METALS AND METALLIC COMPOUNDS

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IN FOUR VOLUMES

VOLUME IV

METALS OF THE "B" GROUPS

LONDON
EDWARD ARNOLD & CO.
1923

Made and Printed in Great Britain by
Butler & Tanner, *Frome and London*

PREFACE

During the past few years so much fruitful research work has been carried out in metallography, crystallography, electrochemistry, colloid chemistry, and geo-chemistry that we are enabled to approach the subject of metals in an altogether new spirit. It is now possible to suggest reasons for phenomena which at one time appeared inexplicable, and to detect regularities where once the facts seemed chaotic. Advantage should surely be taken of the new aspect of the subject in the textbooks. The traditional practice of giving long "catalogues of salts" and empirical accounts of metallurgical processes, is no doubt of use for books of reference. But in books intended for continuous reading, such a method is far too uninspiring, and should be abandoned now that knowledge has advanced sufficiently to offer something better.

In this book, an attempt is made to correlate cause and effect, and to introduce such theoretical views as will serve to connect the known facts in an ordered and elegant sequence. The book is intended for the advanced student of inorganic and metallurgical chemistry, and for those engaged in research in these subjects. The industrial chemist will, I hope, also find it of assistance, whilst certain portions (e.g. those dealing with work-hardening, recrystallization, the effect of impurities on metals, and corrosion) should prove useful to the engineer.

The difficulties which I have experienced in writing the book have served to convince me that the work is really needed. Much information which I regard as being of the greatest importance I have found scattered through the recent volumes of the scientific and technical journals—in many cases in journals which are not commonly considered as being devoted to chemistry at all, and which appear sometimes to have escaped the notice of the writers of standard chemical textbooks.

Of the four volumes, the first is of a generalized character. It begins with an Introduction in which I have endeavoured to condense the elementary principles of general chemistry, physics and geology, a knowledge of which the reader is assumed in the body of the work to possess. The body of Volume I is divided into two parts, "The Study of the Metallic State" (Metallography) and "The Study of the Ionic State" (Electrochemistry). The metallographic portion includes the effects of deformation, annealing and alloying on the properties of metals; the electrochemical portion includes such subjects as the structure of precipitates, the colloidal state, electro-deposition and corrosion; it closes with a chapter on radioactivity. By the treatment of the metallography and electrochemistry of metals in a general fashion, with examples chosen from individual metals, these two subjects are presented in a more satisfactory manner than if they were introduced piecemeal in the sections devoted to the different metals. In addition, a great deal of wearisome repetition is avoided in the subsequent volumes.

The chapters dealing with electrochemistry have presented special difficulties. I do not believe it possible to obtain a proper understanding of the chemistry of metals without some knowledge of electrochemistry and colloid chemistry. In order to throw open these subjects to all, I have made the treatment, as far as possible, non-mathematical. A great obstacle to the attractive presentation of electrochemical principles is the barbarous character of the nomenclature in use; I have not felt justified in introducing a new nomenclature, but have tried to make the best of the existing terms, selecting a terminology which will be definite, even if it is not dignified.

In Volumes II, III and IV, I deal one by one with the individual metals. The order observed is based upon the Periodic Table in a form similar to that made popular by Sir James Walker. The old form of the Periodic Table which classes sodium along with copper has now—it is to be hoped—few active supporters, although it still ornaments the walls of our lecture theatres, and appears to find favour with the authors of chemical treatises based upon the classical model. In the new table, which accords well with the chemical and electrochemical properties of the elements and is in harmony with modern ideas of the structure of the atom, the elements can be divided into three main classes, and I have allocated a different volume to each class. Volume II deals with the metals of the "A Groups," Volume III with the "Transition Elements" ("Group VIII" of the old table), whilst Volume IV deals with the metals of the "B Groups."

