose to form a complex iron-cellulose. C. Doelter observed that when the hydrosol is shaken with a soln. of calcium or magnesium chloride, ferric hydroxide is precipitated. Silver nitrate does not precipitate a chloride from the hydrosol, even though T. Graham, R. Ruer, J. G. Ufer, etc., have demonstrated the presence of chlorides. A. Hantzsch and C. H. Desch said that the failure of silver nitrate to produce the chloride reaction is because of the formation of a complex between the hydrated ferric oxide and the ferric chloride. R. Ruer showed that the phenomenon is more likely to be due to the protective action of the ferric chloride on the colloid. As indicated above, A. W. Thomas and A. Freiden, and A. J. Rabinowitsch and V. A. Kargin considered that the colloidal particles owed their stability as a hydrogel to the adsorbed ferric chloride;

and R. Ruer suggested that in the sol state, the chloride is partially ionized, owing to the invariable presence of, say, ferric chloride in the colloidal ferric oxide produced from that salt.

Many observers—J. Duclaux, A. W. Dumansky, E. Jordis, N. Kühnl and W. Pauli, H. Picton and E. Linder, G. Malfitano and co-workers, L. Michel, M. Neidle, P. Nicolardot, W. Pauli and co-workers, A. W. Thomas and A. Freiden, and G. N. Wyrouboff and A. Verneuil—considered the colloid to be a chloride of a polymerized or condensed ferric hydroxide or an oxychloride of variable composition, $[(FeO_3H_3)_nFe]^{\cdots}(Cl')_3$. N. J. Harrar and F. E. E. Germann studied the effects with salts of organic acids. The work of H. W. Fischer, F. K. Cameron and W. O. Robinson, F. Giolitti, and R. B. Smith and P. M. Giesy furnishes no support for the hypothesis that an oxychloride is formed. P. Nicolardot obtained complexes with eq. ratio of Fe : Cl=125 : 6. A. Béchamp gave 7 : 1 ; J. M. Ordway, 3 : 1 ; G. N. Wyrouboff and A. Verneuil, 8 : 1 ; and J. Duclaux, 300 : 1. The subject was discussed by G. Malfitano, and L. Michel. According to N. Kühnl and W. Pauli, the hydrosols of ferric oxide prepared by peptization of precipitated hydrated oxide with ferric chloride contain on the average ten times as much iron and twenty times as much chlorine as those prepared by hydrolysis. The ratio of active to total chlorine is from 1 : 5 to 1 : 6 in hydrolyzed sols and is little affected by dialysis ; but it decreases from 1 : 3 to 1 : 17 on dialysis of peptized sols, whilst the total oxychloride per colloid eq. increases more than sixfold. The extent to which chlorine is substituted by sulphate and oxalate anions on coagulation is throughout considerably higher for hydrolyzed than for peptized sols. By dialysis, the oxychloride portion of the sol-substance is progressively diminished, more markedly so in hydrolyzed soln. Transport numbers are much the same for both varieties. M. Neidle believed that this particular ratio is more due to chance, but suggested that a complex is formed with the ratio at 21 : 1 ; and A. W. Thomas and A. Freiden considered that it requires a mol. of ferric chloride to keep 21 mols. of ferric oxide in the colloidal state. There is a very wide variation in the Fe : Cl ratio found by different observers. Thus, M. Neidle obtained 84 : 1 ; R. Bradfield, 396 : 1 ; and J. G. Ufer, 2700 : 1. M. Neidle also showed that the maximum degree of purity attainable before coagulation occurs increases with decreasing iron-content of the soln. H. Siebourg studied the effect of dilution on the equilibrium between the hydrosol and the dispersion medium.

E. Heymann observed that with aged soln. of ferric chloride in which the proportion of colloidal hydrated ferric oxide is constant, the quotient of the active masses $[HCl]^3/[FeCl_3]$ is not constant, but undergoes a steady change with a variation of about 30 per cent. This indicates that the active mass of the colloidal ferric hydroxide cannot be regarded as constant. The size of the particles also influences the equilibrium, and the chlorine-content of the colloid particles is greater when they have been formed by hydrolysis than when the system has been prepared by adding hydrochloric acid to colloidal ferric hydroxide—*vide infra*, the hydrolysis of ferric chloride. All this means that, as H. B. Weiser puts it, investigators who assume the existence of definite compounds are unable to agree on their composition. The subject was discussed by E. I. Spitalsky and co-workers. R. Zsigmondy considered the hydrosol to consist of electrically charged mycelial particles with entrained mother-liquor ; and a similar hypothesis was favoured by P. Bary, A. Cotton and H. Mouton, S. I. Diatschkowsky, J. Duclaux and R. Titéica, J. Duclaux, H. Freundlich, G. Malfitano, L. Michel, and R. Wintgen and O. Kühn. J. Duclaux said that there is a state of equilibrium between the chloride ions in soln. and in the mycelia ; although A. W. Dumansky said that the partition of ammonium chloride between the soln. and the mycelia does not follow Henry's law. Wo. Ostwald, H. Freundlich, A. Lottermoser and P. Maffia, and P. Maffia, however, observed that the adsorption agrees with the usual adsorption formula. R. Ruer considered that part of the adsorbed chloride is partially ionized, whilst R. Wintgen and co-workers estimated that 70 to 90 per cent. of the adsorbed chloride is not ionized. The subject was also discussed by W. Pauli, A. W. Dumansky, J. Matula, and R. Zsigmondy. H. Freundlich considered that the mycelia are built up of positively-charged $\mathrm{FeO}^{\cdot}$-ions or $\mathrm{Fe}^{\cdot\cdot\cdot}$-ions associated with the complex. Thus:

$$\begin{bmatrix} n\mathrm{Fe_2O_3} \\ m\mathrm{Cl}.p\mathrm{H_2O} \end{bmatrix}\mathrm{FeO}^{\cdot}+\mathrm{Cl}' \quad \text{or} \quad \begin{bmatrix} n\mathrm{Fe_2O_3} \\ m\mathrm{Cl}.p\mathrm{H_2O} \end{bmatrix}\mathrm{Fe}^{\cdot\cdot\cdot}\mathrm{Cl}'_3$$

where in one case it was estimated that $n=75{\cdot}35$, and $m=7{\cdot}86$. According to J. Böhm, the X-radiograms of fresh hydrosols show that a basic salt is present, but the deposit from old soln. consists of goethite. H. Freundlich and S. Wosnessensky also discussed this subject. G. L. Clark, A. Krause and W. Buczkowsky, P. P. Lazareff, and J. Duclaux and R. Titéica studied the mycellar equilibrium of the hydrosol. G. Schikorr, and A. W. Thomas and E. R. Hamburger studied the hydrosol of the corresponding ferric oxybromide.

The colloidal hydrated ferric oxide as usually prepared is a **positive hydrosol,** but **negative hydrosols** have been obtained. H. Rose found that the presence of glycerol, mannitol, sucrose, and glucose prevent the precipitation of hydrated ferric oxide by the addition of alkali-lye, or a soln. of ammonia to a soln. of a ferric salt. H. W. Fischer dialyzed a soln. obtained by adding a sodium hydroxide soln. to a mixture of ferric chloride and glycerol; and P. Rona and F. Lipmann used a somewhat similar process. E. Riffard said that invert sugar is seven times as effective as cane-sugar in preventing precipitation. There is a converse action, the presence of traces of hydrated ferric oxide hinders the crystallization of cane-sugar, and higher proportions of molasses are formed if raw sugar is kept in iron vessels. E. Grimaux attributed the solubility of the hydrated oxide to the formation of a negative sol stabilized by the preferential adsorption of hydroxylions. A. W. Dumansky and T. P. Tyazhelova obtained the negative hydrosol from ferric chloride in the presence of a soln. of alkaline citrate. F. Hazel and C. H. Sorum obtained the negative hydrosol by the hydrolysis of prussian blue. N. G. Chatterji and N. R. Dhar observed that hydrated ferric oxide can be peptized by adding an alkali hydroxide to a soln. of a ferric salt in the presence of glycerol, or sucrose; and N. R. Dhar and K. C. Sen found that boric, molybdic, malonic, and tartaric acids could be used as peptizing agents; and K. C. Sen and co-workers, sodium arsenite, tartrate, or citrate. A. Schmauss, and J. Billitzer found that the colloid obtained by the spluttering of iron electrodes from an arc under a soln. of gelatin is negatively charged; and the hydrosols obtained by E. Grimaux, D. Vorländer, and P. A. Thiessen and A. Koerner are also negatively charged. A. Boutaric and G. Perreau studied the mutual flocculation of the positive and negative hydrosol.

F. Powis, and A. Boutaric obtained a stable, negative sol without protective colloid; he found that by adding colloidal hydrated ferric oxide to a dil. soln. of sodium hydroxide of suitable conc., it may be changed from positive to negative, coagulation being prevented by mixing in this order. It may also be directly prepared as a negative colloid by allowing the hydrated ferric oxide particles to form in the presence of a dil. soln. of sodium hydroxide. The view is taken that the potential difference at the surface of colloidal particles is due to adsorption of ions from the soln., and that its sign depends on whether the cations or anions are in excess in the layers nearest the particles. The negative sol so prepared is brownish-yellow, and showed no sign of precipitation after standing for three weeks. Sols of ferric oxide prepared by the electrical disintegration of iron electrodes under water are usually charged positively, but, according to T. Malarsky, filtration through filter-paper, fat-free cotton, glass-wool, or sand, may make the charge less positive, neutral, or negative, and he explained the phenomenon as an effect of contact electrification. By successive filtration of the sol of hydrated ferric oxide through filter-paper, the potential difference of the double layer is diminished, and consequently, the velocity in an electrical field is also diminished; repeated filtration will reduce the potential difference to zero and finally change the sign of the charge. H. Freundlich and S. Wosnessensky found that a hydrosol obtained by oxidizing iron pentacarbonyl with hydrogen dioxide and flocculated by boiling, furnishes a negative hydrosol when peptized by sodium or potassium hydroxide; the positively charged hydrosol is also discharged by shaking it with dil. alkali-lye. H. R. Kruyt and J. van der Spek also found that the positively-charged hydrosol is discharged by shaking it with a soln. of sodium hydrophosphate; H. Mayanagi, that potassium ferrocyanide acts similarly; and P. Rona and F. Lipmann, that the positive hydrosol becomes negative when shaken with sodium citrate.

The clear soln. of ferric peptonate prepared by M. Robin by adding ammonium chloride to a mixed soln. of glycerol, peptone, and ferric chloride, was a negative soln. of hydrated ferric oxide peptized by glycerol and peptone. Ordinary positive colloidal soln. of hydrated ferric oxide cannot be used for intravenous injections, since it precipitates the negatively charged serum of the blood, but a negative soln. containing alkali and glycerol does not precipitate serum, and was recommended by H. W. Fischer in arsenical poisoning, and by L. Dozzi, in the treatment of anæmia.

H. B. Weiser and G. L. Mack prepared **alcoholsols** of ferric oxide with methyl and propyl alcohols. P. Rehlinder and E. Wenström studied the stabilizing of suspensions of ferric oxide in benzene, toluene, and heptane.

According to A. Cotton and H. Mouton, the hydrosol of hydrated ferric oxide contains particles of two kinds. The particles in the lower part of the sol are specifically heavier, and have positive birefringence, whilst those in the upper part have a negative birefringence. N. P. Peskoff, and A. Szegvari also found two kinds of particles in the hydrosol, and discussed what is called *barophoresis*. X-radiograms by J. Böhm, J. Böhm and H. Niclassen, H. Freundlich, H. Zocher, H. Zocher and K. Jacobsohn, H. Zocher and W. Heller agree that the lower layers of particles are richer in ferric hydroxide than the upper layers. P. Bary also considered that his experiments on the drying of the hydrosols showed that two kinds of particles are present. G. Quincke also studied this subject. According to H. Freundlich, H. Diesselhorst and H. Freundlich, and B. Lange, the optical properties of the hydrosol show that the aged hydrosol is anisotropic, and contains tabular, and rod-like particles--H. Zocher said disc-shaped. R. Wintgen and M. Biltz, W. Pauli and co-workers, and L. Tieri made estimates of the sizes of the particles; R. Wintgen, A. W. Dumansky, and N. Kühnl and W. Pauli, of their density; and R. Wintgen and O. Kühn, and N. Kühnl and W. Pauli, of the magnitude of the charge. G. Jander and A. Winkel found that in the hydrolysis of the ferric salts, a series of basic states are produced which are stable under definite conditions of equilibrium. The state of equilibrium is very sensitive to the $H^{\cdot}$-ion concentration. The stable states range from the unimolecular ferric salt to the polymolecular ferric hydroxide. Small changes in the $H^{\cdot}$-ion concentration produce large changes in the mol. wt. of the product of hydrolysis.

F. Giolitti showed that the physical character of the precipitated hydrogel of hydrated ferric oxide varies with the nature of the precipitating agent. Thus, the hydrogel produced by the addition of a trace of sulphurous, sulphuric, selenious, iodic, periodic, boric, or phosphoric acid, is gelatinous, and it is not re-peptized by water; while the hydrogel produced by adding traces of hydrochloric, hydrobromic, hydriodic, nitric, perchloric or perbromic acid, is a finely divided, brick-red powder; and the hydrogel produced by the addition of a larger proportion of the monobasic acid is readily peptized by water. H. B. Weiser found that this anomalous behaviour is independent of the valency of the precipitating ion. The most voluminous precipitates are formed when there is a rapid coagulation throughout the entire soln., and when the precipitating agent has no solvent action on the particles. Gelatinous precipitates are formed when the finely divided particles of the hydrate are produced under conditions favouring the formation of a network enmeshing the mother-liquor. Just as large crystals are formed by the slow deposition from a super-saturated soln., and small crystals, by rapid precipitation, a condition which may also form a gelatinous mass, so, in L. P. de St. Gilles' soln., finely-divided particles are present which, if allowed to agglomerate slowly, may form more or less granular masses entangling very little water; but, if allowed to agglomerate rapidly, the particles have not time for orientation and a network may form entangling a relatively large amount of mother-liquor. This produces a relatively voluminous precipitate. Low concentrations of polyvalent ions cause rapid coagulation, and produce gelatinous precipitates. The solvent action of the precipitant also comes into play; thus, potassium chloride has no solvent action, and the stabilizing influence of the potassium ion is slight, hence rapid coagulation and a voluminous precipitate is formed, but with hydrochloric acid, the H'-ion has a stabilizing influence, and the precipitate is slightly soluble in the acid. The smallest particles are most readily attacked, and this will hinder the formation of a network enmeshing the mother-liquor, and restrict the amount of mother-liquor which can be entangled in the precipitate. This reduces the vol. of the precipitate; actually, the precipitate is usually granular. The colour of the precipitate furnished by L. P. de St. Gilles' soln. is not always brick-red; it varies with the conditions of precipitation. H. B. Weiser found that it is possible to make a transition from brown to yellow by increasing the size of the particles. This may be effected by heating water to which ferric chloride has been added. The yellow colloidal hydrated oxide is not readily dehydrated at 100° and probably contains adsorbed ferric salt. A yellow colloidal soln. was prepared by L. P. de St. Gilles' method by allowing the acetate soln. to remain for a few days before diluting and boiling. The slow hydrolysis of the acetate favours the formation of yellow hydroxide stabilized by adsorbed ferric salt. When the soln. is boiled, a stable yellow colloid is formed instead of the usual brick-red one. J. N. Mukherjee studied the effect of dilution on the stability of the hydrosol; A. F. G. Cadenhead and W. H. Vining, the reversibility of the process; and H. Handovsky, the effect of ageing the soln.

According to G. H. Ayres and C. H. Sorum, the **size of the particles** in the hydrosols of ferric oxide, prepared by the hydrolysis of soln. of ferric chloride between 100° and 145°, range from $52\mu\mu$ to $76\mu\mu$—average $60\mu\mu$. The size is not influenced by the temp. of preparation, or by the conc. of its reactants. The **colour** of colloidal hydrated ferric oxide varies from yellow to brick-red and brownish-red. According to E. F. Holden, the colour of colloidal soln. of hydrated ferric oxide when a thickness of 10·5 cms. is viewed against a white background, is pale yellow for soln. with 0·0007 per cent. Fe_2O_3; yellowish-orange, with 0·0034 per cent.; orange, with 0·0059 per cent.; red, with 0·034 per cent.; and dark red, with 0·068 per cent. G. Malfitano, and H. W. Fischer recognized that the variation in colour from yellow to red to brown is associated with an increase in the size of the particles—*vide supra*, ferric oxide. E. A. Schneider observed that the hydrosol becomes brick-red when heated to 200°; and observations were also made by L. P. de St. Gilles. H. B. Weiser's experiments on the hydrolysis of ferric chloride showed that the two factors are co-related. Finely-divided brown particles can be transformed into larger yellow, and still larger brick-red particles by heating them under suitable conditions. J. B. Nichols and co-workers, P. L. du Noüy, R. Audubert, R. Zsigmondy and C. Carius discussed the sizes of the colloidal particles. The observations of U. Antony and G. Giglio, Wo. Ostwald, E. Schaer, T. Svedberg, R. Bradfield, H. M. Goodwin, and C. L. Wagner on the hydrolysis of ferric chloride soln. whereby a colourless, dil. soln. changes spontaneously first to yellow and then to reddish-brown, make it appear that the yellow particles are smaller than the brown. The colour of a dil. colloidal soln. is not necessarily the colour of the particles. R. Bradfield found that a colloidal soln. of hydrated ferric oxide contains varying proportions of small, highly hydrated, reddish-brown particles and also larger, less hydrated yellowish-brown particles which can be separated from one another by the centrifuge. Both forms can be converted into larger, still less hydrated, brick-red particles by heating them to 100°. If the conditions are such that the red particles remain in colloidal soln., then L. P. St. de Gilles' sol is formed.

A yellow St. Gilles' sol does not become red by a prolonged boiling of the soln.; this is attributed by H. B. Weiser to the fact that the yellow particles, formed under certain conditions, lose water at 100° less readily than the reddish-brown particles. W. D. Bancroft pointed out that the yellow colloid is formed under conditions where the adsorption of a ferric salt is possible. H. B. Weiser showed that the adsorption of the ferric salt does not always produce the yellow colloid, but it may be that the yellow colloid, which is not converted to red by heating at 100°, is stabilized by the adsorbed ferric salt. The subject was discussed by G. D. Grane, P. P. Lazareff, H. W. Kohlschütter and H. Siecke, and B. W. Desai and co-workers. M. Annetts discussed the filtration of colloids.

R. Wintgen found that the **specific gravity,** at 25°/4°, of the hydrosol prepared by the dialysis of a soln. of ferric nitrate with the conc. of $Fe(OH)_3$, expressed in grams per 100 grms. of the dispersion medium:

$Fe(OH)_3$	0·23036	0·60683	1·0030	1·0728	2·2759
Sp. gr. . . .	0·99856	1·00095	1·00356	1·00405	1·01199

K. Grossmann expressed the conc. in grams Fe per 100 c.c. of soln., and found:

$Fe(OH)_3$.	0·408	0·815	1·222	1·630	2·445	3·260
Sp. gr. . .	1·0031	1·0084	1·0135	1·0187	1·0291	1·0392

Observations were also made by N. Sahlbom, and G. H. Ayres and C. H. Sorum. A. Gatterer peptized the hydrogel with acetic acid, and evaporated the dil. soln. by warming it under reduced press. The following are the results, Table LXXXIX, reduced to water at 4°, determined in vacuo. Both R. Wintgen, and A. Gatterer observed that the sp. gr. and the **specific volume** of the hydrosol are a linear function of the concentration. H. Picton and E. Linder, and H. R. Kruyt and J. van der Spek observed that a small dilation, just exceeding the errors of observation, occurs when the hydrosol coagulates.

TABLE LXXXIX.—SPECIFIC GRAVITIES OF THE HYDROSOL OF HYDRATED FERRIC OXIDE.

$Fe(OH)_3$ (per cent.)	5°	10°	15°	20°	25°	30°
0	1·0000	0·9997	0·9991	0·9982	0·9971	0·9957
0·252	1·0011	1·0008	1·0002	0·9993	0·9982	—
0·425	—	1·0024	1·0018	1·0009	0·9998	0·9984
0·514	1·0030	1·0027	1·0023	1·0014	1·0002	—
1·042	1·0066	1·0063	1·0057	1·0048	1·0037	—
1·196	—	1·0072	1·0066	1·0057	1·0046	1·0031
1·825	1·0115	1·0112	1·0106	1·0098	1·0087	—
1·875	—	1·0114	1·0109	1·0100	1·0089	1·0075
3·103	—	1·0197	1·0191	1·0182	1·0171	1·0157
3·446	1·0221	1·0218	1·0211	1·0202	1·0191	—

H. Picton and E. Linder found that the coagulation of the hydrosol is attended by an expansion. They attempted to measure the **osmotic pressure** of colloidal soln. of hydrated ferric oxide prepared in various ways, but consistent results could not be obtained. H. Picton and E. Linder observed no perceptible change of temp. during the coagulation of the hydrosol of ferric oxide by the addition of electrolytes. Observations were also made by F. van der Feen, W. Biltz and A. von Vegesack, and G. Malfitano. J. Duclaux said that the osmotic press. increases with concentration but is not proportional to it; R. Zsigmondy, and J. Duclaux found that the osmotic press. decreases slightly with a rise of temp.; and J. Duclaux, and G. Malfitano found that the osmotic press. of the soln. do not vary directly with the electrical conductivity—the latter decreases with dilution more rapidly than the former. It is assumed that the colloidal soln. contain hypothetical, complex oxy-salts possessing the very properties under investigation! It is not surprising that the colloidal soln. show a slight osmotic press., and f.p. effect, because, generally, some adsorbed soluble salts are present. J. Lindemann showed that the electrolyte content of a sol can determine the osmotic press. The more dil. the hydrosol, the less the relationship between osmotic press. and the conc., and this is attributed to negative osmosis. S. Horiba and co-workers found that the osmotic press. of the hydrosol does not increase in light. T. Yamatori studied the dialysis of the hydrosol, and found that ferric ions dialyze completely when the H'-ion conc. is p_H=3·7 to 3·9. H. Freundlich and co-workers (1932) discussed the action of **sound waves** on the thixotropic gels. R. Wilson and T. C. Poulton found that the hydrosol is immediately coagulated when subjected to a **pressure** of 300 atm., and in 30 mins. when the press. is 100 atm.

H. Picton and E. Linder found that the **surface tension** of water is not affected by the presence of the colloid. N. Sahlbom made some observations on the capillary movements of the hydrosol. W. L. Rolton and R. S. Troop observed no change in the surface tension of the hydrosol in a magnetic field of 16,000 gauss. J. Alexander discussed the relation between surface tension and the kinetic activity. G. Jander and A. Winkel measured the relation between the coeff. of **diffusion** and the H'-ion concentration; and E. Ullmann, the rate of diffusion of ferrum oxydatum saccharatum solubile. K. Grossmann found that with hydrosols of ferric hydroxide having C grms. of Fe per c.c., the **viscosity**, η, at 25°, is:

C . . .	0·408	0·815	1·222	1·630	2·445	3·260
η . . .	0·00914	0·00952	0·00981	0·01030	0·01105	0·01215

Measurements were also made by N. Sahlbom, and A. du Pré Denning. H. Freundlich and E. Schalek, E. Schalek and A. Szegvari, G. H. Ayres and C. H. Sorum, J. H. Yoe and E. B. Freyer, R. N. Mittra and N. R. Dhar, A. Gatterer, N. R. Dhar and V. Gore, H. Meerbrei, and H. W. Woudstra observed the effect of *pressure*, p mm., to be such that with hydrosol, over 4 years of age, containing 9·5 per cent. Fe_2O_3, at 20°, the viscosities in arbitrary units were:

p . . .	10	20	30	40	50
Viscosity .	0·0338	0·0313	0·0299	0·0289	0·0280

A 10 per cent. hydrosol did not change its viscosity, η=0·1368, at 20°, over the range p=10 to 50 mm., and the sol was therefore about 13 times more viscous than water. More dil. hydrosols have perceptibly smaller values. The effect of *temperature* was measured by H. Meerbrei, N. R. Dhar and D. N. Chakravarti, and A. Gatterer. H. W. Woudstra observed:

	20°	25°	30°	35°	40°	45°	50°	55°	60°
η	0·01069	0·00950	0·00849	0·00766	0·00703	0·00639	0·00585	0·00534	0·00490

A. W. Thomas and E. R. Hamburger's results with the hydrosols of ferric oxychloride (Cl) and oxybromide (Br) are summarized in Fig. 531. A. G. Banus and M. Masriera studied the effect of a magnetic field on the viscosity. The effect of ageing is to decrease the viscosities in both cases. The observations of H. W. Woudstra, N. R. Dhar and D. N. Chakravarti, and K. Grossmann show that by reducing the dispersion of the hydrosol by raising the temp., or by the addition of small proportions of an electrolyte, the viscosity decreases until the viscosity curve attains a minimum value. A. Fernau and W. Pauli observed also that the *β-rays* of radium at first depress the viscosity, and then rapidly augment it. J. H. Yoe and E. B. Freyer studied the effect of the H'-ion conc. on the viscosity of the hydrosol, and C. H. Sorum, the diffusion. G. Rossi and A. Marescotti found that the surface tension and stability are not altered by the addition of 0·04 per cent. of gelatin. N. R. Dhar and S. Prakash observed that a mixture of 4 c.c. 0·5M-$FeCl_3$, 1 c.c. M-$(NH_4)_2SO_4$, 2 c.c. 3·5N-$CH_3.COONa$, 12·5 c.c. of water, and 0·5 c.c. of 2·34N-NH_4OH sets to a jelly in 6 hrs. The viscosities of the soln. at 30° were:

Age . .	0	30	60	90	107	132 mins.
Viscosity .	0·009324	0·009324	0·009349	0·1158	0·01731	0·01928

F. Doerinckel found the **specific heat** of the hydrosol and hydrogels of hydrated ferric oxide:

Fe_2O_3	1·6	3·3	6·5	8·6	10·8 per cent.
Sp. ht. Hydrosol	0·982	0·966	0·938	0·915	0·901
Sp. ht. Hydrogel	0·981	0·979	0·967	0·946	0·941

A. Brann, J. H. Walton and A. Brann, and H. Freundlich and F. Oppenheimer observed that under-cooled hydrosols of hydrated ferric oxide freeze more rapidly than is the case with water alone, and the crystals are tabular. Measurements of the lowering of the **freezing-point** were made by F. Krafft, G. Malfitano and L. Michel, H. Picton and E. Linder, A. W. Thomas and A. Frieden, A. Sabanejeff, A. W. Dumansky, A. Gatterer, and G. Bruni and N. Pappada, but the effect, if any, is outside the limits of the experimental errors of observation. F. L. Browne found that the effect of dextrose on the f.p. of the colloidal soln. shows that practically all the water in the sol acts as solvent for the substances dissolved in the sol. J. H. Gladstone and W. Hibbert obtained a lowering of the f.p. corresponding with a mol. wt. of 5000; A. W. Dumansky calculated a mol. wt. of 3120; J. Duclaux, 115,000; and R. Wintgen and co-workers, 32,000. These results, however, have no particular meaning. G. Malfitano discussed the size of the colloidal particles, since the whole basis of the calculation is invalid. G. Bruni and N. Pappada obtained negative results in the attempt to measure the effect of the colloid on the **vapour pressure** of water.

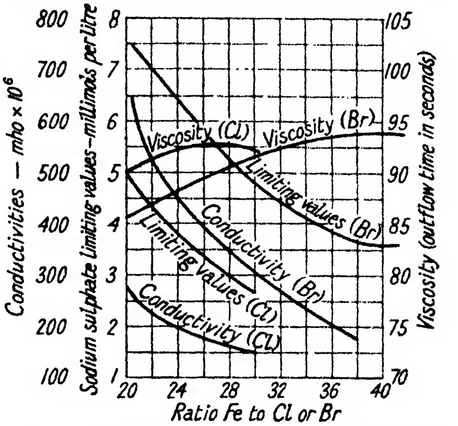

Fig. 531.—Properties of the Hydrosols of Ferric Oxybromide (Br) and Oxychloride (Cl).

M. Berthelot, and H. Picton and E. Linder observed that there is a small evolution of heat during the coagulation of the hydrosol—**heat of coagulation.** F. L. Browne, and F. L. Browne and J. H. Mathews obtained the same value for the heat of coagulation with sols prepared by three different methods, indicating that ferric oxide hydrosols represent an equilibrium which is defined by the temp., press., conc., and purity. The change in the degree of dispersion of ferric oxide during coagulation does not involve a measurable heat effect. The heat effects observed during the coagulation of sols of low purity are due to the dilution of the ferric chloride and hydrochloric acid contained in the sols, to the mixing of these electrolytes with the added coagulating electrolyte, and to changes in the adsorption equilibria. The subject was studied by F. Doerinckel; and H. R. Kruyt and J. van der Spek observed with sodium sulphate coagulation, the heat developed is about 2 cals. per gram of Fe_2O_3, and it increases with the conc. of the chloride in the sol. The heat of coagulation varies greatly with concentration of the hydrosol; and it increases with the proportion of adsorbed salt. The heat of coagulation with potassium oxalate is three times as great as with aluminium sulphate; the heat of coagulation is greater in dil. than in conc. soln., but no heat is developed when the hydrosol is diluted with water. Differences in the results with different preparations of the same hydrosol are due to differences in the proportion of adsorbed salts. F. Doerinckel observed that the **heat of dilution** of an aged 10·8 per cent. hydrosol was zero; but F. L. Browne and J. H. Mathews found that fresh hydrosols have a positive heat of dilution, and that the value decreases during the dialysis, becoming zero, then negative, and finally zero. G. J. Bouyoucos discussed the heat of reaction with soln. of the alkali hydroxides.

H. Picton and E. Linder, and A. Gatterer studied the **dispersion** of the hydrosol as exhibited by the Tyndall effect—1. 13, 7. Ultramicroscopic observations were made by H. Diesselhorst and H. Freundlich, H. Freundlich and co-workers, T. Tevreli, A. Boutaric and C. Tourneur, A. W. Dumansky, N. Kühnl and W. Pauli, B. Kuriloff, R. Wintgen and M. Biltz, and R. Wintgen and O. Kühn. B. Lange found the depolarization of the Tyndall's beam of light by the particles of the hydrosol is much greater with green light than it is with red light. R. Wintgen found that the **index of refraction,** μ, of the hydrosol μ/D is a linear function of the concentration, where D represents the sp. gr. of the soln.; and that with hydrosols having a concentration of C grms. of $Fe(OH)_3$ per 100 grms. of dispersion medium, the indices are:

C . . .	0·23036	0·60683	1·0030	1·0728	2·2759
μ . . .	1·33300	1·33364	1·33443	1·33463	1·33697

S. Prakash studied the extinction coeff. during the coagulation of the hydrosol.

V. Henri and A. Mayer, and C. Doelter observed no coagulation in **radium rays**; but A. Righi, A. Fernau and W. Pauli, and W. P. Jorissen and H. W. Woudstra observed a slow coagulation. J. A. N. Friend made some observations on this subject. P. Lal and P. B. Ganguly studied the action of **ultra-violet light**; S. S. Bhatnagar and co-workers, and J. A. Crowther and J. A. V. Fairbrother, the action of **X-rays**; A. Cotton and H. Mouton, and O. Scarpa, the rotation of the plane of polarization in a magnetic field; and F. Allison and E. J. Murphy, and W. Heller and H. Zocher, the magneto-optic properties. W. Zimmermann observed that the **photoelectric effect** is not perceptible.

O. Majorana observed that hydrosols of hydrated ferric oxide are **birefringent** in a magnetic field, the so-called *Majorana effect*. The hydrosol traversed by a ray of light at right angles to the lines of magnetic force exhibits double refraction sometimes as great as that of quartz. The birefringence disappears when the magnetic field is extinguished. O. Majorana, and A. Cotton and H. Mouton found that the birefringence is accompanied by a perceptible dichroism of the hydrosol. A. Schmauss inferred that the magnetic field caused an orientation of the particles. The phenomenon was discussed by O. Wiener, Lord Rayleigh, J. Kerr, L. Tieri, A. du Pré Denning, R. Gans and H. Isnardi, A. Pontremoli, H. Freundlich, and F. Braun. A. Cotton and H. Mouton observed that after ultra-filtration through collodion, the filtrate remained inactive, while the double refraction of the colloidal residue was increased. While ordinary coagulation gives an inactive gel, coagulation in a magnetic field gives a gel with a permanent double refraction even in the absence of a magnetic field. The turbidity and double refraction depend on the age of the hydrosol; and the ageing is hastened by raising the temp.—thus, 4 hrs.' heating at 100° raised the birefringence forty-fold. The turbidity and viscosity increase during the warming so that the greater the grain-size of the particles, the greater is the birefringence. Some sols prepared by the electric process have particles which are visible under the ordinary microscope, and the long particles become oriented in the magnetic field, and the hydrosol is then birefringent. The double refraction is, therefore, attributed to the orientation of lamellar or rod-like particles in the magnetic field, but the rods or flakes do not form threads. The reason the small particles give a smaller effect is due to the more vigorous brownian movement disturbing the orientation. A. Cotton and H. Mouton inferred that the Majorana effect is due to the nature of the particles themselves as well as to their orientation; and this is in accord with the observations of H. Freundlich, G. Quincke, H. Diesselhorst and co-workers, D. Graffi, A. Pontremoli, and L. Tieri, that the ferric oxide hydrosol exhibits double refraction when stirred mechanically, or when an electric current is passed through the liquid. C. von Nägeli had previously explained the optical and other properties of colloids on the assumption that they consist of anisotropic ultramicrons having a great resemblance to minute crystals. A. W. Ewell, L. Tieri, and O. M. Corbino studied the effect of a variable magnetic field on the Majorana effect.

The colour and dichroism of the hydrosol have been previously discussed. B. Lange studied the absorption of light by the hydrosol of ferric oxide. O. Scarpa found that the **absorption spectra** of the hydrosols are not in accord with Beer's law; with a decreasing concentration, the absorption in the red increases, and decreases in the violet. The absorption spectra observed by B. E. Moore with hydrolyzed soln. of ferric chloride, and hydrosols of hydrated ferric oxide, are summarized in Fig. 532. B. Jirgensons found that when the hydrosol is coagulated, the limit of absorption is at first displaced towards the red, but with complete coagulation, it is displaced towards the violet. A. Boutaric also studied the effect of flocculation on the coeff. of absorption; G. Jander and A. Winkel, the effect of the H'-ion concentration; and V. Petrescu, the depolarization of light by the colloidal soln. M. Matsui and co-workers, B. Kuriloff, and S. Prakash investigated the change in the **extinction coefficient** with the ageing of the hydrosol, and with the hydrosol mixed with different proportions of hydrochloric acid. B. Lange applied Lambert and Beer's law to the hydrosol. T. Ewan observed that when a completely hydrolyzed soln. of ferric chloride is diluted, the extinction coeff., k, has a higher value—wave-length of light constant; and that when the conc. of the hydrosol is C mols. of $Fe(OH)_3$ per litre, and the mean wave-length of the light is λ:

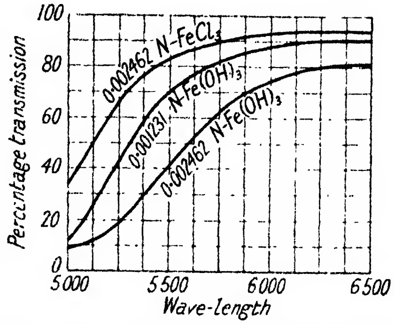

FIG. 532.—The Absorption Spectra of Hydrosols of Hydrated Ferric Oxide.

$C=0·0001254$	λ . .	570·0	513·2	480·2	423·8	442·8
	k . .	22·23	107·2	202·4	263·4	431·6
$C=0·0005680$	λ . .	536·0	497·2	461·2	444·2	434·1
	k . .	53·1	146·8	216·3	263·8	320·7
$C=0·02531$	λ . .	663·8	588·0	550·2	539·2	528·0
	k . .	5·61	14·35	33·04	47·76	61·05
$C=0·09855$	λ . .	665·2	608·0	577·0	552·0	540·5
	k . .	6·12	10·91	17·87	33·1	44·5

S. S. Bhatnagar and co-workers observed no marked change in the velocity of cataphoresis before and after exposing the hydrosol to **X-rays.** The **electrophoresis,** or rather the **cataphoresis,** of the positive colloid was studied by W. Biltz, H. Picton and E. Linder, J. N. Mukherjee and co-workers, S. H. Whang, F. Hazel and G. H. Ayres, W. B. Hardy, A. Reychler, R. Audubert, and W. Spring. The negative form of the colloid was discussed above, likewise also the reversal of the electric sign of colloids by adding varying proportions of positive or negative anions. The speed of migration of the colloidal particles of the positive hydrosol with a potential difference of 1 volt per cm. was found by R. Wintgen and M. Biltz to be 24·1 to 35·1 cms. per sec.; A. J. Rabinowitsch and V. A. Kargin gave 37·1 cms. per sec.; W. Pauli and co-workers—N. Kühnl, L. Engel, F. Rogan, and G. Walter—approximately 4·4; and W. Pauli and J. Matula, 57 to 336. The latter value is considered by R. Wintgen and M. Biltz to be too large, because the conductivity of the intermycellary fluid was ignored. H. Puiggari measured the electrical transport of the colloidal particles for the hydrosol, at 17° using a current of 0·003 amp. and an e.m.f. of 23 volts across the electrodes. The amount of spongy, dark-orange coloured coagulum which separated on the platinum cathode was directly proportional to the current, averaging 304×10^{-5} g. per amp. pet sec. for currents of 0·003 to 0·01 amp., irregularly and progressively smaller for 0·036 to 0·065 amp., and invisible for less than 0·0003 amp. The electrical transport is increased by rise of temp. The subject was discussed by S. S. Bhatnagar and D. C. Bahl, A. Boutaric and G. Perreau, H. Puiggari, F. Hazel and co-workers, A. J. Rabinowitsch and

E. Fodiman, and H. Freundlich and G. Lindau. H. Freundlich and S. Wosnessensky, P. Rona and F. Lipmann, and F. Powis discussed the speed of migration, or rather the **anaphoresis,** of the colloidal particles of the negative hydrosol, and the value works out to be between 15 and 30 cms. per sec. The speed of migration of the cataphoretic particles was found by H. Freundlich and H. P. Zeh to be lowered by the addition of complex cyanides proportionally with the valency; and H. Freundlich and G. V. Slottman found that the lowering of the speed by salts of the sulpho-acids increases as the salts rise in the homologous series. H. Freundlich and P. Rona observed that substances like camphor or thymol lower the speed of migration; and S. W. Young and L. W. Pingree found that light produces a similar result. The subject was discussed by L. Engel and W. Pauli. E. H. Büchner and A. H. H. van Royen found that when a thin stream of the hydrosol of ferric hydroxide flows through the dispersion medium between two vertical electrodes, the stream broadens out in all directions. The effect is not one of cataphoresis, and it is attributed to differences in electrical conductivity of the hydrosol and the dispersion medium. A. Lottermoser and Ta-Yü Chang studied the effect of dilution on the electric charge of the sol.

The sp. **electrical conductivity** of the hydrosol varies within wide limits and it depends on the proportion of chloride associated with the hydrosol. R. Wintgen and M. Biltz found the sp. conductivity in mhos for hydrosols with the following atomic proportions of Cl : Fe to be :

Cl : Fe .	0·1472	0·1354	0·1238	0·1236	0·1132	0·0994	0·0605
Mho × 10^3 .	1·525	1·246	0·8509	0·7544	0·6460	0·5073	0·4622

Observations were also made by W. Kopaczewsky, R. Wintgen and co-workers—M. Vöhl, and O. Kühn—W. Pauli and co-workers—N. Kühnl, G. Walter, J. Matula, F. Rogan, and L. Engel—A. Gatterer, A. Hantzsch and C. H. Desch, N. R. Dhar, and N. R. Dhar and D. N. Chakravarti. The conductivity of the sol increases with ageing, and approaches a constant value. K. C. Sen and co-workers gave 30×10^{-6} to 244×10^{-6} mho for the conductivity of the negative hydrosol. G. Malfitano found that soln. of ferric chloride will pass through a collodion membrane without causing a change in electrical conductivity; but J. Duclaux observed that Graham's sol, with 0·032 gram-atom of iron per litre, gives a colourless liquid by ultra-filtration through a collodion membrane, so as to separate the mycelia from the intermycellary liquid. The original soln. had a conductivity of 113×10^{-8} mho; the filtrate, a conductivity of 82×10^{-6} mho; and the residue, one-tenth the original, had a conductivity of 280×10^{-6} mho. The removal of the mycelia decreased the conductivity; the intermicellary liquid is not changed by its passage through the membrane. The adsorption of the electrolyte by the membrane is negligible. This subject was discussed by R. Wintgen and M. Vöhl, R. Wintgen and M. Biltz, J. Duclaux, E. Heymann, A. Lottermoser, R. Zsigmondy, and Wo. Ostwald. According to H. Handovsky, the longer the hydrosol of ferric oxide is dialyzed, the greater the increase in conductivity with the ageing of the sol; the increase in conductivity is said to take place chiefly in the intermycellary liquid into which the ions move slowly from the mycelia. A. W. Thomas and E. R. Hamburger's results with the hydrosols of ferric oxychloride (Cl), and oxybromide (Br) are summarized in Fig. 532. The effect of ageing is to increase the conductivity in both cases.

R. Wintgen and co-workers attempted to calculate the number of molecules in a single colloidal particle from measurements of the electrical conductivity and the transport numbers, involving a number of very debatable assumptions. It was found that an aged hydrosol, with 1·601 grms. Fe_2O_3 and 0·06014 grm. Cl per 100 grms. of sol, assuming all the particles have the same size, had the average composition of $[75{\cdot}35Fe_2O_3.7{\cdot}86HCl.xH_2O)FeO]^{\cdot}10{\cdot}230+10{\cdot}230Cl'$. A. Lottermoser found that the $H^{\cdot}$-ion conc. of the ultra-filtrates from an aged sol to be the same as that of the sol itself, and the mycelia are supposed to contain neutral chloride and chloride ions. The positive charge of the colloid is attributed to the stronger adsorption of the H·-ion, and he represented the composition of the particles by $[(x\mathrm{Fe_2O_3}.y\mathrm{HCl}.z\mathrm{H_2O})\mathrm{H^{\cdot}}]_n+(n-q)\mathrm{Cl'}$, where $q\mathrm{Cl'}$ represents the chloride ion corresponding to the adsorbed H·-ion. The sp. conductivity of the sol is greater than that of the ultra-filtrates, and A. Lottermoser regarded the difference as the true conductivity of the mycelia. The mobility of the mycelia rises abnormally with increasing dilution in sol containing but a small proportion of chlorine. This is taken to mean that the mycelia are adsorption complexes, and the abnormality is attributed to the displacement of adsorption and hydrolysis equilibria by dilution. H. B. Weiser added that there is no need to assume that the hydrosol is an electrolyte with complex oxychloride to account for the observed fact that only part of the chlorine present appears to be ionic. He argued that an indefinitely large number of hydrated ferric oxides are possible, and differing amongst themselves in the average grain-size, and therefore also in the amount of salt or salt-ions adsorbed at the surface; as shown by F. L. Browne, and P. Maffia, the colloid of Graham's sol adsorbs ferric chloride and hydrochloric acid as well as Fe···-, H·-, and Cl′-ions, in proportions dependent on the nature of the colloid, the sp. adsorption, and the conc. The preferential adsorption is in favour of the ferric and hydrogen ions—the chloride ion is not adsorbed so strongly. There is a state of equilibrium between the proportion adsorbed and the proportion in soln. Prolonged dialysis involves a loss of the adsorbed ions, and this decreases the stability of the sol. The adsorbed chloride is masked or protected by the hydrated ferric oxide, and does not respond to the ordinary tests, and it has a negligible effect on a chlorine electrode and is not detectable by the potentiometer. Hence, continued H. B. Weiser, it is to be expected that the amount of ionic chlorine is less than the total chlorine of the soln. W. L. McClatchie studied the **H·-ion concentration** of sols of ferric hydroxide. H. Puiggari prepared the hydrosol, with the H·-ion conc. eq. to $p_{\mathrm{H}}=3{\cdot}8$, by gradually adding aq. ammonia (90 grms. of 28 per cent. $\mathrm{NH_3}$ and 180 c.c. of water) to 1000 grms. of a soln. of hexahydrated ferric chloride in 2000 c.c. of water, and dialyzing for 264 hrs. The conc. of the H·- and Cl′-ions were determined electrometrically by W. Pauli and J. Matula, N. Kühnl and W. Pauli, A. J. Rabinowitsch and V. A. Kargin, P. Rona and F. Lipmann, R. Wintgen and M. Biltz, F. L. Browne, and A. W. Thomas and A. Frieden. A. J. Rabinowitsch and V. A. Kargin, and H. Pallman studied the H·-ion activity of the dispersed phase. A. Lottermoser and W. Riedel compared the electrolytic and electrokinetic potentials. S. S. Kistler discussed the **dielectric constant.**

A. Turpain and B. de Lavergne observed that a **magnetic field** has no effect on the dispersion of ferric hydroxide, but if some iron, nickel, cobalt, or chromium is present, coagulation occurs. S. Berkman and H. Zocher obtained $\chi=-0{\cdot}03\times10^{-6}$ for the **magnetic susceptibility** of the hydrosol prepared by the dialysis of a soln. of ferric chloride; P. Pascal gave $-0{\cdot}019\times10^{-6}$ for a hydrosol with 4·93 grms. Fe per litre; and O. Scarpa obtained $-0{\cdot}4\times10^{-6}$ to $0{\cdot}7\times10^{-6}$ for hydrosols prepared by electrical spluttering. The magnetic susceptibility was also examined by G. Wiedemann, and A. du Pré Denning. W. Hagen observed that the magnetic susceptibility decreased linearly with the temp.; and R. Gans and H. Isnardi found that it decreased with the temp., and increased with the field-strength.

According to H. Freundlich, the smallest concentrations in mols per litre, required for the precipitation of the hydrogel from the hydrosol of hydrated ferric oxide, are:

$\mathrm{KNO_3}$	$\frac{1}{2}\mathrm{Ba(NO_3)_2}$	NaCl	$\frac{1}{2}\mathrm{BaCl_2}$	$\mathrm{K_2SO_3}$	$\mathrm{MgSO_4}$	$\mathrm{K_2Cr_2O_7}$
0·0119	0·0140	0·00925	0·00964	0·00020	0·00022	0·00019

The negative ion apparently exerts the dominant action, and bivalent ions are more effective than univalent ions. H. Freundlich found the order of the precipitating power of the anions to be: chromate>sulphate>hydroxide>salicylate>benzoate>chloride>nitrate>bromide>iodide; and H. B. Weiser and E. B. Middleton, using L. P. de St. Gilles' sol, found: ferrocyanide>ferricyanide>-dichromate>

tartrate>sulphate>oxalate>chromate>iodate>bromate>thiocyanate>chloride >chlorate>nitrate>bromide>iodide. According to H. B. Weiser, hydrochloric acid has two precipitation values for L. P. de St. Gilles' sol, one above the other with a zone of non-precipitation between, in which the colloid is less stable than the original colloid. The degree of reversibility of the precipitation of hydrous ferric oxide is determined mostly by the specific adsorbability of the precipitating ion, although the physical character of the precipitate has an influence. Non-electrolytes, even in conc. soln., have very little action. A. W. Dumansky found that when the hydrosol is boiled with Fehling's soln., the colloid is precipitated along with cuprous oxide. O. Baudisch and W. H. Albrecht studied the subject. N. R. Dhar and R. N. Mittra discussed the rhythmic coagulation of ferric hydroxide sol.

Observations on the **coagulation** of the hydrosol by electrolytes were made by H. Freundlich and co-workers—H. P. Zeh, K. Jacobsohn, V. Birstein, G. V. Slottman, S. Wosnessensky, A. Brossa, and M. Aschenbrenner—E. Weitz and H. Stamm, H. R. Kruyt and J. van der Spek, J. Traube and E. Rackwitz, A. W. Dumansky and co-workers, E. Schalek and A. Szegvari, W. Knaust, F. Hardy, H. D. Murray, S. I. Dyachkovsky, J. N. Mukherjee and co-workers, B. N. Desai and P. M. Barve, J. Lisiecky, N. R. Dhar and V. Gore, C. H. Sorum, S. Liepatoff, H. Mayanagi, S. G. Chaudhury and A. Ganguli, H. Picton and E. Linder, E. S. Moore and J. E. Maynard, M. N. Chakravarti and co-workers, G. Rossi and A. Marescotti, W. V. Bhagwat and N. R. Dhar, A. J. Rabinowitsch and V. A. Kargin, E. Deiss and G. Schikorr, A. von Buzagh, W. Pauli and co-workers, A. Yanek, K. Jablczynsky and co-workers, A. Ivanitzkaja and L. Orlova, W. P. Jorissen and H. W. Woudstra, W. B. Hardy, A. Boutaric and co-workers—M. Dupin and G. Perreau—N. Pappada, S. Ghosh and N. R. Dhar, N. R. Dhar, D. Deutsch and S. Loebmann, W. W. Taylor, S. S. Joshi and V. L. Narayan, and P. Rona and F. Lipmann. The results show that univalent anions like the Cl′- Br′- and I′-ions are not very different in their action, but the F′-, CyS′-, and OH′-ions have a particularly high coagulating value. Soln. of sodium phosphate act between two limiting concentrations; the coagulating value of the complex cyanides increases with their valency; and the coagulating values of the fatty acids, and of the sodium salts of the sulpho-salts, are greater the higher their position in the homologous series. K. Hakozaki attempted to express the coagulating power of electrolytes by an empirical formula. H. Freundlich, and S. Ghosh and N. R. Dhar found the coagulating values are independent of the age of the hydrosol. A. Boutaric and G. Perreau, H. Freundlich, K. C. Sen and co-workers, H. B. Weiser and H. O. Nicholas, H. R. Kruyt and J. van der Spek, and O. Fodor and R. Riwlin observed that the coagulating power increases with the concentration of the hydrosol, but T. Takamatsu found that whilst the coagulating powers of the OH′-, SO_4''-, CO_3''-, HPO_4''-, $FeCy_6''''$-, and Cr_2O_7''-ions are proportional to the conc. of the hydrosol, that of the I′-, and CH_3COO'-ions is dependent on the conc. of the hydrosol, and that of the Cl′- and NO_3'-ions is independent of the conc. of the hydrosol. E. F. Burton and E. Bishop found that with some colloids: The precipitating power—pp.—of univalent ions increases, that of bivalent ions remains unchanged, and that of tervalent ions decreases with a decreasing concentration of the sol. H. B. Weiser and H. O. Nicholas observed that the rule does not apply for the hydrosol of hydrated ferric oxide; their results, plotted in Fig. 533, were obtained with a hydrosol having 1·7 grms. of the colloid per litre as 100 per cent.:

Conc. of colloid		100	50	25	12·5 per cent.
Pp. value	$KBrO_3$	40·1	34·4	28·0	25·0
	K_2SO_4	0·68	0·41	0·25	0·16
	K_4FeCy_6	0·57	0·30	0·16	0·08

On the other hand, R. C. Judd and C. H. Sorum found that with a hydrosol quite free from chlorides, the coagulation follows E. F. Burton and E. Bishop's rule.

Under these conditions, the amount of coagulating univalent ion decreases as the conc. of the sol increases. N. R. Dhar and co-workers found that the more concentrated the highly purified sols the greater the amount of electrolyte required for coagulation, irrespective of the valency of the coagulating ion.

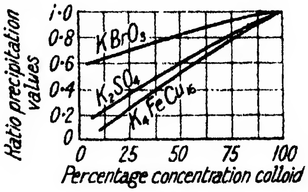

FIG. 533.—The Coagulation of the Hydrosol of Ferric Oxide.

A. W. Thomas and E. R. Hamburger studied the limiting value, or the average of the amounts of sodium sulphate, in millimols per litre, required just to precipitate and just not to precipitate the hydrosols of ferric oxychloride (Cl) and oxybromide (Br), and the results are summarized in Fig. 532. J. Duclaux found that in the coagulation of ferric oxide hydrosol, 10 c.c. of the hydrosol, with 0·0203 gram-atoms of iron and 0·00166 gram-atom of chlorine per litre, required almost eq. quantities of anions for coagulation, regardless of their valency.

SO_4''	$(CH_2)_2C(OH)(COO)_3'''$	CrO_4''	CO_3''	
17×10^{-6}	$16\cdot5\times10^{-6}$	$15\cdot2\times10^{-6}$	17×10^{-6}	
PO_4'''	OH'	$FeCy_6''''$	NO_3'	Cl'
19×10^{-6}	$16\cdot1\times10^{-6}$	13×10^{-6}	1880×10^{-6}	2000×10^{-6}

The nitrate and chloride ions were found to be exceptional. The amount of sulphate or hydroxide ion necessary for precipitation was almost eq. to the chloride-content of the hydrosol. He thus regarded the process of coagulation as a definite stoichiometrical, chemical action, *i.e.* a double decomposition of the ordinary type. F. Hazel and C. H. Sorum, H. Freundlich and G. Lindau, and P. Rona and F. Lipmann found that the coagulating value increases with the H˙-ion conc. of the soln., but the order of the coagulating power of the anions is but little affected by the conc. of the H˙-ion. Graham's sol is stabilized by adsorbed H˙-ions, and probably also by ferric ions. Different concentrations of electrolytes are required to neutralize the adsorbed ions and to precipitate the sol. The conc. of the acids required for precipitation are greater than those of the potassium salts because the stabilizing H˙-ion is more strongly adsorbed than the K˙-ions. W. Pauli and co-workers—J. Matula, G. Walter, F. Rogan, and W. Kühnl—discussed the displacement of the chloride associated with the hydrosol by the coagulating anion; and A. J. Kabinowitsch and V. A. Kargin, the effect of the H˙-ion concentration on the exchange of ions.

H. Freundlich and G. Lindau studied the coagulation value of albumen · egg-albumen, hæmoglobin, paraglobulin, gelatin, globin, and trypsin; and A. Janek and B. Jirgensons, methyl, ethyl, propyl, and isobutyl alcohols. H. M. Stark found that the hydrosol is coagulated by bubbling some gases through the liquid; carbon dioxide caused no coagulation; but the iron precipitated by a litre of gas was 273×10^{-7} grm. with nitrogen; 317×10^{-7} grm. with air; 428×10^{-7} grm. with hydrogen; and 453×10^{-7} grm. with oxygen. A. W. Dumansky found that when a soln. of carbamide is added to a colloidal soln. of hydrated ferric oxide, the time of coagulation increases as the conc. of the carbamide is diminished, but the conc. of the colloid has no effect on the process. Until the occurrence of coagulation, the conc. of the coagulating substance is less than its calculated value, but after coagulation the colloid retains hardly any of the coagulating substance. The process of coagulation is assumed to occur thus: carbamide passes readily through the walls of the bubbles of the colloid suspended in the water, consequently no coagulation appears at first, but the carbamide soln. is concentrated within the cells of the colloid until the strain causes them to burst and coagulation takes place. Under certain conditions, the bubbles of the colloid do not burst, but they stretch, thus occupying a larger vol. and finally cause the formation of a jelly. A. W. Dumansky prepared colloidal soln. of hydrated ferric oxide containing 8·69 grms. of barium nitrate, or 2·152 grms. of potassium chloride, or 4 grms. of potassium nitrate. Conductivity measurements of mixtures, in various proportions, of colloidal hydrated ferric oxide soln. and ammonium chloride soln., show that in these mixed soln. the ammonium chloride distributes itself between two solvents, namely, water and the mols. of the colloid. C. E. Linebarger concluded that it is very unlikely that the coagulation or gelatinization of the hydrosol is comparable with crystallization from supersaturated soln., because the addition of a small amount of a substance having the power to start coagulation in one part of a colloidal soln. does not cause the coagulation to spread at a certain rate throughout the whole soln., such as would occur with crystallization from a supersaturated soln. K. Jablczynsky and M. Soroczynsky studied the kinetics of the process of coagulation of sols of ferric hydroxide by electrolytes; K. Jablczynsky and M. Knaster showed that the speed of coagulation increases with the temp. between 5° and 45°; and K. Jablczynsky and co-workers found that the coagulation velocities with different univalent anions are in the proportions $I' : Br' : NO_3' : Cl' = 1 : 7{\cdot}92 : 72{\cdot}9 : 169$. A. Fordor and R. Riwlin discussed the speed of coagulation of the hydrosol. According to G. H. Ayres and C. H. Sorum, the flocculation of hydrosols showed no regular variation with the temp. of preparation, but samples heated to different temp. were less stable to a flocculating agent the higher the pre-heating temp. Opaque sols of an orange-red colour, produced at a high temp., showed considerable sedimentation on standing. The colour and turbidity of the sols indicate that the oxide is less hydrated the higher the temp. of preparation, and the oxide is then less stable towards electrolytes than sols prepared at a lower temp. The decrease in stability and increase in turbidity are not due to an increase in the grain-size of the particles. W. Knaust discussed the coagulation of the sol peptized by phosphoric acid. E. S. Hedges and R. V. Henley studied the periodic coagulation of the hydrosol.

The coagulation of the negative hydrosol of ferric oxide by electrolytes was studied by H. Freundlich and S. Wosnessensky, P. Rona and F. Lipmann, K. C. Sen and co-workers, and A. Boutaric and G. Perreau.

Mixtures of some electrolytes instead of additively strengthening one another's action, reduce their mutual effect; hence the term **antagonistic electrolytes.** Thus, mixtures of ferric and potassium chlorides, or of aluminium nitrate and potassium sulphate, act as antagonistic colloids in the flocculation of the hydrosol of hydrated ferric oxide. The phenomenon was first observed by H. Picton and E. Linder in connection with the effects of pairs of electrolytes on the coagulation of the hydrosols of arsenic trisulphide. The subject was discussed by K. C. Sen, A. Rabinerson, A. Lottermoser and K. May, and S. Ghosh and N. R. Dhar. It is supposed that the antagonistic effect is due to the interference of the one precipitating ion on the adsorption of the other. A. Boutaric and M. Dupin observed that in the mutual flocculation of the hydrosols of hydrated ferric oxide, and arsenious sulphide, when an insufficient quantity of either sol to cause the flocculation of the other, is added, and the mixture is allowed to stand a few days, the soln. becomes increasingly sensitive to further additions, so that a total quantity of so little as one-twentieth of the quantity required on a first addition is needed to produce flocculation. The phenomenon is analogous with *anaphylaxis*, where an animal, a few weeks after a single injection of protein, becomes extremely sensitive to a second injection which would otherwise be harmless. N. P. Peskoff and V. I. Sokoloff found that when the hydrosol is treated with just sufficient magnesium sulphate to start coagulation, the addition of low concentrations of hydrochloric acid increase the stability of the colloid, whilst high concentrations decrease it, although coagulation is never complete. When sulphuric acid is used as coagulant, the presence of hydrochloric acid increases the instability to a greater extent than in the case of magnesium sulphate.

Protective colloids, or **retarders**, act by hindering the coagulation of hydrosols, and thus make hydrosols more stable—*vide supra*. Some substances, called

sensitizers, increase the sensitiveness of the hydrosol to coagulation by electrolytes —particularly by univalent chlorides, bromides, iodides, or nitrates which have a weak coagulating value. Thus, H. Freundlich and P. Rona observed this to be the case in the presence of urethane, camphor, thymol, amyl alcohol, acetone, phenolthiourea, and tributyrine. Electrolytes which have a stronger coagulating value—like the fluorides, sulphates, and citrates—do not have so marked an effect. H. R. Kruyt and C. F. van Duin observed that the presence of phenol, or, better, of isoamyl alcohol, favours the coagulation power of potassium chloride or sulphate; A. Janek and B. Jirgensons observed that methyl, ethyl, propyl, and isobutyl alcohols have a similar effect on the precipitation value of soln. of sodium chloride; B. N. Ghosh found that thymol, urethane, and amyl alcohol accelerate the coagulation of the hydrosol; H. Freundlich and G. Lindau, egg-albumen, and serum paraglobulin; and S. G. Chaudhury and A. Ganguli found that the hydrosol is more sensitive towards coagulation in the presence of methyl and ethyl alcohols, and pyridine; urea sensitized it towards potassium chloride and sulphate; and glycerol, towards potassium sulphate and ferrocyanide.

According to A. Brossa and H. Freundlich, when the hydrosol is added to a soln. of albumin, free from electrolytes, the particles of albumin and of hydrated ferric oxide are positively charged, but not so strongly as the particles of hydrated ferric oxide when alone. Hence, the hydrosol of hydrated ferric oxide and albumin behaves as a positive suspensoid, which is precipitated by small conc. of electrolytes. In the precipitation by electrolytes the nature of the anion, its valency, and tendency to adsorption are of importance. The quantity of electrolyte necessary to precipitate the complex sol is much less than that required to precipitate the pure hydrated ferric oxide sol; consequently the complex sol has become more sensitive. The sensitiveness can be further increased by adding albumin sol to the albumin-ferric oxide sol. With large conc. of electrolytes, the particles first precipitated are re-dissolved; in this case, as in the peptization of globulin and casein sols, the nature of the anions is determinative, in so far as the high valency anions and organic anions (for example, SO_4'', picrate ion, citrate ion) show their action at much smaller conc. than the others. Albumin is not quantitatively combined with the hydrated ferric oxide sol, but divided between the sol and the soln. The partition does not follow a simple adsorption isotherm, but the quantity adsorbed is proportional to the concentration for small albumin conc.; whilst at high conc., a saturation value is reached. The adsorption does not appear to be reversible. With increasing conc. of hydrated ferric oxide, the sensitiveness of the complex sol decreases, and approaches more nearly to the pure hydrated ferric oxide sol in its properties. The albumin hydrated ferric oxide sol is somewhat more turbid than the hydrated ferric oxide sol, but it cannot be resolved into its constituents in the ultra-microscope. This is easier in the region where no precipitation is possible, and most easy in those sols to which an excess of albumin soln. has been added. The whole of the phenomena of precipitation and re-solution are explained by the adsorption of the anions of the soln., and depend on the discharge and then re-charging of the particles. If instead of adding an electrolyte to a hydrated ferric oxide-albumin sol an albumin sol containing an electrolyte is precipitated with hydrated ferric oxide sol, it is seen that in many respects the relationships are identical, particularly in the amount of hydrated ferric oxide combined with the albumin. Differences noticeable in the nature of the precipitation can be explained by assuming that the changed conditions have affected the rate of coagulation. The action was also studied by W. Pauli and L. Flecker, H. Freundlich and G. Lindau, H. Freundlich and co-workers—G. Lindau, and S. Wosnessensky—and J. Reitstötter. A similar effect was observed with soln. of albumin, paraglobulin, hæmaglobin, and globin; and W. Beck found that lecithin and cholesterin, R. Wintgen and E. Meyer, gelatin, and S. Ghosh and N. R. Dhar, gelatin, albumin, and tannin, act in the same manner. The sensitization effect is attributed to the lowering of the surface charge on the particles as a result of the adsorption of a substance with a lower dielectric constant than water;

but L. Michaelis and P. Rona could not detect any adsorption of these non-electrolytes by the hydrosol of ferric oxide, nor could they detect any effect due to their presence on the adsorption of electrolytes. The subject was discussed by H. Freundlich and co-workers—P. Rona, and G. Lindau—and by W. Pauli and L. Flecker. Y. Matsuno, V. Henri and A. Mayer, and W. P. Jorissen and H. W. Woudstra found also that exposure to the β-rays of radium favours the coagulation of the hydrosol by electrolytes.

H. B. Weiser and E. B. Middleton showed that when a positive colloid like hydrated ferric oxide is coagulated by electrolytes, the negative precipitating ion is adsorbed; but the order of precipitating power and the order of adsorption are not the same. This is because the adsorption measured is ion adsorption plus adsorption of neutral salt, so that one effect may mask the other. H. Freundlich observed that colloids may show a kind of **acclimatization,** for the hydrosol of ferric oxide requires less electrolyte for precipitation when it is added all at once to what is required, than when it is added step-wise with long intervals of time, and particularly when the slow addition produces a fractional precipitation of the sol. This is expressed by saying that the colloid becomes acclimatized to its surroundings when the electrolyte is added slowly, and so more is required to produce a given result. V. N. Krestinskaja and O. S. Moltschanova said that the effect is due to slow chemical changes produced by a reaction of the colloid with the added electrolyte. H. B. Weiser added that the effect of the addition is not necessarily due to the adaptability of the colloid to the electrolyte, because fractional precipitation not only removes ions by adsorption but it alters the stability of the soln. by decreasing its concentration. The factors which determine the excess for slow rates of precipitation are: (i) the extent of the fractional precipitation; (ii) the adsorbing power of the colloid; (iii) the adsorption of the precipitating ions; and (iv) the effect of the dilution of the soln. on the precipitation conc. of electrolytes.

The **mutual coagulation** of hydrosols.—A. Lottermoser, and W. Biltz observed that a positively charged hydrosol like that of hydrated ferric oxide is coagulated by a negatively charged hydrosol. Complete flocculation occurs only within certain limiting proportions of the two hydrosols; with other proportions, the coagulation is incomplete. The phenomenon was observed with silicic acid, by T. Graham, W. M. Simakoff, W. Biltz, A. W. Thomas, and N. Pappada; with the hydrosols of selenium, cadmium sulphide, stannic acid, tungsten-blue, molybdenum-blue, and platinum, by W. Biltz; with humus, by H. Udluft; with mastic, by M. Neisser and U. Friedemann; with arsenic or antimony trisulphides, by W. Biltz, H. Freundlich, A. W. Thomas, J. Billitzer, and M. Neisser and U. Friedemann; manganese dioxide, by E. Deiss, H. Udluft, and W. M. Simakoff; with vanadic acid, by W. Biltz, and H. Freundlich and W. Leonhardt; with ferrous hydroxide, by E. Deiss and G. Schikorr; with gold, by W. Biltz, and A. Galecki and M. S. Kastorskij; and with silver, by A. Rabinerson, and F. Doerinckel, who found that the heat of coagulation reaches a maximum with 60 to 70 per cent. of silver hydrosol, and then falls off rapidly. Optimum coagulation occurs with 70 to 80 per cent. of silver colloid. R. Wintgen and E. Meyer, R. Wintgen and M. Vöhl, D. C. Bahl, H. B. Weiser and co-workers, and H. Freundlich and G. Lindau observed that the hydrosol of gelatin coagulates the hydrosol of hydrated ferric oxide. According to R. Wintgen and E. Meyer, when constant amounts of a sol of hydrated ferric oxide are mixed with increasing amounts of gelatin soln. and water to give constant final vols., two types of flocculation are obtained according as the necessary amount of water is added to the hydrated ferric oxide or the gelatin soln. When the water is added to the gelatin soln., flocculation commences at a well-defined point and the amount of precipitate increases to a maximum. When water is added to the sol of hydrated ferric oxide, for increasing amounts of gelatin, the commencement of the flocculation is well marked, this is followed by an increasing flocculation to a rather indefinite maximum, there is then a sudden fall to a point of no flocculation, and finally, a renewal of increasing flocculation. The amount of gelatin required for the first flocculation decreases with increase in the conc. and the age of the initial gelatin soln. For a series of dilutions of ferric hydroxide sols of different origin, the amount of gelatin required for flocculation decreases in a linear manner with the dilution for typical colloidal sols, but decreases in a linear manner with the conc. of semi-colloidal sols, containing much hydrochloric acid. The first case is regarded as a simple mutual flocculation, and the second as involving, in addition, an increasing dispersion of the gelatin with increasing amounts of hydrochloric acid. H. Udluft found also that coagulation occurs when the hydrosol of hydrated ferric oxide is mixed with humus; A. Rabinerson, with prussian blue, night blue, dextrin, albumin, or silver; M. Neisser and U. Friedemann, with mastic; and R. Ellis, with oil emulsion. E. A. Schneider observed no flocculation of the hydrosol of hydrated ferric oxide by the hydrosol of gold sulphide.

According to W. Biltz, complete coagulation occurs only when a sol of one sign is neutralized by adsorption of an amount of colloid carrying eq. ions of the opposite sign. The amounts required for the purpose vary with their nature. In one case, the positive hydrosol of ferric oxide was more effective than the hydrosol of cerous oxide, and less effective than the hydrosol of thoria in coagulating the hydrosol of gold; while the hydrosols of both thoria and cerous oxide were more effective than positive hydrosols of hydrated ferric oxide in coagulating the hydrosols of antimony and arsenic sulphides. A. W. Thomas and L. Johnson found that there is a chemical equivalence between the peptizing agents of the positive hydrosol of hydrated ferric oxide peptized by ferric chloride and hydrosols of silicic acid peptized by sodium silicate, provided the ratio of the peptizing agent to the disperse phase falls within a certain range; outside this range, the coagulation appeared to be erratic. The precipitations showing chemical equivalence between the peptizing agents at maximum coagulation exhibit little variation in the coagulation ratios with dilution, whilst those showing a divergence from chemical equivalence approach the chemical equivalence on dilution. The mutual coagulation of hydrosols of hydrated ferric oxide and silicic acid is thus assumed to be due to the removal of the peptizing agent by chemical action between them. It is also possible that the mutual coagulation of the hydrosols of arsenic trisulphide and of hydrated ferric oxide is due to the chemical reaction: $\mathrm{S}''+2\mathrm{Fe}^{\cdot\cdot\cdot}=\mathrm{S}+2\mathrm{Fe}^{\cdot\cdot}$. H. B. Weiser added that in order to obtain data supporting the chemical reaction theory, it appears to be necessary to choose the experimental conditions to fit the case. R. Wintgen and H. Löwenthal found the reciprocal coagulation of oppositely charged sols is a maximum when the conc. of the sols expressed in equivalent aggregates are the same, meaning when equal numbers of charges of opposite sign are mixed. J. Billitzer found that gelatin forms a positive sol in acid or neutral soln., and so precipitates negative sols, but not positive ones like the hydrosol of hydrated ferric oxide; on the other hand, gelatin in ammoniacal soln. forms a negative sol, and precipitates the hydrosol of hydrated ferric oxide. If gelatin is first added to the colloidal ferric oxide and afterwards ammonia, a stable mixture of positive sols is changed to a stable mixture of negative sols.

F. Powis observed that the positively charged hydrosol of hydrated ferric oxide is precipitated by the negatively charged hydrosol, and vice versa. The positively charged hydrosol of ferrous hydroxide was found by A. Schmauss to be coagulated by the negatively charged hydrosol of hydrated ferric oxide; but D. Vorländer found that, in general, the negative hydrosol of hydrated ferric oxide is not coagulated by negative hydrosols.

N. Pappada observed that, in general, the **coagulation of the hydrosols by non-electrolytes** does not occur; thus, A. Janek found that the hydrosol of hydrated ferric oxide is not coagulated by benzene, chloroform, and ether, or by mixtures of these liquids, but a partial coagulation was produced by carbon disulphide. Y. Matsuno found that sugar soln. are inactive, but conc. soln. of ethyl alcohol flocculate the hydrosol. A. W. Dumansky found that urea coagulates the hydrosol very slowly; whilst P. P. von Weimarn and A. W. Alexejeff observed that when the hydrosol is shaken with turpentine, a coagulum collects at the boundary surface of the two liquids; and H. Freundlich and S. Loebmann obtained an analogous result with benzene.

A. W. Dumansky observed that the **coagulation of the hydrosol by mechanical agitation** can be produced. For instance, the hydrosol is slowly coagulated when it is treated in a centrifuge having 4000 revolutions per minute. H. Freundlich and H. Kroch observed that the hydrosol obtained from iron pentacarbonyl coagulates readily during 20 hrs.' stirring with 500 revolutions per minute, but not so with the hydrosol produced by the hydrolysis of ferric chloride. H. Freundlich and S. Loebmann compared the result with the coagulation produced with turpentine or benzene—*vide supra*—but here the coagulation occurs at the boundary surface of hydrosol and air. According to E. Schalek and A. Szegvari, if a 5 or 10 per cent. hydrosol of hydrated ferric oxide is mixed with a small proportion of an electrolyte, it gradually forms a pasty hydrogel which easily becomes liquid when it is agitated. Gelatinization again occurs on standing, and the alternate sequence of changes: sol→gel→sol→ . . . can be repeated indefinitely. This isothermal, reversible transformation: Sol⇌Gel, by mechanical agitation, was called by T. Peterfi, **thixotropy**—from *θίξις*, the act of touching; and *νρέπειν*, to change. The phenomenon was studied by H. Freundlich and co-workers—A. Rosenthal, W. Rawitzer, and K. Söllner—N. Marinesco, A. de Waele, A. Paris, E. A. Hauser, S. S. Kistler, W. Heller, D. Deutsch, P. Barry, E. L. McMillen, H. A. Ambrose and A. G. Loomis, and A. Kutzelnigg and W. Wagner. The speed of gelatinization is reduced in the presence of some hydroxylic hydrophiles like the amino-acids, sugar, and increasing conc. of the $H^{\cdot}$-ions; and it is increased by a rise of temp., the addition of sensitizers—like ethyl alcohol, agar-agar, gelatin, and saponin—and by electrolytes with anions of a high valency. R. Wilson and T. C. Poulton found that there is a **coagulation by pressure** of a colloidal soln. of ferric hydroxide—in 30 mins. at 100 atm., and immediately at 300 atm. press.

N. Sahlbom found that **coagulation by capillary action** occurs when long strips of filter-paper are immersed in positive hydrosols, the precipitation takes place at the surface of contact; but negative hydrosols rise through the capillary network without hindrance. The precipitation of the positive colloids is not due to chemical action, but to the setting up of an e.m.f. as a consequence of the streaming of the liquid through the capillaries; this potential difference brings about the discharge of the positively charged colloidal particles. If the capillaries are not sufficiently narrow, the resulting e.m.f. is not large enough to give rise to complete precipitation, and a rise of the positive colloid is observed. According to F. Fichter, when a drop of a dialyzed hydrosol of hydrated ferric oxide is placed on a glass plate, and a second plate is allowed to sink slowly so as to make a pair of parallel plates, the thin layer of soln. between the plates exhibits a sharply defined, circular, opalescent zone in consequence of the precipitation of the positive colloid. The critical distance between the plates necessary for the precipitation is 0·0322 mm. Negative colloids do not show the phenomenon; and A. W. Thomas and J. D. Garard observed the phenomenon only with concentrated, positive hydrosols.

H. Picton and E. Linder observed that in many cases **coagulation by freezing** occurs so that the hydrosol is flocculated by freezing, or by alternate freezing and thawing, but with the hydrosol with much adsorbed chloride, no change occurs. Similar results were obtained by O. Bobertag and co-workers, A. Heiduschka, N. Ljubawin, and A. W. Thomas and A. Frieden. S. I. Dyachkovsky found that the coagulation by freezing is prevented by alcohol. The **coagulation by heat** was examined by N. R. Dhar and S. Prakash. T. Katsurai and T. Watanabe heated the hydrosol between 120° and 180° in an autoclave, and found the products all possessed good quality red colours with X-radiograms like that of hæmatite—*vide infra*, hydrogels. W. Knaust found that the hydrosol of ferric hydroxide coagulated in 45 mins. at 100°; in 150 mins. at 80°; and in 480 mins. at 60°. H. Stintzing, S. Roy and N. R. Dhar, J. R. I. Hepburn, A. Lottermoser and F. Langenscheidt and A. Boutaric and Y. Manière observed no tendency to **coagulation by exposure to light**; but P. Lal and P. B. Ganguly noted the coagulation of the hydrosol in ultra-violet light, and A. Boutaric and J. Bouchard found that if fluorescent substances—eosin, rhodamine, fluorescein or erythrosin—are present in the soln. the flocculation is faster in daylight, and faster still in ultra-violet light. V. Henri and A. Meyer, and W. P. Jorissen and H. W. Woudstra observed no tendency to **coagulation by exposure to the β-rays** of radium, although A. Boutaric and M. Roy, and A. Fernau and W. Pauli said that coagulation does occur with a prolonged exposure to the β-rays. H. Picton and E. Linder, and W. Biltz observed that **coagulation by an electric current** occurs as a flocculation about the cathode—*vide supra*, electrophoresis. H. Puiggari observed that the rate of coagulation is proportional to the current-strength and time; with a current-strength of 0·003 ampère, no coagulation occurs. A rise of temp. favours coagulation. B. N. Ghosh found that the coagulation of the hydrosol, by potassium chloride, sulphate, oxalate, or ferricyanide, by sodium hydroxide, or by aniline sulphate, begins when the electrokinetic potential falls below 32 millivolts.

Adsorption phenomena.—According to H. Udluft, dolomite adsorbs the hydrosol of ferric oxide but not that of manganese dioxide; clay adsorbs both. The two hydrosols exert a protective action on one another, but humus precipitates from the hydrosol hydrated ferric oxide but not hydrated manganese dioxide. Hydrocarbonates precipitate hydrated ferric oxide when unprotected, but not hydrated manganese dioxide and humus soln. M. Geloso also examined the adsorption of the hydrosol by manganese dioxide. N. Carli observed that china clay adsorbs the hydrosol very slightly, if at all. P. Rohland pointed out that the adsorptive powers of clays depends on the colloidal matter present in the clay; and some clays contain virtually none. H. Freundlich and A. Poser, and H. Udluft also observed that china clay adsorbs the hydrosol. A. Fodor and A. Rosenberg found that china clay adsorbs colloidal ferric hydroxide from soln. of ferric chloride, partially hydrolyzed, but colloidal alumina is not adsorbed, so that a separation of the two can be effected. The acid formed by the hydrolysis is not adsorbed by the clay, so that the hydrolysis reaches a state of equilibrium. Talc also adsorbs the colloidal hydroxide and also neutralizes the acid, so that talc causes a complete hydrolysis of the soln. of ferric chloride. Finely-ground sea-sand was also found to adsorb the hydrosol. H. Freundlich and A. Poser observed no adsorption by alumina. E. Wedekind and H. Rheinboldt observed that the hydrosol is decolorized when it is shaken with hydrated zirconium oxide. N. Carli found that the adsorption of the hydrosol by animal charcoal does not follow the usual adsorption law, for the amount of adsorption is independent of the vol. of the hydrosol and the amount of colloid present, but is directly proportional to the weight of the charcoal. On the other hand, A. W. Thomas and T. R. le Compte said that purified charcoal adsorbs no hydrosol. The action of technical charcoal is not due to adsorption, but to a flocculation in consequence of the presence of electrolytes. A. Fodor, and H. Freundlich and A. Poser also observed the flocculation of the hydrosol by charcoal.

According to Y. Matsuno, the hydrosol of ferric oxide readily adsorbs acid-dyes; H. Haber studied the adsorption of potassium ferricyanide, and potassium cuprous cyanide; H. Freundlich and W. Rawitzer, tyrosine; and L. Michaelis and P. Rona, albumen—grape sugar is not adsorbed. A. Boutaric and F. Banès observed that the mycelial liquid adsorbs dyes more readily than does the coagulum. E. Baur and O. Nagel said that the hydrosol can be employed to adsorb the noble metals from sea-water. The adsorption of electrolytes has been previously discussed in explaining some of the phenomena connected with the flocculation of the hydrosol. The subject was discussed by N. Schiloff and A. Iwanitzkaja, and S. Ghosh and N. R. Dhar. A. Lottermoser and P. Maffia, and Wo. Ostwald found that the adsorption of chlorine ions by the mycelia proceeds in accord with the normal isotherm. S. Ghosh and N. R. Dhar found that the H$^{\cdot}$-ions are strongly adsorbed.

H. B. Weiser, and H. B. Weiser and E. B. Middleton noted that the adsorption of the anions proceeds in the following order: phosphates>citrates>tartrates>oxalates>sulphates>iodates>dichromates; and H. B. Weiser and E. E. Porter found that with increasing p_H-values, the oxalates are less and less adsorbed.

The **solubility of gases** in the hydrosol of hydrated ferric oxide.—According to A. Findlay and B. Shen, the solubility of *hydrogen* in the hydrosol of hydrated ferric oxide is not appreciably different from its solubility in water; and G. Geffcken made a similar remark with respect to *oxygen*, for the solubility of that gas in the hydrosol at 25° is 0·03084, and in water, 0·03080. The solubility of *nitrous oxide* in the hydrosol at 25° is less than it is in water, for the respective solubilities in the hydrosol and in water are 0·5793 and 0·5942. A. Findlay and H. J. M. Creighton observed for the solubility, S, at different press., p mm., of soln. with C grm. of $Fe(OH)_3$ per 100 c.c. of sol:

C = 0·625	p .	758	846	934	1010	1121	1383 mm.
	S .	0·590	0·586	0·584	0·588	0·588	0·588
C = 1·49	p .	734	828	935	1078	1215	1432 mm.
	S .	0·586	0·579	0·577	0·581	0·585	0·586
C = 4·061	p .	754	835	883	1093	1208	1358 mm.
	S .	0·578	0·573	0·571	0·574	0·579	0·580

Observations were also made by A. Findlay and O. R. Howell. A. Gatterer found for the solubility of *acetylene* in the hydrosol, expressed in terms of the vol. of gas absorbed by unit vol. of liquid at the given temp. and press.:

		30°	25°	20°	15°	10°
S	0·871N- . .	0·9400	1·018	1·111	1·227	1·364
	0·521N- . .	0·9360	1·016	1·111	1·224	1·364
	0·336N- . .	0·9495	1·029	1·126	1·241	1·383
	0·12N- . .	0·9450	1·026	1·126	1·236	1·379

The solubility of *carbon dioxide* in the hydrosol is greater than it is in water alone; and it does not follow Henry's law. G. Geffcken stated that with carbon dioxide there is a comparatively rapid initial adsorption followed by a slow continuation of the adsorption. A. Findlay and H. J. M. Creighton found that the slow adsorption is barely appreciable even at high press., and, in general, for press. below atmospheric, the increase in solubility is proportional to the conc., C grm. $Fe(OH)_3$ per 100 c.c. of the hydrosol.

C = 0·569	p .	750	846	928	1015	1146	1356 mm.
	S .	0·848	0·843	0·841	0·842	0·845	0·846
C = 0·854	p .	750	847	923	1090	1234	1322 mm.
	S .	0·862	0·858	0·856	0·857	0·860	0·861
C = 1·277	p .	746	841	985	1071	1133	1256 mm.
	S .	0·886	0·881	0·880	0·878	0·878	0·887
C = 1·661	p .	747	831	918	1002	1150	1267
	S .	0·904	0·901	0·896	0·900	0·900	0·902

A. Gatterer found the effect of temp. on the solubility, expressed as the vol. of gas absorbed by unit vol. of solvent, at the given temp. and press., to be:

		30°	20°	15°	10°	5°
S	0·071N- . .	0·8533	0·9610	1·095	1·267	1·471
	0·144N- . .	0·8764	0·9870	1·123	1·297	1·503
	0·293N- . .	0·9063	1·016	1·154	1·326	1·534
	0·513N- . .	0·9526	1·066	1·204	1·379	1·584
	0·967N- . .	1·032	1·149	1·291	1·470	1·680

Observations were also made by A. Findlay and co-workers—W. H. Harby, O. R. Howell, G. King, and T. Williams. The deviations of the solubility of carbon dioxide in the hydrosol were attributed by R. Luther and B. Krsnjavi to the formation of complexes.

H. B. Weiser and G. L. Mack[2] obtained **organosols** with methyl and propyl alcohols. J. Duclaux,[3] and R. J. Kepfer and J. H. Walton studied the catalytic action of the colloid on hydrogen dioxide; and R. Stumper, the effect of the colloid on the rate of evaporation of water.

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§ 32. The Hydrated Ferric Oxides—Hydrogels

A highly gelatinous precipitate of **hydrated ferric oxide,** the so-called **ferric hydroxide,** is thrown down when an alkali is added to a soln. of a ferric salt which is not too dil. According to W. Hampe,[1] the precipitates obtained from soln. of ferric chloride at different temp. have the following compositions:

	0°	20°	25°	30°	40°	60°	80°	100°
Fe_2O_3 . . .	54·6	51·4	50·4	46·1	43·9–52·2	66·2	70·1	72·3–92·7
H_2O . . .	45·4	48·6	49·6	53·9	56·1–47·8	33·8	29·9	27·7– 7·3

There is here no evidence of the formation of definite hydrates. After the precipitation of the hydrated oxide by adding aq. ammonia to a cold or hot soln. of a ferric salt, it is washed by decantation with water, and kept in a desiccator over sulphuric acid or potassium hydroxide, and pressed between porous tubes or washed with alcohol and ether. This is the ordinary mode of preparation, and it was used by G. Almkvist, J. M. van Bemmelen, E. Brescius, K. Endell and R. Rieke, O. Hahn and M. Biltz, W. G. Mixter, J. H. Perry, T. W. Richards and G. P. Baxter, O. Ruff, E. Selch, S. Veil, E. Wedekind and W. Albrecht, H. Wolfram, etc.—*vide infra.* L. T. Wright, and A. Simon and T. Schmidt emphasized the tenacity with which the chlorides are retained by the precipitated colloid. G. F. Hüttig and H. Garside washed the precipitate until the wash-water gave no turbidity with silver nitrate, and yet retained 0·12 per cent. of chlorine. J. Jeannel, and C. F. Cross also emphasized the adsorption, or rather the tenacity, with which the hydrogel retains saline and other impurities. R. Willstätter and co-workers prepared the colloid as follows:

A soln. of 100 grms. of ammonium ferric sulphate in 200 c.c. of water at ordinary temp. is powdered into a soln. of 10·8 grms. of ammonia, 27·5 grms. of ammonium sulphate, and 800 c.c. of water, with vigorous stirring. After being stirred for half an hour, the clear liquid is decanted, and the product is washed many times by decantation with ammoniacal water. The gel is mixed with dry acetone, and centrifuged. The last traces of acetone are removed by decantation with ether, and the hydrogel is then exposed to a high vacuum.

L. Schaffner said that if the precipitation is made with aq. ammonia, the precipitate is free from contamination by the precipitant. If alkali-lye be used in place of aq. ammonia, R. Fricke, W. Ramsay, and H. Wolfram found that the precipitate is difficult to wash. The alkali hydroxide may even decompose the nitroprussides (L. Playfair, J. M. van Bemmelen and E. A. Klobbie, O. Pavel, and G. Städeler), and the nitrosyl salts of Z. Roussin as shown by Z. Roussin, J. M. van Bemmelen and E. A. Klobbie, and J. O. Rosenberg. J. J. Berzelius noted that entrained alkali is retained very tenaciously; and according to J. Huggett and G. Chaudron, a small proportion of sodium ferrite may be formed, otherwise the precipitate is considered to be insoluble in an excess of lye. J. Hausmann noted the layer formation of the colloid when a soln. of potassium hydroxide diffuses into gelatine containing some ferric chloride. W. Ramsay found that baryta-water, V. Vincent, lime-water, H. Rose, and A. Mailhe, mercuric oxide, and D. Vitali, silver oxide, precipitate the hydrated oxide from soln. of ferric salts.

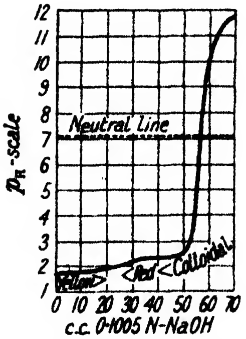


Fig. 534.—Electrometric Titration of an Acidic Solution of Ferric Chloride.

L. J. Curtman and A. D. St. Johns found that the precipitation occurs in the presence of 0·062 mgrm. of iron in soln. H. E. Patten and G. H. Mains said that colloidal hydrated ferric oxide is precipitated from soln. containing 0·03 per cent. Fe, by ammonia or sodium hydroxide, when the H'-ion conc. is $p_H=3{\cdot}3$. H. T. S. Britton found that with 100 c.c. of a soln. containing $0{\cdot}0202N$-HCl and $0{\cdot}0133M$-$FeCl_3$, the electrometric titration with $0{\cdot}1005N$-NaOH furnished the results indicated in Fig. 534. Freshly prepared soln. of ferric chloride, or soln. containing an excess of free acid are only slightly coloured, but the soln. on standing begins to redden, and finally the colour approaches that of hydrated ferric oxide. It was found that the end of the neutralization of the free acid is indicated by an inflexion, at 20·1 c.c. of sodium hydroxide. As the soln. was rendered more basic, the colour gradually changed from yellow to red. It became quite red after addition of 30 c.c. of sodium hydroxide, when the composition of the solute had become $Fe(OH)_{0{\cdot}74}Cl_{2{\cdot}26}$, and with 39 c.c. it began to opalesce. Afterwards the soln. became increasingly colloidal and became opaque at p_H3, which, as will be seen from the curve, occurred just when the sudden change in hydrion concentration had begun. Coagulation set in when the p_H had become 6·6 and 58 c.c. of alkali had been added, the composition of the basic chloride then being $Fe(OH)_{2·85}Cl_{0·15}$. The colloidal soln. persisted until nearly all the chloride had reacted; attempts were made to prevent coagulation during the abrupt fall in H˙-ion concentration. Aq. soln. of ferric chloride more dil. than 0·04*N*-, on boiling, acquired a deep red colour, and often remained colloidal on treatment with 0·10*N*-alkali in slight excess. Small, red, amorphous precipitates separated in some cases, but even then the precipitation was incomplete and the solids did not settle until several hours had elapsed. The presence of a little hydrochloric acid in the soln. before heating had some stabilizing effect on the colloidal soln. which were subsequently produced. In one case the colloidal soln. remained stable for nearly 3 months. This soln. was prepared by adding 55 c.c. of 0·10*N*-sodium hydroxide to 500 c.c. of a boiling soln. containing 100 c.c. of 0·04*N*-ferric chloride and 10 c.c. of 0·10*N*-hydrochloric acid. It seems certain that the red colour of boiled ferric chloride soln. was due to dispersed ferric hydroxide particles, and consequently the increase in the size of the basic chloride particles caused by rendering the soln. alkaline was not so great as that occurring in an unboiled soln., and therefore did not produce coagulation. The increased stability of the colloidal soln. prepared from acidified ferric chloride soln. was probably due to the effect of the acid in suppressing the growth of the colloidal particles on boiling, thereby giving rise to a more highly dispersed and more stable colloidal soln. Prolonged boiling decomposed these alkaline colloidal soln., and they were readily coagulated on addition of electrolytes in sufficient amounts. In accord with the generally accepted theory of the structure of gels (**6**. 40, 21), H. B. Weiser said that when alkali-lye or aq. ammonia is added to the soln. of a ferric salt, there is a relatively large supersaturation before precipitation occurs, and this favours the formation of minute particles; the orientation of these particles into a network of mycelia entraining the mother-liquor, produces the hydrogel. The bulky mass, on standing, gradually loses water and becomes more compact and granular.

Colloidal ferric hydroxide, or hydrated ferric oxide, is a product of numerous reactions. It is formed when iron rusts in the presence of water and oxygen—*vide supra*—as noted by M. Hall, N. J. B. G. Guibourt, D. Tommasi, A. Payen, A. Ackermann, W. R. Dunstan and co-workers, P. Fireman, and L. P. de St. Gilles; by the action of an acidified soln. of hydrogen dioxide on iron, as observed by G. C. Weltzien, and G. T. Moody; by the action of soln. of ammonium salts and air on iron, as found by W. Vaubel, and A. Frickhinger: and by the anodic oxidation of iron in soln. of potassium nitrate, potassium hydroxide, ammonium sulphate, etc., as observed by R. Lorenz, O. Faust, and G. A. le Roy. Colloidal ferric hydroxide is formed during the oxidation of ferrous hydroxide by air or oxidizing agents (E. Deiss and G. Schikorr, A. Krause, and F. Haber), or anodically (H. Becquerel, O. Faust, and V. Paissakowitsch).