The space devoted to each metal is divided into three main sections. The first deals with the metal and its compounds from the point of view of the academical laboratory. The pure chemistry of the metal and its compounds is here discussed; no reference to ores, technical processes and industrial application is made in this section, which is therefore fairly concise. The section ends with a summary of the methods of analysis of the metal in question, although the book is not intended as a practical analytical handbook.

The second section deals shortly with the terrestrial occurrence of the metal in question, starting with its origin in the rock-magma, and discussing the probable mode of formation of the important ores and minerals, both primary and secondary.

The third section—which is often the longest—is of a technical character. We start with the ore or mineral, and follow the metal through the processes of concentration and smelting, and finally consider the practical uses of the element, and of compounds containing it; I have tried to show why the properties of the individual metal—as stated in the theoretical section—render it suitable for the various uses to which it is put, and to make the technical section a correct survey of industry carried on at the present time; I have only referred to obsolete methods of procedure in a few places where such a reference is thought to be instructive.

Stress has been laid on the important points, which have been illustrated by a few chosen examples in order to avoid burdening the reader with a mass of names and numbers, which he will not retain, and which can be looked up when required in a table of physical constants or in a detailed book of reference. Proper names have largely been concentrated in the foot-notes, and thus kept out of the text; I have written a book about chemistry—not about chemists. Likewise the figures are frankly diagrammatic, drawn to emphasize the salient points; in the diagrams of technical plants much that is of merely structural importance is omitted. I have only employed the historical order of description where it happens also to be the logical order.

Throughout the book numerous references are given, in foot-notes, to scientific and technical literature; these should be consulted by the reader who wishes to study any given part of the subject in greater detail. In selecting these references, I have not given preference to the work of the actual originators of the various theories or processes, but have sought rather to provide the reader with the most recent information regarding the matter under discussion. The recent papers themselves will include references to the earlier ones, whilst the converse is clearly not true.

In subjects regarding which disagreement prevails at present, I have in most cases departed from the usual custom of giving in turn a summary of the views advanced by the various disputants, as this practice is apt to leave the reader hopelessly bewildered. Rather, I have endeavoured to suggest a standpoint which the average reader may safely adopt as a working hypothesis, until further research finally decides the question under dispute. If, however, the subject happens to be one of special interest to the reader, he should consult the references in the foot-notes, and form his own opinions. In these foot-notes, he will find references to many authorities whose views are not held by the present writer.

As already stated, great efforts have been made to render the book as "up-to-date" as possible, but I have not concealed the fact that uncertainty still prevails on many parts of the subject, and that research is continually being conducted to settle these doubtful points. I have endeavoured to prepare the reader to revise his own opinions without undue reluctance every time he may open a scientific journal.

I wish to return thanks to the numerous friends who have very kindly given information or advice. Especially would I mention Mr. C. T. Heycock, Dr. E. K. Rideal, Prof. H. C. H. Carpenter, and Mr. Maurice Cook. Mr. Cook has prepared the micro-photographs accompanying Volumes I, III and IV of the book, and has shown much skill and patience in obtaining results which illustrate clearly the points described in the text.

U. R. E.

CAMBRIDGE, 1923.