The oxidation of chalybeate waters, or water containing ferrous hydrocarbonate in soln., furnishes hydrated ferric oxide as observed by G. Bischof, F. Behrend, and H. Molisch. As shown by H. Klut, O. Kröhnke, and A. Schmidt and K. Bunte, chalybeate waters also deposit iron in the form of hydrated ferric oxide, and, as indicated by D. Ellis, D. D. Jackson, E. M. Mumford, etc.—*vide infra*—the action is favoured by the so-called iron-bacteria. S. de Luca, and A. Krause studied the oxidation of ferrous carbonate by air in the presence of water. The hydrated ferric oxide is formed when many ferrous salt soln. are oxidized by hydrogen dioxide (G. C. Weltzien), sodium dioxide (G. Kassner, and T. Poleck), barium dioxide (W. Kwasnik), potassium hypochlorite (F. Muck), potassium chlorate (R. Phillips, and R. H. Parker), or auric chloride (E. Beutel). F. Behrend, and H. Molisch observed that soln. of ferrous sulphate, acidified with citric acid, give a precipitate of hydrated ferric oxide when exposed to light; O. Baudisch and L. W. Bass, H. W. Fischer, J. Matuschek, and C. F. Schönbein obtained a similar result by exposing a soln. of potassium ferrous cyanide to light; and W. A. Macfadyen observed that the hydrated oxide is formed during the electrolysis of a soln. of ammonium ferrous sulphate.

The hydrogel of ferric oxide is formed during the hydrolysis of some ferric salt soln.—*e.g.* G. Keppeler and J. d'Ans observed that it is deposited during the hydrolysis of basic ferric sulphate—and in the decomposition of aq. soln. of ferrites, perferrites, and ferrates (*q.v.*). O. Hauser observed that the hydrated oxide is deposited during the evaporation of a soln. of ammonium ferric carbonate; G. Kassner, and G. Grube, during the hydrolysis of a soln. of potassium ferricyanide, and, according to C. F. Schönbein, and J. Matuschek, the reaction is favoured by exposure to light; J. H. Paterson, by the electrolysis of soln. of ferric salts with platinum electrodes, a low conc., and a small current density. L. Mond and co-workers, and M. Berthelot found that the hydrolysis of iron pentacarbonyl furnishes the hydrated oxide. S. Kern found that an aq. soln. of ferric chloride in contact with magnesium yields hydrated ferric oxide; H. W. Fischer obtained a similar result with zinc; and G. McP. Smith, by the action of mercury in the presence of alkali hydroxide. If an alkaline soln. of potassium ferricyanide be heated with an excess of ferrous sulphate, H. Bollenbach and E. Luchmann found that hydrated ferric oxide is precipitated.

The **hydrogel** may be also produced by the coagulation of the hydrosol under suitable conditions. The formation of the hydrogel from the hydrosol was observed by L. P. de St. Gilles, N. R. Dhar and D. N. Chakravarti, R. Griessbach and J. Eisele, S. Veil, J. Böhm and H. Niclassen, A. Simon and T. Schmidt, E. Wedekind and W. Albrecht, K. Charitschkoff, etc.—*vide supra.* Slow, uniform precipitation of the hydrosols throughout their entire mass produces the so-called **ferric oxide jellies,** whilst rapid, uneven precipitation results in contraction and the formation of a gelatinous precipitate. E. Grimaux's sol, obtained by the addition of water to an alcoholic soln. of ferric ethylate—*vide supra*—forms a jelly more readily than Graham's sol because, being produced by rapid hydrolysis in the cold, it contains finer, and more hydrated particles; and for a similar reason, Graham's sol is more readily coagulated to a jelly than is the case with St. Gilles' sol. R. Bradfield used the centrifuge for isolating the hydrogel. E. Schalek and A. Szegvary, and H. Freundlich and A. Rosenthal obtained the coagulum from Graham's sol as a jelly by adding electrolytes in amounts below the precipitation values to colloidal soln. containing 6 to 10 per cent. of ferric oxide, and allowed the sols to stand quietly. The mixture set to a clear jelly. The jelly formed a sol on shaking up and this solidified slowly to a hydrogel. The logarithm of the time required for solidification after the shaking of the jelly, was found to be inversely proportional to the temp. and to the conc. of the coagulating electrolyte—*vide supra,* thixotropy. No change in the average distance of the particles and no formation of secondary particles could be detected by the ultramicroscope during the liquefaction. The subject was studied by H. Freundlich and W. Rawitzer, and H. Freundlich and K. Söllner. H. B. Weiser attributed the reversible sol-gel transformation to a breaking up and subsequent re-alignment of the orienting forces amongst the particles.

E. Grimaux's sol coagulates spontaneously to form a transparent jelly when it is allowed to stand without agitation, at room temp., or more rapidly when heated; or when it is treated with electrolytes—carbonic, sulphuric, or tartaric acid; nitrate, chloride, or bromide of potassium; the chloride of sodium, barium, etc. E. Grimaux also prepared a jelly by the dialysis of a negative sol prepared by the peptization of hydrated ferric oxide with alkali-lye and glycerol; if ammonia is used in place of alkali-lye, and the sol be exposed to air, the slow loss of the peptizing agent, ammonia, by evaporation, forms a jelly. H. W. Fischer also produced a firm jelly by the prolonged dialysis of a hydrosol containing 1 per cent. of iron. This preparation formed a gelatinous mass when it was warmed, stirred, or frozen. H. B. Weiser also mentioned the formation of a jelly by the slow evaporation of a conc. Graham's sol of a high degree of purity. S. Prakash and N. R. Dhar studied the formation of the gel. D. H. Ghosh obtained ferric hydroxide as a rhythmic precipitate.

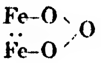
A. W. Bull and J. R. Adams' observations on the adsorption of alkali by hydrated ferric oxide are indicated in connection with sodium ferrite. W. N. Simakoff studied the reciprocal action of sols of ferric hydroxide, aluminium hydroxide, manganese dioxide, and silicic acid. The sparing solubility or insolubility of many hydrated oxides is, according to J. Jeannel, connected with the presence of traces of sulphate, but J. Attfield did not agree with this. According to F. Muck, the hydrated oxide forms a voluminous, gelatinous precipitate which shrinks considerably on drying to form a yellowish-brown, brittle mass. This product loses water when gently heated, and, as the temp. is raised, it becomes calorescent—*vide supra*—without further loss in weight, to form a black, lustrous mass, hard enough to scratch glass. On the other hand, the hydrated ferric oxide, prepared by the oxidation of hydrated ferrous oxide, is pulverulent—particularly if prepared from hot soln.; it does not shrink much on drying, and then forms a friable mass. This product does not exhibit calorescence when heated, and it forms a reddish-brown, friable mass without lustre. This recalls the previous discussion on the St. Gilles' sol, and Graham's sol, and the supposed **allotropic forms** of the hydrated oxide. According to L. T. Wright, recently precipitated, gelatinous ferric hydroxide, when suspended in water and saturated with hydrogen sulphide, is completely soluble in a soln. of potassium cyanide forming potassium ferrocyanide and sulphide: $FeS+6KCy=K_2S+K_4FeCy_6$; but if the ferric hydroxide be kept some time, a certain proportion is converted into an inactive form, not affected by hydrogen sulphide.

According to D. Tommasi, there are two series of hydrated oxides, yellow, and red or brown, which are isomeric or allotropic forms of one another. The members of the red series are produced by precipitating a soln. of a ferric salt with an alkali; the product is voluminous, soluble in dil. acids, and, according to A. E. Davies, is dehydrated by boiling water. The members of the yellow series are obtained by the oxidation of hydrated ferrous oxide or carbonate—say, by potassium chlorate, potassium hypochlorite, or if iron be slowly oxidized under water. R. Phillips found that if the chlorate be added to the ferrous sulphate and sodium carbonate in small portions at a time, black ferrosic oxide is formed, and is not oxidized to red ferric oxide by subsequent addition of the chlorate. The yellow hydrates are denser than the red, they are sparingly soluble in conc. acids, require a higher temp. for dehydration, and retain a mol. of water even when boiled for a long time under water. D. Tommasi thus summarizes the properties of the two series of hydrated ferric oxides:

RED OR α-SERIES.	YELLOW OR β-SERIES.
1. Obtained by precipitating a ferric salt with alkali-lye.	1. Obtained by oxidizing hydrated ferrous or ferrosic oxide, or ferrous carbonate.
2. The dihydrate begins to dehydrate at 50°.	2. The dihydrate begins to dehydrate at 105°.
3. The monohydrate is dehydrated at 92°.	3. The monohydrate is dehydrated at 150°.
4. The anhydride is brown.	4. The anhydride is red or yellowish-red.
5. The sp. gr. of the anhydride is 5·11.	5. The sp. gr. of the anhydride is 3·95.
6. The hydrates are soluble in dil. acids, and in soln. of ferric chloride.	6. The hydrates are sparingly soluble in conc. acids, and in soln. of ferric chloride.
7. The hydrates are dehydrated in boiling water.	7. The hydrates are dehydrated in boiling water.

A. Krause said that the yellow oxide, which he called *meta-ferric oxide* or *β-ferric oxide*, is the more stable form, because the brown oxide, which he called *ortho-ferric oxide* or *α-ferric oxide*, passes into it when kept under water. Contrasting the two oxides, he said that when dried in air, the ortho-oxide breaks up, forming black pieces which furnish a brown powder, which contains some carbon dioxide, and when dried, 70·0 per cent. of Fe_2O_3. The meta-oxide when dried forms a vitreous mass which does not break up, and furnishes a yellow powder with a reddish tinge.

It contains no carbon dioxide, and the dried mass has 82·5 per cent. Fe_2O_3. Both forms are soluble in conc. hydrochloric acid. The ortho-oxide dissolves almost completely in conc. acetic acid forming a brick-red soln. which yields crystals of the acetate; the meta-oxide is almost insoluble in conc. acetic acid, and the soln. does not form crystals of the acetate. The ortho-oxide is peptized by dil. acetic acid, and the hydrosol is yellow, orange, or dark red, according to the proportion of contained ferric oxide; the meta-oxide forms an orange hydrosol, and when very dil., it is greenish-yellow. The ortho-oxide is not peptized by 10 per cent. aq. ammonia, while the meta-oxide is peptized to a greenish-yellow hydrosol. Boiling 76·4 per cent. soda-lye does not dissolve the ortho-oxide completely, but the meta-oxide readily forms a colourless soln. Ammonium sulphate coagulates the hydrosol of the meta-oxide more readily than the ortho-oxide. J. M. van Bemmelen showed that the ratio of oxide to water in the reddish-brown series depends entirely on the method of treatment, and that all the definite hydrates which have been reported are *nur zufällig* being dependent on the accidental conditions used in drying. D. Tommasi represented the reddish-brown hydrate by the formula:



$$\begin{array}{l}\mathrm{Fe{-}O}\diagdown\\ \;\ddot{}\qquad\quad\mathrm{O}\\ \mathrm{Fe{-}O}\diagup\end{array}$$

and the yellow hydrate O=Fe–O–Fe=O each with one, two, or three mols. of H_2O; but, added J. M. van Bemmelen, *alles dies ist nichts als reine phantasie*. The differences between the yellow and red hydrated oxides are determined solely by differences in physical structure. H. B. Weiser added that the later work of E. Posnjak and H. E. Merwin—*vide infra*—has shown that the greater tenacity of the water in the yellow hydrates may be due to the formation of a definite hydrate. P. Nicolardot considered that he had established the existence of six modifications of hydrated ferric oxide. He said that the majority of the crystalline ferric salts are white, and he therefore concluded that the normal hydrated oxide should also be white. He found that the white hydrated oxide is formed when a freshly prepared, conc. soln. of a ferric salt is added to a cooled soln. of ammonia, but it rapidly becomes coloured. He said that the six different forms of the hydrated oxide differ in their physical and chemical properties, and in their water-content. *Toutes sont des polymères de l'hydrate ferrique*, but their degrees of polymerization are different. G. N. Wyrouboff and A. Verneuil suggested that the ferric oxide obtained at the higher temp., and which is very little affected by acids, and forms a red hydrate on salt dialysis, is a hydrate of a polymerized oxide, $(Fe_2O_3)_{44}$, which he calls *para-oxide*. The product obtained by L. P. de St. Gilles was $(Fe_2O_3)_{44}.4HCl$. The product obtained by the dialysis of cold soln. of ferric hydroxide in a neutral ferric salt contains two polymers both of which can unite with acids to form clear, reddish-brown soln. The one oxide, $(Fe_2O_3)_{44}$, called *meta-oxide*, is polymerized during dialysis to form a hydrate or salt of $(Fe_2O_3)_{56}$. T. Graham's product was represented as $(Fe_2O_3)_{56}.4HCl$. This subject has been previously discussed; J. M. van Bemmelen would also have called all this pure phantasy; while H. W. Fischer said that the hypothesis is *experimentell unzureichend gestütz und verfehlt*.

The ferric ferrite obtained by the interaction of hydrated ortho- and meta-ferric oxide was found by A. Krause to be readily peptized by dil. acids after it had been ignited. The resulting sol contains positively charged particles, and its hydrophobic nature is evident from the readiness with which it deposits a ferric oxide mirror on the walls of the containing vessel. Ortho-ferric hydroxide is partly converted into ferric ferrite by ageing under water, or soda-lye yields the same sol after it has been ignited. Neither ortho- nor meta-ferric hydroxide is peptized by acids after ignition, but the meta-oxide, unlike the ortho-oxide and ferric ferrite, is peptized by dil. aq. ammonia after it has been ignited. The hydrosol of meta-ferric acetate has only a slight tendency to produce a mirror, and ortho-ferric acetate has none, and it even exerts a stabilizing influence on the meta-ferric oxide, and ferric ferrite sols. Hence, A. Krause concluded that there are three series of ferric oxides and hydroxides.

Attempts have been made to find how the water is associated with the hydrated ferric oxides, and to establish the chemical individuality of particular hydrates. So long as the earlier workers relied upon analysis alone, there was no limit to the number of possible hydrates, for, as J. M. van Bemmelen has pointed out, the results depended more or less on the actual choice of the method of drying. In only one case does the hydrate exist in a crystalline form, viz., $Fe_2O_3.H_2O$; in all other cases, the products are amorphous, and have the character of hydrogels. The hydrates are usually hygroscopic substances so that the proportions of water they contain at any moment fluctuates with the temp. and humidity of the atmosphere. Nature also furnishes a series of eight minerals which have the character of hydrated ferric oxide, and of these only two occur in the crystalline state—*vide supra*, the hydrosols. Precipitated ferric, and several other hydroxides may be regarded as soln. of water in ferric oxide, etc., or in one of their lower hydroxides. J. M. van Bemmelen called them adsorption compounds, and considered that the moist precipitates contain (i) water mechanically mixed with the precipitate, and (ii) absorbed water. The amount of absorbed water is dependent on the *structure* of the gelatinous mass which in turn is dependent on (i) the method of formation, (2) the time, (3) temp., and (4) the presence of foreign substances. If the adsorbed water be dissolved in the oxide or lower hydroxide, when the water is gradually withdrawn from the system, the vap. press. of the mixture will remain constant so long as free water is present mechanically mixed with the precipitate, and commence to decrease when the free water has disappeared. The composition of the residue at this stage will represent the composition of the sat. soln. of water in the oxide under consideration. Hence, at a constant temp., hydrated ferric oxide, prepared in different ways, should show the same composition at the point where the vap. press. begins to change, provided the system is in equilibrium. H. W. Foote found this to be the case with ferric, aluminium, and zirconium hydroxides. The composition changes with temp., as would be expected if these hydroxides are but soln. of water in the fundamental oxide or in some lower hydrate. At 25°, with hydrated ferric oxide the critical point occurs when the hydrate contains 47·75 per cent. of ferric oxide; with hydrated aluminium oxide, 50·35 per cent. of alumina; and with hydrated zirconium oxide, 32·12 per cent. of zirconia. The difficulties in accepting this hypothesis depend on the facts: (1) If the dissolved water be removed by evaporation, it can never be completely restored; (2) when a moist hydrate is allowed to dry spontaneously there is no sign of an abrupt change in the rate of evaporation.

W. Ramsay, and G. Tschermak tried to find if the existence of definite hydrates could be established by measuring the rate of the drying of the hydrogel at a given temp. J. M. van Bemmelen's hydration and dehydration curves are illustrated in Fig. 535. In drying, the loss of water is continuous with the decrease in the vap. press. of the water. The general result resembles that obtained with silicic acid. At *O*, the drying gel becomes white and opalescent; the re-hydration of the gel does not follow the same track. R. Zsigmondy and coworkers, W. Bachmann, and J. S. Andersen also measured the vap. press. of the hydrated oxide during drying. T. Carnelley and J. Walker, and A. L. Baikoff studied the dehydration of the hydrogel at different temp. At 55°, the composition of the hydrated oxide approximates $Fe_2O_3.3H_2O$; and as the temp. rises, more water is evolved until, at 385°, the product has the composition $10Fe_2O_3.H_2O$, and the weight remains constant

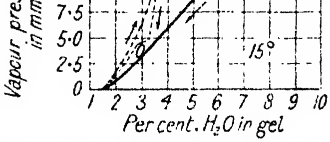


FIG. 535.—Hydration and Dehydration of the Hydrogel of Ferric Oxide.

during several hours' heating between 385° and 415°. At 500°, the dehydration is complete. Observations on the subject have been made by C. F. Cross, A. E. Davies, L. P. de St. Gilles, A. Krieger, L. G. Leroy, F. Limberger, F. Muck, W. Ramsay, G. Rousseau and co-workers, Z. Roussin, L. Schaffner, H. Schiff, W. Spring, D. Tommasi and G. Pellizzari, G. C. Wittstein, D. Balarew and S. Krastew, L. T. Wright, P. A. Thiessen and R. Köppen, and G. F. Hüttig and A. Zörner—*vide infra*. According to the vap. press. curves of J. M. van Bemmelen and co-workers, E. Brescius, T. Carnelley and J. Walker, H. W. Foote and co-workers, W. B. Hardy, W. Ramsay, E. Y. Rode, A. Simon and T. Schmidt, and G. Tschermak, ferric oxide hydrogel does not form a chemical compound. R. Willstätter and co-workers do not consider the results decisive, and the conclusion is not proven. A. V. Rakovsky studied the subject. R. E. Wilson and T. Fuwa investigated the absorbent power of the gel for moisture in air. For the action of heat on the dehydrated gel, *vide supra*, ferric oxide.

E. Wedekind and W. Albrecht found that the magnetic susceptibility of ferric oxide is 4 or 5 times less than that of the hydrated oxide, and they consequently inferred that a compound is formed. R. Willstätter and co-workers treated the gel successively with dry acetone and ether, followed by the preservation of the sample in a high vacuum for some time. This is said to remove all the adherent water. The product treated at 10° to 20° has rather less water than is needed for $Fe(OH)_3$, and the amount decreases slowly when it is kept for a protracted period in contact with water. A preparation dried with acetone at −15° had the approximate composition $Fe(OH)_3.H_2O$. A. Simon and R. Zsigmondy doubted if these products are chemical individuals.

In H. W. Foote and B. Saxton's study of the changes in vol. which occur on freezing the hydrogel, owing to the water expanding when it forms ice, if this amount of water be subtracted from the total loss on ignition, the difference is taken to represent the water chemically combined which cannot be frozen. This corresponded with $Fe_2O_3.4{\cdot}25H_2O$. The water which freezes gradually with a fall of temp. is held in the capillaries—*capillary water*. It was assumed that the loosely attached water freezes at about −5°; and that the capillary water freezes at −30°. The debatable assumption made is that the failure of water to freeze at a given temp. determines whether the water is dissolved or adsorbed. No evidence of the formation of simple ratios between ferric oxide and water was observed during the dehydration of the hydrogels, so that the term chemically combined water was understood to refer to water held in solid soln., in definite proportions, and not adsorbed water. K. Hakozaki discussed the swelling of the hydrogel; P. Barry, and R. E. Liesegang, the structure of the slowly dried gel; and A. and E. Lottermoser, the ageing of the gel.

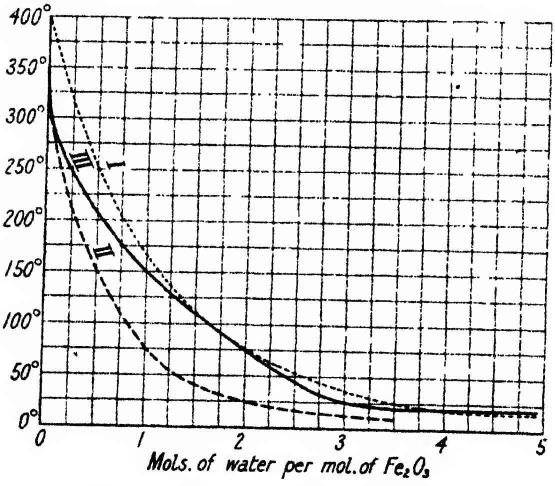


FIG. 536.—Dehydration Curves of the Hydrogel of Ferric Oxide.

A. Simon and T. Schmidt prepared hydrated ferric oxide: I, by precipitation from a soln. of ferric nitrate at 40° by ammonia; II, by precipitation from a cold soln of ferric chloride by ammonia; and III, by the dialysis of a soln. of ferric nitrate until the hydrogel precipitated and the residue was free from nitrate. Sample I was relatively coarse; II, relatively fine; III, was of intermediate fineness. The dehydration curves, Fig. 536, are all continuous, and show no indications whatever of hydrates containing 1, 2, 3, or more mols. of water. X-radiograms showed that I was amorphous when dried in air, but showed amicroscopic crystals of ferric oxide if heated high enough to drive off all the water; while the air-dried oxide III, obtained by slow hydrolysis, showed a weak interference pattern different from that of J. Böhm for anhydrous ferric oxide. This is taken to mean that certain gelatinous substances may contain water in solid soln. between the oriented mols. of the space-lattice, just as E. Posnjak and H. E. Merwin found that water mols. may assume a fixed position in the ferric oxide lattice to form the monohydrate $Fe_2O_3.H_2O$.

J. Böhm showed that the hydrogel, freshly precipitated in the cold, shows no crystalline structure when examined by the X-radiogram process; nor does the hydrogel precipitated from the boiling soln. give any evidence of the formation of a definite hydroxide, but a basic ferric chloride is associated with the precipitate. The main conclusion here indicated agrees with the work of G. F. Hüttig and H. Garside, A. Simon and T. Schmidt, and F. Haber. The subject was also discussed by E. Heymann, E. Wedekind and W. Albrecht, and D. Balarew and S. Krastew. P. A. Thiessen and R. Köppen said that the dehydration curve of the hydrated oxide obtained by exposing a soln. of ferric ethylate, in absolute alcohol, to water vapour, agrees with the assumption that there are eight hydrates $2Fe_2O_3.nH_2O$, with $n=8$, 7, 6, 5, 4, 3, 2, and 1, as well as the more doubtful cases of $n=9$ and 10. W. C. Hansen and L. T. Brownmiller found that no crystalline structure appears when the hydrogel is heated an hour at 200°, but if heated an hour at 300°, the structure of hæmatite appears; aged hydrogels, natural or artificial, were found by J. Böhm and co-workers to show the structure of hæmatite with some distortion which E. Wedekind and W. Albrecht, and A. Simon and T. Schmidt attribute to the introduction of a number of H_2O-molecules in the spaces in the lattice. J. A. Hedvall also found that the dried hydrated hydroxide has a crystalline structure.

According to M. Biltz, the hydrogel has a sponge-like structure in which there are two kinds of capillary canals—primary and secondary. The adsorption of water by the dried gel is due to the fillings of the primary canals followed by the filling of the secondary canals when the vap. press. of the water has attained a high value, so that, according to F. Haber, the gel is built up of aggregates of molecules separated from one another by layers of water. A. Simon and T. Schmidt said that the amount of water associated with the hydrogel depends on the grain-size or degree of dispersion of the molecular aggregates; a preparation with finely dispersed aggregates had $Fe_2O_3 : H_2O = 1 : 36{\cdot}29$; one with medium dispersion, $1 : 30{\cdot}36$; and with a coarser dispersion, $1 : 14{\cdot}58$. The force when the water is retained by the hydrogel is greater the greater is the degree of dispersion. The structure of the hydrogel was also discussed by G. Malfitano and M. Sigaud, and P. P. von Weimarn; W. Kraust found that the X-radiograms of the fresh precipitate showed that the product is amorphous, but on standing, it gradually becomes crystalline.

T. Katsurai observed that when the hydrogel is heated with a slight excess of alkali in an autoclave at 5 to 10 atm. press., a red powder is produced. According to O. Ruff, when red colloidal ferric oxide is heated with water under the enormous press. of 5000 atm., it becomes hydrated. Thus, between about 30° and 42·5°, it yields a yellow hydrate $2Fe_2O_3.3H_2O$, corresponding with natural brown ironstone or limonite; and between 42·5° and 62·5° it yields the yellowish-brown hydrate $Fe_2O_3.H_2O$, corresponding with the mineral goethite; and at a higher temp. it furnishes a hemihydrate $2Fe_2O_3.H_2O$, equivalent in composition to turgite. H. Wölbling said that only the hydrated hæmatites can be hydrated under ordinary conditions of temp. and press.; and added that O. Ruff's products were in all probability mixtures of anhydride and a hydrate. The mol. vols. of brown ironstone, goethite, and turgite are said to be smaller than the mol. vols. of the components, because increasing the press. favours the formation of that compound which is formed with a decrease in vol. The red hydrogel at ordinary temp. gradually passes into a stabler, less hydrated, and denser state, without producing a definite hydrate. It is, therefore, assumed that the hydrogel very slowly loses water and passes into the anhydrous oxide. The dehydration process, however, at ordinary temp. is never complete because another simultaneous reaction occurs so that the hemitrihydrate is formed, and this hydrate, the brown ironstone or limonite of the mineralogist, is the most stable of the hydrates of ferric oxide. O. Ruff represented the successive stages: Colloid→anhydride→hemihydrate→monohydrate→hemitrihydrate. He found that the yellow colloid did not change in the temp. interval 40° to 70°, like the red hydrogel, and he accordingly inferred that the yellow colloid is not really a colloid but a true hydrate, possibly of the character of xanthosiderite; but O. Ruff himself added that limonite at 70° or 75°, and turgite at 40° to 50°, did not behave as they would do if O. Ruff's hypothesis were correct, and form respectively turgite and limonite. H. W. Fischer favoured the hypothesis that many of the colloidal or amorphous ferric oxides are definite compounds. He said that there are three definite hydrates: the yellow hydrates—artificial and natural—of the limonite type; the reddish-black colloid of the hæmatite type; and the reddish-brown colloids studied by J. M. van Bemmelen. He based his opinion regarding limonite on its having a characteristic dehydration curve. This might fit the opinion that the yellow colloids contain a definite hydrate of the goethite type, and C. Hintze regarded limonite as colloidal goethite. H. W. Fischer's remarks on the other colloids are to be regarded more as opinions, since they were not based on experimental work—*cf.* ferrous oxide. J. R. I. Hepburn found that the colloid after a prolonged freezing has some properties usually regarded as characteristic of the crystalline state. G. Graue, and O. Hahn and G. Graue discussed the surface area of the gel.

W. Spring found the **specific gravity** of the hydrogel precipitated by ammonia, and dried in air, to be 2·436 at 15°; G. Berndt gave 1·264 for the impure hydrogel obtained by the slow oxidation of ferrous carbonate in air; A. E. Davies found 4·545 for the sp. gr. of an aged hydrogel, boiled for a long time with water, and containing about 5 per cent. of water; whilst B. Aarnio gave 3·6 for a specimen which had been heated to 200°, and which contained 1·5 per cent. of water. F. Muck emphasized how the freshly-precipitated, voluminous hydrogen shrinks enormously as it dries to a brittle, hard mass; and R. Willstätter and co-workers said that the **drying of the hydrogel** is attended by a marked coagulation of the molecular aggregates. The subject was discussed by E. Brescius, and W. Hampe. B. Aarnio said that the hydrogel precipitated by ammonia, and dried at room temp., retains the following proportions of water on **dehydration** at:

	100°	200°	300°	700°
Retained water . . .	10	1·5	1·0	0·0 per cent.

The subject was discussed by T. Carnelley and J. Walker, W. Ramsay, A. Simon and T. Schmidt, R. Wallach, and R. Willstätter and co-workers—*vide infra*, the special hydrated oxides. T. W. Richards and G. P. Baxter emphasized the difficulty involved in driving off the last traces of moisture from the hydrogel, due in part, said N. A. Tananaeff, to the formation of hard crusts on the surfaces of the grains. H. Freundlich noted the liquefaction of the gel by **ultrasonic waves.** For the **calorescence** when heated, *vide supra*, ferric oxide. The ageing, and possible crystallization of the hydrated oxide when subjected to **freezing,** was discussed by J. M. van Bemmelen and E. A. Klobbie, H. W. Foote and B. Saxton, and F. Limberger and G. C. Wittstein. According to J. R. I. Hepburn, practically no dehydration of hydrated ferric oxide occurs during freezing; the absence of mother-liquor during freezing does not affect the dehydration curve or the composition after desiccation. In general, the products of freezing are colloidal, but they may present some physical characteristics of the crystalline state; thus, optical activity may be detected, but it is rather the result of strains set up by pressure than the effect of a crystalline structure. J. Thomsen obtained for the **heat of formation** $(2Fe,3O,nH_2O)=191\cdot13$ Cals., and M. Berthelot, 191·2 Cals. The subject was discussed by F. Haber. J. Thomsen gave for the **heat of dissolution** of $Fe_2O_3.nH_2O$ in sulphuric acid, 33·75 Cals.; in chloric acid, 32·34 Cals.; and in hydrochloric acid, 33·45 Cals.; M. Berthelot gave for dil. hydrochloric acid, 34·2 Cals.; and in hydrofluoric acid, O. Mulert gave 47·55 Cals.; and E. Petersen, 47·72 Cals.

For F. Doerinckel's observations on the **specific heat** of the hydrogel, *vide supra*, the hydrosol. For the **electrical properties,** *vide supra*, the hydrosol. Some observations on the **magnetic properties** of the hydrogel of ferric oxide were made by J. Plücker, S. H. Emmens, S. de Luca, J. L. Smith, and G. Wiedemann; and numerous observations have been made on the mass magnetic susceptibility of the hydrogel prepared in different ways. Thus, E. Wedekind and W. Albrecht found for a sample precipitated by ammonia from ammonium ferric sulphate, and dried by acetone, $\chi=100\times10^{-6}$; it contained 23·5 per cent. H_2O. A sample similarly treated and obtained from ferric sulphate, contained 22·3 per cent. H_2O, and had $\chi=224\times10^{-6}$. When similar samples were dried below 100° to 14·4 per cent. H_2O, E. F. Herroun and E. Wilson observed that $\chi=102\times10^{-6}$ to 115×10^{-6}, and if dried to 10·1 per cent. H_2O, $\chi=127\times10^{-6}$ to 147×10^{-6}. A sample obtained by ultra-filtration of a dialyzed soln. of ferric chloride, and dried by acetone, gave $\chi=32\cdot5\times10^{-6}$, and it contained 22·3 per cent. H_2O; and a sample obtained by the action of hydrogen dioxide on iron pentacarbonyl, when dried in air, gave $\chi=46\times10^{-6}$, and it contained 31·6 per cent. H_2O; whilst a sample dried by acetone gave $\chi=65\times10^{-6}$, and it contained 22·4 per cent. H_2O. S. Berkman and H. Zocher found that a sample obtained by dialyzing a soln. of ferric chloride gave $\chi=39\times10^{-6}$. A. Quartaroli observed that a sample precipitated by ammonia from a cold soln. of ferric chloride gave $\chi=58\cdot16\times10^{-6}$; 24 hrs. after filtration, $\chi=79\cdot9\times10^{-6}$; and when dried between filter-paper, $\chi=118\cdot4\times10^{-6}$. R. Willstätter and co-workers observed that the susceptibility increased during the progressive dehydration of the hydrogel. Thus, with a precipitated and dried hydrogel:

H_2O . .	22·1	24·3	24·7	25·1	30·0	32·8	40·5	42·8 per cent.
$\chi\times10^6$.	155	117	105	103	88	86	73	71

and with a hydrogel prepared by hydrolysis with water in a sealed tube, and dried by acetone:

H_2O . .	24·7	22·4	19·0	12·8	10·1	9·2	6·9	5·9 per cent.
$\chi\times10^6$.	105	150	208	286	155	114	6·9	5·9

E. Wedekind and W. Albrecht, and G. Wiedemann observed that the ageing of the hydrogel at ordinary temp. is attended by a rise in the susceptibility; and S. Veil studied the change which occurs in the susceptibility when the gels are heated with water. W. Albrecht observed that as the proportion of contained water is reduced, the susceptibility rises to a maximum at $\chi=420\times10^{-6}$, and a minimum at $\chi=280\times10^{-6}$. R. Wallach found that when dehydrated at different temp., there is a maximum at 200°, and a minimum at 650°; these temp. alter a little with different preparations. Treatment of the gels with hydrogen dioxide was found by S. Veil to depress the susceptibility; and S. Hilpert found that treatment with persulphate makes the gel strongly magnetic. O. Hauser found that the hydrate $Fe_6O_7.5H_2O$ furnishes strongly magnetic hydrated ferric oxide—not so, added H. Chandra, if $Fe_6O_7.5H_2O$ be treated with soda-lye and hydrogen dioxide. G. Berndt observed that hydrated ferric oxide, obtained by the oxidation and hydration of ferrous carbonate, has a vol. susceptibility which is dependent on the field-strength, and it also exhibits magnetic hysteresis. S. Veil also studied the magnetic properties of the hydrated oxide.

In general, as C. Whitehead showed, several of the acid-forming elements—phosphorus, arsenic, antimony, tin, selenium, and tellurium—are precipitated as insoluble compounds when an excess of ferric salt is added to ammoniacal soln. The **adsorption** of phosphoric acid by hydrated ferric oxide was examined by E. Angelesen and G. Balanesen; and R. Bunsen and A. A. Berthold studied the adsorption of arsenious acid by freshly precipitated, hydrated ferric oxide so that this reagent can be used as an antidote for arsenical poisoning—a subject discussed by D. Maclagan, R. H. Brett, J. M. Clavera, K. C. Sen, A. Boutaric and G. Perreau, J. H. Orton, T. and H. Smith, J. Zeller, and N. J. B. G. Guibourt. While A. Reychler, T. Oryng, etc., hold that complex, sparingly soluble arsenites are formed; W. Biltz showed that the effect is really an adsorption process, for the proportion of arsenic taken up by the hydrated oxide varies continuously with the conc. of the arsenious acid soln. The isothermal curve varies continuously without a break. G. Lockemann and M. Paucke found that the most complete adsorption occurs when the hydrogel is precipitated with a stoichiometrical proportion of ammonia, an excess of ammonia or precipitation with alkali-lye decreases the adsorptive power. R. Bradfield showed that such a proportion of ammonia gives the most finely divided and most readily peptized particles of hydrate. G. Lockemann and F. Lucius found that the equivalent amount of hydrogel, E mgrms., required to adsorb A mgrms. of arsenic is given by $E=kA^p$, where K and p are constants which vary with the temp. M. C. Boswell and J. V. Dickson, and W. Mecklenburg found that the equation is only approximate. For H. W. Fischer, and H. W. Fischer and E. Kuznitsky on the use of colloidal ferric oxide for intravenous injections in arsenical poisoning, *vide supra*. M. C. Boswell and J. V. Dickson showed that the adsorption of arsenious acid is increased if sodium hydroxide be present, and that the adsorption of sodium hydroxide is increased if arsenious acid be present. The adsorption of arsenious acid by hydrated ferric oxide was studied by K. C. Sen, A. Reychler, L. Herboth, and J. M. Clavera—*vide* arsenic trioxide. J. H. Yoe found that the rate of adsorption of arsenious acid by hydrated ferric oxide is very rapid, for 75 per cent. or more is adsorbed in the first few minutes, although the final state of equilibrium is not attained until after 12 hrs. The adsorption power is lessened, as shown in Fig. 537, the higher the temp. of formation of the hydrogel. Those formed at 0° and at 25° follow the simple adsorption equation: $x/m=kC^{1/n}$—*vide* **5**, 39, 9.

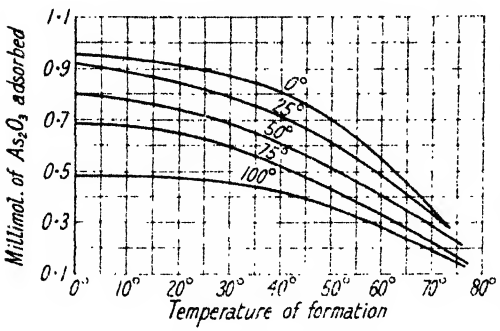


FIG. 537.—The Adsorption of Arsenious Acid by Hydrated Ferric Oxide formed at different Temperatures.

E. Angelesen and G. Balanesen investigated the adsorption of phosphoric acid. H. N. McCoy and C. H. Viol, and J. A. Cranston and co-workers studied the adsorption of the B- and C-members of the radium and thorium series by hydrated ferric oxide. The at. ratio of thorium-B to thorium-C adsorbed is greater than the at. ratio of radium-B to radium-C. O. Erbacher and H. Käding, O. Hahn and M. Biltz, and O. Hahn studied the adsorption of radium emanation by the hydrated oxide; I. Kurbatoff, the effect of the acidity of the soln. on the adsorption of thorium-X by the gel; and D. C. Lichtenwalner and co-workers, the adsorption of salts of magnesium, calcium and potassium by hydrated ferric oxide gels. The order of adsorption of the cations was found to be calcium, magnesium, and potassium; and of the anions, phosphate, sulphate, and nitrate. In the case of nitrates, adsorption was very slight. The time taken to attain equilibrium was considerably greater for phosphates than for other salts. The amount of adsorption of a particular salt increased with increased conc. The adsorption of a cation depended to some extent on the particular anion with which it was associated. Phosphates replaced adsorbed sulphates, but the reverse change did not occur. Sulphates and nitrates adsorbed by hydrogels could be removed by washing, but about two-thirds of the adsorbed phosphate could not be leached out. If hydrated ferric oxide is precipitated by ammonia from soln. containing a copper or a nickel salt, some hydrated copper or nickel oxide is adsorbed, the amount depending on the proportions of the two salts present, and the amount of ammonia added; the hydrated copper and nickel oxides cannot be removed by washing; and A. Charriou observed an analogous result when the precipitation is made in the presence of a calcium salt, and of a magnesium salt. F. Behrend, K. Ruegg, N. R. Dhar and co-workers, E. Toporescu, and A. Charriou studied the adsorption of other hydroxides—Ca, Mg, Cu, Ni, Fe(ous), Zn, Cd; A. C. Chatterji and N. R. Dhar, the adsorption of the hydrosol of ferric oxide; O. Hahn and M. Biltz, thorium emanation; M. Biltz, radiothorium, and radium emanations; and O. Nagel, the effect of adsorption on geochemical processes. M. Geloso observed that precipitated hydrated manganese dioxide likewise adsorbs precipitated hydrated ferric oxide. E. Dittler found that sulphuric acid may be adsorbed by precipitated hydrated ferric oxide; A. Charriou, calcium hydroxide; K. Flerow, potassium nitrate; V. H. Hall, potassium sulphate; F. Ibbotson and H. Brearley, nickel salts; I. M. Levy, copper and nickel salts; H. Busch, manganous, nickel, cobalt, and zinc salts; N. Nikitin, ammonia; W. A. Lazier and H. Adkins, hydrogen and ethylene; A. F. Benton, hydrogen, oxygen, carbon monoxide, and carbon dioxide; Wo. Ostwald and W. Haller, CCl_4, C_6H_{14}, C_6H_6, CH_3Cl, $(C_2H_5)_2O$, $CH_3.COOH$, C_2H_5OH, and $(CH_3)_2CO$; H. N. Holmes and C. J. B. Thor, the adsorption of oleostearine from soln. in volatile organic solvents; H. B. Weiser and E. E. Porter, and C. E. White and N. E. Gordon, P. Rohland, and L. Michaelis and P. Rona, organic dyes; K. C. Sen, citric, racemic, oxalic, sulphuric, malic, succinic, hippuric, and benzoic acids; K. C. Sen's results for the adsorption of some organic acids are summarized in Fig. 538. J. H. Perry found that in the adsorption of vapours from mixtures of vapour and air, (i) the adsorption efficiency is never 100 per cent., and decreases continuously until the saturation value is reached (chloroform, acetone, etc.); (ii) the adsorption is 100 per cent. efficient for some time, and then proceeds to the saturation point, which is reached only after a long time (carbon tetrachloride, ethyl alcohol, benzene); (iii) the curves are almost linear up to saturation, probably indicating chemical reaction (methyl alcohol). The addition of air to sulphur dioxide or ammonia causes a marked lowering of the saturation capacity of the gel. The gel absorbs about 15 per cent. of its weight of water with 100 per cent. efficiency, after which the efficiency falls off up to saturation (18 per cent. of its weight of water). J. C. Philip discussed the reversibility of the adsorptive process as illustrated by the failure of the sorption and desorption curves of ferric oxide gel and benzene to coincide; and B. Lambert and A. G. Foster, the pressure-concentration equilibria

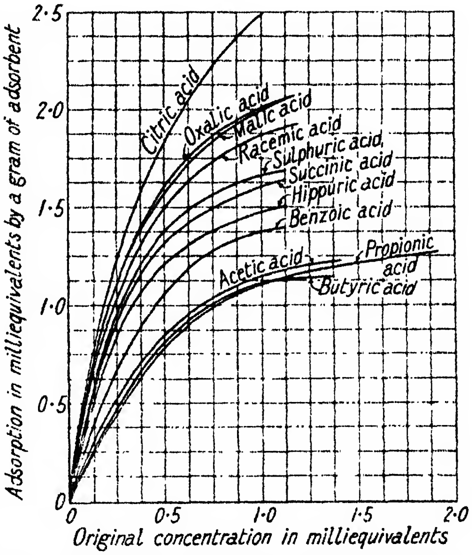


FIG. 538.—The Adsorption of Some Organic Acids by Ferric Hydroxide.

between ferric oxide gels and water, ethyl alcohol, and benzene. J. K. Chowdhury and M. N. Pal, and B. Lambert and A. M. Clark, and A. G. Foster studied the adsorption of benzene; D. P. Grettie and R. J. Williams, piperidine, nicotine, arginine, quinoline, adenine, caffeine, creatine, betaine, acetanilide, urea, acetamide, glucose, succinimide, glycine, vicine, asparagine, glutamic acid, and aspartic acid; G. Malquori, nicotine, caffeine, and quinine; H. Freundlich and G. Lindau, proteins; E. Abderhalden and J. Heumann, trypsin; A. W. Bull and J. R. Adams, sodium alizarin; and A. Boutaric and M. Doladilhe, organic dyes. W. Stollenwerk and M. von Wrangell found that with ferric oxide gels in soln. of sodium hydro-, dihydro-, and normal phosphate, the phosphate is adsorbed in continually increasing amounts until a maximum is attained in about 12 hrs., and after that there is a *retrograde adsorption*, for the adsorbed phosphate is gradually given up again. M. A. Rakuzin observed that neither the anhydrous nor the hydrated ferric oxide exerts a perceptible adsorption when immersed for 24 hrs. in an aq. soln. of egg-albumin. Partly dehydrated or anhydrous ferric oxide has a relatively high adsorptive power for gases at elevated temp. Hence its use in burning hydrogen sulphide for the recovery of sulphur and in a process for making salt cake, discussed by E. Jobling, and E. K. Rideal and H. S. Taylor; and in the contact process for sulphuric acid, discussed by G. Lunge and K. Reinhardt, G. Keppeler and co-workers, J. Krutwig, and L. and P. Wöhler and co-worker; T. Ito studied the action of silver nitrate on hydrazine hydrate, hydroquinone, and sodium hydrosulphite in a medium containing the hydrated ferric oxide.

H. Moissan observed that **hydrogen** at 440° reduces hydrated ferric oxide to ferrosic oxide. The loss of **water,** and the diminution in absorptive power and chemical activity which occur when the hydrogel is kept under water were discussed by J. Lefort, G. A. le Roy, and F. Limberger and G. C. Wittstein. The changes—reduced dispersion, crystallization and loss of water—which occur in the hydrogel when it is heated under water were examined by E. Berl and F. van Taack, J. Böhm, W. Bruhns, A. E. Davies, L. P. de St. Gilles, H. de Sénarmont, E. Wedekind and W. Albrecht, and S. Veil—*vide supra*; and the change which occurs when the hydrogel is heated with water at a high press. was investigated by O. Ruff. For the solubility in water, and for the solubility product, *vide infra*, ferric hydroxide. A. Mailfert observed that the hydrated oxide dissolves in a soln. of potassium hydroxide in the presence of **ozone,** forming potassium ferrate. L. J. Thénard found that hydrated ferric oxide has no action on **hydrogen dioxide.** R. J. Kepfer and J. H. Walton, I. S. Teletoff and E. A. Alekseeva, and G. F. Hüttig and A. Zörner studied the reduction with age in the activity of hydrated ferric oxide as a catalytic agent in the decomposition of hydrogen dioxide. The activity decreased from 18·5 secs. when 14 days old, to 20 secs. when 41 days old, to 22·5 secs. when 55 days old.

According to G. Calcagni, C. E. Janssen, G. A. le Roy, F. Limberger and G. C. Wittstein, B. Reinitzer, O. F. Tower, and G. C. Wittstein, the rate of dissolution of the hydrated oxide in organic and inorganic acids depends on its previous history; the aged hydrogel dissolves in acids slowly. O. Mulert, E. Petersen, and A. Speransky found that the fresh hydrogel dissolves in **hydrofluoric acid,** forming a soln. of ferric fluoride; and for the work of E. Brescius, A. E. Davies, H. R. Ellis and W. H. Collier, F. L. Hahn and M. Hertrich, F. Herrmann, W. G. Mixter, H. Schiff, D. Tommasi and G. Pellizzari, S. Veil, and R. Willstätter and co-workers, *vide supra*. The action of **hydrogen sulphide** is discussed in connection with ferric oxide. P. Berthier, A. Gélis, C. J. Koene, L. Marino, J. Meyer, J. S. Muspratt, K. Seubert and M. Elten, and H. C. H. Carpenter found that with **sulphurous acid** it forms sulphite and dithionate. H. J. Harrar found that 100 c.c. of **sulphuric acid,** at 25°; dissolves during 40 and 60 days' action respectively 12·245 and 14·236 mgrms. of Fe.

F. Ephraim observed that when the hydrogel is rubbed with **sodamide,** much heat is developed and ferric oxide is formed. O. Faust, and A. Guyard found that the hydrogel is not soluble in aq. **ammonia** in the presence of ammonium salts, but if some organic compounds are present, G. P. Baxter and R. A. Hubbard, and others observed that the hydrogel passes into soln. C. F. Cross, and E. Schirm observed that during the washing of the precipitated hydrate, it appears to dissolve —or it may be that the colloid is peptized. According to G. P. Baxter and R. A. Hubbard, " the solubility of hydrated ferric oxide in aq. ammonia is caused by some organic impurity in the ammonia," and they tried, without success, to reproduce the phenomenon by mixing methyl-, ethyl-, diethyl-, and *iso*amyl-amines, ethylenediamine, aniline, and phenyl hydrazine with ammonia. H. von Helmolt said that the hydrogel is soluble in a hot soln. of **ammonium fluoride,** but not in a soln. of **ammonium chloride,** and, according to W. Vaubel, not in a soln. of **ammonium nitrate.** The adsorption of **phosphoric acid** and phosphates has been indicated previously ; E. Erlenmeyer found that it dissolves in a hot, 48 per cent. soln. of phosphoric acid ; and R. M. Caven noticed that the fresh hydrogel reacts with a boiling soln. of **ammonium phosphate** to form ferric phosphate. The adsorption of **arsenious acid** by the hydrogel has just been discussed ; and A. Rosenheim and St. Thon observed that if heated in a sealed tube with a soln. of arsenious acid, basic ferric arsenite is formed—*vide supra*, adsorption. H. N. Hartshorne studied the action of arsenic acid. According to P. de Clérmont and J. Frommel, the fresh hydrogel does not react with **arsenic trisulphide.**

According to J. A. Sokoloff, **carbon monoxide** begins to reduce the hydrogel at about 150°. F. K. Cameron and W. O. Robinson, and P. N. Raikow observed no reaction with **carbon dioxide,** but J. Tillmans and co-workers stated that the hydrated oxide does absorb carbon dioxide. G. MacKinney, N. R. Dhar, G. Rao and A. Ram, G. Rao and N. R. Dahr, and E. Baur and A. Rebmann studied the photo-reduction of carbon dioxide to formaldehyde with colloidal ferric oxide as catalyst. According to E. Wedekind and W. Albrecht, and H. W. Fischer, freshly precipitated ferric hydroxide gradually becomes black in contact with 4 per cent. **hydrocyanic acid,** whilst the liquid acquires an intense reddish-violet colour, the cause of which has not been ascertained. With increasing age of the ferric hydroxide, the colour becomes less intense, and is scarcely perceptible with a preparation 20 days old. With specimens which have been preserved during 5 to 6 weeks, the blackening of the solid or violet colour of the soln. is not observed. The black precipitate consists of a mixture of prussian blue and ferric hydroxide ; it is also formed when freshly prepared ferric hydroxide is brought into contact with prussian blue. The ageing of the hydroxide affects only the first phase of the change, viz., the reduction of ferric to ferrous hydroxide by hydrocyanic acid. G. A. Goyder found that when the hydrogel is treated with a soln. of **potassium cyanide,** potassium ferrocyanide is formed. N. Tarugi, and K. C. Bailey found that the fresh hydrogel dissolves in **thiocyanic acid** to form ferric thiocyanate ; E. Belloni, A. Scheurer-Kestner, and O. F. Tower, that it dissolves in **formic acid.** C. L. Parsons and S. K. Barnes found that the hydrogel is insoluble in a 10 per cent. boiling soln. of **sodium hydrocarbonate.** A. Bette, F. Haber and G. von Oordt, C. E. Janssen, G. Mankiewicz, S. U. Pickering, and B. Reinitzer also found that the hydrogel is soluble in **acetic acid** ; W. G. Bateman and A. B. Hoel, in **chloroacetic acid** ; F. K. Cameron and W. O. Robinson, J. M. Eder and E. Valenta, and A. Rosenheim, in **oxalic acid** ; F. K. Cameron and W. O. Robinson observed that the hydrogel dissolves in oxalic acid to an extent proportional to the conc. of the acid, and no definite basic oxalate was formed at 25°. Soln. of oxalic acid of sp. gr. *S* dissolve the following percentage amounts of hydroxide, estimated as Fe_2O_3 :

S	1·007	1·015	1·031	1·040	1·050	1·064
Fe_2O_3	0·48	0·95	1·86	2·33	2·98	3·62 per cent.

A. Bussy observed that the hydrogel is soluble in **alkali oxalate** soln. ; H. Malfati found that the hydrogel is soluble in **tartaric acid** ; E. Landrin, and S. U. Pickering, in **malonic acid,** tartaric acid, and in **citric acid** ; G. Werther, and E. Soubeiran and H. Capitaine, in **alkali tartrate** soln.; and G. Calcagni, in **glycollic and lactic acids.** According to H. J. Harrer, the solubility of limonite expressed in milligrams of Fe per 100 c.c., at 25°, during 40 and 60 days' action, is for formic acid respectively 4·329 and 4·352; acetic acid, 0·505 and 0·535; **propionic acid,** 0·259 and 0·381; oxalic acid, 6·645 and 3·825; **malonic acid,** 10·520 and 12·125; **succinic acid,** 1·213 and 1·220; **lactic acid,** 8·845 and 10·958; tartaric acid, 10·528 and 16·098; citric acid, 16·159 and 18·582; **benzoic acid,** 5·888 and 6·039; and **salicylic acid,** 21·568 and 21·335. There is a definite relation between the strengths of the acids and the quantities of ferrous and ferric oxides and limonite dissolved. The hydroxy-acids which form complex anions with iron dissolve abnormal proportions, and the soln. undergo striking changes of colour. Some of the supposedly weak organic acids dissolve remarkable quantities of iron, and in natural soln. would be the most effective of all solvents. J. B. Burt found that a 12·5 per cent. excess of citric acid is necessary to dissolve ferric hydroxide. He also examined the reducing action of light on elixir of iron in the presence of quinine and strychnine. J. Wolff observed that the hydrated oxide is soluble in **ammonium salicylate,** and is precipitated from the soln. by hydrogen sulphide. M. Leprince found adsorption products were formed with **methylarsinic acid.** A. Naumann found that the hydrogel is insoluble in **benzonitrile;** and P. Vignon, insoluble in **trimethylamine;** A. Müller observed that the hydrogel is soluble to some extent in **glycerol;** J. M. van Bemmelen and E. A. Klobbie said that it is dehydrated by boiling glycerol; H. Malfatti observed that it is soluble in **polyhydric alcohols,** glycerol, and **sugar** soln.; and G. Buchner, that it is soluble in soln. of **albumen.** C. F. Schönbein found that **tincture of guaiacum** is not oxidized by hydrated ferric oxide.

G. Rousseau and J. Bernheim found that the hydrated oxide dissolves in fused **sodium hydroxide**—*vide infra*, goethite. G. Zirnité observed that if a current of air be passed into hot, conc. soda-lye containing hydrated ferric oxide in suspension, a little ferric oxide dissolves without colouring the liquor, and when the soln. has stood for some days, it becomes turbid owing to the separation of hydrated oxide. The turbid soln. is clarified when it is warmed—*vide infra*, alkali ferrites, and ferrates. The hydrogel dissolves in some soln. of **metallic salts** to form complex salts. C. L. Parsons and S. K. Barnes found that the hydrogel is insoluble in a 10 per cent. boiling soln. of **sodium hydrocarbonate.** H. Ost observed no reaction with soln. of **magnesium chloride,** and O. T. Christensen, that when fused with **potassium hydrofluoride,** potassium ferric fluoride is formed. W. O. Hickok observed that a soln. of **stannous chloride** acts on goethite. J. Jeannel, and P. Nicolardot found that soln. of the hydrated oxide in one of **ferric chloride** have an acidic character, they decompose carbonates, and are said to contain an oxychloride or basic chloride (*q.v.*). According to E. A. Schneider, the hydrated oxide dissolves in a conc. soln. of **aluminium sulphate,** forming a brown liquor which can be evaporated without decomposition, but if water be added, a basic sulphate is precipitated. A. Charriou studied the adsorption of ferric hydroxide by precipitates of **barium sulphate,** and **calcium oxalate.** E. S. Hopkins discussed the use of hydrated ferric oxide as a flocculant in the purification of water.

A red, earthy ore, sometimes mistaken for limonite and called *red ochre*, as well as *hæmatite*, occurs in the Turginsk copper-mine near Bogoslovsk, Urals; in the Kolyvan district, Altai; near Hof, Bavaria, near Siegen and Düsseldorf, Prussia; etc. A. Breithaupt[2] called it *hydrohæmatite*; and H. R. Hermann, **turgite,** or *turite* or *turjite*, according to the spelling adopted for the Russian name. The word turgite is an incorrect German transliteration from the Russian. Analyses were reported by P. A. Schemjatschensky, J. Samojloff, C. F. Rammelsberg, F. M. Heddle, G. J. Brush, E. Manasse, E. Posnjak and H. E. Merwin, J. Eyerman, H. R. Hermann, and G. C. du Bois. Turgite was also described by E. S. von Fedoroff and S. N. Nikitin, and A. Krasnopolsky. The results in some cases approximate to **hemihydrated ferric oxide,** $2Fe_2O_3.H_2O$. With the analyses of N. S. Kurnakoff and E. F. Rode, the percentage water in hydrohæmatite ranges from 5·91 to 7·98, and a sample of red Gloskopf had 0·60 per cent. J. D. Dana regarded turgite as identical with hydrohæmatite. G. Tschermak, F. Zirkel, F. Klockmann, and P. Groth discussed the right of turgite to be regarded as a definite mineral species; L. J. Spencer found that the dehydration curve is different from those of limonite and goethite, and he favoured the hypothesis that the mineral is a distinct mineral species, and M. Bauer represented it by the formula $H_2Fe_4O_7$. H. W. Fischer did not regard it as a definite individual, and E. Posnjak and H. E. Merwin found that the facts fitted the assumption that it is a solid soln. of hæmatite and goethite with enclosed (or capillary) and adsorbed water. O. Ruff obtained a hemihydrate by heating ferric oxide and water under a press. of 5000 atm. above 62·5°. H. Wölbling regarded the product as a mixture of anhydride and hydrate. According to E. Posnjak and H. E. Merwin, turgite is not necessarily a dehydration product of goethite or lepidocrocite; but pseudomorphous turgite may have resulted from the dehydration of fibrous goethite, and from the oxidation and slight hydration of magnetite and the martites. Pseudomorphous turgite is intermediate between hæmatite and primary turgite. A. Pelikan, who observed turgite—which he called limonite—on some fibrous goethite, concluded that turgite could not have been formed by the dehydration of goethite, but was rather deposited there directly. H. Stremme, and F. Cornu considered that the dehydration of the higher hydrates of ferric oxide takes place in nature under the influence of salt soln. or by atmospheric weathering, since it is impossible for several hydrates to be stable under a given set of conditions. E. Posnjak and H. E. Merwin, however, question whether the assumed series of hydrated ferric oxide really exists. The monohydrate is probably stable at any temp. which the earth's surface may normally reach, and it is therefore unlikely that in nature the red ferric oxide is derived by the *direct* dehydration of the yellow. It is probable that both red and yellow substances may be formed at ordinary temp. by somewhat different chemical reactions; both are relatively stable under the conditions usually met with near the earth's surface. According to J. Böhm, the naturally-occurring hydrated ferric oxides, except ruby mica, consist of impure goethite; in the case of turgite, the X-radiograms correspond with the hæmatite structure, so that turgite is partially dehydrated goethite. X-radiograms of the hydrogels give no indication of the presence of any crystalline hydroxide, but if they be heated with 2*N*-KOH, at 150°, the lines of goethite appear. The hydrosols appear to contain a basic salt, but aged sols show the goethite lines. E. Davies prepared what he regarded as the hemihydrate, $2Fe_2O_3.H_2O$, by adding aq. ammonia, or soda-lye, or potash-lye to a soln. of a ferric salt, heating the precipitate with the mother-liquor for 100 hrs. at 100°, or 1000–2000 hrs. at 50°–60°, washing the precipitate, and drying it between 50° and 100°.

L. J. Spencer said that turgite usually occurs as a layer on limonite, and forms hard, lustrous, mamillated or botryoidal masses with a radially-fibrous and concentric-shelly structure. It is black often with a reddish tinge of colour. The streak is dark cherry-red, and very thin fibres transmit a crimson colour. E. Davies' product had a sp. gr. of 4·545. A. Breithaupt gave 4·29 to 4·681 for the sp. gr. of the mineral turgite; H. R. Hermann gave 3·54 to 3·74; J. Samojloff, 4·63; G. J. Brush, 4·14; and C. Bergemann, 4·681. N. S. Kurnakoff and E. J. Rode gave 4·41 to 4·57 for the sp. gr. of hydrohæmatite. E. Posnjak and H. E. Merwin found that the sp. gr. of turgite ranges from 4·607 to 4·978 at 25°/25°; and if corrected for the contained silica and siderite, the sp. gr. ranges from 4·648 to 5·050; with sp. vols. from 0·198 to 0·215. If the water is adsorbed, turgite should have very nearly the sp. vol. of the sum of the sp. vols. of water and ferric oxide (sp. gr. 5·2). The sp. vol. curve would then be that represented by the thin line in Fig. 539. The observed results deviate from this, and lie more nearly on the sp. vol. curve of mixtures of hæmatite and goethite represented by the thick line in Fig. 539. This agrees with the assumption that turgite is a solid soln. of ferric oxide (hæmatite) and monohydrated ferric oxide (goethite). L. J. Spencer found that the hardness of turgite is near 6·5; and that turgite decrepitates violently when heated. The dehydration curve, with a 4 months' heating at each temp., is a continuous line. This was confirmed by E. Posnjak and H. E. Merwin, who found that the curve is different from the corresponding curves of goethite, limonite, lepidocrocite, and xanthosiderite—*vide infra*. The smooth curve shows that the water is given off gradually, as the temp. rises. There is no sudden decomposition anywhere. It is therefore inferred that the water is adsorbed or in solid soln., or both. The rehydration of dehydrated turgite was not successful, so that the dehydration is not a reversible process, and consequently it is doubtful if the water is merely adsorbed. The water is supposed to be held in solid soln. E. Posnjak and H. E. Merwin found the heating curve of turgite shows a slight exothermal break at 110°, and no other singularity occurs between that temp. and 600°. The heating curve is unlike the corresponding curves with the other hydrates. If turgite be a solid soln. of hæmatite and goethite, it might have been expected that the heating curve would resemble that of goethite—*vide infra*.

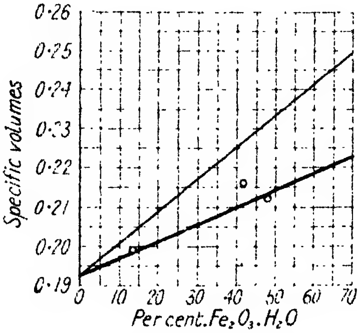


FIG. 539.—Specific Volumes of Mixtures of Goethite and Hæmatite.

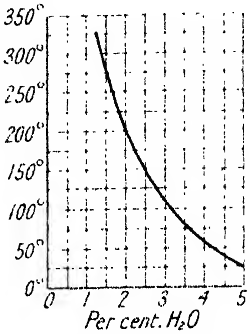


FIG. 540.—Dehydration Curve of Turgite.

N. S. Kurnakoff and E. J. Rode showed that the dehydration curves of the natural hydrated ferric oxides can be subdivided into three groups, and they furnish three phases. The first group, illustrated by curve I, Fig. 541, has a continuous dehydration curve analogous to the dehydration curves of the zeolites. There may be a break at 125° to 130°—*vide infra*. This group includes the turgites and the hydrohæmatites. The sp. gr. is 4·4 to 4·8. The colour is red, and the streak differs from the streaks of the substances in the other classes. The second group, illustrated by curve II, includes goethite, lepidocrocite, and limonite with 8 or more per cent. of water. These substances have 9·9 to 13·2 per cent. of water. Water exceeding $Fe_2O_3.H_2O$—*i.e.* 10·1 per cent.—is probably present in solid soln. The sp. gr. is 3·5 to 4·2; and the streak is pale yellow to dark brown. The dehydration curves have a characteristic terrace—the goethite terrace—in the vicinity of 200°, shown by curves II and III. This terrace corresponds with the beginning of the breaking of the α-phase-solid soln. of water in hæmatite. The hydrates of group I are typically α-solid soln. In substances with the higher proportions of water there is a terrace between 125° and 135°, corresponding with the

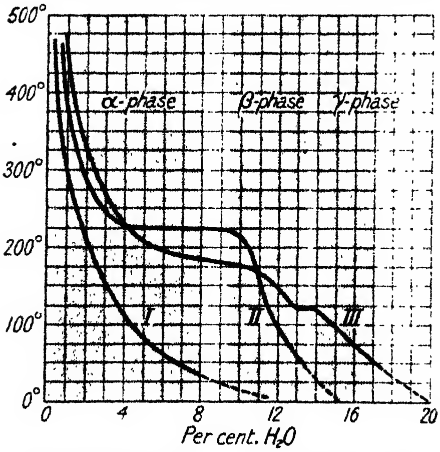


FIG. 541.—Dehydration curves of the Natural Hydrated Ferric Oxides.

beginning of the breaking up of the β-phase or solid soln. of water in goethite. The third group, illustrated by curve III, includes xanthosiderite, bog ores, and limonite. They have 13·8 and more per cent. of water. The dehydration curves show the goethite terrace; and the terrace at 120° to 150° where the β-phase or solid soln. begins to decompose; below that temp. there is the γ-phase, or what N. S. Kurnakoff and E. J. Rode call the xanthosiderite soln., or the γ-solid soln. is present. Curve III represents the decomposition of the bog iron ore, the sp. gr. of which is 2·7 to 3·8, and the streak pale yellow or dark brown. P. A. Thiessen and R. Köppen's study of the dehydration curves of goethite shew that it is a hemihydrate; the vap. press. curves of hydrated ferric oxide, at different temp., had breaks corresponding with the *tetrahydrate*, $Fe_2O_3.4H_2O$; the *hemiheptahydrate*, $2Fe_2O_3.7H_2O$; the *trihydrate*, $Fe_2O_3.3H_2O$; the *hemipentahydrate*, $2Fe_2O_3.5H_2O$: the *dihydrate*, $Fe_2O_3.2H_2O$; the *hemitrihydrate*, $2Fe_2O_3.3H_2O$; the *monohydrate*, $Fe_2O_3.H_2O$: and the *hemihydrate*, $2Fe_2O_3.H_2O$. There are probably also the *pentahydrate*, $Fe_2O_3.5H_2O$; and the *hemienneahydrate*, $2Fe_2O_3.9H_2O$. G. F. Hüttig and A. Zörner, G. F. Hüttig and H. Garside, O. Ruff, and C. Slonim studied this subject.

Turgite is optically negative. E. Manasse found that it is not doubly refracting. According to E. Posnjak and H. E. Merwin, fibrous red oxide of iron containing variable amounts of water—4 to 6 per cent.—cannot be definitely characterized. Detached splinters have parallel extinction, negative elongation, and negative, apparently uniaxial, optical properties. The refractive indices range from α (or ϵ) $=2\cdot3$ to $2\cdot6$, and β (or ω) $=2\cdot5$ to $2\cdot7$. They found $\alpha=2\cdot46$ to $2\cdot58$ for Na-light, and $\beta=\gamma=2\cdot38$ to $2\cdot52$ for Li-light. T. W. Case found that the resistance does not change on exposure to light. E. Davies found the artificial product dissolves readily in hydrochloric acid, and slowly in nitric acid.

In 1789, J. P. Becher[3] described what he called *Rubinrotherz Eisenglimmer*, which occurred at Siegen, in thin scales of a ruby-red colour; and later L. A. Emmerling, an *Eisenglimmer* with a colour, red, steel-grey or black; F. Mohs, a fibrous ironstone, coloured hyacinth-red, or blood-red, and forming four-sided plates; while J. F. L. Hausmann said that *Brauneisenstein* occurs (i) in thin, red, scaly or tabular crystals, in *Rubinglimmer*, a name synonymous with J. C. Ullmann's *pyrrhosiderite*—from *πυρρός*, fiery red; *σίδηρος*, iron—and which D. G. J. Lenz called **goethite**—after J. W. Goethe; (ii) scaly and fibrous, *e.g.* the *lepidocrocite* or *lepidokrokite*—*λεπίς*, scale; and *κροκίς* or *κροκύς*, fibre—of J. C. Ullmann; (iii) acicular, or capillary (not flexible) crystals, or in slender prisms sometimes grouped, *e.g.* the yellowish-red, fibrous *needle-ironstone* or *Nadeleisenerz* of A. Breithaupt. K. Willmann considers rubinglimmer and nadeleisenerz to be definite varieties. A variety occurring at Pribram, has a velvety surface and was called *Sammetblende* or *velvet blende*, and it is the *przibramite* of E. F. Glocker. There is also (iv) a brown or black, fibrous variety called *Glaskopf*; (v) a drossy variety corresponding with J. C. Ullmann's *stilpnosiderite*—*στιλπνός*, shining—which is a form of limonite (*q.v.*); (vi) a compact form; and (vii) an ochreous variety—both the compact and ochreous varieties are probably limonites. The *stainerite* of V. Cuvelier, and A. Schoep and V. Cuvelier approximates $(Co,Fe,Al)_2O_3.H_2O$. The *chileite* of A. Breithaupt is a form of goethite, and the acicular goethite which penetrates the quartz found on an island in Lake Onega, Russia, was called *onegite* by C. C. André, and *fullonite*—after a Mr. Fullon—by A. Breithaupt. F. Cornu called a colloidal variety with the "composition" of goethite, *Ehrenwerthite*—after A. Ehrenwerth. The crystals in some forms of *flèches d'amour*, and in some *aventurine* felspars—*e.g. sunstone*—are supposed to be goethite. F. von Kobell showed that needle-ironstone, goethite, and lepidocrocite have the general formula $Fe_2O_3.H_2O$, while varieties of limonite have the composition $2Fe_2O_3.3H_2O$. Analyses of goethite were also reported by A. Breithaupt, G. J. Brush, I. Domeyko, P. A. Dufrénoy, C. W. von Gümbel, B. J. Harrington, T. Häege, F. M. Heddle, H. R. Hermann, A. Lacroix, E. Manasse, J. J. Nöggerath, W. F. Pfaff, E. Posnjak and H. E. Merwin, C. F. Rammelsberg, G. Rose, J. B. Schober, M. Weibull, K. Willmann, and P. Yorke. N. S. Kurnakoff and E. J. Rode found 9·89 to 11·17 per cent. of H_2O in the samples they analyzed. The analyses of goethite and lepidocrocite are in general agreement with the formula for the **monohydrated ferric oxide,** $Fe_2O_3.H_2O$, or, with less justification, **ferric oxyhydroxide,** FeO(OH). N. S. Kurnakoff and E. J. Rode, however, are not satisfied that this substance is really a chemical individual. The formation of goethite in nature has been discussed by F. Babanek,[4] W. Bornhardt, O. Mügge, and A. E. Reuss, from which it appears that in some cases, limonite represents an intermediate stage in its formation, but in other cases—*e.g.* the inclusions of geothite in quartz, etc.—it is not probable that it was formed from limonite. According to L. P. de St. Gilles, when a soln. of a ferric salt is treated with ammonia, and the precipitate washed until free from ammonia, and then dried at 100°, the colour slowly changes from yellowish-brown to brick-red, and it then contains water eq. to $Fe_2O_3.H_2O$. G. Fownes obtained an analogous product by the action of potassium hydroxide on ammonium potassium ferric sulphate. Observations on this subject were made by C. W. C. Fuchs, H. Schiff, H. de Sénarmont, H. Debray, and F. W. C. Krecke. According to G. Rousseau, this hydrate is obtained in crystals by the action of boiling water on ferric oxychloride. F. Muck obtained the amorphous monohydrate by the action of a mixture of sodium carbonate and hypochlorite on a boiling soln. of ferrous sulphate; and G. Rousseau and J. Bernheim reported violet plates contaminated with a little soda, to be formed at 1100° by the action of dry, hydrated ferric oxide on sodium carbonate. The needle-like crystals produced by the last-named were said to be rhombic and different from ordinary goethite, so that this hydrate was said to be dimorphous. J. D. Dana, however, did not accept these statements; and C. Doelter could not obtain the dimorphous crystals, and said that the synthesis must be regarded as very doubtful. For D. Tommasi's observations on the α- and β-monohydrate, *vide supra*. D. Tommasi oxidized hydrated ferrous carbonate or hydrated manganosic oxide with potassium chlorate, he also oxidized ferrous hydroxide, and oxidized iron under water to form in all cases the yellow hydrogel hydrated ferric oxide. F. Muck said that the oxidation is complete when sodium hypochlorite is employed. O. Ruff, J. M. van Bemmelen, and E. Posnjak and H. E. Merwin regarded the yellow hydrogel as a true monohydrate. H. W. Fischer obtained a yellow hydrogel by the hydrolysis of a hot soln. of ferric chloride; S. Veil, and V. Rodt by the oxidation of ferrous or ferric sulphide suspended in water by means of a current of air; O. Baudisch and co-workers, the action of an azide or organic base on ferric chloride; and A. Krause, by oxidizing ferrous hydroxide.

H. Brunck and C. Gräbe obtained a substance resembling goethite from a molten sodium hydroxide, at 400°, contained in an iron boiler. According to W. L. Dudley, iron is attacked by fused sodium dioxide to form dark red, tabular crystals of the monohydrate. A. Frickhinger, obtained the monohydrate by the action of a soln. of ammonium chloride on iron in a closed vessel; and F. Wibel, by the action of soln. of ferrous salts on copper or on cuprous oxide. Z. Roussin obtained this hydrate by heating iron nitrosylsulphide, or sodium nitroprusside with conc. alkali-lye. J. M. van Bemmelen and E. A. Klobbie found that the hexagonal plates of sodium ferrite, $NaFeO_2$, when treated with water at 15°, furnish a *ferrous acid*, $H.FeO_2$; the crystals lose water at 100°, and consequently this hydrate cannot be the same as goethite, which retains its water at a much higher temp. They also doubted if goethite can be produced under the conditions of temp. which prevailed in G. Rousseau's, and H. Brunck and C. Gräbe's experiments. A. Vesterberg obtained monohydrated ferric oxide, pseudomorphous after ferric sulphate, by drying his dihydrate—*vide infra*—in a desiccator. The product was not very stable, for it began to lose water at 100°; and, unlike some other forms, it is hygroscopic. E. Posnjak and H. E. Merwin found that the yellow hydrated ferric oxide resembling the natural, amorphous oxide was formed below approximately 120°, but only above that temp. was red, hydrated ferric oxide, resembling turgite and hæmatite, produced. O. Ruff obtained the monohydrate, goethite, by heating the hydrated oxide with water between 42·5° and 62·5°; at a higher temp. a less hydrated oxide was formed, and at a lower temp. a more hydrated product was produced—*vide supra*. H. Wölbling regarded O. Ruff's product as a mixture of anhydride and hydrate. C. Doelter found that the precipitate of hydrated ferric oxide becomes crystalline after being shaken for 88 days; and that the gelatinous precipitate gradually forms the crystalline monohydrate when heated on the water-bath. The syntheses of crystalline goethite here reported are not, in general, satisfactory; and those of the monohydrated ferric oxide which yield a colloidal or amorphous product leave it open for debate whether or not the proportion of water observed is only due to an arbitrary selection of the conditions of drying. According to W. H. Albrecht, and E. Wedekind and co-workers, what F. Haber called the *a-hydrate*, a-FeO(OH), identical with goethite, is prepared by oxidation of ferrous hydrogen carbonate soln. by hydrogen dioxide, by a current of air or oxygen, or by a prolonged exposure of the soln. to air at 37°. In the last case, ferrous iron is present as well. The *γ-hydrate*, γ-FeO(OH), identical with lepidocrocite, is obtained by the oxidation of very dil. soln. of a ferrous salt by the eq. amount of sodium iodate in presence of sodium thiosulphate. Both hydrates are crystalline. The temp. of decomposition of the synthetic hydrates is markedly lower than that of the natural substances. The ratio $H_2O : Fe_2O_3$ is not constant, the water-content being usually higher than the theoretical.

H. Freundlich and S. Loebmann, and P. von Mutzenbecher prepared a colloidal soln. of goethite by centrifuging a mixture of perhydrol and iron pentacarbonyl. They found the speed of coagulation to be a quadratic function of the rate of stirring. Coagulation occurs at the interface of sol and air. The speed of coagulation passes through a minimum on adding increasing amounts of electrolytes. Small amounts of propyl alcohol favour coagulation, larger amounts delay it. *Iso*amyl alcohol favours coagulation, methyl alcohol inhibits it. H. Freundlich and B. S. Greensfelder also studied the subject.

Goethite occurs in reniform or stalactitic masses with a concentric and radiated structure; it also occurs fibrous and foliated or in scales, as well as in prismatic crystals which are vertically striated, and often flattened into scales or plates parallel to the (010)-face. The colour is yellowish-, reddish-, and blackish-brown; often blood-red by transmitted light. The streak is brownish-yellow or ochre-yellow. J. L. C. Schröder van der Kolk [5] said that the colour of the powder is like that of a ripe orange; and E. Posnjak and H. E. Merwin added that the fine powder is dull orange-yellow. The thicker grains show a slight pleochroism in orange-yellow and browns; but the thinner grains are not perceptibly pleochroic, and they are clear yellow. K. Willmann said that the mineral is feebly pleochroic—yellowish-orange in the direction of the *c*-axis; and brownish, perpendicular to that axis. O. Mügge said that when thin plates are warmed, between crossed nicols, the colour passes from green to red, but the green colour returns on cooling. According to W. Phillips, the rhombic crystals of needle ironstone have the axial ratios $a : b : c = 0{\cdot}9185 : 1 : 0{\cdot}6068$; and E. Posnjak and H. E. Merwin gave 0·90 (to 0·92) : 1 : 0·600 (to 0·605). The elongation of the prismatic, bladed, and fibrous varieties is parallel to (001). The (010)-cleavage is perfect, and the (100)-cleavage is good. In one sample, the optic axial angle $2E = c.\ 80°$ for 600$\mu\mu$; and in another sample, $2E = 90°$ for 675$\mu\mu$, and 120° for 546$\mu\mu$, or $2V = 35°$ to 40°. E. Palla gave $2E = 50°$; A. Pelikan, $2E = 58° 31'$ for red light, and 67° 42′ for yellow light. O. Mügge found that with the 577$\mu\mu$ and 579$\mu\mu$ yellow mercury double line, the effect of temp. on the optical axial angle is:

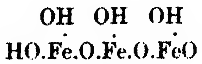
θ .	12·0°	31·0°	55·7°	63°	74·1°	102·5°	116·3°
$2E$.	83° 11′	63° 14′	24° 05′	0°	46° 22′	96° 11′	119° 20′

The optical character is negative. R. Gaubert found that the effect of temp. on the variation of the dispersion of the optic axes of goethite and limonite, and the action of hydrochloric and hydrofluoric acids show that fibrous limonite is impure goethite. K. Willmann regarded the scaly rubinglimmer, and acicular needle-ironstone as two different forms of the monohydrate, so that goethite is considered to be dimorphous, and rubinglimmer is called γ-**goethite,** and needle-ironstone, α-**goethite.** The γ-form is taken to include lepidocrocite—*vide infra*—and pyrrhosiderite. For the coagulation of colloidal soln., *vide* hydrosols of ferric oxide. O. Baudisch and L. A. Welo dehydrated $\gamma\text{-Fe}_2O_3.H_2O$ by friction, forming red $\gamma\text{-F}_2O_3$.

According to J. Böhm, the X-radiograms show that precipitated hydrated ferric oxide is amorphous, but after slow drying it gives hæmatite, and when heated with potash-lye, goethite. The α-monohydrate has a rhombic holohedral lattice with $a=4\cdot60$ A., $b=10\cdot01$ A., and $c=3\cdot04$ A., or $a:b:c=0\cdot459:1:0\cdot303$, and a sp. gr. 4·195; the γ-form has $a=385$ A., $b=12\cdot5$ A., and $c=3\cdot07$ A., or $a:b:c=0\cdot308:1:0\cdot246$, and a sp. gr. 3·97. These values for the *a*- and *c*-axes are about half those generally accepted. J. Böhm gave for the dimensions of the elementary cell, $a=4\cdot60$ A., $b=10\cdot01$ A., and $c=3\cdot04$ A. S. Goldsztaub gave $a=6\cdot64$ A., $b=10\cdot0$ A., and $c=3\cdot03$ A. for goethite; and for lepidocrocite, $a=3\cdot87$ A., $b=12\cdot4$ A., and $c=3\cdot06$ A.; and W. F. de Jong gave for goethite, $a=4\cdot55$ A., $b=9\cdot90$ A., and $c=3\cdot01$ A.; and he said that it is not isomorphous with stainerite—*cf.* ferrous oxide. G. Tunell and E. Posnjak, and P. F. Kerr studied the X-radiograms of goethite. J. Böhm gave for *Nadeleisenerz* the axial ratios $a:b:c=0\cdot918:1:0\cdot606$; and for *Rubinglimmer*, $0\cdot64:1:0\cdot43$. Observations on the crystals were also made by F. Babanek, M. Bauer, A. Breithaupt, K. Busz, J. Cates, G. Cesaro and A. Abraham, J. H. Collins, J. D. Dana, A. P. Dufrénoy, R. P. Greg and W. G. Lettsom, F. M. Heddle, A. Johnsen, G. A. Kenngott, A. Lacroix, A. Michel-Lévy and A. Lacroix, L. Michel, E. Palla, A. Pelikan, F. A. Quenstedt, C. F. Rammelsberg, A. E. Reuss, G. Rose, H. Traube, and D. F. Wiser.

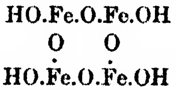
For the sp. gr., G. Rose gave 4·7; D. F. Wiser, 4·111; F. M. Heddle, 3·768 to 4·146; A. Breithaupt, 4·006; J. D. Dana, 4·0 to 4·4; and O. Mügge, 4·193 to 4·481; and after dehydration, the sp. gr. was 4·318 to 4·524. E. Posnjak and H. E. Merwin found the sp. gr. of their samples ranged from 4·091 to 4·263 at 27°/27°; and when corrected from the analyses for the contained siderite, manganite, and silica, they ranged from 4·29 to 4·32 at 27°/27°; N. S. Kurnakoff and E. J. Rode gave 4·20 for the sp. gr. The hardness is between 5 and 5·5.

The α-form is also called **ferric metahydroxide,** and the γ-form **ferric orthohydroxide.** According to A. Krause, and O. Baudisch and L. A. Welo, the metahydroxide has acidic properties, its isoelectric point being $p_H=5\cdot2$. whilst the orthohydroxide is more basic than acidic having an isoelectric point $p_H=7\cdot7$; whilst goethite, J. Böhm's α-Fe.O.OH, has no acidic properties. For the ferrous ferrites from these two hydrated ferric oxides, *vide infra*, ferrous ferrites. Since orthoferric hydroxide furnishes $Ag_3H(FeO_2)_4$, when heated with silver nitrate, A. Krause and K. Pilawsky suggested that not all the OH-groups have the same value, and, in the absence of a knowledge of the mol. wt., suggested that the graphic formulæ of the ortho- and meta-hydroxides are respectively as follows:—



$$\begin{array}{c}\text{OH}\;\;\text{OH}\;\;\text{OH}\\ \text{HO.}\dot{\text{F}}\text{e.O.}\dot{\text{F}}\text{e.O.}\dot{\text{F}}\text{eO}\end{array}$$

Orthohydroxide



$$\begin{array}{c}\text{HO.Fe.O.Fe.OH}\\ \text{O}\;\;\;\;\text{O}\\ \text{HO.}\dot{\text{F}}\text{e.O.}\dot{\text{F}}\text{e.OH}\end{array}$$

Metahydroxide

According to G. Schikorr, the X-radiograms of rust show that both α- and γ-FeO(OH) can be formed in the rusting of iron. The two forms are crystallographically different and they are represented by the minerals goethite—or α-FeO(OH)—and lepidocrocite—or γ-FeO(OH). G. Schikorr observed that when ferrous chloride in aq. soln. is oxidized spontaneously in air, α-FeO(OH) is formed; when ferrous hydroxide is rapidly oxidized in water through which oxygen is passed, α-FeO(OH) is formed; and α-FeO(OH) is produced when the hydroxide is slowly oxidized. When a soln. of ferrous hydroxide in ammonium chloride is rapidly oxidized, α-FeO(OH) is formed, and if slowly oxidized, γ-FeO(OH) is produced; and if a soln. of ferrous hydrocarbonate in saturated carbonic acid is slowly oxidized α-FeO(OH) is formed, but if the carbonic acid is in only slight excess, some γ-FeO(OH) is formed. E. Stirnemann observed the formation of the γ-form in the hydrolysis of ferric oxychloride. According to G. Schikorr, rust which is formed in contact with iron, under water, consists of γ-FeO(OH), presumably because it has been produced by the oxidation of a ferrite; whereas rust formed at some distance from the iron consists of α-FeO(OH), presumably because it has been formed by the direct oxidation of a ferrous salt. R. D. Williams and J. Thewlis prepared crystals of the γ-hydroxide, *i.e.* lepidocrocite, by precipitation from a soln. of ferrous chloride with calcium hydroxide, and subsequent oxidation at room temp. The crystals are of the order 10^{-5} cm. across, and those of the α-oxide, are of the order 10^{-4} cm. across. When heated, the α-hydroxide passes into cubic ferric oxide, and later into the rhombohedral oxide. The transformation from the γ-hydroxide to the γ-oxide (cubic) is roughly between 250° and 300°. R. Kattwinkel, F. Haber, O. Kröhnke, H. Schwiersch, and F. Drexler also studied this subject. The dehydration of the oxyhydroxide was examined by O. Ruff, H. W. Fischer, P. Nicolardot, G. F. Hüttig and co-workers, J. Böhm, and A. Simon and T. Schmidt. G. Schikorr represented by Fig. 542 the dehydration curves of the two forms prepared by slow and rapid oxidation of soln. of ferrous hydroxide in aq. soln. of ammonium chloride. W. H. Albrecht and E. Wedekind thus summarized the relations between the different oxides and hydrates: A. Krause and co-workers concluded from their study of silver ferrite that the ferric hydroxides include:

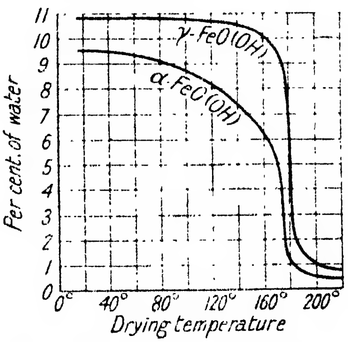
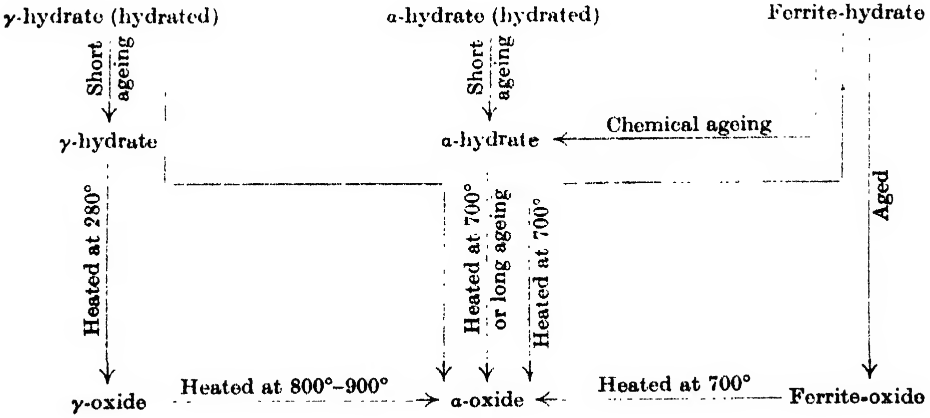
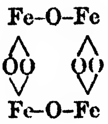


Fig. 542. — The Dehydration Curves of the two Ferric Oxyhydroxides.

I.—The orthohydroxide and polyorthohydroxide with chain-like molecules.

II.—Yellow hydroxide with ring-like molecules—*e.g.* the metahydroxides—embracing (1) the ferrous acid, $(HFeO_2)_n$ either amorphous, or crystalline γ-FeO(OH); and (2) goethite, $(Fe_2O_3.H_2O)_n$, to which the α-hydroxide and amorphous goethite belong.





J. W. Gruner's limonite was probably goethite, and he found :

> The stability of limonite in the presence of water was tested at 250° and 300° in sealed, thick-walled pyrex tubes. At 250° limonite showed no change. At 300° it was found that limonite in the tube above the water turned a brilliant red, whereas the limonite under water remained unchanged. The time of the experiment was 21 days. On analysis it was found that the whole sample in the tube contained 5·95 per cent. volatile matter after drying at 105°, and the ignition loss of the original material after drying at 105° was 12·13 per cent. This very peculiar behaviour of ferric hydroxide at these temperatures will be investigated further. It is probable, however, that, as J. M. van Bemmelen pointed out long ago, limonite is stable in the presence of water and under corresponding pressures at temperatures which approach 300°.

According to G. Tunell and E. Posnjak, the conversion of goethite to hæmatite probably proceeds at a much lower temp., for with boiling 0·1*N*-HCl, goethite passes into hæmatite ; and in J. W. Gruner's experiments, a product with a slow rate of decomposition was mistaken for a stable state. Variations were observed owing to differences in the rates of heating, and differences in the physical character of the substance—*e.g.* size of grain. Dehydration experiments in which the substance was heated for 4 months at different temp., and the losses of weight determined, showed that the dehydration curve consists of three parts, Fig. 543. The middle portion represents the loss of water attending the decomposition of the goethite, and it is accompanied by a change in colour from yellow to red. The upper and lower portions of the curve represent losses of water not chemically combined, and which is in all probability adsorbed and capillary water held in proportions which vary largely with the structure of the material. The re-hydration curves show that, roughly, the proportion of water taken up by the dehydrated material in a humid atmosphere is the same as the amount lost in the first stage of the heating. Goethite which was crystalline before dehydration, took up very little water ; while the fibrous varieties, and particularly the amorphous varieties, took up larger proportions. L. J. Spencer also found a break in the dehydration curve of goethite just below 250° ; and O. Mügge also obtained one at approximately 250°. N. S. Kurnakoff and E. J. Rode's observations on this subject have been discussed in connection with turgite—*vide supra.* E. Posnjak and H. E. Merwin's break at 200° was obtained with a 4 months' heating at the different temp. ; the others were obtained with a few hours' heating, so that equilibrium was more nearly attained than was the case with L. J. Spencer's, and O. Mügge's measurements. Expressing the time in hours and in brackets, the percentage losses of water at different temp. with a sample of coarse-grained goethite, from Crystal Park, were as follows (the sample when dried at 126° suffered an insignificant loss) :

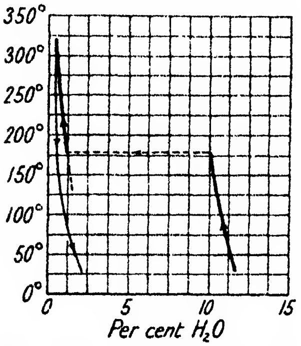


FIG. 543.—Dehydration and Re-hydration Curves of Goethite.

	153° (3)	192° (3)	244° (7)	264° (3)	282° (2)	303° (21)	305° (24)	376° (16)
Loss . .	0·04	0·05	0·24	0·90	1·37	7·77	9·62	9·72 per cent.

The loss over 376° (4) was 10·38 per cent. With a fine-grained sample, the losses were :

	132° (1)	220° (16)	275° (22)	304° (7)	353° (16)	400° (22)	>400° (0·5)
Loss . .	0·19	0·54	6·28	9·51	9·74	9·79	10·06 per cent.

Hence, the finer the grain-size, the faster the dehydration at the lower temp. The powder dehydrated at 354°, took up only 0·04 when exposed to a humid atmosphere. There is a sharp change in the optical properties of the sample heated to 250°. The sp. gr. rose from 4·193 to 4·318. C. F. Cross found that monohydrated ferric oxide, obtained by drying at 100° the ordinary precipitate, when exposed to a sat. atmosphere at 18°, gradually absorbs moisture, forming in about 67 hrs. a mixture eq. to $Fe_2O_3.3H_2O$, and in 192 days, one eq. to $Fe_2O_3.11H_2O$. The daily fluctuations of temp. gave variable results for the composition of the hydrated oxide. Observations were made by L. Hackspill and E. Stempfel, and P. A. Thiessen and R. Köppen.