CONTENTS OF VOLUME IV

LIST OF JOURNALS REFERRED TO IN VOLUME IV AND ABBREVIATIONS EMPLOYED

Amer Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Amer. Machinist	American Machinist.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Anal.	Annales de Chimie Analytique.
Ann. Chim. Appl.	Annali di Chimica Applicata.
Ann. Phys.	Annalen der Physik.
Analyst	Analyst.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Board of Trade J.	Board of Trade Journal.
Brit. Assoc. Rep.	British Association for the Advancement of Science, Report.
Brit. J. Photo.	British Journal of Photography.
Brit. Med. J.	British Medical Journal.
Bull. Acad. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Amer. Inst. Min. Eng.	Bulletin of the American Institute of Mining Engineers.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull Soc. Chim.	Bulletin de la Société chimique de France.
Bull. Soc. Chim. Belg.	Bulletin de la Société chimique de Belgique.
California Min. Bur. Bull.	California State Mining Bureau, Bulletin.
Cham. Comm. J.	Chamber of Commerce Journal.
Chem. News	Chemical News
Chem. Trade J.	Chemical Trade Journal.
Chem. Weekblad.	Chemisch Weekblad.
Chem. Zeit.	Chemiker-Zeitung.
Chim. et Ind.	Chimie et Industrie.
Comptes Rend.	Comptes rendus hebdomadaires des Séances de l'Academie des Sciences.
Dental Cosmos	Dental Cosmos.
Discovery	Discovery.
Econ. Geol.	Economic Geology.
Electrochem. Ind.	Electrochemical Industry.
Engineering	Engineering.
Eng. Min. J.	Engineering and Mining Journal.
Gazetta	Gazetta chimica italiana.
Helv. Chim. Acta.	Helvetica Chimica Acta.
Int. Cong. App. Chem.	International Congress of Applied Chemistry.
Int. Zeitsch. Met.	Internationale Zeitschrift für Metallographie.

Iron Coal Trades Rev.	Iron and Coal Trades Review.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical and Mining Society of South Africa.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Geol.	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Met.	Journal of the Institute of Metals.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Phys.	Journal de Physique.
J. Phys. Chem.	Journal of Physical Chemistry.
J Prakt. Chem.	Journal für praktische Chemie.
J. Roy. Soc. Arts	Journal of the Royal Society of Arts.
J. San. Inst.	Journal of the Sanitary Institute.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Wash. Acad. Sci.	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
Koll. Zeitsch.	Kolloid-Zeitschrift.
Lancet	Lancet.
Machinery	Machinery (London).
Mech. World	Mechanical World.
Met. Ind.	Metal Industry (London).
Met. Ind. (New York)	Metal Industry (New York).
Met. et. Alliages	Métals et Alliages.
Met. u. Erz.	Metall und Erz.
Met. Chem. Eng.	Metallurgical and Chemical Engineering (also called " Chemical and Metallurgical Engineering ")
Metallurgie	Metallurgie.
Metallographist	Metallographist.
Min. Eng. World	Mining and Engineering World.
Min. Ind.	Mineral Industry.
Min. Mag.	Mining Magazine.
Min. Met.	Mining and Metallurgy.
Min. Sci. Press	Mining and Scientific Press.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Mon. Sci.	Moniteur Scientifique.
Nature	Nature.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Photo. J.	Photographic Journal.
Phys. Rev.	Physical Review.
Phys. Zeitsch.	Physikalische Zeitschift.
Proc. Amst. Acad.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Chem. Soc.	Proceedings of the Chemical Society.

Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. Trav. Chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. Met.	Revue de Métallurgie.
Rep. Insp. Alkali Works	Reports of the Chief Inspectors on Alkali (etc.) Works.
Sitzungsber. Preuss. Akad.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenchaften zu Berlin.
Stahl. u. Eisen	Stahl und Eisen.
Times Eng. Supp.	"The Times," Engineering Supplement.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Met.	Transactions of the American Institute of Metals.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Can. Min. Inst.	Transactions of the Canadian Mining Institute.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. Met.	Transactions of the Institution of Mining and Metallurgy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Univ. Miss. Bull.	University of Missouri Bulletin.
U.S. Bur. Stand. Circ.	United States Bureau of Standards, Circular.
U.S. Bureau Stand. Sci. Paper	United States Bureau of Standards, Scientific Paper.
U.S. Bur. Stand. Tech. Paper	United States Bureau of Standards, Technologic Paper.
U.S. Geol. Surv. Bull.	United States Geological Survey, Bulletin.
U.S. Geol. Surv. Min. Res.	United States Geological Survey, Mineral Resources.[1]
Zeitsch. Anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. Angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. Anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Metallkunde	Zeitschrift für Metallkunde.
Zeitsch. Phys.	Zeitschrift für Physik.
Zeitsch. Phys. Chem.	Zeitschrift für Physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. Wiss. Photo.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.