E. S. Larsen gave for the indices of refraction of the rhombic crystals, $\alpha=2{\cdot}21$, and $\beta=\gamma=2{\cdot}33$ to $2{\cdot}35$ for Li-light. E. Posnjak and H. E. Merwin gave $\alpha=2{\cdot}26$, $\beta=2{\cdot}394$, and $\gamma=2{\cdot}400$ for rhombic goethite; and said with respect to fibrous goethite, that aggregates of thin blades and fibres, sub-parallel with respect to the *c*-axis, vary considerably physically and chemically. They usually appear microscopically homogeneous, but their refractive indices are low; they contain water, silica, etc., as impurities, and they show confused interference figures; they are uniaxial at shorter wave-lengths than is the case with goethite, owing to lack of parallel orientation with respect to the *a* and *b* axes. If the fibres or blades, elongated parallel to *c*, are fine—below $0{\cdot}5\mu$ in diameter—they can be packed without pore-space and with random orientation with respect to *a* and *b*, then slices of the apparently parallel-fibrous aggregates would have a maximum refractive index, parallel to the elongation, equal to 2·40, and a minimum, throughout the plane perpendicular to the elongation, equal to 2·33. Absorption would be slightly greater in the direction of the elongation. If instead of the random orientation, there is a tendency towards parallelism, there will be for any bundle of fibres considered as a unit, three principal refractive indices, namely, $\gamma=2{\cdot}40$, β variable between 2·40 and 2·33, and α variable between 2·26 and 2·33. Observations were also made by E. Palla, A. Michel-Lévy and A. Lacroix, and G. Cesaro and A. Abraham. F. Beijerinck found that goethite is a non-conductor of electricity. T. W. Case observed no change in the resistance of goethite on exposure to light. W. H. Albrecht found the magnetic susceptibility of artificial goethite to be 40×10^{-6} mass unit; J. Huggett and G. Chaudron studied the magnetic properties. E. F. Herroun and E. Wilson gave $28{\cdot}5\times10^{-6}$, and added that the susceptibility of α-$Fe_2O_3.H_2O$ does not change when it is heated. According to J. Huggett and G. Chaudron, goethite is paramagnetic, but it becomes ferromagnetic when heated in air at 360°. The magnetizability increases in vacuo owing to the removal of water, and at 570° it diminishes further. Goethite dehydrated in vacuo at 600° behaves like magnetite. Lepidocrocite, and rust conduct themselves similarly. G. F. Hüttig and H. Kittel studied the subject. G. Grenet gave 360×10^{-6} for the coeff. of magnetization of goethite. S. Berkman and H. Zocher studied the magnetic properties of $FeO(OH)$. G. F. Hüttig and H. Kittel found the magnetic susceptibility to vary from $30{\cdot}7\times10^{-6}$ to $43{\cdot}7\times10^{-6}$ mass unit according to the mode of preparation—*vide supra*, ferric oxide. G. Chaudron studied the magnetization curve of goethite; and lepidocrocite, heated in air. There is the magnetic transformation of magnetite at 570°, and an anomaly with ferric oxide at 660°. Goethite dissolves slowly and completely in conc. hydrochloric acid, but more easily in nitric acid. A residue of insoluble silica may appear.

G. F. Hüttig and H. Garside examined the hydrogel and found that when freshly-prepared it is amorphous, and that most of the water is united chemically with the ferric oxide, possibly as $Fe(OH)_3$ or $Fe(OH)_3.H_2O$, but a certain proportion of water in the colloid is mobile. If dehydrated to $Fe_2O_3.H_2O$, it is probable that water is all chemically united with the ferric oxide, and it cannot be removed without the application of heat. The heat transforms a part of the substance into crystalline ferric oxide. During ageing, the hydrogel becomes less active chemically, and the sp. ht. changes. The end-product of the ageing is $Fe_2O_3.H_2O$, or crystalline ferric oxide associated with water not chemically bonded. The stable form between 77° and 228° is goethite, and above 228°, crystalline ferric oxide associated with water not chemically combined. In ageing, part of the amorphous hydrogel forms crystalline ferric oxide, and a part forms goethite. The X-radiograms show that the space-lattice of the unstable ferric oxide associated with the water is expanded, but becomes normal when it passes into the stable form. The sp. ht., Table XC, and the vap. press. of the unaged hydrogel is less, and its activity in the catalytic decomposition of hydrogen dioxide is greater, than that of the aged hydrogel. S. Loebmann discussed the mechanical coagulation of goethite sols. P. P. von Weimarn and T. Hagiwara found that goethite can be transformed into hæmatite by mechanical disintegration.

TABLE XC.—SPECIFIC HEAT OF HYDRATED FERRIC OXIDE, $Fe_2O_3.nH_2O$.

Sample	Age in days	n	Temp.	Mean sp. ht.	Mol. ht.	Deviation from sum of mol. hts.	Apparent heat capacity of water	Apparent mol. ht. of water	Apparent mol. ht. of ferric oxide
A_1	2	3·791	3·85°–57·6°	0·3818	87·02	−6·893	61·35	16·18	18·77
	14	3·721	2·8°–36·8°	0·3780	85·68	−6·97	60·00	16·13	18·70
	36	3·721	3·7°–48·3°	0·3758	85·18	−7·47	59·50	15·99	18·20
	80	3·721	3·9°–52·1°	0·3659	82·93	−9·72	57·25	15·38	15·95
A_2	2	2·085	4·2°–82·2°	0·3006	59·28	−3·93	33·60	16·11	21·75
	23	2·247	4·2°–73·3°	0·3062	61·28	−4·84	35·60	15·84	20·84
	41	2·247	4·6°–81·5°	0·3010	60·24	−5·88	34·56	15·38	19·80
	78	2·247	4·0°–71·9°	0·2909	58·22	−7·90	32·78	14·59	17·78
A_3	3	1·2095	4·2°–85·2°	0·2401	43·55	−3·899	17·87	14·78	21·78
	14	1·233	3·7°–85·6°	0·2340	42·56	−3·31	16·88	13·69	20·36
	36	1·233	3·7°–85·7°	0·2415	43·94	−1·93	18·27	14·81	21·75
	79	1·233	3·55°–82·4°	0·2403	43·70	−2·166	18·03	14·62	21·51
A_4	3	0·2667	3·55°–83·9°	0·1837	30·87	+0·39	5·19	19·46	26·07
	21	0·237	3·5°–85·2°	0·1842	30·20	+0·25	4·52	19·07	25·93
	40	0·237	3·7°–90·4°	0·1855	30·41	+0·46	4·73	19·96	26·14
	70	0·237	3·7°–89·1°	0·1856	30·43	+0·48	4·75	20·04	26·16
B_1	—	1·00	5·4°–92·7°	0·2040	36·40	−7·30	10·72	10·72	18·40
C_1	2	0·872	3·3°–90·2°	0·2155	37·80	−3·57	12·12	13·90	22·11
C_2	2	0·0269	3·5°–89·4°	0·2047	35·00	−1·96	9·32	14·87	23·78
C_3	36	0·1442	3·7°–97·0°	0·1795	29·13	−0·77	1·82	12·62	26·54
C_4	?	0·0858	3·2°–87·8°	0·1707	27·52	+0·30	1·84	21·44	25·98

A_1 is the hydrogel $Fe_2O_3.3·721H_2O$; A_2 is the same preparation dried at 30° for 5 hrs.—$Fe_2O_3.2·247H_2O$; A_3, the same dried another 5 hrs. at 30°—$Fe_2O_31·233H_2O$; A_4, is A_3 dried over phosphorus pentoxide at 40°—$Fe_2O_3.0·237H_2O$. B_1 is goethite from Bohemia; C_1 is ferric oxide dried in air at 60°, and C_2, C_3, and C_4 are preparations dehydrated in vacuo at 200° over phosphorus pentoxide; and n, mols. of H_2O.

A. Lacroix [6] stated that the optical properties of the reddish, scaly crystals of rubinglimmer and **lepidocrocite**—*vide supra*—show that they should be classed together as one mineral species, but are separated from goethite, with which they had previously been regarded as similar. J. Samojloff, and P. A. Schemjatschensky reported crystals of a mineral optically similar to lepidocrocite, but containing more water than goethite, and he called the mineral **hydrogoethite.** The mineral was found associated with limonite near Lipetzk, and Dankoff, Government Tula, Russia. The mineral is sometimes regarded as the γ-goethite. F. L. Hahn and M. Hertrich obtained it by boiling a neutral or feebly acidic soln. of a ferrous salt with sodium thiosulphate and iodate; or a ferric salt soln. with sodium thiosulphate. The reaction was studied by A. Stock and C. Massaciu. V. Rodt, and W. Mecklenburg and V. Rodt obtained it by exposing ferric sulphide, in the presence of alkalies, to air; and W. H. Albrecht, by oxidizing a soln. of ferrous chloride in the presence of pyridine. J. Huggett obtained lepidocrocite by the prolonged immersion of iron in aerated water.

The analyses of J. Samojloff, P. A. Schemjatschensky, and K. A. Nenadkewitsch correspond with $3Fe_2O_3.4H_2O$. N. S. Kurnakoff and E. J. Rode found 10·89 to

11·22 per cent. H_2O in the samples they analyzed. The analyses of E. Posnjak and H. E. Merwin closely approximate to $Fe_2O_3.H_2O$, so that the composition is taken to be the same as that of goethite. The colour and streak are brick-red, or orange-red. The pleochroism in thicker grains shows α=clear yellow, β=dark reddish-orange, and γ=a darker reddish-orange; in thinner grains, α is nearly colourless or slightly yellow, β and γ are orange to yellow according to the thickness. K. Willmann also discussed the colour and pleochroism of the mineral. The mineral forms red or orange-red, micaceous or scaly crystals on goethite; and it also occurs in bladed, fibrous, or scaly aggregates. The crystals are rhombic, and, according to E. Posnjak and H. E. Merwin, and G. Cesaro and A. Abraham, the axial ratios are $a:b:c=0·43:1:0·64$—*vide supra*, γ-goethite. J. Böhm found that the X-radiograms agreed better with halving the values for the a- and c-axis, thus making $a:b:c=0·308:1:0·246$, and a sp. gr. of 3·97. The dimensions of the elementary lattice are a=3·85 A., b=12·5 A., and c=3·07 A. The (010)-cleavage is perfect, and the (001)-cleavage is not so good. The optic axial angle $2V=83°$, and the axial dispersion is slight. The optical character is negative. P. Gaubert found that goethite and lepidocrocite behave differently in the variation of the dispersion of their optical axes with temp. P. A. Schemjatschensky gave 3·53 for the sp. gr., and J. Samojloff, 3·73. N. S. Kurnakoff and E. J. Rode found the sp. gr. to be between 3·88 and 3·95. E. Posnjak and H. E. Merwin gave 3·841 to 3·854 for the sp. gr. at 25°/25°, and when corrected for the contained siderite, silica, and manganite, 4·07 to 4·12 at 25°/25°. The sp. gr. is therefore smaller than that of goethite. The hardness is 4. The heating curve closely resembles that of goethite, and similarly also with the dehydration curve. The γ-monohydrate is not altered when it is heated in a sealed tube with water at 100°. The indices of refraction are, $\alpha=1·94$, $\beta=2·20$, and $\gamma=2·51$. Hence, although the chemical composition of lepidocrocite is the same as that of goethite, the crystallographic constants, the sp. gr., and the refractive index of the crystals are quite distinct. Consequently, monohydrated ferric oxide is dimorphous, and the two forms are represented by goethite and lepidocrocite; while hydrogoethite is a variety of lepidocrocite. According to W. H. Albrecht and co-workers, and O. Baudisch and W. H. Albrecht, the magnetic properties of artificial specimens of the hydrated ferric oxide show a distinct change with the age of the specimen, whereas determinations of the water-content and the X-radiograms indicate stability. Ageing under water causes a diminution of the susceptibility of both hydrates, whereas desiccation at 100° in a current of air diminishes the susceptibility of the α-hydrate but increases greatly that of the γ-hydrate. The natural or synthetic α-hydrate is more stable than the γ-hydrate; dehydration of the α-hydrate affords the α-oxide, whereas the γ-hydrate gives the γ-oxide which passes at a higher temp. into the α-oxide. W. H. Albrecht observed that the preparation obtained from the ferrous salt soln. had a magnetic susceptibility between 37×10^{-6} and 74×10^{-6}; E. F. Herroun and E. Wilson gave 42×10^{-6}. When heated, the susceptibility rises rapidly to $39,500\times10^{-6}$, and then falls again. For J. Huggett and G. Chaudron's observations, *vide* goethite.

In the first century of our era, Dioscorides, in his *Περί ὕλης ἰατρικῆς* spoke of the *σχίστος λίθος*, and Pliny, in his *Historia naturalis*, of the *schistos*; and G. Agricola,[7] J. G. Wallerius, and A. Cronstedt regarded these minerals as equivalent to the red iron ore, or *Glaskopf*—that is, with black, brown, or red *hæmatites hemisphæricus*. This subject was discussed in connection with hæmatite or ferric oxide. The *ὤχρα*, or *ochres*, mentioned in the *Περί λίθων* of Theophrastus about 315 B.C., is represented by the *ochra nativa* or the *Berggeel* of G. Agricola; the *ochra nativa*, the *Berggelb*, and the yellow ochre of C. Gesner; and the *ochriger Brauneisenstein* of A. G. Werner, and D. L. G. Karsten. J. G. Wallerius, A. G. Werner, R. Hermann, L. A. Emmerling, and A. Breithaupt co-ordinated with the iron ores—*Brauneisenstein*, and *Raseneisenstein*—various earths including *minera ferri subaquosa*, *minera ferri lacuotris*, and *minera ferri palustris*, as well as *brown ironstone*, *brown hæmatite*, *brown ochre*, *marsh ore*, *bog ore*, *meadow ore*, etc., and *Sumpferz*, *Modererz*, *Pfennigerz*, *Morasterz*, *Wiesenerz*, etc. J. S. Kennedy objects to the use of the term "brown hæmatite" for limonite. J. F. L. Hausmann included in the term *Brauneisenstein* various iron ores: *Rubinglimmer*, or *ruby mica*, ledpidocrocite, and *Sammetblende*; drossy, compact, and ochreous iron ores; *Pecheisenstein* or *Eisenpecherz*; *Glanzeisenstein*; *Hyposiderite*; *Quellerz*; *Gelbeisenstein*, etc., mentioned by C. K. Stifft, J. Brunner, J. L. Jordan, and J. C. Ullmann. The yellow, waxy, pitch-like ore was called by J. C. Ullmann *stilpnosiderite*—from στιλπνός, shining; and σίδηρος, iron—only in very exceptional cases can this be regarded as a shining ore; and D. L. G. Karsten, and M. H. Klaproth, *pittizite*—from πιττίζω or πισσίζω, waxy; but J. F. L. Hausmann's term **limonite**—from λεμών, a meadow—is usually employed for *Eisenoxydhydrat mit dem Minimum des Wassers*. F. S. Beudant employed the term "limonite" in a more general sense than the "yellow bog ore" of J. F. L. Hausmann. A. Breithaupt, F. von Kobell, C. C. von Leonhard, and E. F. Glocker made observations on this subject. The early analyses reported by J. F. d'Aubuisson de Voisins, R. J. Haüy, J. F. L. Hausmann, J. C. Ullmann, J. L. Proust, and M. H. Klaproth showed that the varieties of yellow bog ore had a composition ranging from $2Fe_2O_3.3H_2O$ to $Fe_2O_3.2H_2O$; while R. Hermann's *Quellerz* was represented by $Fe_2O_3.3H_2O$, and J. D. Dana applied the term **limnite**—from λίμνη, a lake—to this earth, while $2Fe_2O_3.3H_2O$ was regarded as the composition of limonite, the term **xanthosiderite**—from ξανθός, yellow; σίδηρος, iron—was applied by E. E. Schmid to the yellow ochreous, bog ore, or the *Gelbeisenstein* of J. F. L. Hausmann, to which the formula $Fe_2O_3.2H_2O$ had been assigned. This subject was discussed by G. Tschermak, J. Böhm, M. Bauer, and C. Hintze. The Hungarian *kaliphite* of M. Ivanoff is, according to J. D. Dana, a mixture of limonite, manganese oxides, and silicates of calcium and zinc.

J. D. Dana said that limonite has various shades of brown, generally dark and dull, and that it sometimes has a black, varnish-like, or pitch-like exterior; and when earthy, it is brownish-yellow, or ochreous-yellow. The streak is yellowish-brown. It does not occur crystalline, and commonly occurs in stalactitic, botryoidal, or mammillary forms having a fibrous or sub-fibrous structure; it also occurs concretionary, massive, and earthy. The varieties are: (i) *Compact*—with a submetallic or silky lustre, often stalactitic, botryoidal, etc. It includes brown *Glaskopf*. (ii) *Ochreous*—is brownish-yellow to buff-yellow and earthy; and it often contains impurities like clay, sand, etc. (iii) *Bog ore*—from marshy places, is loose or porous in texture, and contains fossilized leaves, wood, etc. (iv) *Brown clay ironstone*—in compact masses or concretionary nodules with a brownish-yellow streak different from the streak of clay ironstone. Brown clay ironstone may be (*a*) *pisolitic*, or in aggregate concretions the size of peas—*bean ore* or *Bohnerz*; and (*b*) *oolitic*. The brown limonite, found in Luxemburg, Lorraine, and the Rhineland, consists of oolitic grains bound together by a cement of chalk, clay, or silica. It is called minette. According to E. Schroedter, W. Gill, and H. Wandesleben, it is used in the manufacture of basic steel. Numerous analyses of limonite have been reported.

For example, L. C. Beck, C. Borgemann, A. W. G. Bleeck, R. Böttger, G. C. du Bois, A. Breithaupt, A. Brunlechner, G. J. Brush, C. F. Bucholz, A. H. Church, E. Cohen, J. D. Dana, A. S. Eakle, C. F. Eichleiter, J. Eyerman, G. Einecke and W. Köhler, R. Fluhr, H. B. von Foullon, C. Gäbert, C. W. von Gümbel, E. Hatle, C. von Hauer, S. Haughton, F. M. Heddle, R. Hermann, T. C. Hopkins, T. S. Hunt, W. Jaworsky, C. von John, F. Katzer, W. Knaust, G. A. Kenngott, F. Klockmann, F. von Kobell, W. Kohlmann, F. Kretschmer, A. Lacroix, H. Leitmeier and M. Goldschlag, T. Liebisch, E. Manasse, A. Müller, T. L. Phipson, J. J. Pohl, B. Popoff, E. Posnjak and H. E. Merwin, F. Prime, C. F. Rammelsberg, G. von Rath, R. W. Raymond, A. Sachs, J. Samojloff, P. A. Schemjatschensky, E. E. Schmid, J. B. Schober, H. Schönberg, A. von Schrötter, H. Simons, E. G. Smith, J. L. Smith, J. W. E. Söchting, H. Struve, J. Thiel, G. Tschermak, J. C. Ullmann, N. Watitsch, F. Weltzien, A. J. F. Wiegmann, T. Wiese, and S. Wittich and B. Neumann. N. S. Kurnakoff and E. J. Rode found 10·85 to 16·58 per cent. of H_2O in the samples they analyzed.

Many of the samples of limonite contain silica, according to F. Wöhler, mainly as silicates, or clay; others contain alumina as clay, bauxite, or laterite—a subject discussed by M. Bauer; phosphates, sulphates, and manganese compounds are commonly present; R. Böttger, T. Bodemann, A. Müller, F. J. Otto, V. Merz, L. R. von Fellenberg, and T. L. Phipson found vanadium present in some of the limonites; and W. N. Hartley and H. Ramage detected spectroscopically, sodium, potassium, rubidium, silver, copper, calcium, manganese, nickel, thallium, chromium, gallium and indium in different limonites. The *ochres* are yellow earthy varieties of limonite contaminated with clay, etc. They were discussed by G. Gin, G. H. Hurst, A. Bouchonnet, F. Rose, A. G. Gentèle, G. Zerr and R. Rübencamp, etc. Likewise also with the *terra di siena*, or the *siennas*, which derive their name from the Italian town of Sienna. The siennas are redder than the ochres, and they were discussed by G. H. Hurst, F. Rose, A. G. Gentèle, G. Zerr and R. Rübencamp, etc. Some of the red earths are called *bole*, *Indian red*, *Venetian red*, raddle, etc. The umbers are browner than either the ochres or the siennas. Their name is derived from Umbria, an Italian town now known as Spoleto. They were discussed by G. H. Hurst, F. Rose, A. G. Gentèle, G. Zerr and R. Rübencamp, etc. Some dark brands of umber are called *Cassel brown*, and *Cologne earth*.

Attempts to find a formula for limonite gave F. von Kobell, E. Manasse, and F. S. Beudant **hemitrihydrated ferric oxide,** $2Fe_2O_3.3H_2O$, or $H_6Fe_4O_9$, results commonly used to represent the composition of limonite. J. F. L. Hausmann said that J. L. Proust's analysis agreed better with $Fe_2.O_3.2H_2O$. E. Posnjak and H. E. Merwin found that when an allowance is made for impurities, and for capillary and adsorbed water, the composition approximates closely to $Fe_2O_3.H_2O$; and this agrees with F. von Kobell's hypothesis, that limonite or stilpnosiderite is *wahrscheinlich Goethite im amorphen Zustande*. C. Hintze also supported the hypothesis that limonite is **colloidal monohydrated ferric oxide,** or **colloidal goethite**—*vide infra*. P. A. Thiessen and R. Köppen found that the dehydration curves agreed best with the assumption that limonite is a hemihydrate, like goethite, but with adsorbed water. R. Gaubert came to a similar conclusion in his study of the dispersion of the optic axes of the two minerals, and also of the action of hydrochloric and hydrofluoric acids on fibrillar limonite and goethite.

There are numerous deposits of limonite and the hydrated ferric oxides being formed as deposits from spring waters, etc., at the present day. H. Leitmeier and M. Goldschlag observed brown xanthosiderite on the walls of a mine in Payerbach, Austria, where, after two years' exposure to the atmosphere, the colour darkened, and the structure became granular and crystalline. Thus, E. C. Case[8] found a deposit being formed by the well water near Lawrence close to the Kansas River. The cellular structure of the so-called *boxwork limonite* was discussed by F. P. Boswell and R. Blanchard. E. Cohen observed stilpnosiderite in the meteorite from Beaconsfield, Australia. C. G. Ehrenberg noticed that yellow ochre or limonite contains extremely delicate branched threads indicating the presence in the original waters of an organized body containing an extremely large proportion of iron. J. C. Brown, D. Ellis, and H. Molisch have shown that the slimy streamers which develop in water conduit pipes, and on the walls and bottoms of shallow, water-storage reservoirs, are masses of hydrated ferric oxide whose existence is due to the activities of *iron bacteria*—Leptothrix ochracea, Gallionella ferruginea, Spirophyllum ferrugineum, Crenothrix polyspora, Cladothrix dichotoma, etc. The nodular excrescences, and tubercular incrustations found in iron pipes conveying water are due to the chemical action of dissolved carbon dioxide in the water, and the local enrichments of carbon dioxide facilitate the change of iron into soluble carbonate which is then oxidized to hydrated ferric oxide. The ferruginous incrustations found on the walls of iron conduit pipes (the walls, however, are not corroded) are considered to be the work of iron bacteria, assisted possibly by other organisms. The formation of spongy iron in iron water-pipes is due to the attack of acids in the water, or soil, and not to iron bacteria. This subject has been discussed by

O. Aschan, J. M. van Bemmelen, A. Beythien and co-workers, O. Casagrandi, N. Cholodny, F. Cohn, C. L. Dake, W. D. Francis, N. Gaidukoff, J. W. Gruner, E. C. Harder, N. J. Harrar, W. H. Herdsmann, C. R. van Hise, K. Höflich, A. Irving, D. D. Jackson, J. D. Kendall, J. Lafar, C. Mettenheimer, W. Migula, A. Molisch, E. M. Mumford, B. V. Pyaskovsky, E. Raumer, O. Rössler, W. Rullmann, C. Sauvageau and M. Radais, J. B. Schober, H. Schwers, H. C. Sorby, R. L. Starkey and H. O. Halvorson, C. Tolomei, S. Winogradsky, C. Zapffe, and W. Zopf—*vide supra*, the corrosion of iron. J. W. Gruner summarized his conclusions on the action of humic acids as follows:

> Soln. from decaying plants dissolve all oxides and carbonates of iron, and most of the silicates, but do not seem to attack pyrite appreciably. The strength of such soln. is similar to that of carbonic acid. It is possible that carbonic acid is the chief acid of the so-called "natural organic acids" but the organic colloids in such soln. give special properties to them. One of the differences between natural organic soln. and carbonic acid is that the organic soln. reduce ferric iron compounds to soluble ferrous salts, while carbonic acid does not.

The solvent action of carbonated waters was discussed by W. B. and R. E. Rogers, R. Müller, W. P. Headden, and J. W. Gruner—*vide infra*. O. Schreiner and E. C. Shorey observed that:

> Hydroxy-acids of the fatty series are very widely distributed in the vegetable kingdom—malic, citric, tartaric, glycollic, lactic, butyric, formic, and acetic acids; there is no doubt that vegetable acids of this group are added to soils in large quantities and become, temporarily at least, a part of the organic matter of the soil;

while E. C. Harder stated that "according to the extent to which organic acids are present, iron may be carried in soln. as salts of those acids. It is not impossible that such organic salts as iron formate, iron butyrate, iron lactate, or iron citrate may occur in iron-bearing waters." The subject was investigated by N. J. Harrar.

There are many and varied deposits of limonite in various parts of the world. The limonite is in all cases assumed to have been formed by the alteration of ferruginous minerals and rocks by exposure to air, moisture, etc. The subject was reviewed by F. W. Clarke,[9] C. Doelter, and F. Beyschlag and co-workers. Pseudomorphs of limonite after copiapite, cerussite, and copper pyrites were mentioned by A. F. Rogers; after anhydrite and diabantite, by B. V. Emerson; and after marcasite, by H. Laubmann, P. von Jeremejeff, P. N. Tschirwinsky, H. B. North, N. Watistsch, and L. Dürr. Outcrops of sulphide ores—*e.g.* pyrite or chalcopyrite—are often altered to masses of porous limonite: and pseudomorphs after pyrite are very common—*e.g.* R. W. Raymond, etc. The gossan caps of limonite on sulphide ores have also been formed by the oxidation and hydration of the mineral—*vide* the formation of manganese deposits, **12.** 64, 2. E. Newton said that the manganiferous iron ores of Minnesota were partly formed by the leaching of ferruginous limestone by alkaline soln.; and the removal of iron by the leaching of iron silicate rocks was discussed by J. W. Gruner, T. S. Lovering, L. Cayeux, and R. A. F. Penrose; while L. Dieulafait, J. P. Kimball, C. W. Hayes, C. W. Hayes and E. C. Eckel, S. W. McCallie, H. C. Sorby, G. Keller, and A. F. Foerste discussed the pseudomorphous replacement of limestone by percolating soln. of iron salts, and the formation of residual limonite from ferruginous limestone by the simultaneous oxidation of ferrous carbonate, and the dissolution of calcium carbonate. The formation of limonite from pyrite and marcasite has been described by G. Bischof, P. N. Tschirwinsky, M. Watanabe, E. Cohen, H. M. Chance, F. Cornu and H. Leitmeier, O. Mügge, A. Pelikan, and J. von Roth; and from siderite by G. Bischof, K. von Bülow, E. Hatle, R. Helmhacker, and K. A. Redlich. E. V. Shannon said that the presence of chlorides promotes the formation of hydrated ferric oxide.

Limonite may be found as a residual deposit where it was formed, and, according to C. K. Leith and W. J. Mead, J. F. Kemp, W. G. Miller, W. E. Pratt, G. O. Smith and B. Willis, A. C. Spencer, and C. M. Weld, it may have been formed by processes analogous to those concerned in the production of laterites—**5**. 33, 8. Limonite, like clays, may have been mechanically transported by streamlets from surrounding hills and deposited as bog ore in marshy places, and in pools where the velocity of the streamlet is sluggish, and the excess may be carried by rivers into the sea. The iron may also be transported in soln. dissolved as (i) hydrocarbonate in carbonated waters, (ii) as sulphate in water with acids derived from the oxidation of the sulphur in pyrites, or (iii) as a salt of an organic acid in peaty and other waters. It may have been deposited from such waters in the form of bog ore, or in stalactitic, tuberose, and other concretionary forms. Carbonated waters extract iron as ferrous hydrocarbonate from silicate rocks or from disseminated magnetite, and the soln. of the hydrocarbonate in carbonated waters, or the soln. of iron as sulphate from oxidized pyrites may deposit limonite when oxidized either by exposure to air, or, according to N. S. Shaler, by contact with oxygen given off by the respiration of aquatic plants —*e.g.* bog ores are more abundant along the margins of swamps, and are often wanting at the centre. The decomposition of the soln. of ferrous hydrocarbonate may be facilitated or produced by iron-bacteria which adsorb iron and re-deposit it in the form of hydrated ferric oxide, as indicated by G. Tolomei, J. M. van Bemmelen, W. D. Francis, E. C. Harder, etc.—*vide supra*—and E. S. Moore discussed the formation of bog ore by the action of algæ and lower plants on chalybeate waters. H. Molisch, for instance, found that under the influence of light, there is a separation of hydrated ferric oxide from soln., and an evolution of oxygen. Sulphate soln. may oxidize on exposure to air to form hydrated ferric oxide, and sparingly soluble basic salts; or they may precipitate the hydrate by contact with limestone or other carbonates, or phosphates, or with organic matter. In illustration of the solvent action of the organic acids in peaty and swamp waters, A. Kindler said:

> On the declivities of sand-hills planted with pine trees, and where springs, lying lower down, cause falls of earth, dead roots which penetrate through the ferruginous quartz sand absorb the rain-water filtering through. A decomposition commences, by which acids are formed, which are capable of dissolving large quantities of ferrous or ferric oxide; for in a few months the sand becomes as white as if it had been treated with acid. The action of a root, two lines in thickness, extends to a distance of from one to two inches. This phenomenon also presents itself in woods and gardens, for decolorized sand is found everywhere under rotting leaves.

R. J. Hartman and R. M. Dickey discussed the formation of banded iron formations by the diffusion of iron salts in silica gels.

A. Daubrée also observed this decolorization of ferruginous sands by roots. If a decaying root and quartz sand coloured with iron oxide be often moistened with water, the filtrate will be found to contain iron. When such soln. are oxidized, hydrated ferric oxide is deposited. As mentioned by G. Bischof, the rusty deposits about chalybeate springs, and the iridescent films of hydrated ferric oxide on the surface of marshes and swamp waters illustrate this reaction. This subject was discussed by J. M. van Bemmelen, W. Spring, and O. Aschan. W. H. Weed explained the formation of *iron-sinter* by an analogous process. When the waters deposit their ferruginous load where air has free access, limonite is formed, but if the deposition occurs in the presence of decaying organic matter and carbon dioxide, ferrous carbonate or siderite may be deposited. Hence, also—as noticed by H. Taylor, R. Phillips, and P. Kremers--the presence of ferrous iron in ferruginous clays, and soils. O. C. S. Carter observed a ferruginized tree in which part of the wood was replaced by brown hæmatite. H. Hess found some stag antlers changed to iron ore in the bog-iron ore deposit of Posen. The cementing action of hydrated ferric oxide in rocks like sandstones was discussed by W. Spring. According to K. Endell, rust, or hydrated ferric oxide is found in meteorites penetrating into the iron mass in the form of a tube which exhibits a rhythmic structure. The formation is held to be due to the setting up of local electric currents when the mass is moist, whereby ferrous hydroxide is first formed; this is oxidized, and the ferric hydroxide is deposited. R. J. Hartman and R. M. Dickey discussed the rhythmic phenomenon in the iron ores of Lake Superior.

The formation of limonite was also discussed by B. Aarnio, J. Ahlburg, J. P. Arend, O. Aschan, A. Bergeat and A. W. Stelzner, R. Blanchard and P. F. Boswell, A. W. G. Bleeck, R. A. Brauns, E. van den Broeck, A. Brongniart, K. von Bülow, J. M. Campbell, L. Cayeux, C. L. Dake, A. Daubrée, C. Deffner, E. Döll, G. Einecke and W. Köhler, A. Gärtner, A. Gressley, A. de Grossouvre, G. D. Hubbard, P. von Jeremejeff, F. Katzer, K. Keilhack, J. F. Kemp, A. Kindler, J. Klärding, P. Krusch, A. E. Kupffer, M. Lazarevic, C. K. Leith and W. J. Mead, A. Leppla, J. Levallois, A. Merle, W. G. Miller, E. S. Moore, M. Neumayr, J. S. Newberry, H. W. Nichols, W. E. Pratt, R. W. Raymond, G. Reinders, G. Schmidt, F. Senft, H. Sjögren, G. O. Smith and B. Willis, A. C. Spencer, F. M. Stapff, M. Tecklenburg, E. Thirria, L. Tokody, P. von Tschirwinsky, A. Vierschilling, C. M. Weld, B. A. Wendeborn, and F. Zirkel. The formation of pisolitic ores was discussed by A. Bergeat and A. W. Stelzner, F. Beyschlag, M. Brauhäuser, C. Chelius, C. Deffner, R. Delkeskamp, B. Fach, O. F. Fraas, L. Hoffmann, E. Hollmann, F. Klockmann, W. Kuhn and W. Meigen, R. Lang, A. Moos, H. Münster, F. W. Pfaff, H. Simons, H. Stremme, H. Tasche, and F. W. Voit; and the formation of oolitic ores or mimette, by A. Bencke, L. Cayeux, F. Gaub, L. Hoffmann, J. M. Jegunoff, W. Kohlmann, A. E. Kupffer, B. Popoff, H. Schneiderhöhn, C. H. Smyth, J. Thoreau, and L. van Werveke.

The hemitrihydrated ferric oxide, $2Fe_2O_3.3H_2O$, formerly supposed to represent the composition of limonite, was reported by J. J. Berzelius [10] to be formed as *iron-rust*, or *crocus martis aperitivus*, when iron oxidizes in aerated water. J. Lefort obtained this hydrate by precipitating a hot soln. of a ferric salt with alkali-lye and drying the washed product over sulphuric acid; L. P. de St. Gilles used aq. ammonia as precipitant, and dried the product in vacuo. F. Muck said that the *tritapentahydrate*, $3Fe_2O_3.5H_2O$, is produced when a basic ferric sulphate is added to molten potassium hydroxide, and after a short time the product is cooled, washed with water, and dried at 100°. O. Ruff obtained a similar hydrate by heating red, colloidal ferric oxide with water between 30° and 42·5°, and at 5000 atm. press. H. Wölbling regarded O. Ruff's products as mixtures of anhydride and hydrate. From the preceding discussion, it follows that despite plausible formulæ based on analyses, there is nothing to show that a definite hydrate is formed as a chemical individual, for the composition depends on the arbitrary conditions selected for the desiccation. G. C. Wittstein added that if the amorphous hydrate be kept under water a couple of years it becomes crystalline. According to A. Krause, ferrous hydroxide precipitated from a soln. of ferrous sulphate by an equimolar quantity of sodium hydroxide, yields on atm. oxidation, hydrated ferric oxide, but if the soda-lye is highly concentrated, the oxidized product always contains ferrous oxide, the highest ratio being $FeO : Fe_2O_3 = 0·3 : 1$. As the ferrous oxide increases, the colour changes from yellow to black, with a decrease in the water-content corresponding with a change from *meta*ferric hydroxide to ferrous ferrite. The isoelectric point of the hydroxide with the composition approximately $Fe_2O_3.2H_2O$, is nearly $p_H = 5·2$. Confirmation of this hypothesis of ferrite formation is obtained by oxidizing ferrous hydroxide in the presence of magnesium hydroxide, when magnesium ferrite is formed. The meta-form of ferric hydroxide differs from the brown ortho-form in having its isoelectric point $p_H = 7·7$, its ease of peptization, and its greater grain-size. The ortho-form is less stable under water, where it gradually passes to the meta-form. This change is much accelerated by the presence of OH′-ions, and at the same time, the isoelectric point changes from $p_H = 5·2$ to 7·7. The dried meta-oxide contains less water than the ortho-form, it is brownish-yellow instead of black, is more friable, and adheres more firmly to glass. The meta-oxide can be readily peptized by either dil. acid or ammonia, but not so with the ortho-oxide.

The **colour** of limonite ranges from dark brown to light yellowish-brown, dark yellow, and ochre-yellow. A. Bergeat [11] considered that the colour depends on the proportion of contained clay, and not on the proportions of iron or manganese. He found with three samples:

	Clay	Fe per cent.	Mn per cent.
Dark chestnut-brown . . .	scarcely any	59·90	0·17
Chestnut-brown	a little	67·61	0·11
Ochre-brown	much	44·00	0·29

W. D. Bancroft attributed the colour to adsorbed iron salts—*vide supra.* For R. Gaubert's observations on the identity of fibrillar limonite with goethite, *vide supra,* goethite. J. Böhm examined the X-radiograms of xanthosiderite, limonite, and limnite. E. Wedekind and W. Albrecht noted the appearance of interference lines in the X-radiograms during the ageing of the gels. J. W. E. Söchting gave 3·40 to 4·17 for the **specific gravity** of limonite; C. Bergemann, 3·908; E. Posnjak and H. E. Merwin, 3·841 to 4·172 at 25°/25°; and when an allowance is made for the contained siderite, manganite, and silica, 4·30 to 4·34 at 25°/25°. N. S. Kurnakoff and E. J. Rode found the sp. gr. to range from 2·7 to 4·01. Brown compact limonite has a **hardness** of about 5, and when freshly dug, sometimes over 5; but the hardness of other kinds ranges from 1 to 5. F. D. Adams found a cubic pseudomorph of limonite after pyrite was crushed to powder under a compression of 43,000 lbs. applied in 17 mins., without showing signs of plastic deformation. J. Joly found the mean **specific heat** of limonite to be 0·2263 between 13·3° and 100°; and of limonite pseudomorphous after pyrite, 0·2215 between 13·6° and 100°. The values calculated by the additive rule are respectively 0·22632 and 0·22155. R. Ulrich gave 0·2235 for the sp. ht. between 17° and 98°. E. Posnjak and H. E. Merwin found that the **heating curves** of limonite may show a slight thermal effect at about 100°. N. S. Kurnakoff and E. J. Rode's observations on this subject have been discussed in connection with turgite (*q.v.*). H. W. Fischer found that the **dehydration curves** of limonite show that water is lost rapidly below 100°, then sparingly, though continuously, up to 165°, and beyond that temp. the loss is very large, and is accompanied by a change in colour from yellow to red. He said that this behaviour is characteristic of that of a colloidal hydrate, and a marked effect at about 300°. By measuring the loss of water when specimens are kept at different temp. over 4 months, they obtained a curve very similar to that obtained with goethite. This, coupled with the sp. gr. data, etc., favours the hypothesis that limonite is colloidal goethite or monohydrated ferric oxide. When bog-iron ore is heated to 325° to 400°, F. Muck, N. S. Kurnakoff and E. J. Rode, etc., found that a calorescence occurs—*vide supra,* hæmatite. The subject was studied by R. Gaubert. E. Posnjak and H. E. Merwin found that limonite contains layers, splinters, filaments, or other portions with a **refractive index** 1·99 to 2·07; and in some cases with a red material having a refractive index of 2·2 to 2·3 resembling turgite, and in other cases having a refractive index of 2·4 and a strong double refraction like turgite. A. Pelikan gave $\gamma-\alpha=0{\cdot}048$ for the **double refraction.** As a result of their examination of various limonites, E. Posnjak and H. E. Merwin said: When monohydrated ferric oxide is precipitated and hardened under natural conditions which do not permit definite crystallization, a porous mass is formed containing considerable excess of water, besides other impurities. So indefinite is the material that it cannot be characterized very satisfactorily. Its colour in fine powder is scarcely distinguishable from that of fibrous goethite. Although often occurring in compact layered or botryoidal forms, it does not possess decided fibrous fracture. The earthy varieties consist of minute, loosely agglomerated spheroidal grains. Air-dried material possesses some pores of such size that, although microscopically invisible, they readily fill with such liquids as are used to immerse the grains for microscopic study. Thus, refractive index determinations cannot be definitely interpreted; air-dried material does have observed apparent refractive indices within the rather narrow limits of about 2·00 to 2·10 when saturated with a liquid of corresponding refractive index. Such material is here regarded as limonite. Double refraction is common in such material, usually it is indefinite and not strong, but occasionally it reaches 0·04 and is almost as definite as in fibrous goethites. For example, in the cylindrical crusts around stalactites and in the spheroidal grains, the ray vibrating along the radius is not strongly refracted as in fibrous goethite. In rare cases a decided tendency for minute fragments to be splintery makes this material look somewhat like fibrous goethite. E. Puseddu and A. Marini found that limonite from Bena de Padru, Sardinia, contains radioactive impurities. F. Beijerinck observed that the **electrical conductivity** is negligible. R. D. Harvey studied the subject. T. W. Case observed no change in its resistance on exposure to light. E. E. Fairbanks found the **dielectric constant** to be 9·9 to 15. H. B. Kosmann observed that the limonite from Harteberg, Silesia, is **magnetic.** F. Stutzer and co-workers gave 222×10^{-6} for the coeff. of magnetization of limonite; and G. Grenet obtained values ranging from 27×10^{-6} to 160×10^{-6}. A. Abt observed that a sample of limonite shows scarcely any magnetic moment. For the magnetic susceptibility, *vide infra*, the *trihydrate*. The magnetic separation of limonite was discussed by C. Jones, W. B. Phillips, and H. A. J. Wilkens and H. B. C. Nitze. A. Quartaroli prepared a magnetic variety—*vide supra*, magnetic ferric axide.

According to L. P. de St. Gilles, the hydrated ferric oxide dissolves in **acetic acid.** The presence of a little ammonia hinders the dissolution. F. Cornu found that limonite may exhibit a strong acidic reaction, possibly owing to the presence of basic sulphates—which E. Cohen found in limonites derived from pyrite. Limonite is soluble in **hydrochloric acid,** and it may leave behind a siliceous skeleton—the silica in limonite was discussed by F. Wöhler, J. F. L. Hausmann, C. H. Smyth, F. M. Stapff, and L. van Werveke. The action of hydrofluoric acid and of hydrochloric acid was studied by R. Gaubert; of hydrogen sulphide, by M. Mainz and M. Mühlendyck; and the reducing action of methane, by O. Meyer and W. Eilender.

J. F. L. Hausmann [12] found silky needles of hydrated ferric oxide associated with the manganese ores at Ilmenau, and elsewhere. It was called **xanthosiderite** —*vide supra*—by E. E. Schmid. It forms golden-yellow needles or fibres which may also appear brown or brownish-red. As an ochreous earth it is different shades of brown or brownish-red. The needles may occur in radiating or concentric aggregates. Xanthosiderite may have a silky, greasy, pitch-like, or an earthy lustre; and the streak is ochreous yellow, or pale brown to dark brown. Analyses were reported by J. F. L. Hausmann, E. E. Schmid, C. F. Rammelsberg, and S. Haughton, and as a result it came to be regarded as **dihydrated ferric oxide,** $Fe_2O_3.2H_2O$, or, with less justification, $Fe_2O(OH)_4$. J. L. Proust's analysis of a substance like limonite agreed with the dihydrate formula. N. S. Kurnakoff and E. J. Rode found 11·84 to 13·83 per cent. of water. Samples examined by E. Posnjak and H. E. Merwin had 9·92 to 10·22 per cent. water, and then had more the character and composition of goethite. J. Lefort said that dihydrated ferric oxide is produced when it is precipitated from a cold soln. of a ferric salt by cold alkali-lye, and dried over sulphuric acid; and F. Weltzien, by mixing a soln. of ferrous sulphate with potash-lye, and then with an excess of hydrogen dioxide, and drying the product at 100°. E. Brescius found that when the precipitate obtained by adding ammonia to ferric chloride is washed and dried over sulphuric acid, for 3 months, it contains 13·6 per cent. of water; while if the precipitate be washed with alcohol and then with ether, and dried for 2 months under the same conditions, its composition corresponds with the dihydrate $Fe_2O_3.2H_2O$, which loses half its water at 100°. For D. Tommasi's observations on the α- and β-dihydrates, *vide supra*. A. Vesterberg obtained the dihydrated oxide, pseudomorphous after ferric sulphate, by adding reduced iron powder to hot, dil. sulphuric acid (1 : 1), and heating the mixture until the acid begins to fume and the iron is transformed into a faintly red, crystalline powder of ferric sulphate. The acid is poured off as completely as possible and the crystals, without being washed, are placed in water and shaken with a soln. of sodium hydroxide (1 : 2). The copper-coloured, crystalline meal is finally washed with hot water and dried at the ordinary temp. The substance forms six- or eight-sided, isotropic plates, has a yellowish-brown or reddish-brown colour, and is very friable. The sp. gr. of xanthosiderite, reported by N. S. Kurnakoff and E. J. Rode, is 3·76; A. Vesterberg gave 3·234 at 15°.

E. E. Schmid gave 2·5 for the hardness. A. Vesterberg's product passed into the monohydrate in a desiccator, and lost more water at 100°. J. Lefort's product also lost water at 75°. E. Posnjak and H. E. Merwin obtained a dehydration curve very like that obtained for goethite (*q.v.*). H. W. Fischer discussed this subject; and N. S. Kurnakoff and E. J. Rode's observations are also indicated in connection with goethite. It is supposed that a colloidal γ-solid soln. of xanthosiderite and water decomposes at 120°–150°, forming the β-solid soln. of goethite and water; and that this, at about 200°, forms the α-solid soln. of hæmatite and water. F. Muck said that the dihydrate does not show a calorescence when heated. E. Posnjak and H. E. Merwin's samples of xanthosiderite had fibres with the index of refraction α near 2·27, β near 2·33, and γ near 2·37, but all were variable. The yellow colour was attributed to the presence of minute pores and inclusions. A. Vesterberg said that the dihydrate dissolves rapidly in 20 per cent. hydrochloric acid.