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[1] The year stated is always the year of the series; the year of publication is invariably later.

NOTE ON MICRO-PHOTOGRAPHS IN PLATE

(Prepared specially by Mr. Maurice Cook, M.Sc.)

Fig.

A. **α-Brass:** 70% copper, 30% zinc. *Chill Cast.* Etched with ferric chloride and hydrochloric acid. Magnification, × 60.

B. **α-Brass:** 70% copper, 30% zinc. *Cold worked and annealed.* Etched with ferric chloride and hydrochloric acid. Magnification, × 40.

C. **αβ-Brass:** 60% copper, 40% zinc. Etched with ferric chloride and hydrochloric acid. Magnification, × 60.

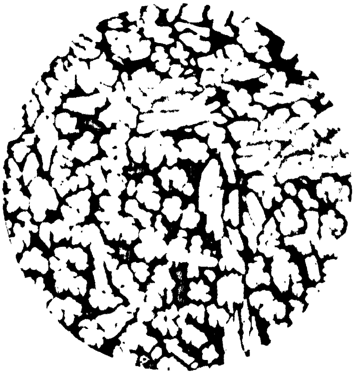
D. **Aluminium Bronze:** 89% copper, 11% aluminium. *Annealed* at 525° C. for half an hour. Etched with ferric chloride and hydrochloric acid. Magnification, × 440.

E. **Aluminium Bronze:** 89% copper, 11% aluminium. *Water-quenched* from 750° C. Etched with ferric chloride and hydrochloric acid. Magnification, × 60.

F. **Bearing Metal:** 87% tin, 9% antimony, 4% copper. *Chill Cast.* Etched with alcoholic nitric acid. Magnification, × 60.

(A) α-BRASS CHILL-CAST

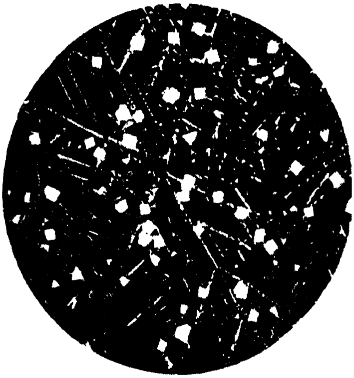
(B) α-BRASS WORKED AND ANNEALE



(C) αβ-BRASS

(D) ALUMINIUM BRONZE ANNEALED

(E) ALUMINIUM BRONZE QUENCHED



(F) BEARING METAL

(For preparation see page xii)

GROUP IB

	Atomic Weight.	Normal Electrode Potential (Hydrogen Scale).
Copper . .	63·57	+ 0·3469 volts
Silver . .	107·88	+ 0·7987 ,,
Gold . .	197·2	+ 0·985 ,, (approx.)

In passing from the transition elements to Group IB, we return to metals which appear to be monovalent, at least in one class of salts. In the older form of the Periodic Table, copper, silver and gold were classed along with the alkali-metals, although it is impossible to say that the three metals resemble the alkali-metals in any respect other than in valency. In this book a form of the Periodic Table is employed, which shows the " B " groups distinct from the " A " groups; the employment of this newer form of the table renders it unnecessary to waste space in attempting to discover similarities and analogies between copper and potassium, which do not, in truth, exist.

Two metals of the group, copper and gold, have a second series of salts in which a valency higher than one is exerted, and in these cases of variable valency we find coloured compounds. It is interesting to note that the metals themselves are coloured; that is, the surface reflection of those rays to which our eyes are sensitive is of a selective character. In most of the metals hitherto considered, the lustre has been a " white " one. In silver, the valency is almost invariably monovalent, and the metal is white. Most of the salts of silver also are almost colourless; such selective absorption as occurs is in the ultra-violet region of the spectrum to which our eyes are not sensitive.

The metals themselves are malleable and ductile substances, which are exceptionally good conductors of heat and electricity. They stand rather towards the " noble " end of the Potential Series, and are easy to deposit quantitatively from aqueous solution by electrolysis. On the other hand, copper and silver show far less tendency towards passivity or valve-action than the metals hitherto considered, and can usually be dissolved quantitatively from an anode. As in the transition elements, the " noble " character of the elements in the group increases as the atomic weight rises.

COPPER

Atomic weight . . . 63·57

The Metal

Compact copper is a reddish metal which can be polished to display a brilliant lustre. The red colour appears more intense if light is reflected at a copper surface several times before reaching the eye. The colour is due to the fact that the red rays are reflected at the surface more completely than the green and blue, and it is not surprising to find that the light which passes *through* a thin copper leaf contains a preponderance of the shorter rays. Thus, although red by reflected light, copper appears bluish-green by transmitted light.

Pure copper is a very soft metal, but the hardness is considerably increased by cold-working, and still more by the presence of other metals in solid solution—matters which will be considered in further detail in the technical section. The specific gravity is 8·9 and the melting-point 1,083° C.

Copper is extremely malleable and can be rolled out into sheets, or beaten into foil or thin leaf ; it is also ductile, and can be drawn into wire. It is an exceptionally good conductor of heat and of electricity, but here again impurities have a considerable effect, which will be considered in the technical section.

Copper crystallizes in the cubic system. Well-formed octahedral crystals of copper are found in nature, and are sometimes produced accidentally in the working of a Daniell cell. Crystalline growths of copper, showing octahedral faces, are also produced sometimes in the electrolysis of a copper sulphate solution at the corner of a cathode, where the conditions are such as to allow an individual crystal to develop freely.[1] In ordinary electrolytic copper, however, the crystals growing out from the cathode surface grow into contact laterally with one another, and the structure is columnar.[2] If, owing to high current density combined with absence of stirring,

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[1] Compare L. Addicks, *Electrochem. Ind.* **3** (1905), 267.

[2] O. Faust, *Zeitsch. Anorg. Chem.* **78** (1912), 201. W. Blum, H. D. Holler and H. S. Rawdon, *Trans. Amer. Electrochem. Soc.* **30** (1916), 159. M. von Schwartz, *Int. Zeitsch. Met.* **7** (1915), 124. A. Sieverts and W. Wippelmann, *Zeitsch. Anorg. Chem.* **91** (1915), 1; **93** (1915), 287.

the concentration at different portions of the cathode has been unequal, mossy or dendritic growths will be observed, whilst at a still higher current density dark, spongy, incoherent copper is obtained. The causes of the differences in the structure of the electrolytic deposits of copper have been considered in Chapter XI (Vol. I).

In micro-sections of ordinary copper cast from the fused state, the usual polygonal grains common to most cast metals are generally observed. When the metal undergoes deformation the grains become elongated, and sections of copper wire show a fibrous structure; on annealing, the fibrous structure gradually disappears.[1] The internal crystal-structure of copper has been studied by the X-ray method, and it is found that the atoms are arranged on a face-centred cubic space-lattice.[2]

A smooth copper surface loses its initial brightness when exposed to damp air, taking on a dull brownish colour, which may be regarded as due to a very thin oxidized-layer. The action is, however, confined to the surface, and no further oxidation takes place at ordinary temperatures. At a higher temperature oxidation occurs even in dry air and may cause interference colours; at a red heat, a dark layer of oxide of appreciable thickness is formed, but even at this temperature, the effect of oxidation does not extend far below the surface, because the rate of diffusion of oxygen through the oxide-layer quickly falls off as the thickness of the layer increases.[3] The dark oxide layer appears to be cupric oxide (CuO) on the outer surface and cuprous oxide (Cu_2O) in the lower portions. Finely divided copper—obtained by reduction of the oxide—is oxidized readily by air even at low temperatures.