According to J. D. Dana,[13] the analyses of A. H. Church, R. Hermann, and C. J. B. Karsten of bog ore, the *Quellerz* of R. Hermann, and *Raseneisenerz,* approximate in composition to **trihydrated ferric oxide,** $Fe_2O_3.3H_2O$, and J. D. Dana called the earth **limnite**—from λίμνη, a marsh—*vide supra.* E. F. Glocker had previously proposed the term as a substitute for limonite. It occurs as an earthy, yellow ochre; and in stalactites and tuberose forms resembling limonite. It is not regarded as a definite mineral species, but rather as a hydrated limonite; the hydrate is also designated **ferric hydroxide,** $Fe(OH)_3$, but here again there is little evidence in favour of the assumption of a definite hydroxide in the chemical sense of the word. P. A. Thiessen and R. Köppen's dehydration curves indicate that limonite is goethite with absorbed water. G. C. Wittstein obtained what he regarded as this substance by adding ammonia to a soln. of ferric sulphate, and washing the product, and drying it first at a gentle heat and then at 100°. The amorphous, yellow product, under freezing water, forms a granular, yellowish-brown powder which appears to consist of microscopic crystals. P. Fireman, and R. S. Penniman and N. M. Zoph observed the formation of a hydrated oxide with 13·63 per cent. of water by passing air through a soln. of an iron salt in the presence of iron. J. Matuschek observed the formation of the hydrated oxide when soln. of potassium ferrocyanide are exposed to light. F. L. Hahn and M. Hertrich obtained the hydrated oxide in a heavy, powdery form which is easily filtered and washed, and which is free from basic salt, by warming on a water-bath a neutral soln. of a ferric salt—containing, say, 0·2 grm. Fe_2O_3 per 400 c.c.—with sodium thiosulphate until the soln. is colourless; the soln. of ferrous salt is then warmed with a slight excess of potassium iodate: $2Fe^{\cdot\cdot}+3H_2O+IO_3'+4S_2O_3''=2Fe(OH)_3+I'+2S_4O_6''$. H. V. Kohlschütter studied the product obtained by the action of aq. ammonia on crystals of ferric sulphate. D. N. Ghosh observed the rhythmic precipitation of the hydroxide. N. J. Harrar and F. E. E. Germann studied the colours of soln. of ferric hydroxide in various acids; and G. G. Rao and N. R. Dhar, the catalytic action on the photo-synthesis of formaldehyde from alkali hydrocarbonates. According to H. Molisch, hydrated ferric hydroxide is precipitated by the action of light on certain dil. soln, containing salts of iron; for example, iron ammonium citrate; whilst a soln. of ferrous sulphate and ferrous hydrogen carbonate deposits ferric hydroxide on remaining even in the dark. J. Thomsen gave for the **heat of formation** $(2Fe,3O,3H_2O)=191:15$ Cals.; and $(2Fe(OH)_2,O,H_2O)=54·59$ Cals. K. Inoue studied the heat of dehydration of bog-iron ore. K. Jellinek and H. Gordon gave 10^{-38} for the solubility product $[Fe^{\cdot\cdot\cdot}][OH']^3$, and G. F. Hüttig and H. Kittel found that the magnetic susceptibility varies with the mode of preparation. Samples with $Fe_2O_3.nH_2O$, with $n=3·162$, 2·434, and 1·699, had the respective values $105·4\times10^{-6}$, $114·3\times10^{-6}$, and $124·5\times10^{-6}$ mass unit.

Observations on the magnetic susceptibility were made by M. Faraday, C. B. Greiss, and A. Abt. E. F. Herroun and E. Wilson obtained for limonite $31·6\times10^{-6}$ mass unit; G. Wistrand, $123·8\times10^{-6}$; and F. Stutzer and co-workers, $59·4\times10^{-6}$. S. Veil found that the magnetic susceptibility depends on the previous states through which the material has passed, and the temp. to which it has been heated. W. Albrecht found that the magnetic susceptibility of the hydrated ferric oxides depends on the mode of preparation, etc.—*e.g.* dehydration in open or sealed tubes under water at 100° ; interaction of iron pentacarbonyl and an alcoholic soln. of hydrogen dioxide ; adding anhydrous ferric sulphate, or ammonium ferric sulphate to 35 per cent. ammonia, etc. With hydrated oxides containing varying proportions of water, there is a maximum in the curve corresponding approximately with $Fe_2O_3.3H_2O$, but hydrates having almost identical proportions of water may differ greatly in their magnetic properties. P. Hausknecht found the susceptibility of the trihydrated oxide to be five times as great as that of the anhydrous oxide—*vide supra*, ferric oxide.

J. W. Gruner observed that peat-water dissolved 14 parts of iron per million from limonite in 77 days, and 30 parts in 182 days. B. Aarnio found that hydrated ferric oxide precipitated by ammonia, and dried at 100°, contains 10 per cent. of water, and has a **hygroscopicity** of 34 per cent. ; when dried at 200°, the corresponding values are 1·5 and 42 per cent. ; dried at 300°, respectively 1·0 and 29·6 per cent. ; and when dried at 700°, the hydrate becomes anhydrous, and loses its hygroscopicity. When various hydrated oxides are heated in chlorine to 900°, W. Kangro and R. Flügge found that 88 to 100 per cent. of the iron is removed as ferric chloride in about 150 mins. The trihydrated oxide readily dissolves in acids to form ferric salts. According to G. Bodländer, the **solubility** of this hydrate in **water** is represented by $3·73 \times 10^{-12}$ gram-equivalent of $Fe(OH)_3$ per litre ; G. Almkvist gave $1·51 \times 10^{-4}$ grm. per litre for the solubility at 20° ; K. Jellinek and H. Gordon, 3×10^{-10} mol per litre ; and E. Müller, $1·35 \times 10^{-9}$ mol per litre. G. Bodländer represented the **solubility product** as $[Fe^{\cdot\cdot\cdot}][OH']^3 = 6·5 \times 10^{-47}$ on the assumption that the ionization is complete. H. T. S. Britton said that the solubility product with very weak bases like hydrated ferric oxide, has probably very little meaning. K. Jellinek and H. Gordon's value for the solubility product $[Fe^{\cdot\cdot\cdot}][OH']^3 = 10^{-37·9}$. O. Ruff and B. Hirsch's value is $1·1 \times 10^{-36}$; and E. Müller's $6·5 \times 10^{-47}$. K. Jellinek and H. Gordon measured the $H^{\cdot}$-ion conc. with the hydrogen electrode of soln. of ferric chloride, containing potassium chloride to coagulate the colloidal soln., to which varying amounts of sodium hydroxide had been added. H. T. S. Britton added that if it be assumed that in the titration the appearance of opalescence marked the point at which ferric hydroxide actually began to separate, and that the amount of free ferric ions was eq. to the remaining amount of alkali to be added to decompose the ferric chloride completely, the value for the solubility product becomes $10^{-37·7}$. Thus, opalescence occurred on the addition of 39 c.c. of $0·10N$-alkali ; $p_H = 2·3$. Hence, $[OH'] = 10^{-11·8}$ and $[Fe^{\cdot\cdot\cdot}] = 10^{-2·3}$—*vide supra*, hydrated ferric oxide. P. P. von Weimarn estimated the solubility to be much less than that of hydrated alumina because of the concentration of the soln. required for the separation of gelatinous precipitate. G. Almkvist gave for the solubility, 0·151 mgrm. of $Fe(OH)_3$ per litre at 20°—*vide supra* for the hydrosol.

E. Reichardt and E. Blumtritt found that 100 grms. of air-dried hydrated ferric oxide absorbed 375 c.c. of gas from the air, and the gas contained 26 per cent. of N_2, 4 per cent. of O_2, and 90 per cent. of CO_2 ; and A. von Dobeneck found that hydrated ferric oxide absorbed 6·975 grms. of carbon dioxide at 0°, 5·702 grms. at 10° ; 5·054 grms. at 20° ; and 4·274 grms. at 30°. L. P. de St. Gilles observed that when trihydrated ferric oxide is boiled with water for several hours, it gradually becomes brick-red, and passes into the monohydrated oxide. P. Nicolardot inquired why is hydrated ferric oxide not white when the normal ferric salts are white ? He found that by adding a freshly prepared, conc. of soln. of ferric salt to cooled, aq. ammonia, the hydrate obtained is white, but it rapidly turns brown, due, he supposed, to polymerization—*vide supra.* D. Tommasi and G. Pellizzari found that when hydrated ferric oxide is kept under water for a year, it loses its gelatinous structure, and changes in colour from brown to yellowish-red. About

30 per cent. passes into a modification insoluble in dil. acids, and about 0·3 per cent. is converted into a soluble modification identical with Graham's colloidal hydrate. The change is very slightly, if at all, affected by light. For the solubility of limonite in various menstrua, *vide supra*, hydrated ferric oxide. O. Meyer and W. Eilender discussed the reduction of limonite with methane. For W. von W. Scholten's observations on the solid soln. of ferrous and ferric hydroxides, *vide supra*, ferric oxide. H. Handovsky found that ferric hydroxide, but not iron, ferrous sulphate, ferrosic oxide or the hydrosol of ferric oxide, acts catalytically in the oxidation of leucine.

A mineral was obtained by L. J. Igelström from the Längban iron-mine in Sweden, and he called it **pyriaurite**; M. F. Heddle obtained a similar mineral from the serpentine of Haaf-Grunay, Scotland, and called it *igelströmite*. The analysis by L. J. Igelström, M. F. Heddle, and G. Aminoff and B. Broome corresponds with magnesium ferric hydroxide, $Fe(OH)_3.3Mg(OH)_2.3H_2O$. It occurs in golden or silvery, six-sided plates, and with an obscure fibrous structure. G. Aminoff and B. Broome found that the crystals are of two types: (i) The six-sided plates have X-radiograms corresponding with a hexagonal cell having $a=3{\cdot}097$ A., and $c=15{\cdot}56$ A., or $a:c=1:5{\cdot}024$; and (ii) small rhombohedral crystals having a trigonal cell with $a=3{\cdot}089$ A., and $c=23{\cdot}23$ A., or $a:c=1:7{\cdot}520$.

According to A. S. Eakle and W. T. Schaller,[14] a mineral occurs in Esmeralds Co., Nevada, and it was accordingly called **esmeraldite.** Its composition approximates **tetrahydrated ferric oxide,** $Fe_2O_3.4H_2O$, after making due allowance for impurities. It occurs in the earthy limonite as pod-shaped masses of a coal-black colour; bright, vitreous lustre; and glassy fracture. The edges are translucent, and appear yellowish-red by transmitted light. The streak is yellowish-brown. The sp. gr. is 2·578; and the hardness of the brittle mineral is 2·5. W. Spring reported a tetrahydrate to be formed when the voluminous precipitate of hydrated oxide, obtained by adding ammonia to a dil. soln. of ferric sulphate or chloride, is allowed to dry in air. The black, vitreous mass appears red by transmitted light. Its sp. gr. is 2·436 at 15°; it is not decomposed by press.; and it loses water in a desiccator. P. A. Thiessen and R. Köppen obtained the tetrahydrate by the slow hydrolysis of a boiling, dil. soln. of ferric ethylate in absolute alcohol. The crystals are probably cubic; and the sp. gr. is 3·0 to 3·1.

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§ 33. The Ferrites and Perferrites

Ferric oxide unites with many bases to form salts commonly called **ferrites**, just as the salts of chromic oxide with the bases are called *chromites*, and those of manganic oxide with the bases, *manganites*. To keep the nomenclature more or less uniform, the salts of the acid anhydride MnO_2 are called *permanganites*, and those of the acid unknown anhydride, FeO_2, are called **perferrites.** Similarly, the salts of the acid anhydride CrO_3 are called *chromates*, those of MnO_3, manganates, and those of FeO_3, ferrates. The ferrites can thus be regarded as salts of a monobasic *ferrous acid*, $HFeO_2$, which was obtained by J. M. van Bemmelen and E. A. Klobbie [1] as indicated below. It may be convenient to regard the ordinary ferrites as **metaferrites,** $R'FeO_2$, and the acid, $HFeO_2$, as **metaferrous acid.** The **orthoferrites,** $R_3'FeO_3$, are then regarded as salts of a tribasic **orthoferrous acid,** H_3FeO_3. The " ous " and " ic " nomenclature unfortunately goes wrong with the

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chromites, manganites, and ferrites; the orthoferrous acid, H_3FeO_3, is analogous with ferric hydroxide, $Fe(OH)_3$; and the iron is in the "ic" form. In a special case, discussed previously, it was convenient to consider ferric oxide, Fe_2O_3, as *ferric orthoferrite*, $Fe(FeO_3)$. Some **polyferrites** are known. The ferrites were discussed by L. E. R. Dufau, H. le Chatelier, S. Hilpert, etc.

A. Chondew observed that a ferrite is probably formed when potassium hydroxide is fused in an iron crucible, for, when the cold mass is boiled with water, some ferric oxide remains in soln.; and a similar soln. is produced when hydrated ferric oxide is boiled with conc. alkali-lye. The alkali ferrites are formed by the interaction of fused or conc. aq. soln. of the alkali hydroxides and ferric oxide or iron-rust. The removal of ferrites from caustic alkali-lye picked up in the evaporators is an important operation in the finishing of commercial caustic alkalies. Reducing agents—*e.g.* sulphur—is one method employed in reducing the ferrites and causing the iron hydroxides to separate from the soln. and ultimately to settle as a deposit at the bottom of the caustic pot. The dilution of the lye to less than 40 per cent. NaOH will precipitate most of the iron as hydrated oxide. G. C. Wittstein said that hydrated ferric oxide is slightly soluble in conc. alkali-lye, but L. Schaffner observed that this is a mistake, for the ferric oxide is only in a state of fine mechanical suspension. A. W. Bull and J. R. Adams studied the adsorption of sodium hydroxide by hydrated ferric oxide, and the results are summarized in Fig. 544. There is here no sign of the formation of a ferrite.

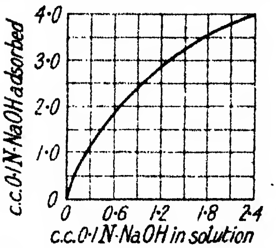


FIG. 544.—The Adsorption of Sodium Hydroxide by Hydrated Ferric Oxide.

E. Posnjak and T. F. W. Barth prepared **lithium ferrite,** $Li(FeO_2)$, or $Li_2O.Fe_2O_3$, by heating a conc. soln. of lithium hydroxide and ferric hydroxide in a press. bomb below 600°. The crystals were anisotropic. If the temp. exceeds 600°, an isotropic, cubic modification is produced, and also when lithium carbonate and ferric oxide in theoretical proportions are heated to redness. The X-radiograms show that the cubic form has one $Li_2O.Fe_2O_3$-molecule per unit cube which is of the sodium chloride type. The length of one edge is 4·141 A.; the sp. gr. is 4·368; and the refractive index, 2·40 for Li-light. S. Hilpert and co-workers studied the magnetization of this salt.

F. von Schaffgotsch prepared **sodium ferrite,** with the formula—presumably from the analyses of W. F. Salm-Horstmar, and J. M. van Bemmelen and E. A. Klobbie—$Na_2O.Fe_2O_3$, or $NaFeO_2$. F. von Schaffgotsch found that a mixture of a mol, or 78 parts of ferric oxide and a small excess of anhydrous sodium carbonate at a red-heat, gives off a little more than a mol or 23·9 parts of carbon dioxide, forming a liver-brown sodium ferrite which does not readily melt. The fracture is waxy and conchoidal. On exposure to air, sodium ferrite becomes reddish-brown and dull. Hot and cold water extract the alkali, leaving ferric oxide behind. W. F. Salm-Horstmar, O. Loew, and E. Mitscherlich prepared the salt in a similar way; M. O. Charmandarian and G. V. Martschenko, by heating a mixture (3 : 1) of iron oxide and sodium carbonate at 950°; and E. Mitscherlich, by calcining sodium ferric oxalate in air. The yellow product is decomposed by acids. J. d'Ans and J. Löffler obtained the ferrite by the action of ferric oxide on sodium hydroxide; and G. Rousseau and co-workers, by heating hydrated ferric oxide mixed with sodium hydroxide or carbonate up to 800° or 1000°. J. M. van Bemmelen and E. A. Klobbie prepared the alkali ferrites by the prolonged heating of ferric oxide with conc. alkali-lye, the resulting ferrite is partially soluble and gradually crystallizes. The crystals of the sodium salt appear at first to be crossed prisms, but they afterwards form hexagonal plates which sometimes become rhombohedral and spherical, or else they form long needles. The same crystals are produced when ferric oxide is heated with fused alkali carbonate or chloride. Excepting the hexagonal plates, the crystals of sodium ferrite are decomposed by water when they assume at first a pseudocrystalline form, and then pass into amorphous, hydrated ferric oxide.

The hexagonal plates of sodium ferrite, when treated with water, furnish *ferrous acid*, $Fe_2O_3.H_2O$, or $HFeO_2$, with the same crystalline form, transparency, and optical properties as the original ferrite. S. Goldsztaub found that the rhombohedral crystals have the parameters a=5·59 A., α=35° 20′, and the density 4·23. Ferrous acid is not hygroscopic, and it begins to lose water at 100°, whereas goethite can be heated to 300° without losing water.

According to G. Zirnité, when a strong current of air is blown into a hot, conc. soln. of soda containing about 34 per cent. of hydroxide, standing in an iron vessel, or to which finely divided hydrated ferric oxide has been added, perceptible quantities of iron are dissolved without colouring the liquid. The soln. remains clear and colourless for several days at the ordinary temp., but ultimately becomes turbid, yellow, and finally red, owing to the separation of the hydrated ferric oxide; this colour, however, disappears again on heating. When the colourless soln. is diluted, the ferric oxide is precipitated in about half an hour, but is re-dissolved by concentrating the dil. soln. Hydrogen sulphide at first produces a deep, cherry-red coloration in the colourless liquid, and on continuing the action a greenish-black precipitate is formed, leaving a clear soln. free from iron, but slightly yellow from the presence of sodium sulphide. G. Zirnité assumed that sodium ferrate is formed, but this hypothesis does not agree with F. Haber's observations, which show that sodium ferrite is produced. According to F. Haber, when a soln. of sodium ferrate is boiled for a sufficiently long time, it becomes colourless or pale yellow, provided that care has been taken to use materials which are free from manganese. The yellowish soln. contains a soluble ferrite, and when kept, deposits colourless crystals of a compound which very quickly decomposes when it is removed from the strongly alkaline liquid. The same soln. of ferric oxide is obtained by boiling ferric hydroxide with a conc. soln. of sodium hydroxide. Addition of an alkaline sulphide gives a red coloration, due to the formation of the double alkali iron sulphide to which the red liquors of Leblanc's alkali manufacture owe their colour. When pure iron is boiled gently for a few minutes with conc. sodium hydroxide soln., the liquid is found to contain ferrous oxide. When exposed to air, this soln. readily oxidizes to the ferric oxide soln. Both the soln. of ferrous and ferric oxide are readily oxidized to ferrate by electrolytic oxygen. O. Loew said that the salt is soluble in a conc. soln. of sodium hydroxide; but O. Sackur observed that it is insoluble in molten alkali chlorides or carbonates, and in molten alkaline earth chlorides. W. G. Mixter gave for the thermal value of the reaction: $Fe_2O_3+nNa_2O=Fe_2O_3.nNa_2O+58$ Cals. M. Matsui and co-workers found for the heat of the reaction $Na_2O+Fe_2O_3=2NaFeO_2+44·82$ Cals.; $Na_2CO_3+Fe_2O_3=2NaFeO_2+CO_2-32·06$ Cals.; $(2Na,2Fe,2O_2)=2Na_2FeO_2+248·08$ Cals.; and $2NaFeO_2+H_2O=2NaOH_{aq.}+Fe_2O_3-101·32$ Cals. V. I. Sokoloff found that the decomposition of sodium ferrite by water is endothermal—55·14 Cals.—and the heat of formation $(Na_2O,Fe_2O_3)=58$ Cals. The reaction between ferric oxide and sodium carbonate begins at 820°; and the press. of the gas is given by $\log p=-7539·6T^{-1}+1·75 \log T-0·001626T+6·0808$, from which it follows that $2NaFeO_2+CO_2=Na_2CO_3+Fe_2O_3+34·873$ Cals. at 25°. G. Grube and H. Gmelin showed that when iron which has been rendered active by cathode treatment is anodically polarized by a low-current density in a 40 per cent. soln. of sodium hydroxide and in complete absence of air, it passes into soln., in the bivalent condition, as *sodium hypoferrite*, Na_2FeO_2. at 80°, with a current density of 0·166 amp. per sq. dcm., 0·026M-soln. of sodium ferrite is formed. Sodium ferrite can be obtained by the anodic oxidation of an alkaline soln. of ferrous hydroxide, or by the cathodic reduction of sodium ferrate using platinum electrodes. A soln. of sodium ferrite is much more complex than an alkaline soln. of ferrous hydroxide. The anodic soln. of bivalent iron in 40 per cent. sodium hydroxide takes place at 80° at potentials ϵH −0·84 to −0·82 volt. At a slightly higher potential, ϵH --0·8 to —0·7, the oxidation process $2FeO_2'' + 2\oplus \rightleftharpoons Fe_2O_4''$ takes place. In 40 per cent. sodium hydroxide soln., the equilibrium potential of the process $Fe + 2\oplus \rightleftharpoons 2Fe''$ lies at $\epsilon H = -0·86$ volt. The subject was discussed by L. Rolla and R. Salani. S. Hilpert and co-workers studied the magnetization of the ferrites. W. G. Mixter reported the ferrite Na_3FeO_3; T. Wallace and A. Fleck, $Na_2Fe_3O_6$ or $Na_3Fe_5O_9$; and W. H. Schramm, $Na_2Fe_2O_5$.

W. F. Salm-Horstmar, E. Mitscherlich, and J. M. van Bemmelen and E. A. Klobbie prepared **potassium ferrite,** $K_2O.Fe_2O_3$, or $KFeO_2$, by the process employed for the sodium salt. The crystals of the potassium salt appear at first to be rhombic plates, but, as the heating is continued, and the water expelled, they become regular octahedra. W. F. Salm-Horstmar's analysis agrees with $3K_2O.4Fe_2O_3$, but J. M. van Bemmelen and E. A. Klobbie found $KFeO_2$. According to G. Rousseau and J. Bernheim, potassium ferrate is rapidly decomposed by fused potassium chloride or hydroxide to form potassium ferrite and oxygen. The alkalinity of the flux has no influence on the result, as is also the case with barium ferrate. If potassium hydroxide be employed, the ferrite is not changed by continued heating at bright redness, but if the flux is a mixture of hydroxide and chloride, the ferrite is gradually converted into reddish, transparent crystals of hydrated ferric hydroxide, containing about 3 per cent. of alkali. The general properties of potassium and sodium ferrite are similar. S. Hilpert and co-workers found that the alkali ferrites prepared in the wet way are indifferent in a strong magnetic field, but when prepared in the dry way, they are strongly magnetic. The magnetic properties are lost at 150°. S. Hilpert and A. Lindner prepared the potassium ferrites $K_2O.Fe_2O_3$, $K_2O.2Fe_2O_3$, and $K_2O.7Fe_2O_3$, and examined their X-radiograms. Similarly with the **rubidium ferrite,** $Rb_2O.Fe_2O_3$; and with the **cæsium ferrite,** $Cs_2O.Fe_2O_3$.

C. Friedel found a dark grey mineral on the lithomarge of Ekaterinburg, Siberia, and he called it **delafossite**—after G. Delafosse. It occurs in small, tabular crystals which are cleavable into thin, opaque laminæ of sp. gr. 5·07. According to A. F. Rogers, delafossite occurs in mines at Bisbee, Arizona, and the analysis corresponds with **cuprous ferrite,** $CuFeO_2$. The rhombohedral crystals are trigonal with the axial ratio $a : c = 1 : 1·94$. The hardness is 5·5. The mineral fuses easily and becomes magnetic. It is soluble in hydrochloric and sulphuric acids, but not in nitric acid. S. Hilpert melted together cuprous oxide and ferric oxide at 1250° in an atm. of nitrogen and obtained a black, magnetic mass; by treating a mixed soln. of cuprous and ferric salts with alkali, cuprous ferrite is formed, as a flocculent black mass which becomes crystalline at 900°. A. C. Halferdahl found that copper ferrite melts at 1458°; and F. S. Wartman and G. L. Oldright said that copper ferrite probably exists in the slags from pyrite smelting. E. V. Shannon discussed the formation of ferromagnetic $CuO.Fe_2O_3$. K. List obtained **cupric ferrite,** $Cu(FeO_2)_2$, by heating a powdered mixture of cupric and ferric oxides; V. Y. Mostovich and G. S. Uspensky said that the reaction begins at 600°, and proceeds rapidly at 750°. P. T. Walden recommended heating the mixture in an electric furnace, and removing the excess of ferric oxide by a magnet and levigation; and W. Stähl recommended heating a mixture of 5 grms. of cuprous oxide and 16·7 grms. of ferric oxide at 750° to 800° in a covered porcelain crucible in a muffle. K. List also obtained it by heating to redness a mixture of cupric and ferrous nitrates, and by adding potash-lye to a mixed soln. of ferric chloride and cupric sulphate to precipitate all the copper and iron. The dirty yellow precipitate when dried in vacuo over sulphuric acid forms a cinnamon-brown powder of the *pentahydrate*. It becomes anhydrous at a red-heat. K. List also prepared cupric ferrite by treating a soln. of ferric chloride with cupric oxide, when a brownish-yellow precipitate is formed. S. Holgersson found that the X-radiograms of the spinel-like crystals had the lattice parameter $a = 8·445$ A. This was confirmed by H. Forestier. W. Biltz and co-workers found that the $Cu(FeO_2)_2$ spinel had the mol. vol. 45·3, where the CuO has the mol. vol. 12·6, and the Fe_2O_3, 32·7. H. Forestier found that the curve showing the expansion at different temp. has a break at 455°. S. Loria and C. Zakrzewsky found the indices of refraction, μ, and the coeff. of extinction, k, for light of wave-length, λ, to be :

λ .	4390	4660	5530	5896	6330	7040
μ .	2·77	2·76	2·73	2·71	2·67	2·59
k .	0·69	0·59	0·47	0·29	0·25	0·16

The brownish-black cupric ferrite is magnetic. S. Hilpert obtained cupric ferrite as in the case of cuprous ferrite ; and by compressing a mixture of powdered cupric and ferric oxides, and sintering at 100°. The magnetic permeability disappears at 280°. O. C. Ralston observed the formation of zinc and copper ferrites in the roasting of sulphide ores at about 650°, and the cupric ferrite so formed resists the action of the 5 to 10 per cent. sulphuric acid used in leaching, so that losses occur. H. Forestier and G. Chaudron obtained the ferrite by precipitation from a mixture of the component chlorides,by sodium hydroxide, and then heating the precipitate. The mean magnetic susceptibility of copper ferrite obtained by H. Forestier and G. Chaudron, is 102×10^{-3} mass unit between 0 and 100 gauss. S. Hilpert and co-workers, and A. Serres made observations on this subject. H. Forestier observed that the magnetization decreases slowly with rise of temp., but there is an abrupt decrease at 420° which ends at 450°, a temp. corresponding with the Curie point. The relation between the strength of the magnetic field and the intensity of magnetization is shown in Fig. 545. A. Serres, and S. Veil studied the magnetic properties of copper ferrite. E. Wilson and E. F. Herroun found that the ferrites have higher magnetic susceptibilities than ferric oxide, and observed values for cupric ferrite. V. Y. Mostovich and G. S. Uspensky found that the ferrite is insoluble in soln. used for extracting copper oxide in hydrometallurgy. It is decomposed by sulphur dioxide at 500° to 600° ; and by calcium oxide, and other strong bases. P. T. Walden said that no blue precipitate is formed when cupric ferrite is treated with a soln. of potassium ferricyanide.

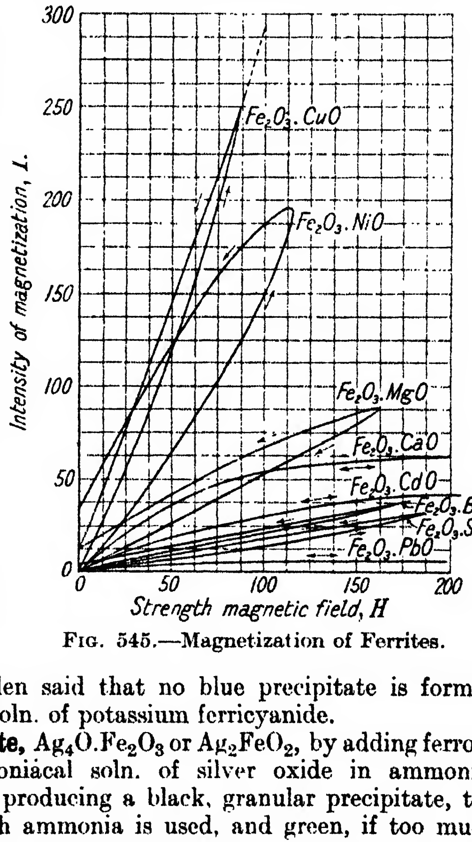


FIG. 545.—Magnetization of Ferrites.

H. Rose prepared **silver hemiferrite,** $Ag_4O.Fe_2O_3$ or Ag_2FeO_2, by adding ferrous sulphate to an excess of an ammoniacal soln. of silver oxide in ammonia. N. W. Fischer found that instead of producing a black, granular precipitate, the colour is yellowish-brown if too much ammonia is used, and green, if too much ferrous sulphate is added. Ammonia extracts a little silver oxide from the precipitate and colours it yellowish-brown. Hydrochloric acid converts it into ferric chloride and a precipitate of reddish-grey silver chlorides, and if the precipitate be treated with ammonia, metallic silver remains undissolved, suggesting that the precipitate contains silver suboxide. It is probable that this product contains some ferric hydroxide associated with colloidal silver. According to M. C. Lea, a soln. of ferric alum readily dissolves silver at the ordinary temp., with production of a ferrous salt, and if the ferric compound is in excess, the whole of the silver is dissolved. When ferrous sulphate soln. is mixed with successive quantities of silver oxide until a fresh quantity of the latter is no longer affected, the whole of the iron is precipitated, and a black product is obtained which is probably the compound $Ag_4O.2FeO.Fe_2O_3$ obtained by H. Rose in the same way. When a soln. of ammonium ferric alum is mixed with a large excess of finely divided silver in a well-closed vessel and allowed to remain for several days, with frequent agitation, the liquid acquires a deep red colour, which may persist for several days, but then gradually disappears, the soln. becoming greenish, although it still contains a considerable quantity of ferric salt. It follows that the reducing action of silver on ferric salts is limited and ceases before reduction is complete, even when the silver is present in large excess. K. Pilawsky, and A. Krause and K. Pilawsky prepared **silver ferrite,** $(AgFeO_2)n$, by the action of a soln. of silver nitrate on yellow metaferric hydroxide, FeO.OH, obtained by the action of air on ferrous hydroxide, or ferrous acid, $(HFeO_2)_n$, in soln. of $p_H=5{\cdot}2$, and peptized in $0{\cdot}01N$-acetic acid; if brown orthoferric hydroxide, obtained by the action of alkali on a ferric salt, $p_H=7{\cdot}7$, is used, then **silver hydroferrite,** $Ag_3H(FeO_2)_2$, is formed. The salt was studied by A. Krause and W. Buczkowsky.

The bleaching action of calcium oxide on the yellowish or reddish-brown colour produced by ferric oxide in clays has long been known in the ceramic industries, and attributed to the formation of a calcium ferrite of paler tint. Thus, the effect is mentioned by H. Seger. According to J. Percy, ferric oxide forms fusible compounds with calcium oxide if the mixture in theoretical proportions for **calcium ferrite,** $CaO.Fe_2O_3$, or $(CaFeO_2)_2$, be heated to whiteness in an oxidizing atmosphere. The mass of dark brown, interlacing, acicular crystals is magnetic, and it has a sp. gr. 4·693. The composition is said to be analogous to that of magnetite with ferrous oxide replaced by calcium oxide, or to that of a spinel with alumina replaced by ferric oxide. S. Hilpert and A. Lindner examined the X-radiograms of $CaO.Fe_2O_3$. H. O. Hofmann and W. Mostowitsch prepared a crystalline calcium ferrite by heating equimolar proportions of calcium sulphate and ferric oxide. Sulphur dioxide and oxygen were given off at 1100°, and at 1250° the mass was molten. The calcium ferrites in Portland cements were described by H. Kühl, and R. Nacken and M. E. Grünewald. C. E. Swartz and F. C. Krauskopf obtained non-magnetic calcium ferrite by heating calcium oxide and ferric oxide above 650°. L. Jacqué found that the first clear signs of fusion with mixtures of ferric and calcium oxides were obtained at the following temp.:

CaO .	0	5	10	20	26	30	40	50	60	70 per cent.
Temp. .	>1500°	1455°	1290°	1230°	1220°	1220°	1245°	1370°	1430°	>1500°

If the mixtures are kept until completely fused, a portion of the ferric oxide is dissociated, and some ferrous oxide is formed. This reduces the f.p. of the mixture. The ratio $Fe_2O_3 : FeO$ approaches 2·22 on prolonged heating, and the ratio 2·22 corresponds with Fe_3O_4. J. Pelouze obtained a product, which he represented by the formula $4CaO.Fe_2O_3$, by adding an excess of potash-lye to a soln. containing a mol of ferric and 4 mols of calcium chloride; H. Forestier and G. Chaudron obtained calcium ferrite by a similar process; K. List, by adding lime-water to a soln. of ferric chloride, washing the product with lime-water, and heating it to redness. S. Hilpert prepared calcium ferrite by the fusion process. J. Guillissen did not obtain definite results for the temp. at which the reaction between ferric oxide and calcium carbonate begins. H. Forestier observed that the ferromagnetic crystals are not cubic, and may have a face-centred, tetragonal lattice with $a : c=1 : 0{\cdot}8$. The ferromagnetic property relates to an unstable state which is lost at higher temp.

S. Hilpert and E. J. Kohlmeyer studied the binary system, $CaO-Fe_2O_3$, thermally, and their results are summarized in the curve, Fig. 546. Under the conditions of the experiments, mixtures with less than 31 molar per cent. of ferric oxide were very viscid, and the last portion solidified at 1410°. The calcium oxide formed well-developed crystals. With less than 75 molar per cent. of calcium oxide, the primary crystallization is that of **calcium orthoferrite,** $3CaO.Fe_2O_3$, which melts at 1410°, and disintegrates, like calcium orthosilicate, when cooled. The next compound formed is $3CaO.2Fe_2O_3$, or **calcium tetraferrite,** which melts at 1450°. This solid, at 1220°, undergoes a reaction forming a compound **pentacalcium hexaferrite,** $5CaO.3Fe_2O_3$, resembling the corresponding aluminate, $5CaO{\cdot}3Al_2O_3$. E. D. Campbell obtained a ferrite, $5CaO.3Fe_2O_3$, and said that it is isomorphous with $5CaO.3Al_2O_3$. R. Nacken and M. E. Grünewald examined the red crystals of this salt and found them to be doubly refracting. N. M. Yasuirkin gave 6·9 Cals. for the heat of formation of $3CaO.Fe_2O_3$; and 2·9 Cals. for that of $4CaO.Fe_2O_3$.

J. Pelouze, and W. Pukall reported $4CaO.Fe_2O_3$; W. Pukall, and E. Diepschlag and E. Horn, $3CaO.Fe_2O_3$; R. Nacken and M. E. Grünewald, $5CaO.3Fe_2O_3$; F. Martin and O. Fuchs, $3CaO.2Fe_2O_3$; and Z. Weyberg, $2CaO.5Fe_2O_3$. E. Martin reported the hydrate, $CaO.4Fe_2O_3.6H_2O$, or $CaO.3Fe_2O_3.5H_2O$; and $CaO.2Fe_2O_3.2H_2O$; $CaO.Fe_2O_3.H_2O$; $3CaO.2Fe_2O_3.3H_2O$; $4CaO.2Fe_2O_3.3H_2O$; $6CaO.2Fe_2O_3.3H_2O$; W. Michaelis, $3CaO.Fe_2O_3.3H_2O$; and H. le Chatelier, $4CaO.Fe_2O_3.12H_2O$.

Returning to S. Hilpert and E. J. Kohlmeyer's diagram, Fig. 546, there is a eutectic at 1200°, and 50 mol. per cent. of calcium oxide; and a second maximum at 1400°, corresponding with **dicalcium hexaferrite,** $2CaO.3Fe_2O_3$. Below the eutectic temp., **calcium metaferrite,** $CaO.Fe_2O_3$, or $Ca(FeO_2)_2$, is present. The behaviour of mixtures rich in ferric oxide is complicated, partly owing to the escape of oxygen, and the formation of magnetite. Calcium metaferrite was also prepared by W. C. Hansen and co-workers—*vide infra*—W. F. Salm-Horstmar, W. Pukall, K. List, S. Peacock, K. Endel, C. E. Swartz and E. C. Krauskopf, H. O. Hofmann and W. Mostowitsch, O. Schott, H. Moissan, and J. Percy; whilst E. Diepschlag and E. Horn prepared the 2 : 1, 5 : 3, and the 1 : 1 ferrites. R. B. Sosman and H. E. Merwin could not confirm S. Hilpert and E. J. Kohlmeyer's five calcium ferrites. The equilibrium diagram is summarized in Fig. 547, and only two ferrites were observed. The compound $2CaO.Fe_2O_3$ dissociates and is in equilibrium with calcium oxide and liquid at 1436°, and all mixtures with less than 36 molar per cent. of calcium oxide, up to pure calcium oxide, liquefy in part at this temp., leaving pure calcium oxide as the solid phase in excess. The compound $CaO.Fe_2O_3$ dissociates and is in equilibrium with $2CaO.Fe_2O_3$, and liquid at 1216°, and all mixtures between about 35 and 62 molar per cent. Fe_2O_3 liquefy in part at 1216°, forming liquid, and $2CaO.Fe_2O_3$ as solid phase in excess. This dissolves as the temp. rises and disappears at the liquidus curve. The compound $CaO.Fe_2O_3$ dissociates and is nearly all liquefied at 1216°—J. Konarzewsky gave 1251°—and at 1250° the solid phase, $2CaO.Fe_2O_3$, formed by dissociation, all disappears. The

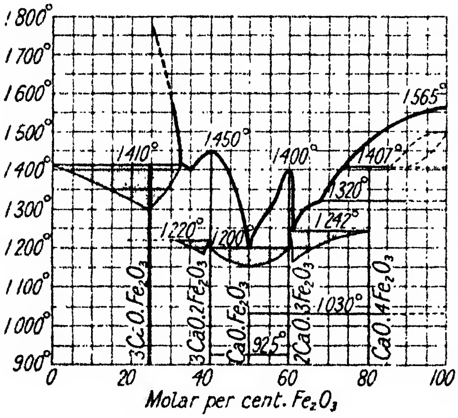


FIG. 546.—Freezing-point Curves of the Binary System : $CaO–Fe_2O_3$.

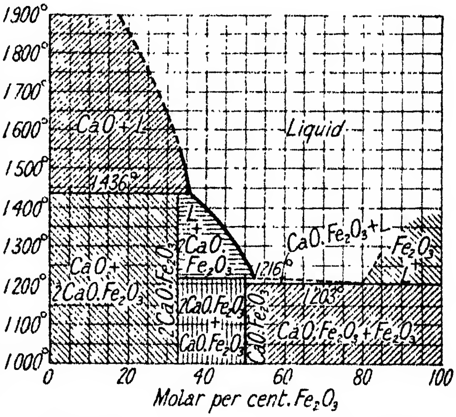


FIG. 547.—Freezing-point Curve of the System : $CaO–Fe_2O_3$.

eutectic at 1203° between calcium metaferrite and ferric oxide has between 75 and 90 per cent. ferric oxide and is probably nearer the former amount. No optical evidence of solid soln. of calcium oxymetaferrite with calcium oxide or calcium metaferrite, or of calcium metaferrite with calcium oxymetaferrite or ferric oxide was observed. M. E. Grünewald verified the results with 40 to 65 molar per cent. of calcium oxide. E. D. Campbell studied the mixed crystals with calcium aluminate. N. M. Yasuirkin gave 1·5 Cals. for the heat of formation of $CaO.Fe_2O_3$. S. Nagai and K. Asaoka found that calcium metaferrite is not acted on by water. E. Diepschlag and E. Horn said that the orthoferrite reacts with calcium sulphide at 800°, but not with ferrous sulphide below 1150°. **Calcium oxymetaferrite,** or *calcium oxyferrite*, $2CaO.Fe_2O_3$ or $Ca_2O(FeO_2)_2$, is formed at 1436° in well-developed, black crystals, which are yellowish-brown by transmitted light. M. E. Grünewald also obtained tabular crystals of calcium oxymetaferrite. E. Martin gave 1300° to 1325°, R. Nacken and M. E. Grünewald, 1380° to 1420°; J. Konarzewsky, 1440°; O. Schott, 1500°; and O. Andersen, 1436° for the incongruent m.p. of the oxymetaferrite. This compound was also prepared by C. W. Hansen and co-workers, and by S. Nagai and K. Asaoka, W. Pukall, V. Vincent, W. Lerch and R. H. Bogue, and O. Schott—*vide infra*. According to R. B. Sosman and H. E. Merwin, the melted substance may be under-cooled to 1385°, but it always shows traces of the dissociation products, calcium metaferrite and oxide. Calcium oxymetaferrite furnishes positive, biaxial crystals with a moderate optic axial angle. N. M. Yasuirkin gave 32·03 Cals. for the heat of formation of $2CaO.Fe_2O_3$. The indices of refraction for Li-light are: $\alpha=2{\cdot}200$, $\beta=2{\cdot}220$, and $\gamma=2{\cdot}290$; and for Na-light, $\alpha=2{\cdot}25$, whilst β and γ have a lower dispersion. The transition temp. at which the metaferrite dissociates and is in equilibrium with the oxymetaferrite is 1216°. Calcium metaferrite forms deep red crystals which are negative, and uniaxial. E. Martin gave 1225° to 1250°; R. Nacken and M. E. Grünewald, 1220° to 1230°; H. O. Hofmann and W. Mostowitsch, 1250°; S. Hilpert, 1200°; and O. Andersen, and R. B. Sosman and H. E. Merwin, 1216°, for the incongruent m.p. of the metaferrite. According to R. B. Sosmann and H. E. Merwin, the refractive indices are: $\omega=2{\cdot}465$ and $\epsilon=2{\cdot}345$ for Li-light; and for Na-light, $\omega=2{\cdot}58$ and $\epsilon=2{\cdot}43$. S. Nagai and K. Asaoka observed that $2CaO.Fe_2O_3$ is slowly decomposed by water. According to R. B. Sosman and H. E. Merwin, a considerable amount of ferrous oxide or magnetite was formed with mixtures containing less than 50 mol. per cent. of lime, but with higher proportions of lime, the amount of ferrous oxide formed below 1500° is relatively small.

O. Andersen, R. Nacken and M. E. Grünewald, and E. D. Campbell obtained results confirming R. B. Sosman and H. E. Merwin's view that there are only two definite calcium ferrites. According to E. Martin, the calcium ferrite which is formed on heating a mixture of ferric oxide and calcium carbonate depends on the proportions in which the ingredients are mixed, and not on the temp. attained; thus, at 1200°, the 1 : 1 mixture furnishes the metaferrite, and the 1 : 2 mixture, the oxymetaferrite. The powdered metaferrite has a sp. gr. near 4, it is magnetic, and non-hydraulic; the powdered oxymetaferrite has a sp. gr. below 4, it is magnetic, and has a hardness of 6. H. Forestier said that the structure, from the X-radiograms, is not cubic. R. Nacken and M. E. Grünewald said that in the presence of much molten calcium chloride, the metaferrite forms rhombic needles, and the oxymetaferrite, plates. Only these two compounds are formed in the presence of an excess of molten calcium chloride. When equimolar proportions of ferric and calcium oxides with half their weight of calcium chloride are melted 2 to 4 days at 1200°, $5CaO.3Fe_2O_3$ is formed, and if 3 mols or more of calcium oxide and 1 mol of ferric chloride be treated in a similar way, calcium oxymetaferrite is formed. The fusion curve of calcium metaferrite and aluminate is shown in Fig. 547.

According to S. Hilpert and E. J. Kohlmeyer, molten mixtures of calcium and ferric oxides furnish brown to black products—those with a large proportion of ferric oxide are steel-grey, and the colour becomes paler with increasing proportions of calcium oxide. Many different tints were observed, according to the temp. at which the different mixtures were sintered. M. E. Grünewald found the crystals of $CaO.Fe_2O_3$ are rhombic. The hardness decreases with increasing proportions of calcium oxide. The sp. vol. curve shows a sharp change of direction when $CaO.Fe_2O_3$ is formed, and another, less distinct break occurs near 20 molar per cent. CaO. The following is a selection from the sp. gr. and sp. vol. data for different molar percentages of calcium oxide of sp. gr. 3·316, and ferric oxide, of sp. gr. 5·190:

CaO .	10	17·5	22	27	41	50	56	64
Sp. gr. .	5·025	4·878	4·844	4·785	4·724	4·683	4·480	4·213
Sp. vol. .	0·1982	0·2018	0·2064	0·2089	0·2177	0·2135	0·2232	0·2374

R. Nacken and M. E. Grünewald gave 5·08 for the sp. gr. of $CaO.Fe_2O_3$; 3·98 for that of $2CaO.Fe_2O_3$; and 4·02 for that of $5CaO.3Fe_2O_3$. The electrical conductivity is very small even with fused ferric oxide, which is only 10^{-10} of that of iron. Solid soln. are not formed. The magnetic properties diminish with the proportion of iron, and become insignificant with over 67 molar per cent. of calcium oxide. H. Forestier and G. Chaudron gave $42·3\times10^{-3}$ mass unit for the mean magnetic susceptibility of calcium ferrite between 0 and 100 gauss; and they found that it loses its magnetic properties irreversibly when heated to 700°. The heating and cooling magnetization temp. curves coincide, unless the heating has been above the Curie point, in which case the Curie point is depressed from 425° to 150°, so that it is completely transformed into a paramagnetic substance if kept at a high temp. for some time. H. Forestier's observations on the relation between the strength of the magnetic field, and the intensity of magnetization were discussed in connection with Fig. 545. S. Hilpert and co-workers added that this ferrite loses its magnetic permeability at 160°. The calcium ferrites were also studied by S. Nagai and K. Asaoka. S. Hilpert and E. J. Kohlmeyer observed that the calcium ferrites are much less readily attacked by reagents than the silicates, and hence they are better than silicates in cements for resisting the attack of sea-water. Mixtures with 60 to 70 molar per cent. of calcium oxide are hydraulic. W. Pukall, S. Nagai and K. Asaoka, E. Martin, and J. Konarzewsky said that $CaO.Fe_2O_3$ is not changed by long contact with water, and it possesses no hydraulic properties, but O. Schott, and K. Zulkowsky did not accept this conclusion. J. Konarzewsky, W. Pukall, S. Nagai and K. Asaoka, and K. Zulkowsky noted that $2CaO.Fe_2O_3$ does possess hydraulic properties in hardening under water, but not so much as Portland cement. Calcium ferrites are less readily reduced than ferric oxide. W. Odling said that hydrogen sulphide does not attack calcium ferrite. According to E. Martin, the metaferrite is insoluble in 10 per cent. acetic acid, and in a hot or cold soln. of sodium carbonate, or of ammonium chloride. It is slightly soluble in a soln. of lime and sugar, and it is slowly attacked by oxalic acid. An excess of alumina decomposes the ferrite at a high temp., 1200°, whilst with silica, silicoferrites are formed. The oxymetaferrite resembles the metaferrite in its chemical behaviour, except that it is attacked slowly by 10 per cent. acetic acid, it is also slightly attacked by a boiling soln. of sodium carbonate, and is entirely decomposed by a hot soln. of ammonium chloride. W. H. MacIntyre and W. M. Shaw observed that whilst ignited ferric oxide shows no tendency to absorb appreciable amounts of calcium sulphate, freshly precipitated ferric oxide and lime, in the proportions $3CaO : Fe_2O_3$, readily does do. H. le Chatelier, and K. List obtained a **calcium dichlorometaferrite,** $CaCl_2.Ca(FeO_2)_2$, or $Ca(Cl)FeO_2$, in bright, prismatic crystals, by dissolving calcium and ferric oxide in fused calcium chloride. It is not decomposed by water or air.