Copper cannot under ordinary circumstances evolve hydrogen as a gas from dilute hydrochloric or sulphuric acid. It is, however, appreciably attacked by these acids if an oxidizing depolarizer, such as hydrogen peroxide or sodium hypochlorite, is present[4]; dilute sulphuric acid slowly attacks copper in the presence of air. Likewise, the metal dissolves in oxidizing acids; it is attacked by hot concentrated sulphuric acid, sulphur dioxide being evolved, and also by nitric acid with the production of various oxides of nitrogen. In the latter case, the action is rather slow at first, but afterwards becomes very rapid; it appears that nitrous acid, which is one of the products of the reaction, acts as a catalyst.

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[1] See H. Baucke, *Int. Zeitsch. Met.* **4** (1913), 155.

[2] W. L. Bragg, *Phil. Mag.* **28** (1914), 355.

[3] N. B. Pilling and R. E. Bedworth, *J. Inst. Met.* **28** (1923).

[4] Compare O. P. Watts and N. D. Whipple, *Trans. Amer. Electrochem. Soc.* **32** (1917), 257.

If a substance, like urea, which destroys nitrous acid, is added to the nitric acid, the attack upon the copper is almost entirely prevented.[1]

A piece of copper immersed in nitric acid of specific gravity 1·108, and caused to rotate rapidly is only slightly attacked; but it is seriously dissolved, when allowed to remain at rest in the same acid.[2] The explanation is simple: when the copper is at rest, the nitrous *acid, formed by the reaction, remains at the surface of the metal and aids further dissolution. But, if the surface of the metal is in* constant motion, the nitrous acid is carried away from the metal as soon as it is formed, and the catalytic acceleration of the action does not occur.

When compact copper is immersed in water containing dissolved oxygen, it soon becomes dulled, owing to the formation of a thin oxidized layer (" tarnish "). The character of this layer depends somewhat upon the preliminary treatment of the metallic surface, and upon the conditions of immersion, but it is often of a highly resistant character and will protect the metal from further attack.[3] A light (straw-coloured) tarnish appears usually to be more resistant than a dark (reddish) tarnish.

Copper is attacked readily by aqueous ammonia or ammonium nitrate in the presence of oxygen, deep violet-blue ammino-compounds being produced.[4] In fact, if bright dry copper be placed in moist air containing ammonia, the surface soon blackens, and becomes covered with drops of a deep violet-blue liquid.[5]

It is interesting to note that copper—unlike iron or nickel—is seriously attacked by fused caustic alkalis. If caustic soda be heated at 350° C. in a copper crucible, the fused substance quickly becomes blue, and a number of small solid scales appear suspended in the " melt." At higher temperatures (500° C.) the melt becomes dark brown, and dark crystalline matter, apparently cupric oxide (CuO), appears at the bottom of the crucible.[6]

Although copper becomes passive much less readily than the metals of previous groups, it can be rendered passive by immersion in a solution of potassium dichromate; when in the passive con-

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[1] V. H. Veley, *Proc. Roy. Soc.* **46** (1889), 216; *J. Soc. Chem. Ind.* **10** (1891), 204.

[2] J. H. Stansbie, *Trans. Faraday Soc.* **9** (1913), 11. Actually an electrode of platinum plated with copper was used in the experiment, no external E.M.F. being applied.

[3] G. D. Bengough and O. F. Hudson, *J. Inst. Met.* **21** (1919), 102.

[4] H. Bassett and R. G. Durrant, *Trans. Chem. Soc.* **121** (1922), 2630, find that the ammonia becomes largely oxidised, the main product being the nitrite $[Cu(NH_3)_4]\ (NO_2)_2$.

[5] U. R. Evans, *Trans. Faraday Soc.* (1923).