H. Forestier prepared **strontium ferrite,** $SrO.Fe_2O_3$, and observed an irregularity in the dilation curve near 480°, the Curie point. The relation between the magnetic field and intensity of magnetization are shown in Fig. 545. H. Forestier said that the X-radiogram indicates a hexagonal lattice with the ratio $a:c=0:1·8$. F. Martin and O. Fuchs prepared $2SrO.Fe_2O_3$; and H. Borck reported a hydrated strontium ferrite. S. Hilpert and A. Lindner studied the X-radiograms of the strontium ferrites $SrO.Fe_2O_3$, $2SrO.3Fe_2O_3$, $SrO.2Fe_2O_3$, and $SrO.4Fe_2O_3$. E. Martin prepared **barium ferrites** as in the case of calcium ferrites; and similarly with E. J. Maumené, and W. Mostowitsch. J. Guillissen found that the reaction between ferric oxide and barium carbonate begins at about 830°, and with barium oxide at about 1300°. The reaction was studied by J. Guillissen and P. J. van Rysselberghe. G. Rousseau and J. Bernheim found that if barium ferrate is introduced into barium chloride or barium bromide fused at 800° to 1300°, it rapidly decomposes with effervescence, owing to the liberation of oxygen, and leaves a residue of ferric oxide. If, however, about 3 grms. of barium ferrate are added gradually to a fused mixture of 15 grms. of barium chloride or bromide, and 5 grms. of barium oxide, and the product is treated with water, it yields brownish-black crystals of barium ferrite. At 1100°, about 6 grms. of barium oxide are required to prevent the decomposition of the ferrite, and at an orange-red heat 12 grms. are necessary. It follows from these results, that whereas barium ferrate, if heated alone, decomposes into oxygen, ferric oxide, and barium oxide, yet, when heated with barium oxide, it yields oxygen and barium ferrite. The decomposition of the ferrate in presence of neutral or slightly basic fluxes is analogous to the decomposition of alcoholates by dilution, but the latter is progressive whilst the former takes place suddenly as soon as the proportion of barium oxide has fallen below a certain limit. If barium carbonate is present, it crystallizes from the oxychloride which is formed, and the crystals are not readily separated from those of the ferrite. S. Hilpert prepared barium ferrite in the wet way as in the case of calcium ferrite. It is non-magnetic unless it has been heated to 800° and cooled. S. Hilpert and A. Lindner studied the X-radiograms of the barium ferrites $BaO.Fe_2O_3$, $2BaO.3Fe_2O_3$, $BaO.2Fe_2O_3$, $BaO.3Fe_2O_3$, and $BaO.4Fe_2O_3$. H. Forestier said that the X-radiogram of $BaO.Fe_2O_3$ corresponds with a hexagonal lattice. H. Forestier and G. Chaudron prepared barium ferrite as in the case of calcium ferrite, and found that its mean magnetic susceptibility is $9·9\times10^{-5}$ mass unit between 0 and 100 gauss. H. Forestier observed a break in the dilation curve near 445°, and this temp. is also the Curie point. The relation between the strength of the magnetic field, and the intensity of magnetization is shown in Fig. 547. S. Hilpert and co-workers studied the magnetic properties of these ferrites.

H. Forestier and M. Galand prepared **beryllium ferrite,** $Be(FeO_2)_2$, and found that the crystal lattice has the structure of lepidocrocite; so that BeO in the ferrite plays the part of water in lepidocrocite. The ferrite decomposes at 360° into BeO and Fe_2O_3. S. Hilpert and co-workers studied the magnetic properties. C. F. Rammelsberg described crystals of a mineral resembling magnetite which was obtained in the vicinity of the fumaroles of Vesuvius, and particularly about those of the eruption of 1855. He called the mineral *magnoferrite*, G. A. Kenngott, *magneferrite*, and J. D. Dana, **magnesioferrite.** The crystals and their associations were described by A. Scacchi, G. vom Rath, H. Bücking, G. Leonhard, A. Lacroix, and F. Zambonini. Before C. F. Rammelsberg's examination, the crystals had been mistaken by T. Monticelli and N. Covelli, D. F. Wiser, A. Scacchi, and A. Krantz, for magnetite, hæmatite, or martite. According to F. Cornu, magnesite crucibles made from sintered magnesite contain crystals of periclase and of magnesioferrite. The analyses of C. F. Rammelsberg correspond with $3MgO.4Fe_2O_3$, but the presence of ferric oxide as an impurity in the samples lead him to suggest the formula for **magnesium ferrite,** $MgO.Fe_2O_3$, or $Mg(FeO_2)_2$. W. Weyl, and S. Holgersson obtained crystals by sintering at 1200° a mixture of equimolar parts of magnesia and ferric oxide, and heating the product with three times its weight of potassium chloride at 1200° in a platinum crucible for 40 hrs. K. A. Hofmann and K. Höschele found that magnesium chloride is an excellent mineralizer for making crystals of this spinel. Analyses were reported by T. L. Watson, G. S. Rogers, and E. Hugel. K. A. Hofmann and K. Höschele heated the mixture with an excess of magnesium chloride; H. Müller heated ferric oxide with an excess of potassium magnesium sulphate; and F. Hundeshagen heated the metal with molten hydrated magnesium chloride. H. St. C. Deville, E. Posnjak, and R. Nacken and M. E. Grünewald prepared magnesioferrite crystals by heating a mixture of magnesia and ferric oxide in a current of hydrogen chloride. J. Morozewicz obtained crystals of magnesioferrite, associated with spinel, on heating silicate magma rich in ferric oxide, magnesia, and alumina. T. Weyl, and R. Nacken and M. E. Grünewald said that the constituent oxides do not react at temp. up to 1200°, but K. Endel, L. E. R. Dufau, C. W. Parmelee and co-workers, and C. E. Swartz and F. C. Krauskopf obtained magnesium ferrite by heating an intimate mixture of magnesia with ferric oxide above 650°—H. Forestier said that the reaction commences at about 350°; W. C. Hansen and L. T. Brownmiller recommended a calcination temp. of 1450°. K. A. Redlich reported that some black crystals he observed in some magnesite refractories employed in the lining of a steel furnace were probably those of magnesium ferrite.

H. S. Roberts and H. E. Merwin studied the ternary system $MgO-FeO-Fe_2O_3$ above 1000°, and with an oxygen pressure on the isobar 0·2 atm. They observed two solid soln. fields: The solid soln. *A* begins at MgO below 1000° and extends with increasing temp. towards $Mg(FeO_2)_2$ and FeO. In Fig. 548, the field *A* is bounded by curve I, the $MgO-Fe_2O_3$ side of the triangle. A liquid phase appears at 1770°, where the solid soln. contains iron oxide equivalent to 73 per cent. of Fe_2O_3. The solid soln. *B* extends with increasing temp. from $Mg(FeO_2)_2$ towards the iron oxide boundary which it reaches at 1386°. Solid soln. of about 1 per cent. of MgO in $Mg(FeO_2)_2$ may occur between 1750° and about 1000°. In Fig. 548, the field *B* is bounded by the curves III and V. The isotropic grains had the index of refraction 2·34 for Li-light. X-radiograms of the crystals were obtained. It forms a solid soln. with 91 per cent. $MgO.Al_2O_3$. The structure was also studied by H. Forestier, and T. F. W. Barth and E. Posnjak. For solid soln. of magnesium ferrite with ferric oxide and with magnesia, see Fig. 548. The subject was discussed by H. S. Roberts and H. E. Merwin, R. Nacken and M. E. Grünewald, C. E. Swartz and F. C. Krauskopf, and R. Schenck and T. Dingmann.

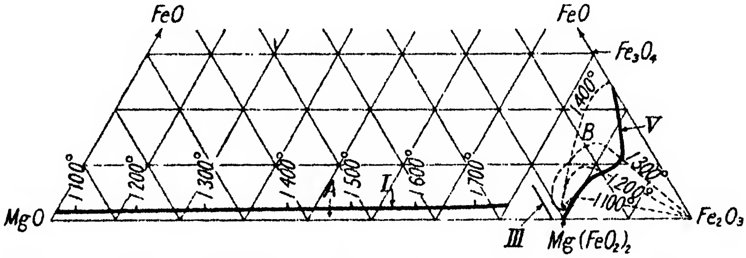


FIG. 548.—Portion of the Equilibrium Diagram of the Ternary System: $MgO-FeO-Fe_2O_3$.

According to C. F. Rammelsberg, and H. St. C. Deville, the cubic crystals of magnesioferrite occur in octahedra, or octahedra with truncated edges. W. Weyl's observations with the X-radiograms show that the crystal-lattice is of the spinel type. E. Posnjak found a=8·36 A., for the unit lattice containing 8 mols. $Mg(FeO_2)_2$ per unit cell; G. L. Clark and co-workers gave a=8·366 A.; and S. Holgersson gave a=8·342 A.; and L. Passerini, a=8·360 A. M. L. Huggins discussed the electronic structure. E. Posnjak found that the calculated density is 4·518 and the observed 4·481. L. Passerini gave 4·436; and S. Holgersson, 4·53; W. Biltz and co-workers found the mol. vol. to be 44·1 with 11·3 belonging to MgO, and 3·28 to Fe_2O_3. The index of refraction for Li-light is 2·34. The sp. gr. ranges from 4·568 to 4·654; A. Bergeat gave 4·998 to 5·247. The hardness ranges from 6·0 to 6·5. H. Forestier observed a reversible break in the dilation curve at about 315°. R. Nacken and M. E. Grünewald found the m.p. to be too high for them to obtain an equilibrium diagram of the binary system MgO–Fe_2O_3. They observed no reaction occurred with the well-mixed, powdered components at 1200°. K. A. Hofmann and K. Höschele obtained magnesium ferrite in solid soln. with magnetite, and in octahedral crystals by fusing mixtures of magnesia and ferric oxide with an excess of dehydrated magnesium chloride. R. Nacken and M. E. Grünewald examined the effect of heat on various mixtures of the components and in every case obtained no complex other than $Mg(FeO_2)_2$; they employed H. St. C. Deville's process and obtained black, octahedral crystals of sp. gr. 3·6. There was evidence that between 1350° and 1450° some change occurs in the crystals; there was no sign of fusion at 1550°. H. S. Roberts and H. E. Merwin said that this compound dissociates slightly and begins to melt at 1750°, and they observed the formation of a solid soln. with magnesia. H. Forestier gave 1650° to 1700° for the m.p. F. Beijerinck said that magnesioferrite is a good electrical conductor. H. Forestier and G. Chaudron gave 1700° for the m.p. and added that it is stable below that temp. They observed the temp. of the magnetic transformation of mixtures of magnesia with 2 to 50 per cent. of ferric oxide to remain constant at 310°, and magnesium ferrite remains in the free state; with 50 to 56 per cent. of ferric oxide, the temp. rises to 400°, and a solid soln. of the ferrite in ferric oxide is formed; with 56 to 100 per cent. of ferric oxide, the temp. is 675° corresponding with that of ferric oxide alone. The mean magnetic susceptibility of magnesium ferrite is 54×10^{-3} mass unit. The Curie point observed by H. Forestier with different mixtures is shown in Fig. 549. The relation between the strength of the magnetic field and the intensity of magnetization is shown in Fig. 545. S. Hilpert and co-workers, A. Serres, S. Holgersson and A. Serres, and E. Wilson and E. F. Herroun studied the susceptibility of magnesium ferrite. S. Hilpert said that magnesium ferrite prepared in the wet way is non-magnetic until fused. A. Serres studied the magnetic properties of magnesium ferrite. H. St. C. Deville observed magnesium ferrite is insoluble in hot nitric acid; and C. E. Swartz and F. C. Krauskopf, that it is insoluble in alkali-lye, and in dil. acids, but soluble in conc. hydrochloric acid.

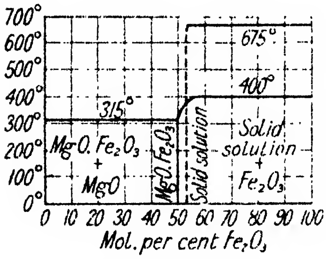


FIG. 549.—The Curie Point with the MgO–Fe_2O_3 System.

K. Kraut added a mixed soln. of a mol of a ferric salt and 6 mols of a magnesium salt to potash-lye of sp. gr. 1·1, and boiled the mixture for some hours. The brown precipitate first formed becomes white. It can be dried without change of colour at 120°, but if heated to redness, it becomes a rust-brown colour. Its composition was assumed to be that of the *enneahydrate* of **magnesium pentoxyferrite,** $5MgO.Mg(FeO_2)_2.H_2O$. It attracts carbon dioxide from the air; it becomes green when in contact with ammonium sulphide for 24 hrs.; it is not changed by ammonia; and when it is heated with ammonium chloride, it forms ferric oxide and magnesium chloride. According to L. J. Igelström, golden yellow or silvery white scales of a mineral occur in the iron-mine of Långban, Wermland, Sweden, and it was called **pyroaurite**—M. F. Heddle proposed calling it *igelströmite*. The mineral approximates to the *pentadecahydrate*, $5MgO.Mg(FeO_2)_2.15H_2O$, or $Fe(OH)_3.3Mg(OH)_2.3H_2O$. It occurs in six-sided plates belonging to the hexagonal system, or else in masses with a fibrous structure—*vide supra*, ferric hydroxide. H. Sjögren, and G. Flink described the yellow to yellowish-brown crystals of pyroaurite, and said that they are optically negative with a low birefringence. The axial ratio is $a : c = 1 : 1·6557$. The sp. gr. is 2·07, and the hardness 2·5.

P. Berthier described a mineral from Franklin Furnace, New Jersey, and named it *franklinite*—after B. Franklin. The mineral also occurs near Eibach, Nassau; and at Altenberg near Aix-la-Chapelle. It is now called **franklinite.** Analyses reported by P. Berthier, T. Thomson, H. Abich, G. J. Brush, H. Steffens, C. F. Rammelsberg, F. von Kobell, G. H. Seyms, G. C. Stone, and C. Palache correspond with $(Fe,Mn,Zn)O.(Fe,Mn)_2O_3$, with the **zinc ferrite,** $Zn(FeO_2)_2$, or $ZnO.Fe_2O_3$, predominant. A. Daubrée prepared crystals of zinc ferrite by passing the vapours of the chlorides of zinc and iron over red-hot calcium oxide; J. J. Ebelmen heated a mixture of the component oxides with boric acid at a high temp.; F. Reich, and C. E. Swartz and F. C. Krauskopf, by strongly heating an intimate mixture of finely divided zinc and ferric oxides; J. Guillissen and co-workers found that ferric and zinc oxides react at about 620° to 650° yielding zinc ferrite; and O. C. Ralston pointed out that the zinc ferrite formed in the roasting of sulphide ores is difficult to extract by 5 to 10 per cent. sulphuric acid usually employed in the leaching of the roasted ore. The ferrite can be decomposed by treatment with hot 20 to 30 per cent. sulphuric acid near the b.p.; or by hot dil. acid acting for a long time. The zinc ferrite being ferromagnetic can be removed by magnetic concentration and treated separately; or the ferrite can be decomposed by using a carbonaceous reducing agent—say, by sprinkling coal-dust on the hot calcine before it is discharged from the roasting furnace. Y. Kato and T. Takei obtained zinc ferrite by heating a mixture of zinc and ferric oxides above 700°, and extracting the product with a soln. of ammonium chloride so as to leave insoluble zinc ferrite. The compound forms with appreciable velocity at 600°, and rapidly above 700°. The reaction was studied by J. Guillissen and P. J. van Rysselberghe, G. L. Oldright and D. P. Niconoff, E. H. Hamilton and co-workers, G. Murray and D. McIntosh, C. W. Parmelee and co-workers, V. Tafel and H. Grosse, and K. List. W. Florence reported that he had obtained crystals by fusion in a mixture of lead oxide and borax. According to A. Gorgeu, the crystals are formed when a soln. of a mol of sodium sulphate, 1 to 2 mols of zinc sulphate, and 0·25 to 0·5 mol of ferric sulphate is evaporated to dryness, and the product fused at a cherry red-heat, a small quantity of the mixture being removed from time to time and treated with boiling water. When nothing but octahedra appear in the liquid, together with some basic zinc sulphate, fusion is stopped, and the cooled mass is extracted with boiling water, the basic zinc sulphate being removed by means of dil. acetic acid. The formation of zinc ferrite under these conditions is due to the action of the ferric oxide, formed by the decomposition of the ferric sulphate, on the mixture of sodium sulphate and basic zinc sulphate. The ferrite can, in fact, also be obtained by the action of powdered hæmatite on a mixture of zinc and sodium sulphates, fused at a cherry red-heat. If the hæmatite contains sand, crystals of willemite appear after the formation of franklinite, and before the formation of crystallized zinc oxide. This fact assists in explaining the association of these three minerals in certain veins. Franklinite can also be formed from zinc chloride or fluoride. The chloride is heated in moist air with ferric chloride, or with powdered hæmatite. In the case of the fluoride, 4 parts are mixed with 6 parts of potassium fluoride, and 2 parts of ferric fluoride or 1 part of ferric oxide. Any crystals of zincite which are formed are removed by treatment with dil. acetic acid. A franklinite identical with the natural mineral is obtained by fusing together sodium sulphate and 10 per cent. each of zinc, manganese, and ferric sulphates, and adding a small quantity of a reducing agent, such as ferrous sulphide, during fusion. The small quantity of ferrous oxide thus formed combines with some of the ferric oxide and forms magnetite, which crystallizes with the zinc ferrite. K. List, and H. Forestier and G. Chaudron obtained zinc ferrite by adding sodium hydroxide to a mixed soln. of zinc and ferric chlorides, and strongly heating the precipitate; and S. Hilpert used a somewhat similar method. J. S. Wells reported the compounds $2ZnO.Fe_2O_3$, and $4ZnO.Fe_2O_3$.

Franklinite is an iron-black mineral with a reddish-brown or black streak; artificial zinc ferrite is reddish-brown with a yellowish-red streak. Franklinite may occur in coarse or fine granular or compact masses, and in octahedral crystals belonging to the cubic system. There is an octahedral pseudo-cleavage or parting as with magnetite. F. Becke found that the corrosion figures with 17·5 per cent. hydrochloric acid resemble those of spinel or magnetite; and O. Mügge obtained similar results with potassium hydrosulphate, etc. Observations on the crystals were also made by A. H. Phillips, F. R. van Horn, W. J. Mead and C. O. Swanson, and H. Mierke; and J. Königsberger studied the optical anisotropy. A. Gorgeu said that the artificial crystals appear in regular octahedra modified by facets of the rhomboidal dodecahedron. P. F. Kerr studied the X-radiograms. E. Posnjak found the cubic space-lattice is of the spinel type with eight molecules per unit cell, and with $a=8·41$ A.; G. L. Clark and co-workers gave $a=8·423$ A.; and S. Holgersson gave $a=8·403$. M. L. Huggins discussed the electronic structure. The calculated density is 5·349, and the observed 5·290. G. C. Stone gave 5·09 to 5·215 for the sp. gr. of franklinite; A. Gorgeu, 5·09, and for artificial zinc ferrite, 5·33, while J. J. Ebelmen gave 5·12. W. Biltz and co-workers found that the mol. vol. is 44·6, of which 14·3 belongs to ZnO, and 30·3 to Fe_2O_3. The hardness of franklinite is 5·5 to 6·5; and of artificial zinc ferrite, 6·5. H. Forestier observed no anomaly on the dilation curve up to 800°. G. Spezia said that the mineral is infusible before the blow-pipe. E. S. Larsen gave 2·36 for the index of refraction; and E. Posnjak, 2·31 for Li-light. E. T. Wherry found franklinite to be a medium radiodetector. F. Beijerinck found that the mineral is a good conductor of electricity, particularly at high temp. E. E. Fairbanks gave >81 (water 81) for the dielectric constant. A. Gorgeu said that the artificial ferrite is non-magnetic, while franklinite is magnetic; S. Hilpert found that artificial zinc ferrite is non-magnetic until it has been fused; and H. Forestier and G. Chaudron stated that zinc ferrite gives a magnetization-temp. curve with no discontinuity, and which is reversible throughout. The mean magnetic susceptibility of zinc ferrite is $0·16\times10^{-3}$ mass unit. F. Stutzer and co-workers found the coeff. of magnetization of franklinite to be $35·64\times10^{-6}$; and E. F. Herroun and E. Wilson, the magnetic susceptibility to be 455×10^{-6}, and W. R. Crane, 33×10^{-6}. According to Y. Kato and T. Takei, the most highly magnetic products are obtained by heating zinc and ferric oxides in the proportion 2 : 3. The product obtained by heating this mixture at 1130° and then quenching, was black and almost non-magnetic, but if allowed to cool slowly in the air it was reddish-brown and either magnetic or non-magnetic, according to the rate of cooling. Black specimens turned reddish-brown and became more magnetic when heated at 450°. The magnetic character of the brown specimens is attributed mainly to mechanically mixed ferric oxide. Magnetite can form solid soln. with zinc ferrite and thereby greatly increase its magnetic character. S. Hilpert and co-workers, and S. Holgersson and A. Serres studied the magnetic properties of the ferrites. H. Kittel and G. F. Hüttig said that mixtures of the component oxides when calcined at 620° show no marked change in magnetic properties or in their X-radiograms; at 620° to 670°, the magnetic susceptibility is increased; and at 670° to 770°, the compound becomes ferromagnetic, and there is a change in internal structure. H. A. J. Wilkens and H. B. C. Nitze discussed the magnetic separation of franklinite. H. Forestier could not fix a definite Curie point. A. Gorgeu said that zinc ferrite is attacked very slowly by acids; franklinite dissolves in hydrochloric acid with the evolution of a little chlorine—this is attributed to the effect of the admixed manganic oxide. C. E. Swartz and F. C. Krauskop found that zinc ferrite can be partially decomposed by calcium oxide or magnesium oxide at 850°. V. Tafel and H. Grosse observed that at 1050°, zinc ferrite is reduced by charcoal as rapidly as zinc oxide, but below this temp., it is reduced more slowly; zinc oxide is more easily reduced by metallic iron; the addition of some lime to the ferrite favours reduction. The transformations of franklinite in nature were discussed by J. Roth; and A. R. Leeds reported a pseudomorph of franklinite after calcite.

H. Forestier and G. Chaudron prepared **cadmium ferrite**, $Cd(FeO_2)_2$, by the methods they employed for zinc ferrite. The magnetic properties disappear on heating, and ultimately disappear at the Curie point, about 400°, but are restored on cooling; the heating and cooling curves give coincident curves unless heated above the Curie point, when this point is depressed, and by keeping the ferrite at a high temp. for some time it can be transformed into a paramagnetic form. E. Posnjak found that the cubic space-lattice is of the spinel type with 8 mols. per unit cell, and a=8·67 A.; the calculated density is 5·835, and the observed. 5·764. S. Holgersson gave a=8·731 A. W. Biltz and co-workers found the mol. vol. is 50·0, of which 15·8 belongs to CdO, and 34·2 to Fe_2O_3. H. Forestier said that the lattice is hexagonal with the ratio $a : c$=1 : 1·64. Paramagnetic cadmium ferrite loses its magnetism when heated. There is an allotropic change with the ferromagnetic state unstable. The index of refraction with Li-light is 2·39. H. Forestier observed that the magnetic transition temp. is not reversible, being about 250° on the heating curve, and 150° on the cooling curve. The relation between the strength of the magnetic field and the intensity of magnetization is shown in Fig. 545.

No **aluminium ferrite** has been prepared. A. Salvétat observed the bleaching action of alumina on ferric oxide. A. Béchamp found that freshly precipitated aluminium hydroxide added to a dil. or conc. soln. of ferric chloride slowly withdraws the iron from soln. as hydrated ferric oxide, but the reverse action does not occur, since freshly precipitated ferric hydroxide does not dissolve in dil. or conc. soln. of aluminium chloride. In some of the bauxites analyzed by P. Berthier, H. St. C. Deville, and M. von Lill, some ferric oxide seems to replace alumina isomorphously. According to N. Kühnl and W. Pauli, when precipitated aluminium hydroxide is peptized with ferric chloride, or ferric hydroxide with aluminium chloride, brown sols are obtained containing roughly equivalent amounts of aluminium and iron, the proportions varying with the mode of preparation. In the replacement of chlorine by coagulating anions, and in the relations exhibited by the transport numbers, and the size of particles, these sols resemble pure ferric hydroxide peptized sols. It is suggested that the sol particles have the same constitution as solid soln. H. Forestier observed that the break in the dilation curve of different mixtures varied as indicated in Fig. 550. S. Hilpert and co-workers studied the magnetic properties of the aluminium ferrites or solid soln.—$Al_2O_3.3Fe_2O_3$. The mineral *hercynite*, analyzed by B. Quadrat, and synthesized by J. J. Ebelmen, is a ferrous aluminate—**5.** 33, 12. According to H. Warth, when mixtures of alumina and ferric oxide are heated before the blow-pipe, they become pure white in colour provided the proportion of the ferric oxide does not exceed 7 per cent.; beyond that stage, the mixtures are brown after they have been heated. The bleaching action of alumina on ferric oxide was observed by A. Salvétat, and attributed by L. A. Keane, F. H. Scheetz, and J. H. Yoe, to be due to the fine particles of peptized ferric oxide being prevented from agglomerating to red ferric oxide by alumina. For *ferric aluminate, vide infra*, ferric chloride.

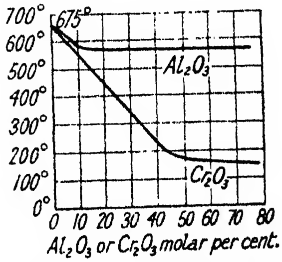


FIG. 550.—Anomalous Point in the Dilation Curve of Mixtures of Ferric Oxide with Aluminium and Chromium Oxides.

According to E. D. Campbell, if a soln. of lime in molten $5CaO.3Al_2O_3$ contains alumina and ferric oxide in the molar proportion 1 : 3, and is slowly cooled, a solid soln. of ferric oxide and alumina crystallizes out in the ratio 1 : 7 until the ratio in the soln. has increased to 1 : 3·5, when crystals of the solid soln. in this ratio crystallize out, and the ratio in the soln. has attained 1 : 1 at about 1370°. The solubility of calcium oxide in fused calcium aluminates in which part of the alumina is replaced by ferric oxide is less than in pure aluminates. H. Forestier and G. Chaudron found that the presence of alumina in ferric oxide does not lower the transition point, 675°, of ferric oxide if the mixture has previously been heated to 400°. This is taken to show a mere juxtaposition of the two oxides, not solid soln. Mixtures heated to 700° afford evidence of the formation of solid soln., which is completed at 900° in 2 hrs. The addition of up to 12 per cent. of alumina decreases the transition point to 575°, but further additions produce no other change. H. le Chatelier believed that a calcium aluminatoferrite, $3CaO.Al_2O_3.Fe_2O_3$, exists; while E. S. Shepherd and co-workers observed that calcium oxyferrite, $2CaO.Fe_2O_3$, reacted with $5CaO.3Al_2O_3$. W. C. Hansen, and L. T. Brownmiller and R. H. Bogue studied a part of the ternary system: Al_2O_3–Fe_2O_3–CaO, and their results are summarized in Fig. 551. The area A is the zone where calcium oxide occurs as primary phase; B, the aluminate, $3CaO.Al_2O_3$; C, the aluminate, $5CaO.3Al_2O_3$; D, the complex $4CaO.Al_2O_3.Fe_2O_3$; and E, the zone of solid soln. of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$. The dotted line is not a true boundary line since, owing to the formation of a continuous series of solid soln., there can be no true boundary line separating the fields where $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ occur as primary phases.

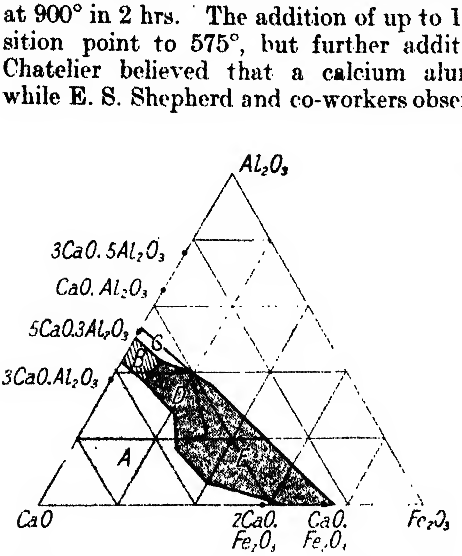


FIG. 551.—Phase Diagram of a Portion of the Ternary System: CaO–Al_2O_3–Fe_2O_3.

Crystalline **calcium aluminatoferrite,** $4CaO.Al_2O_3.Fe_2O_3$—also called *brownmillerite*—is readily formed by heating a mixture of its components below 1400°. It has a sp. gr. 3·77, and it melts congruently at 1415°. The compound is biaxial, and negative; it has a medium optic axial angle; there is occasional polysynthetic twinning, and the prismatic grains have the extinction angle against the prismatic faces very small; the pleochroism γ is brown, and α, yellowish-brown. The indices of refraction are: $\alpha = 1·96$, $\beta = 2·01$, and $\gamma = 2·04$ for Li-light; and $\alpha = 1·98$, $\beta = 2·05$, and $\gamma = 2·08$ for the yellow mercury line, $\lambda = 578$. S. Solacoln established the individuality of this salt. It is stable in the presence of an excess of lime, and forms solid soln. with dicalcium ferrite. According to W. C. Hansen, and L. T. Brownmiller and R. H. Bogue, the f.p. curve of calcium aluminatoferrite with calcium oxide forms a eutectic mixture melting at 1395°, Fig. 552.

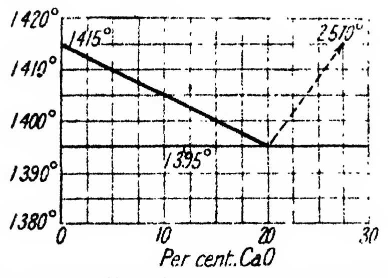


FIG. 552.—Freezing-point Curves of the System: $4CaO.Al_2O_3.Fe_2O_3$ and CaO.

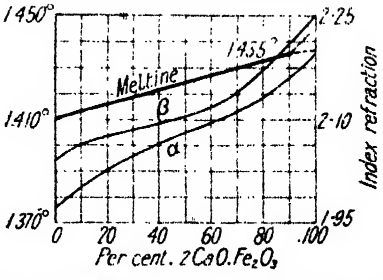


FIG. 553.—Melting-points and Refractive Indices of Solid Solutions of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$.

Mixtures of calcium aluminatoferrite, and calcium oxyferrite, Fig. 553, form a complete series of solid soln. The oxyferrite dissociates at 1435° into calcium oxide and liquid. The indices of refraction of the solid soln. are shown in Fig. 553. Those rich in $4CaO.Al_2O_3.Fe_2O_3$ are negative, those rich in $2CaO.Fe_2O_3$ are positive. Mixtures of calcium aluminatoferrite with calcium dioxytrialuminate, $5CaO.3Al_2O_3$, or $2CaO.3Ca(AlO_2)_2$, have a eutectic at 1335°, Fig. 554. With the system calcium aluminate and ferrite, Fig. 555, there is a eutectic at 1205°. W. C. Hansen and L. T. Brownmiller made a partial study of the f.p. of the system :

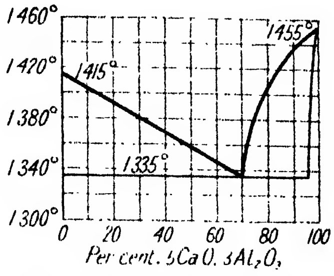


FIG. 554.—Freezing-point Curve of the System : $4CaO.Al_2O_3.Fe_2O_3$ and $5CaO.3Al_2O_3$.

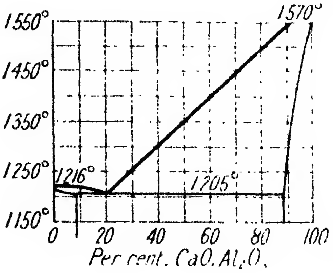


FIG. 555.—Freezing-point Curve of the System : $CaO.Fe_2O_3$ and $CaO.Al_2O_3$.

$MgO–4CaO.Al_2O_3.Fe_2O_3$, and the results are summarized in Fig. 556. The solid soln. dissociate at 1370° ; and undergo a thermal change at 1300°. A **calcium magnesium aluminatoferrite,** $4CaO.2MgO.Al_2O_3.Fe_2O_3$, is formed, which dissociates at 1370°, and changes from an α- to a β-form at 1300°. Its sp. gr. is 3·72 ; the crystals are uniaxial or biaxial, with a very small optic axial angle : α = 1·92, and γ = 1·97 for Li-light. The pleochroic crystals have α = yellowish-brown, and γ = dark brown almost opaque. The X-radiograms were examined. T. F. W. Barth and E. Posnjak studied the ferrite, and favoured the structure $Fe''MgFeO_4$.

H. von Wartenberg and W. Gurr observed that no **zirconium ferrite** is formed by heating mixtures of the constituent oxides—see Fig. 530. S. Hilpert and co-workers studied the magnetic properties of the **stannic ferrites,** $SnO_2.2Fe_2O_3$ and $SnO_2.3Fe_2O_3$. According to K. List, **lead ferrite,** $Pb(FeO_2)_2$, is formed by the action of lead oxide on a soln. of ferric chloride ; according to O. Proske, when lead sulphate is decomposed by ferric oxide ; and, according to H. Forestier and G. Chaudron, and S. Hilpert, by adding alkali-lye to a mixed soln. of lead and ferric chlorides, and heating the precipitate to redness. H. Forestier said that the X-radiograms correspond with a hexagonal lattice. S. Hilpert and A. Lindner examined the X-radiograms of the lead ferrites: $PbO.Fe_2O_3$, $PbO.2Fe_2O_3$, and $PbO.8Fe_2O_3$. E. J. Kohlmeyer obtained cooling curves of mixtures of lead and ferric oxides, and obtained evidence of the possible existence of compounds with the molar ratio, $PbO : Fe_2O_3 = 3 : 1$, 3 : 2, 1 : 1, 2 : 3, and 1 : 2. The microstructure of the mixtures agrees with these results. The sp. gr. and sp.-vol. of the mixtures were :

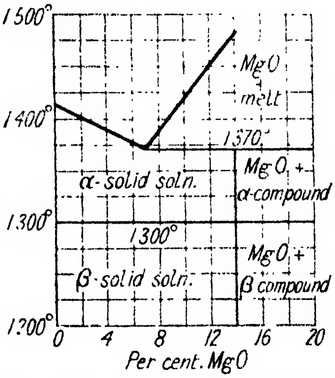


FIG. 556.—Freezing-point Curves of the System : MgO $4CaO.Al_2O_3.Fe_2O_2$.

PbO . .	100	75	60·22	51·48	40·12	28·26	18·39	9·71
Sp. gr. .	9·514	8·170	7·896	6·936	6·337	5·974	5·461	5·353
Sp. vol. .	0·105	0·122	0·137	0·144	0·158	0·167	0·177	0·187

The curve with full data has breaks corresponding with 3 : 1, 3 : 2, and 2 : 3. The hardness increases with increasing proportions of ferric oxide. The curve of the relative magnetic permeabilities has a small maximum with the 1 : 1 compound, and there is a break corresponding with the 1 : 2 compound. E. J. Kohlmeyer, and M. Feiser observed that the lead is less volatile than it is with litharge. According to E. J. Kohlmeyer, the colour of all the mixtures in hydrogen darkens at 220° ; and at 260° to 280° some metal is formed. When heated in air or oxygen some red lead is formed, and water extracts a little lead oxide; if exposed to air and water, a skin of basic lead carbonate is formed; boiling conc. hydrochloric acid extracts the lead oxide; hydrogen sulphide blackens the moist powder; and nitric acid extracts most of the lead but leaves a little behind as lead dioxide. The lead ferrites are decomposed when heated with silica. H. Forestier observed no break in the dilation curve up to 600°; the Curie point is at 335°, and it is nearly reversible. The relation between the strength of the magnetic field and the intensity of magnetization is shown in Fig. 545. H. Sachse studied the Curie point; and S. Hilpert and co-workers, the magnetic properties. A. Serres studied the magnetic properties of lead ferrite. L. J. Igelström, and G. Aminoff described a mineral from the Jacobsberg mine, Nordmark, Wermland, Sweden. He called it **plumboferrite.** Its composition approximates $Pb(FeO_2)_2$ in which part of the lead is replaced by calcium, magnesium, manganese(ous), and iron(ous). It occurs in nearly black, cleavable masses, with a red streak, and a hardness of 5. K. Johansson calculated from the analysis the formula $(Pb,Mn,Fe)O.2Fe_2O_3$. The axial ratio of the hexagonal crystals is $a:c=1:3{\cdot}9719$; and the X-radiograms correspond with a hexagonal lattice having $a=11{\cdot}86$ A., and $c=47{\cdot}14$ A., or $a:c=1:3{\cdot}9747$. There are 42 mols. or 504 atoms in each elementary parallelopipedal cell. The sp. gr. is 6·07. The mineral acts feebly on a magnet. According to H. Forestier and co-workers, the magnetization decreases as the temp. rises, and disappears at the Curie point; the heating and cooling curves coincide; and the mean magnetic susceptibility is $1{\cdot}2\times10^{-3}$ mass unit. S. Hilpert said that lead ferrite prepared in the wet way is non-magnetic until fused. The transformation point of lead ferrite is near 200°. A mixed lead and cupric ferrite is as strongly magnetic as pure cupric ferrite if rapidly cooled from 1000°, but loses this property if slowly cooled, or if melted at 1300°. The permeability is restored by heating to 900° and slowly cooling. H. Sachse, and S. Hilpert studied the subject. G. Aminoff described **magneto-plumbite** as a related mineral from Langban, Sweden. It has a complex composition approximating $2RO.3Fe_2O_3$ or $3RO.4Fe_2O_3$—the X-radiogram favours the former. It occurs in black, acute, hexagonal pyramids with the axial ratio $a:c=1:3{\cdot}91$; the basal cleavage is perfect. The X-radiogram indicates a holohedral, hexagonal crystal with a unit cell of dimensions $a=606$ A., and $c=23{\cdot}69$ A., containing four mols. $2RO.3Fe_2O_3$. The streak of magnetoferrite is brown; the sp. gr., 5·517; and the hardness, about 6. Unlike plumboferrite, magnetoferrite is strongly magnetic. K. Johansson described a mineral from Jacobsberg, Wermland, and he called it **hämatophanite.** It occurs in thin plates with a mica-like cleavage. The mineral is dark reddish-brown; the powder is yellowish-red. When in very thin plates, the colour by transmitted light is blood-red. The analysis corresponds with **lead chloroferrite,** $Pb(Cl,OH).4PbO.2Fe_2O_3$. The tetragonal crystals have the axial ratio $a:c=1:1{\cdot}95$, and the X-radiogram shows that the lattice has $a=7{\cdot}801$ A., and $c=15{\cdot}23$ A., or $a:c=1:1{\cdot}952$. There are 3 mols. in each parallelopipedal cell. The sp. gr. is 7·70; and the hardness, 2 to 3.

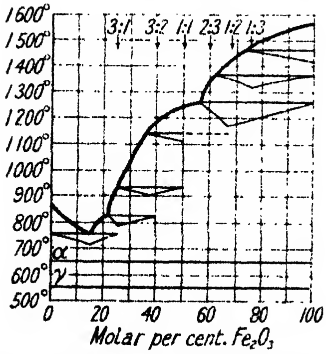


FIG. 557.—Freezing-point Curve of Mixtures of Lead and Ferric Oxides.

No **chromic ferrite** has been prepared—*vide* ferrous chromite. H. Forestier and G. Chaudron observed that the addition of chromic oxide to ferric oxide lowers the transition point of ferric oxide 230° when 40 per cent. has been added, and there is no sharp break in the temperature–chromic oxide curve. With high percentages of chromic oxide, the effect on the transition point is less. Ferric and chromic oxides are miscible in all proportions in agreement with the fact that the ratio of their mol. vols. is nearly unity. H. Forestier observed that the anomalies in the dilation curves of different mixtures of chromic and ferric oxides vary as shown in Fig. 550. S. Hilpert and A. Wille studied the subject. The *chromitite* of M. Z. Jovicic is a mineral from Western Siberia whose analysis corresponds approximately with $Cr_2O_3.Fe_2O_3$, but the ferrous and ferric iron were not separated in the analysis—*vide* chromite. A. Wolff prepared some **tungstatoferrites**—*vide* tungstates, **11.** 62, 14 and 16.

J. H. Andrew and co-workers observed that manganous and ferrous oxides form solid soln.; and P. Oberhoffer and O. von Keil made some determinations of the m.p. of mixtures of the oxides. K. List added alkali-lye to a mixed soln. of equimolar proportions of manganous and ferric chlorides and obtained a dark brown precipitate, which, after calcination, was regarded as a magnetic **manganous ferrite,** $Mn(FeO_2)_2$; but S. Hilpert regarded it as a ferrous manganite. E. Diepschlag and E. Horn, and C. W. Parmelee and co-workers, observed that at a high temp., manganous and ferric oxides unite to form the ferrite. E. Wilson and E. F. Herroun studied the magnetic susceptibility of manganese ferrite A. Damour described a black mineral, **jacobsite,** from Jacobsberg, Wermland, Sweden. Analyses were reported by A. Damour, C. F. Rammelsberg, O. Lindström, L. J. Igelström, G. Flink, and F. Kovar, and the results agree with $(Mn,Fe)O.(Fe,Mn)_2O_3$. The distorted octahedral crystals belong to the cubic system. K. Johansson gave $MgFe_2O_4+(Mn,Fe)Fe_2O_4$. The X-radiograms of the cubic crystals indicate a lattice of side $a=8{\cdot}42$ A., L. Passerini gave $a=8{\cdot}515$ A.; and the lattice is of the magnetite type, with 8 mols., $(Mg,Mn)Fe_2O_4$, per unit cell. The sp. gr. is 4·76; L. Passerini gave 4·436. S. Holgersson gave for artificial $Mn(FeO_2)_2$, $a=8{\cdot}572$ A.; and G. L. Clark and co-workers, $a=8{\cdot}457$ A. A. Damour gave for the sp. gr. 4·75, and for the hardness, 6. W. Biltz and co-workers gave 47·3 for the mol. vol., of which 13·3 belongs to the MnO, and 34·0 to Fe_2O_3. H. Forestier gave 54×10^{-6} for the magnetic susceptibility. S. Hilpert and A. Wille studied the magnetic properties. According to F. A. Genth, a variety of black *Eisenmulm* can be represented as a manganiferous magnetite, $(Fe,Mn)O.Fe_2O_3$; its sp. gr. was 3·76; and M. Weibull, E. Hugel, and A. H. Chester also described manganiferous magnesian magnetites, $(Fe,Mn,Mg)O.(Fe,Mn)_2O_3$. W. M. Bradley described a mineral, **skemmatite,** from Iva, South Carolina. Its composition is $3MnO_2.2Fe_2O_3.6H_2O$, and it is an alteration product of pyroxmangite, $(Fe,Mn)SiO_3$. Its hardness is 5·5 to 6; and it is soluble in hydrochloric acid. P. E. Wretblad observed no sign of the formation of **manganic ferrite,** $Mn_2O_3.Fe_2O_3$.

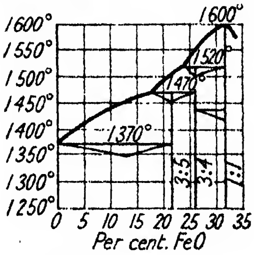


FIG. 558.—Freezing-point Curves of Mixtures of Ferrous and Ferric Oxides.

For **ferrous ferrite,** $Fe(FeO_2)_2$, *vide supra*, magnetite, and ferric oxide, and hydroxide. According to S. Hilpert, ferric hydroxide prepared by oxidizing freshly precipitated ferrous hydroxide with ammonium persulphate is non-magnetic, but if first oxidized by air to the Fe_3O_4-stage, the persulphate gives a highly magnetic product which becomes ordinary ferric oxide at 400°. The ferric hydroxide obtained by the action of air on ferrous carbonate is non-magnetic if rapidly prepared, but if oxidized slowly so that ferroso-ferric oxide is first formed, the final product is magnetic. The magnetic ferrites all contain Fe_2O_3 as an acid-forming oxide, and it is probable that the magnetic ferric oxides described also retain the same constitution: $2(FeO^{+}+2(Fe_2O_3)^{-}+O=(Fe_2O_3{}^{+}.2(Fe_2O_3)^{-}$; this molecular arrangement, however, being unstable, was changed on heating. The results of E. J. Kohlmeyer are summarized in Fig. 558, where there are indications of the formation of the ferrous ferrites, $FeO : Fe_2O_3=1:1$, $3:4$, and $3:5$—*vide supra*, solid soln. of ferric and ferrous oxides; and also ferrosic oxide.