[6] T. Wallace and A. Fleck, *Trans. Chem. Soc.* **119** (1921), 1849.

dition it will not displace silver or mercury from solutions of their salts.[1]

The **anodic attack**[2] of copper differs from that of the metals hitherto described in that a copper anode shows very little tendency to become passive through anodic treatment. If a solution of sodium sulphate is electrolysed in a cell fitted with a copper anode, the solution becomes blue owing to the presence of cupric sulphate. The rate of dissolution of the anode, calculated on the assumption that cupric sulphate is formed, corresponds to a current efficiency of 106–109 per cent.; the fact that the efficiency exceeds 100 per cent. shows that in addition to cupric ions, $Cu^{\cdot\cdot}$, a certain amount of cuprous ions, $Cu^{\cdot}$, are formed. The anode usually becomes covered with red cuprous oxide, but this is not closely adherent, and does not cause passivity. In a solution of sodium chloride, the current efficiency calculated on the same basis is still higher: 185 per cent. is quite usual, whilst 200 per cent. can be reached. This latter figure indicates that only cuprous salts are being formed.

Laboratory Preparation. In a dark, finely-divided state, copper can be produced by heating the oxide in a current of hydrogen; the reaction is auto-catalytic, proceeding slowly at first, but when once a speck of red copper appears at a point, it seems to serve as a nucleus for further reduction and the change proceeds apace at that point.[3] Metallic copper can also be produced as a dark red sponge, by the action of zinc upon the aqueous solution of a copper salt.

If the preparation of compact copper at a low temperature is desired, it can be produced by the electrolysis of a salt solution. From a solution of the sulphate containing sulphuric acid, electrolysis will give a coherent deposit; a much more brilliant deposit is obtained from a violently agitated bath containing nitric acid. If the copper salts employed contain traces of other metals (e.g. iron), this second method generally yields a purer product than the first; but, since much of the current is used up in the reduction of nitric acid, the current efficiency is always low. If a particularly smooth shining deposit of copper is required, it can be obtained from an acidified sulphate bath containing gelatine; such a deposit has a lamellar structure, as opposed to the columnar or fibrous structure obtained from colloid-free baths. It is, however, far from being pure copper, since it contains an important quantity of gelatine.[4]

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[1] W. R. Dunstan and J. R. Hill, *Trans. Chem. Soc.* **99** (1911), 1863.

[2] G. R. White, *J. Phys. Chem.* **15** (1911), 731.

[3] R. N. Pease and H. S. Taylor, *J. Amer. Chem. Soc.* **43** (1921), 2179.

[4] G. Grube and V. Reuss, *Zeitsch. Elektrochem.* **27** (1921), 45; G. Grube, *Zeitsch. Elektrochem.* **27** (1921), 53.

Where it is desired to obtain pure copper from commercial copper in the laboratory, it is possible to adopt on a small scale the process used in technology for the electrolytic refining of copper.

Alleged Allotropy of Copper. Cohen, impressed by certain small changes in the electrical resistance and density of copper brought about by heating, has put forward the view that copper undergoes an allotropic change at about 72° C.[1] Other experimenters[2] have examined this question, and have come to the conclusion that no such allotropic change occurs. It is, of course, well known that any piece of metal which has undergone any mechanical deformation—even of a superficial character—is liable to experience a certain change on heating, namely, recrystallization; in the case of the softer metals (lead, tin, zinc, copper and aluminium) this change may commence to occur—although very slowly—at quite low temperatures, and will undoubtedly have a slight effect on the physical and electro-chemical properties of the metal. It is likely that some at least of the changes which Cohen has observed in many of the softer metals are due to this cause. It is misleading to refer to them as allotropic changes.