Ferrous ferrites can be obtained: (i) *from orthohydroxide.* F. Wöhler, J. Lefort, and L. A. Welo and O. Baudisch obtained ferrous ferrite by treating a mixed soln. of ferrous and ferric salts with alkali; A. Krause and co-workers by the action of an excess of ammonia on a mixture of peptized yellow ferric metahydroxide in 0·01*N*-HCl and ferrous chloride at 18°; and E. Deiss and G. Schikorr obtained it by mixing hydrosols of ferrous hydroxide and ferric orthohydroxide. The product is brownish-black. The ferrous ferrites can also be obtained (ii) from *metahydroxide*. J. Liebig and F. Wöhler, and R. Böttger obtained ferrous ferrite by treating a soln. of a ferrous salt with alkali-lye, and oxidizing the boiling mixture with oxygen; and A. Krause and co-workers, by treating a mixed soln. of ferrous and ferric chlorides with an excess of aq. ammonia at 18°; and E. Kaufmann and F. Haber, by treating a soln. of ferrous sulphate with ammonia, and oxidizing the boiling mixture with sodium nitrate. The product is deep black with a bluish streak.

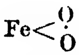
A. Krause and J. Tulecki found that the ferrite prepared from the orthohydroxide is more hydrated than the other ferrite. The ferrite obtained from the metahydroxide, unlike that from the orthohydroxide, is stable in air and not readily oxidized. The ferrite from the metahydroxide contains rather more ferrous iron than that from the orthohydroxide. The preparation richest in ferrous iron had the composition $FeO : Fe_2O_3 : H_2O = 1 : 1·13 : 0·54$, or $Fe''(Fe'''O_2)_2.nH_2O$. Both types are ferromagnetic. W. Biltz and co-workers gave 45·1 for the mol. vol. of ferrous ferrite, and of this, 12·0 belongs to the FeO, and 33·1 to the Fe_2O_3.

T. F. W. Barth and E. Posnjak discussed the titanium salt, $FeTiFeO_4$, or $Ti(FeO_2)_2$—**titanium ferrite.** E. J. Kohlmeyer also reported a **lead ferrous ferrite,** $PbO.FeO.4Fe_2O_3$. For ferric orthoferrite, $Fe(FeO_3)$, see magnetic ferric oxide. H. Forestier and G. Chaudron found the mean magnetic susceptibility to be 80×10^{-3} mass unit. S. Hilpert's product was obtained by precipitating a soln. of a mixture of ferrous and ferric salts with soda-lye. The black precipitate becomes red when calcined in air, and its magnetic transformation point is 525°.

According to S. Hilpert, if a colloidal soln. obtained by treating an aq. soln. of cobaltous nitrate and ferric chloride with *N*-NaOH is treated with ammonia, the precipitated **cobaltous ferrite,** $Co(FeO_2)_2$, is distinctly magnetic. S. Hilpert and A. Wille studied the magnetic properties. The amorphous black powder when dried and heated to 280° to 290° loses its magnetic properties, but they are restored on cooling. S. Holgersson found the spinel-like crystals had the lattice parameter $a = 8·359$ A., G. Natta and L. Passerini gave $a = 8·36$ A.; the vol., 584×10^{-24} c.c.; and sp. gr. 5·19. S. B. Hendricks and W. H. Albrecht gave $a = 8·35$ A., and sp. gr. 5·5. R. J. Elliot obtained cobaltous ferrite by joint precipitation, with ammonia, from a mixed soln. of cobaltous and ferric salts and heating the mixture in a crucible. The sp. gr. is 4·82 at 10°. W. Biltz and co-workers gave 44·5 for the mol. vol., of which 11·7 belongs to the CoO, and 32·8 to the Fe_2O_3. When heated in a current of hydrogen sulphide, it forms a magnetic sulphide. S. Veil observed that the magnetization coeff. of the ferrites are more than 1000 times as great as those of the pure constituents. There is a maximum in the magnetization coeff. of calcined mixtures of the constituent oxides of cobalt ferrite corresponding with that of the pure ferrite. E. V. Shannon discussed the formation of ferromagnetic cobalt ferrite. S. B. Hendricks and W. H. Albrecht found that the X-radiograms of cobalt ferrite prepared by adding a mixed soln. of cobalt chloride and ferrous ammonium sulphate to boiling sodium hydroxide, are analogous to those of Co_3O_4 and Fe_3O_4. Cobalt ferrite is paramagnetic. The compound cannot be completely dehydrated at 100°, the residual water being merely adsorbed. The magnetic susceptibility of preparations oxidized in varying degree indicates an increase of this property with diminishing content of $Co_2O_3.2Fe_2O_3$, the value for the homogeneous material being $45·6 \times 10^{-6}$ mass unit. The oxidized product exhibits the same X-ray spectrum as the oxide, $CoO.Fe_2O_3$, but the lines are less sharply defined. When the substance is heated, the lines become more distinct and completely identical with those of the lower oxide if the temp. has been raised above 250°. The magnetic properties were examined by S. Hilpert, P. Martin, S. Veil, and E. F. Herroun and E. Wilson. S. B. Hendricks and W. H. Albrecht prepared what may be **cobaltic ferrite,** $Co_2O_3.Fe_2O_3$, in the homogeneous state, by adding potassium persulphate to the soln. employed for making cobaltous ferrite.

H. Forestier and G. Chaudron prepared **nickelous ferrite,** $Ni(FeO_2)_2$, by adding alkali-lye to a mixed soln. of nickelous and ferric chlorides, and heating the precipitate to redness. L. Passerini found that the space-lattice of the cubic spinel has the side 8·340 A.; the vol. $580{\cdot}09\times10^{-24}$ c.c.; and sp. gr. 5·268. H. Forestier said that the salt has a spinel lattice. W. Biltz and co-workers gave 44·7 for the mol. vol., of which 11·0 belongs to the NiO, and 33·7 to the Fe_2O_3. J. A. Hedvall, K. List, and S. Holgersson prepared brown magnetic nickel ferrite in a similar manner. H. Forestier and G. Chaudron found that its mean magnetic susceptibility is 78×10^{-3} mass unit; and its magnetic transition point is 590°. H. Forestier observed a break in the dilation curve near 590°, and the Curie point is about the same temp. The relation between the strength of the magnetic field and the intensity of magnetization is shown in Fig. 545. Nickel ferrite is stable at a high temp. A. Serres, and H. Sachse also studied the Curie point, and S. Hilpert and A. Wille, the magnetic properties. S. Veil obtained results with the magnetization coeff. of nickel ferrite similar to those which she obtained with cobalt ferrite. W. Stahl, and A. Serres studied the nickel ferrites. A. F. Grosse described a black nickel magnetite which was called **trevorite.** Analyses by A. F. Grosse, and T. L. Walker correspond with $Ni(FeO_2)_2$. E. V. Shannon discussed the formation of ferromagnetic trevorite. Its sp. gr. is 5·165, and its hardness 5.

Higher oxides than ferric oxide have been assumed to exist. Thus, C. Zimmermann [2] explained the reaction between potassium permanganate and ferrous chloride in the presence of hydrochloric acid on the assumption that a higher iron oxide was formed; J. Brode, the action of hydrogen dioxide on a soln. of ferric chloride; A. Bach, the action of air on iron; and C. W. Bennett and W. S. Burnham, and W. D. Bancroft, the action of nitric acid on iron. Although the oxide with quadrivalent iron, **iron dioxide,** FeO_2, has not been prepared, some salts—**perferrites**—supposed to contain this oxide as an acid anhydride have been reported by L. Möser and H. Borck. According to G. Pellini and D. Meneghini, when hydrogen dioxide acts on ferrous or ferric chloride, or on ferrous or ferric hydroxide, there is formed a very unstable, pale red substance resembling colloidal ferric hydroxide, but having the properties of a true peroxide. The composition could not be established with certainty, but experiments show that the ratio Fe : O is not less than 2 and not greater than 3. It is thought that the product is *iron peroxide*, O=Fe–O–O–Fe : O, or



$$Fe<\overset{O}{\underset{O}{:}}$$

They also found that an alcoholic soln. of ferrous chloride exhibits a yellowish-green coloration, the intensity of which is only slightly diminished by intense cold; with ferric chloride, the soln. has a yellowish-brown colour, which fades appreciably on cooling. The soln. of the ferrous salt reacts energetically with hydrogen dioxide, developing a considerable amount of heat and an intense brown coloration, which is not sensibly lightened by cooling; the soln. of the ferric salt reacts feebly with hydrogen dioxide, the liquid obtained not differing appreciably from the original soln., and losing its colour in the same way on cooling. This behaviour indicates that some sort of chemical combination takes place between the ferrous salt and hydrogen dioxide, whilst with ferric chloride such combination takes place either not at all or only extremely slowly. W. Manchot and F. Glaser supposed that the dioxide is formed when ferrous compounds are oxidized with free oxygen; L. Losana, as ferrous ferrate, $Fe(FeO_4)$, when barium ferrate is treated with a soln. of ferrous nitrate; and C. A. O. Rosell, when barium ferrate is treated with a soln. of ferric chloride. In connection with the ferrates obtained by L. Losana—*vide infra*—ferrous ferrate, $Fe(FeO_4)$, has the ultimate composition FeO_2; and ferric ferrate, $Fe_2(FeO_4)_3$, the ultimate composition Fe_5O_{12}.

According to L. Möser and H. Borck, if a mixture of conc. soln. of a mol of ferric nitrate and 1 to 2 mols of strontium nitrate be evaporated to dryness, and the finely powdered residue heated to a temp. not exceeding 600°, in a current of oxygen, until all the nitrogen oxides are expelled, a compound is obtained whose composition corresponds with **strontium perferrite,** $SrO.FeO_2$, or $SrFeO_3$, and not with $2SrO_2.Fe_2O_3$. A hydrated product is obtained as a yellowish-brown precipitate on warming on a water-bath for some time a suspension of freshly precipitated ferric hydroxide in a conc. soln. of strontium hydroxide. When heated, it loses water and becomes brown, and at temp. exceeding 300°, it absorbs oxygen to form $SrO.FeO_2$. It can also be obtained by oxidizing a mixture of freshly precipitated ferric hydroxide and a conc. soln. of, say, lithium hydroxide, with bromine, and also by heating the ferrate until the oxygen is evolved, and then heating the brown product in air or oxygen so as to re-oxidize it to perferrite. The salt was also prepared by W. Eidmann and L. Möser; and K. Albert and H. Schulz recommended it as a catalyst for the oxidation of sulphur dioxide. L. Möser and H. Borck prepared **barium perferrite,** $BaFeO_3$, by heating to 400°, in a current of oxygen, a mixture of barium and ferric hydroxides; and it was studied by L. Losana. Impure **lithium perferrite,** Li_2FeO_3, was prepared by L. Möser and H. Borck, by oxidizing a mixture of lithium and ferric hydroxides with bromine. If a mixture of barium or sodium and ferric hydroxides be oxidized with bromine, the perferrites are produced.

These perferrites are black substances which are stable below 640°, but beyond that temp. they decompose slowly with the evolution of oxygen; the reaction: $4SrFeO_3 \rightleftharpoons 4SrO + 2Fe_2O_3 + O_2$ is reversible. The perferrites are slowly decomposed by water with the evolution of oxygen: $4SrFeO_3 + 10H_2O = 4Sr(OH)_2 + 4Fe(OH)_3 + O_2$; there is a violent reaction with hydrogen dioxide: $4SrFeO_3 + 2H_2O_2 + 8H_2O = 4Sr(OH)_2 + 4Fe(OH)_3 + 2O_2$; with hydrochloric acid, both chlorine and oxygen are evolved: $2SrFeO_3 + 10HCl = 2SrCl_2 + 2FeCl_3 + 5H_2O + O$, and $O + 2HCl = H_2O + Cl_2$. It can be assumed that an unstable iron tetrachloride, $FeCl_4$, is formed: $2SrFeO_3 + 12HCl = 2SrCl_2 + 2FeCl_4 + 6H_2O$ followed by $2FeCl_4 = 2FeCl_3 + Cl_2$; with sulphuric acid, oxygen is evolved; $4SrFeO_3 + 10H_2SO_4 = 4SrSO_4 + 2Fe_2(SO_4)_3 + 10H_2O + O_2$; with nitric acid, oxygen is vigorously evolved and nitrates are formed; with acetic acid, acetates are formed and oxygen is evolved; with oxalic acid, oxygen and carbon dioxide are formed; there is no perceptible reaction with dry carbon dioxide at ordinary temp., but at a red-heat, the perferrite is completely decomposed; thus, at 600° to 700° the reaction is symbolized: $4SrFeO_3 + 4CO_2 \rightleftharpoons 4SrCO_3 + 2Fe_2O_3 + O_2$, and the reaction is reversible, but there are side reactions: $SrCO_3 \rightleftharpoons SrO + CO_2$, and $6Fe_2O_3 = 4Fe_3O_4 + O_2$; moist carbon dioxide slowly decomposes the perferrite at ordinary temp.; and mixtures of air and alcohol or other inflammable vapours, when led over the heated perferrite, are oxidized to water and carbon dioxide, and when once the combination has started, combustion proceeds of its own accord. The perferrites are fairly stable towards alkaline liquids; thus soln. of the alkali or alkaline earth hydroxides decompose the perferrite less and less with increasing concentration; similarly also with soln. of alkali carbonates and phosphates.

W. Manchot and O. Wilhelms inferred that in the liberation of iodine from potassium iodide by hydrogen dioxide in the presence of a ferrous salt, the iron does not act catalytically but is itself oxidized in such a way that every 2 atoms of ferrous iron require 2 mols of hydrogen dioxide, and 2 atoms of iodine are liberated. Allowing for the oxidation of ferrous to ferric iron, this means that an *iron peroxide*—**iron hemipentoxide,** Fe_2O_5, or iron pentiodide, FeI_5—is formed. Again, if half a mol of hydrogen dioxide be added to a soln. of a mol of ferrous sulphate, the whole of the latter is oxidized to ferric sulphate; but if a mol of ferrous sulphate soln. be added to a soln. of 0·5 mol to 1·4 mols of hydrogen dioxide, both ferrous and ferric salts exist side by side—particularly at 0°—and varying quantities of oxygen are evolved. With a mol of ferrous salt and 1·5 mols of hydrogen dioxide at 0°, between 1 and 1½ mols of hydrogen dioxide are consumed, corresponding, as before, with the formation of iron hemipentoxide. In acidic soln., the interaction of ferrous salts, hydrogen dioxide, and potassium iodide is more complex, the iodine being liberated more slowly; the iron here acts catalytically, and there is no well-defined end-point of the action. The addition of dil. sulphuric acid to a soln. of hydrogen dioxide containing sufficient ferric ammonium sulphate to destroy the whole of the dioxide in about 70 hrs., practically prevented the iron from changing the conc. of the soln. Acid also retards the oxidation of ferrous salts by hydrogen dioxide and the addition of oxygen (or hydrogen dioxide) to ferric salts. Ferric salts destroy hydrogen dioxide more slowly than do ferrous salts. W. Manchot also drew similar conclusions from the action of hydrogen dioxide, potassium permanganate and chromic acid on a ferrous compound in the presence of an acceptor; and N. R. Dhar, for the induced oxidation of sodium formate. The reactions were studied by A. K. Goard and E. K. Rideal, R. Kuhn and A. Wassermann, C. S. Mummery, W. Manchot and G. Lehmann, and H. Wieland and W. Franke.

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§ 34. Iron Trioxide.—Ferric Acid and the Ferrates

G. E. Stahl,[1] in his *Specimene Becheriano* (Franckfurth, 1702), said that when iron is heated with nitre, and the product digested with water, the alkali produced by the decomposition of the nitre takes up some iron to form an amethyst or purple soln. Again, if a very dil. soln. of iron in nitric acid be poured by small portions at a time into conc. potash-lye, and the liquid be agitated, the iron dissolves to form a blood-red soln. According to C. Neumann,

> A mixture of equal parts of iron filings and nitre, injected into a strongly heated crucible, and, after detonation, thrown into water, tinges the liquor of a violet or purple-blue colour. This soln., however, is not permanent. Though the liquor at first passes through a filter without any separation of iron, yet, on standing for a few hours, the metal falls to the bottom in the form of a brick-coloured powder. It is pretty singular, that volatile alkalies instantly precipitate the iron from this fixed alkaline soln.

A. G. Ekeberg also observed that when gadolinite is fused with potassium hydroxide, a dark red soln. is obtained which, on standing, deposits a brick-red precipitate; and he added that the red colour is not due to manganese; for the alkali hydroxide can dissolve iron, producing a beautiful purple colour. A. C. Becquerel found that when ferric oxide is heated with 4 to 6 times its weight of potassium hydroxide in a silver crucible, some ferric oxide dissolves, but separates out again with the simultaneous evolution of oxygen when the product is dissolved in water. The escape of oxygen was attributed to the decomposition of potassium peroxide formed in the reaction. R. Phillips discussed ferric acid in 1843, and E. Frémy, in his *Recherches sur les acids métalliques*, 1844, showed that a salt of a ferric acid, or of **iron trioxide,** FeO_3, is formed and decomposed in A. C. Becquerel's experiment. Attempts to prepare the trioxide have not been successful; it is, however, considered to be the anhydride—*ferric anhydride*—of **ferric acid,** H_2FeO_4, a reputed parent of a series of salts formed by the union of this dibasic acid with the basic oxides. The salts are called **ferrates,** and are symbolized $R_2'FeO_4$. W. Manchot and O. Wilhelms assumed that this oxide is formed as an intermediate product in the oxidation of a ferrous salt with hypochlorous acid; and the subject was discussed by W. D. Bancroft. D. R. Hale supposed that FeO_3 is formed as an intermediate compound when hydrogen dioxide or potassium permanganate acts on neutral soln. of a ferrous salt; and that Fe_2O_4 is the intermediate oxide formed when oxygen acts on ferrous iron in alkaline soln. J. W. Retgers' experiments on the solid soln., or isomorphous mixtures formed by potassium ferrate are in harmony in that definite ferrates are formed. These formulæ are also in accord with the analyses of E. Frémy, J. D. Smith, H. Rose, and J. de Mollins.

According to E. Frémy, if a fireclay crucible containing 5 grms. of iron filings be heated to redness, and 10 grms. of the powder of fused potassium nitrate be projected therein, a lively reaction occurs, and a portion of the mixture may be thrown out of the crucible. The covered crucible is then allowed to cool. A reddish-violet mass of **potassium ferrate,** K_2FeO_4, is formed. H. Trommsdorff recommended projecting a mixture of finely divided iron and nitre, in the proportions 1 : 2, into a crucible at a dull red-heat. If the temp. is too high, the ferrate may be decomposed as fast as it is formed. H. W. F. Wackenroder said that if the crucible be too hot, the nitre fuses without deflagrating, and the mass must then be poured into an iron mortar, powdered, and again projected into the crucible. The crucible should be so heated that it is perceptibly red only at the bottom and a few inches up the sides, and the mixture projected into the middle and somewhat to the side. The deflagration occurs in a few seconds, it is attended by a bright glow, and an intumescence of the mass. The crucible is removed from the fire during or immediately after the deflagration. The product is contaminated with alkali nitrite so that the red soln. it forms with water, quickly loses its colour owing to the reduction of the ferrate. E. Frémy found that the reddish-brown, highly deliquescent mass which is obtained by heating ferric oxide for a considerable time with potassium hydroxide, contains the ferrate; but it is best prepared by strongly igniting a mixture of ferric oxide, and potassium nitrate and hydroxide for some minutes. If the heat is too low, potassium nitrite remains undecomposed, and then, on the addition of water, the ferrate is reduced to ferric oxide. A. W. Hofmann used a similar process. J. D. Smith recommended the following mode of preparation. He said:

> Wash the *ferri sesquioxidum* of the shops with boiling water until free from sulphate of soda, dry and ignite at a low red-heat; this furnishes a very pure oxide of iron and in a state of minute division; 1 part of this is to be intimately mixed with 4 of dried nitre, reduced to fine powder; place this mixture in a crucible of about twice the capacity of the bulk of the mixture, lute a well-fitting cover on, making a few small holes in the lute to allow the escape of gas, and ignite at a full red-heat for about an hour, if 6 or 8 ounces are made: the time of ignition depends much on the quantity prepared, and the temperature should never be raised above a full red-heat. When well prepared it presents the appearance of a dark reddish-brown porous mass, rapidly deliquescing on exposure to the air, so that I have found it advantageous to powder it whilst still warm, when it may be preserved for use, in a well-stoppered bottle, apparently for any length of time.

A soln. of potassium ferrate is formed by dissolving the dry salt in ice-cold water; some heat is developed in the act of soln., and there is always a slight decomposition and an evolution of oxygen, owing, said D. Smith, to the decomposition of potassium peroxide. The soln. must be separated from the undissolved portion by subsidence and decantation, not by filtration through filter-paper. E. Frémy obtained a soln. of the salt by passing chlorine through conc. potash-lye in which ferric oxide is suspended, until the oxide is all dissolved, to form a red soln. of potassium ferrate: $Fe_2O_3.3H_2O+10KOH+3Cl_2=6KCl+8H_2O+2K_2FeO_4$. H. W. F. Wackenroder said that 5 parts of hydrated ferric oxide dried between bibulous paper, 10 parts of potassium hydroxide, and 16 parts of water can be used. The hydrated oxide quickly dissolves as chlorine is passed into the liquid. There is a gradual rise in temp., and potassium chlorate is deposited by the cooling liquid. If too much water, or too much hydrated ferric oxide be used, the liquid remains colourless; and H. Rose added that if an excess of chlorine is used, the ferrate will be decomposed. L. Losana, C. A. O. Rosell, G. Merz, and L. E. Rivot and co-workers also used chlorine as the oxidizing agent; A. Mailfert said that the chlorine can be replaced by ozone; A. Mennet, M. Muspratt and E. S. Smith, G. Blattner, and W. Foster used calcium or sodium hypochlorite; D. K. Goralevich, potassium nitrate; C. L. Bloxam, and C. A. O. Rosell, bromine—iodine did not work satisfactorily; and W. Foster, hypobromite. According to H. G. Elledge, the red colour with some hypochlorite soln. is not due to alkali ferrate, but to permanganate. L. Möser recommended the following process:

> Gradually add 50 grms. of bromine to a suspension of 80 to 90 grms. of hydrated ferric oxide in a cooled soln. of 50 grms. of potassium hydroxide in 80 grms. of water; more potassium hydroxide is then added, and the mixture kept at 50° to 60° for 30 mins. The ferrate from the cold soln. is drained on a tile, and the excess of alkali removed by alcohol. The potassium bromide is then removed by dissolving the product in a little water, and re-precipitating it with alcohol.

F. Haber and W. Pick observed that soln. of ferrous and ferric salts are readily oxidized to ferrate by electrolytic oxygen. J. C. Poggendorff passed a current of electricity from 6 pairs of Grove's batteries for 24 hrs. through an anode of cast-iron into a sat. soln. of potassium hydroxide containing a clay cylinder with the platinum cathode. The whole is cooled by ice. H. Rose said that the preparation is less stable if dil. potash-lye be employed. No oxygen is evolved about the anode excepting just at the beginning or end of the electrolysis. If the current be long continued, microscopic crystals of potassium ferrate may be deposited on the iron anode, and a little iron may collect on the platinum cathode. F. Haber and W. Pick found that immediately after closing the circuit, all varieties of iron are oxidized to ferrate, and that the action is continuous provided a conc. soln. of alkali-lye and a low current density—say, 0·001 amp. per cm.—be employed. The yield of ferrate is greatest with cast iron and smallest with wrought iron; it is also greater with sodium than with potassium hydroxide, possibly on account of the greater solubility of sodium ferrate. The quantity of ferrate reduced at the cathode of platinum wire, in a cell without a diaphragm, is comparatively trifling. The yield of ferrate depends on the temp., so that under comparable conditions, traces only of ferrate were formed at 0°, whilst at 70°, the current efficiency was almost 100 per cent. According to W. Pick, when iron, especially one of the purer kinds, is used as anode in a soln. of an alkali hydroxide, a temporary formation of ferrate occurs; by reversing the current for a short time after the formation of ferrate has ceased, the iron returns to the condition in which it can be oxidized to ferrate, and after several repetitions of the treatment this condition becomes permanent. The same result is obtained by using the iron as anode in a conc. soln. of an alkali hydroxide and passing a very small current for some time. The iron is found to be covered by a dark grey skin which prevents atm. oxidation. G. Grube and H. Gmelin found that increasing the temp. and conc. of the soda-lye increases the yield; and that by increasing the current density, the yield rises to a maximum, and then falls with any further increase in the current density. The current-yield of sodium ferrate can be considerably increased by superimposing an alternating current over the direct current. The increase in the yield for constant direct current reaches a maximum for a definite alternating current density. Using as electrolyte 40 per cent. sodium hydroxide with an iron anode and a platinum cathode, and electrolyzing at 35° with a direct current of 3·33 amps. per sq. dcm. and an alternating current of 5·0 amps. per sq. dcm., an increase of 160 per cent. in the yield of sodium ferrate is obtained. In the preparation of conc. soln. of ferrates, the anode and cathode should be separated, and since ferrates lose oxygen at 50°, and yield a precipitate of hydrated oxide, this temp. must not be exceeded in the preparation, and the velocity of formation must be increased by imposing an alternating current on the direct current. In this way undecomposed sat. soln. and the crystalline salts may be obtained. The oxidation potential for the conversion of a ferrite to a ferrate is 0·78 volt at 20° to 70°; and the potential of conc. alkali-lye towards active iron is —0·6 volt. G. Grube and H. Gmelin also observed that the anodic dissolution of iron in conc. soln. of soda-lye, at a high temp., occurs in two stages; in the first stage, iron dissolves in the bivalent condition; and in the second stage, the iron in soln. passes into the sexivalent condition as ferrate with the simultaneous evolution of oxygen. Nowhere does the iron pass into soln. in the tervalent state—*vide* sodium ferrite. In a 40 per cent. soln. of sodium hydroxide, the equilibrium potential of the process $\mathrm{Fe}+2\oplus\rightleftharpoons\mathrm{Fe}^{\cdot\cdot}$ lies at $\epsilon_H-0{\cdot}86$ volt; that of the process $\mathrm{Fe}^{\cdot\cdot}+\oplus\rightleftharpoons\mathrm{Fe}^{\cdot\cdot\cdot}$ at $\epsilon_H-0{\cdot}69$ volt; and that of the process $\mathrm{Fe}^{\cdot\cdot\cdot}+3\oplus\rightleftharpoons\mathrm{Fe}^{\cdot\cdot\cdot\cdot\cdot\cdot}$ at $\epsilon_H+0{\cdot}55$ volt. Hence, the potential of the reaction $\mathrm{Fe}+3\oplus\rightleftharpoons\mathrm{Fe}^{\cdot\cdot\cdot}$ is $-0{\cdot}80$ volt; and that of the reaction $\mathrm{Fe}+6\oplus=\mathrm{Fe}^{\cdot\cdot\cdot\cdot\cdot\cdot}$ is $-0{\cdot}13$ volt.

According to L. Möser, potassium ferrate forms a reddish-black powder. P. Niggli and W. Nowaski discussed the crystal structure of the ferrates. J. W. Retgers added that a soln. of the ferrate can be kept some days without decomposition, and that it may be crystallized at a gentle heat in black, microscopic, rhombic prisms or pyramids; it forms solid soln. with potassium sulphate, selenate, chromate, tungstate, and molybdate, and it is therefore isomorphous with these salts; but no isomorphous mixtures could be obtained with potassium tellurate. The solid soln. with potassium chromate range in colour from pink through dark red to dark brown. V. L. Bohnson and A. C. Robertson found that the energy of formation of the ferrate ion, FeO_4'', is near —140,000 cals. V. L. Bohnson and A. C. Robertson measured the absorption spectra of soln. of potassium and barium ferrates, and the results are summarized in Fig. 559. The absorption spectrum was examined by E. Baschieri, and E. Hardtmann. L. Möser found that when potassium

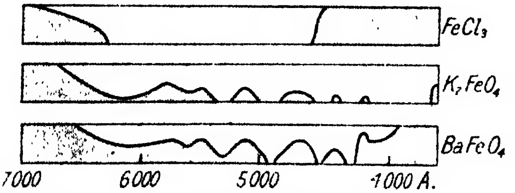

Fig. 559.—The Absorption Spectra of Potassium and Barium Ferrates.

ferrate is ignited, it loses oxygen and passes into green ferrite, which is very deliquescent, and, on exposure to air, rapidly oxidizes into potassium hydroxide, and hydrated ferric oxide. O. Liebknecht and A. P. Wills said that potassium ferrate is paramagnetic, and he measured the susceptibility of the aq. soln.

Potassium ferrate is very soluble in **water,** and the aq. soln. is deep red. E. Frémy, and J. D. Smith found that an aq. soln. of potassium ferrate is of a deep amethyst-red or cherry-red and that it is pervious to light only when it is in thin strata. The aq. soln., on standing for some time, loses its colour, gives off oxygen, and deposits hydrated ferric oxide. L. Möser found that alkali ferrate hydrolyzes in aq. soln., $2Na_2FeO_4+5H_2O\rightleftharpoons4NaOH+2Fe(OH)_3+3O$. This decomposition is faster with the more dil. soln., and when the temp. is raised. A conc. soln. may be kept in closed vessels for several months without complete decomposition, and when evaporated, it leaves a reddish residue. In some cases, the conc. soln. can be boiled without decomposition, but it afterwards deposits hydrated ferric oxide more quickly than if it had not been boiled. The dilution of the soln. of the ferrate with various **alkali salts** makes the soln. more stable than if it is diluted with water. H. Rose, and C. A. O. Rosell observed that if the decomposed soln., after the deposition of hydrated ferric oxide, is green, some manganese salt is present, probably derived from the iron employed in the preparation of the salt, the green colour is not due to the presence of ferrous iron, as was thought to be the case by J. D. Smith. O. Kassner said that the addition of **sodium peroxide** to the aq. soln. precipitates ferric hydroxide. The ferrate is quickly decomposed by reducing agents. C. A. O. Rosell said that in their oxidizing properties, the ferrates resemble the manganates more closely than the chromates. E. Frémy, and J. D. Smith found that **hydrochloric acid** forms a double potassium ferric chloride with the evolution of chlorine, while with a smaller quantity of acid, hydrated ferric oxide is precipitated. H. Rose, and H. W. F. Wackenroder found that by treating the soln. with **hydrogen sulphide,** dark green or black iron sulphide is formed. The green soln. reported by E. Frémy is, according to C. A. O. Rosell, produced by manganese present as impurity. L. Möser said that potassium ferrate is converted by **alkali sulphides** into a green substance, possibly a sulphoferrate. H. Rose observed that **sulphurous acid** forms potassium sulphate and hydrated ferric oxide; and E. Frémy, that **sulphuric acid** forms potassium ferric sulphate with the liberation of oxygen. H. Rose, and H. W. F. Wackenroder observed that **ammonia,** and all **ammonium salts** decompose the ferrate because the ammonia which is evolved reduces the ferric acid to ferric oxide. C. A. O. Rosell made a similar observation with respect to the oxidation of ammonia by the ferrates. C. A. O. Rosell found that the **nitrites** are readily oxidized by ferrates. E. Frémy found that **nitric acid** forms potassium ferric nitrate with the liberation of oxygen.

According to E. Frémy, all **organic substances** reduce the ferrate so that the soln. cannot be filtered through paper without decomposition; and L. Möser observed that paper, wood, and other organic substances are slowly oxidized by a dilute soln. of potassium ferrate, but the action is slower than with potassium permanganate. Potassium ferrate is insoluble in **ether,** and in **chloroform.** L. Möser observed that **alcohol** can have up to 20 per cent. of water. without exercising any solvent action, or without decomposing potassium ferrate. Alcohol precipitates potassium ferrate from its aq. soln. H. Rose found that alcohol is oxidized to aldehyde; while **sugar** decolorizes the soln. quickly with the precipitation of hydrated ferric oxide; and **egg-albumin** decolorizes the soln. without precipitation. H. W. F. Wackenroder found that the soln. of ferrate is decolorized by **potassium ferrocyanide**; and H. Rose, that **alkali racemates, tartrates, and malates** quickly decolorize the soln. without precipitating hydrated ferric oxide; alkali **citrates** act slowly with the occasional precipitation of hydrated ferric oxide; while **potassium oxalate, formate, acetate, and benzoate** decolorize the liquid as slowly as the inorganic salts of potassium; and **potassium succinate** acts still more slowly. C. A. O. Rosell found that the ferrates readily oxidize tartrates, and

glycerol; and also oxalates, alcohol, and **urea,** as well as most soluble organic compounds with the exception of acetates. J. D. Smith observed that when the soln. is treated with a **zinc salt,** oxygen is slowly evolved; with **nickel salts** and **manganese salts,** the peroxides are precipitated; L. Möser found that **silver nitrate** gives a precipitate, probably silver ferrite, and oxygen is given off; and similarly with **mercuric chloride,** and with **copper sulphate**; while H. W. F. Wackenroder showed that alum, and the heavy **metal salts** decolorize the liquid, and the metal base is precipitated along with hydrated ferric oxide—*vide infra.*

According to L. Möser and co-workers, when barium ferrate is digested with alkali carbonate, a soln. of the alkali ferrate is formed, and in this way, **rubidium ferrate,** Rb_2FeO_4, and **cæsium ferrate,** Cs_2FeO_4, were produced. W. Eidmann and L. Möser recommended strontium ferrate in place of the barium salt. E. Frémy found that **sodium ferrate,** Na_2FeO_4, can be prepared by the methods used for the potassium salt (*q.v.*); C. A. O. Rosell could not prepare the sodium salt in the dry way by calcining ferric oxide with sodium hydroxide, carbonate and nitrate, and with mixtures of sodium hydroxide and nitrate, and also with sodium nitrate and carbonate; but it was obtained by heating ferric oxide with sodium dioxide, and, by treating the cold mass with ice, instead of water, a soln. of sodium ferrate was obtained. A soln. of this salt was also prepared by the action of chlorine on soda-lye holding hydrated ferric oxide in suspension. The salt was also prepared by J. d'Ans and J. Löffler. T. Wallace and A. Fleck, and C. Zengelis and S. Horsch passed carbon dioxide over a mixture of sodium dioxide and finely-divided iron; and A. Holt obtained the ferrate by the action of sodium hydroxide on ferric oxide. The treatment of barium ferrate with lithium carbonate furnishes **lithium ferrate,** Li_2FeO_4. W. Eidmann and L. Möser recommended strontium ferrate in place of the barium salt.

L. Losana prepared **copper ferrate,** $CuFeO_4.H_2O$, by the action of copper nitrate on barium ferrate, suspended in water, washing the green powder with water, and drying it over sulphuric acid. The salt decomposes in vacuo over sulphuric acid, so that the anhydrous salt was not obtained. The salt begins to decompose when heated to about 50°, giving off water and oxygen. The reaction: $K_2FeO_4+2AgNO_3=2KNO_3+Ag_2FeO_4$, is not suitable for the preparation of **silver ferrate,** Ag_2FeO_4, but if barium ferrate, suspended in water, be treated with silver nitrate, silver ferrate is produced as a black powder with a pink reflexion. It can be washed and dried at 15° over sulphuric acid. When heated to 30°, the salt begins to decompose in accord with $4Ag_2FeO_4=4Ag_2O+2Fe_2O_3+3O_2$.

When a soln. of potassium ferrate is treated with an excess of a dil. soln. of a barium salt, J. D. Smith, and L. Losana found that a bulky, carmine-red precipitate of **barium ferrate,** $BaFeO_4.H_2O$, is formed. The precipitate is washed, and dried over sulphuric acid, or at 100°. The precipitate when fresh is cochineal-red, but after washing and drying, it is brick-red. C. L. Bloxam prepared barium ferrate as a purple precipitate by adding barium chloride to a soln. of the calcium ferrate; by C. A. O. Rosell, by adding barium carbonate to a soln. of sodium ferrate; and J. A. Hedvall and N. von Zweigbergh, by the action of barium peroxide on ferric oxide. J. D. Smith said that when barium ferrate is heated, it loses water and turns green, and at a higher temp., it gives off oxygen and loses its colour. L. Losana found that the salt begins to lose weight at 105°. The losses in weight of two grams of the salt, after heating it to different temp., was as follows (the time in hours is indicated in brackets):

	50°	100°	105°	108°
Weight .	2·0000	2·0002 (4)	1·9988 (6)	1·8772 (26) grms.
	116°	123°	144°	160°
Weight .	1·8772 (3)	1·7584 (3)	1·7004 (3)	1·7002 (3) grms.

This is the only ferrate examined which did not lose oxygen continuously, so that the decomposition: $4BaFeO_4=4BaO+2Fe_2O_3+3O_2$ is thought to proceed *viâ* the formation of $BaFeO_3$ as an intermediate compound. The anhydride can also be obtained by gently heating the hydrate; but the hydrate is stable over conc. sulphuric acid in vacuo. Barium ferrate was said by C. A. O. Rosell, J. D. Smith, and H. W. F. Wackenroder to be insoluble in water, and before drying to be readily decomposed by all the acids, even carbonic acid; but after drying it is not so easily acted upon. E. Frémy stated that barium ferrate is one of the most stable salts of the series. It can be suspended in water, and boiled without decomposition. A. Baschieri found that dil. hydrochloric acid, of sp. gr. 1·09, decomposes barium ferrate with the formation of ferric and barium chlorides, and the evolution of chlorine; with more dil. hydrochloric acid, in the cold there is a vigorous evolution of chlorine, the precipitate gradually disappears, and the soln. assumes a vermilion colour; this liquid continues to evolve chlorine for about a day and slowly turns colourless. The vermilion colour of the soln. is due, not to the intermediate formation of a chloroferrate, but to the presence of the ion FeO_4''. J. de Mollins found that the reaction $2BaFeO_4+8KI+16HCl=2BaCl_2+2FeCl_2+8KCl+8H_2O+4I_2$ is quantitative. A. Baschieri found that barium ferrate is not decomposed by dil. sulphuric acid, but decomposition increases as the temp. rises until it becomes complete in the boiling acid. The action of sulphuric acid was also discussed by H. W. F. Wackenroder, and J. D. Smith. A. Baschieri found that the salt is instantly decomposed by nitric acid; while the salt dissolves in soln. of organic acids, the solubility and intensity of colour imparted to the soln. increases as the acid becomes more energetic. E. Frémy said that while the salt is decomposed immediately by mineral acids, it forms a red soln. when treated with acetic acid. According to C. A. O. Rosell, an alkali sulphate decomposes barium ferrate if it has not been dried, forming barium sulphate and hydrated ferric oxide, and giving off oxygen. A. Naumann found barium ferrate to be insoluble in acetone. W. Eidmann and L. Möser prepared **strontium ferrate**, $SrFeO_4$, by the double decomposition of potassium ferrate with a sat., neutral soln. of strontium bromide, and washing the precipitate with alcohol and ether. Some admixed ferric oxide is present. L. Losana obtained the strontium salt by the process employed for the barium salt, and found that when dried over sulphuric acid it forms the *dihydrate*, $SrFeO_4.2H_2O$. This salt forms a dark red amorphous powder; it begins to decompose at about 52°, for the weight of 2 grms. after heating 3 hrs. at 25°, was as follows (the time of heating, in hours, is indicated in brackets):

	25°	35°	52°	68°	85°	150°
Weight .	2·0000 (5)	1·9978 (6)	1·7000 (11)	1·5062 (16)	1·5062 (10)	1·5066 (3) grms.

The anhydride can be prepared by gently heating the hydrate. W. Eidmann and L. Möser observed that strontium ferrate is sparingly soluble in water, and that the soln. is readily decomposed with the evolution of oxygen, forming strontium hydroxide and hydrated ferric oxide. It is insoluble in alcohol, and ether. W. Eidmann and L. Möser prepared **calcium ferrate**, $CaFeO_4.2H_2O$, by double decomposition of a calcium salt with strontium ferrate; C. L. Bloxam, by boiling a mixture of ferric chloride and bleaching powder; and E. Frémy, and L. Losana, by the action of a calcium salt soln. on potassium ferrate. A gram of the salt heated 5 hrs. at 20° lost 0·1110 grm. in 18 hrs. at 44°. E. Frémy said that the salt is not soluble in water, but C. A. O. Rosell, and L. Losana found it to be soluble. The anhydride was not obtained, since the dihydrate decomposes in vacuo over sulphuric acid. Observations were made by C. L. Bloxam, and T. L. Bailley and P. H. Jones.

W. Eidmann and L. Möser prepared **magnesium ferrate**, $MgFeO_4$, by double decomposition of strontium ferrate and a magnesium salt; but L. Losana did not succeed in obtaining it by the action of magnesium nitrate on barium ferrate; or by the action of magnesium nitrate on potassium ferrate. L. Losana obtained **zinc ferrate**, $ZnFeO_4$, by the action of a soln. of zinc nitrate on barium ferrate. The rose-coloured powder forms a rose-red soln. with water; and when dried for 3 hrs. at 20°, the salt loses 0·30 per cent. in 4 hrs. at 30°, and 11·32 per cent. in 11 hrs. at 30°.

L. Losana obtained **mercurous ferrate,** Hg_2FeO_4, by the action of a soln. of mercurous nitrate on barium ferrate. The salt decomposes during the drying. No definite **mercuric ferrate,** $HgFeO_4$, was obtained by the action of a soln. of mercuric nitrate on barium ferrate; but with aluminium nitrate and barium ferrate, **aluminium ferrate,** $Al_2(FeO_4)_3$, was obtained as a rose-red powder, which decomposed on drying. L. Losana did not obtain a definite **thallium ferrate,** Tl_2FeO_4, by the action of a soln. of thallous nitrate on barium ferrate; **thorium ferrate,** $Th(FeO_4)_2$, was obtained by the action of thorium nitrate on barium ferrate, but the salt decomposed on drying. L. Losana prepared **lead ferrate,** $PbFeO_4$, by the action of a soln. of lead nitrate on barium ferrate. The rose-coloured powder lost 0·22 per cent. when heated 3 hrs. at 30°, and 3·58 per cent. in 5 hrs. at 40°. In the attempt to prepare **chromium ferrate,** $Cr_2(FeO_4)_3$, by the action of chromic nitrate on barium ferrate, a voluminous yellow precipitate was obtained containing barium chromate and ferric oxide. It is probable that the reaction proceeds $6BaFeO_4+4Cr(NO_3)_3=6Ba(NO_3)_2+2Cr_2(FeO_4)_3$; followed by $2Cr_2(FeO_4)_3+4H_2O=4H_2CrO_4+6FeO_2$, and $6FeO_2=3Fe_2O_3+3O$; while the chromic acid reacts with two-thirds of the barium nitrate: $4H_2CrO_4+4Ba(NO_3)_2=4BaCrO_4+8HNO_3$; and part of the ferric oxide reacts with the nitric acid: $Fe_2O_3+6HNO_3=2Fe(NO_3)_3+3H_2O$. No definite **manganese ferrate,** $MnFeO_4$, was obtained by the action of manganese nitrate on barium ferrate; and **ferrous ferrate,** $Fe(FeO_4)$, obtained by the action of ferrous nitrate on barium ferrate decomposes on drying; and similarly also with **ferric ferrate,** $Fe_2(FeO_4)_3$, obtained by the action of a soln. of ferric nitrate on barium ferrate. L. Losana prepared rose-violet **cobalt ferrate,** $CoFeO_4$, by the action of a soln. of cobalt nitrate on barium ferrate. The powder dried for 5 hrs. at 20° lost 2·18 per cent. when dried 5 hrs. at 25°, and 11·1 per cent. in 18 hrs. at the same temp. Similarly with **nickel ferrate,** $NiFeO_4$, which gives a greyish-green powder. The powder dried for 5 hrs. at 20° lost 1·88 per cent. when heated 3 hrs. at 30°, and 7·46 per cent. in 18 hrs. at the same temp.

O. Baudisch and P. Mayer[2] assumed that **perferric acid,** $FeO_3(OH)_2$, or H_2FeO_4, is produced when freshly precipitated ferrous hydroxide is oxidized by oxygen. D. K. Goralevich said that **iron tetroxide,** or **perferric anhydride,** FeO_4, or perferric acid, H_2FeO_5, is probably formed as a volatile, unstable compound when barium perferrate, $BaFeO_5$, is treated with an excess of dil. sulphuric acid, at a low temp. Perferric anhydride is insoluble in water, but soluble in dil. acids. He prepared bright green **potassium perferrate,** $K_2FeO_5.nH_2O$, by fusing ferric oxide with potassium hydroxide and an excess of potassium nitrate, or, better, chlorate. The salt can be purified by sublimation; it decomposes very slowly when kept in air; explosively, when warmed, on treatment with conc. sulphuric acid, or on impact if mixed with sulphur, phosphorus, or charcoal. It is quite stable in alkaline soln., but acids readily decompose it, with evolution of oxygen and, in the case of hydrochloric acid, chlorine. Oxidizing agents like chlorine and hydrogen peroxide give a deep red soln. of potassium ferrate, with evolution of oxygen. Neutral soln. of the perferrate give no reaction for ferric ions until, on the addition of acid, decomposition has commenced. Similarly with **sodium perferrate,** the alkaline earth perferrates were obtained as white precipitates on adding a soln. of a salt of an alkaline earth to a soln. of potassium perferrate; with barium salt, **barium perferrate,** $BaFeO_5.7H_2O$, is produced; and with a strontium salt, **strontium perferrate,** $SrFeO_5.7H_2O$. These salts are white and insoluble in water, alcohol, and ether.

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