Nevertheless, although the use of the word "allotropy" is unfortunate, the importance of the changes must not be overlooked. The potential of the electrode

Polished or cold-drawn copper | copper sulphate solution

is found to be distinctly variable, depending on the mechanical and thermal history of the metal: only an electrode covered with spongy copper gives a perfectly fixed and constant potential.[3] Cold-drawn copper will therefore differ from annealed copper not only in its mechanical properties, but also in its chemical behaviour.

Compounds

Copper forms two oxides, having the compositions CuO and Cu_2O. Two classes of salts exist, corresponding to these two oxides; they are known respectively as the cupric and cuprous salts. The cupric salts have many points of resemblance to the salts of nickel and of cobalt, metals which stand on the left of copper in the Periodic Table. On the other hand, the cuprous salts present a close relationship to the monovalent salts of silver, which falls

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[1] E. Cohen and W. D. Helderman, *Proc. Amst. Acad.* **16** (1913), 628; **17** (1914), 60. Compare the views of G. Masing, *Zeitsch. Metallkunde,* **10** (1919), 65.

[2] G. K. Burgess and I. N. Kellberg, *J. Wash. Acad. Sci.* **5** (1915), 657.

[3] F. H. Getman, *Trans. Amer. Electrochem. Soc.* **26** (1914), 67.

below copper in the Table. On the whole the cupric salts are much more stable than the cuprous.

A. Compounds of Divalent Copper (Cupric Compounds).

Cupric oxide, CuO, can be obtained, as has been stated above, as a black powder by heating the finely-divided metal in the air, although it is only formed to a very small extent on the surface of ordinary compact copper exposed to air at a high temperature. It is also produced on heating the nitrate or carbonate.

It may be prepared from copper salts by precipitation with caustic alkali. A pale blue precipitate, usually regarded as the **hydroxide,** $Cu(OH)_2$, is first produced, which usually contains alkali; on warming the liquid, the precipitate becomes black, presumably losing part of its water.[1] After being filtered and washed, the precipitate should be heated, so as to drive off the last part of the water and cooled in air, cupric oxide being thus obtained.

It is stated that the blue hydroxide is much more stable if the soluble copper salt is present in slight excess of the alkali used to precipitate it; under such circumstances, the precipitate remains blue even on boiling, being probably stabilized by adsorbed cupric salt.[2]

When heated in hydrogen, cupric oxide is reduced to finely-divided copper. If heated very strongly in air, it may lose part of its oxygen, producing cuprous oxide, but on cooling in air, this oxygen is usually taken up again. The dissociation pressure corresponding to the equilibrium

$$4CuO \rightleftharpoons 2Cu_2O + O_2$$

increases with the temperature; it is only 12·5 mm. of mercury at 900° C., but is 95·3 mm. at 1,000° C.[3]

Cupric hydroxide dissolves in acids yielding pale-blue solutions of cupric salts, and in ammonia giving a deep violet-blue solution of an ammonia compound. Although not appreciably soluble in dilute caustic alkalis under ordinary circumstances, it dissolves in concentrated (30 per cent.) sodium hydroxide, yielding a violet-blue solution.[4] This has been described by some chemists as a colloidal solution, but it probably contains a definite cuprite. The solution appears to be fairly stable if the copper content is only

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[1] Compare the views of V. Kohlschütter and J. L. Tüscher, *Zeitsch. Anorg. Chem.* **111** (1920), 193.

[2] N. G. Chatterji and N. R. Dhar, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 124.

[3] F. H. Smyth and H. S. Roberts, *J. Amer. Chem. Soc.* **42** (1920), 2582; **43** (1921), 1061.

[4] Justin Mueller, *Comptes Rend.* **167** (1918), 779; E. Müller, *Zeitsch. Angew. Chem.* **33** (1920), i, 303; **34** (1921), 371.

small, but a solution containing much copper is apt to deposit a brown precipitate of partly hydrated cupric oxide on standing. The solutions very rich in alkali, however, deposit a blue precipitate which is believed to be sodium cuprite, but the precipitate turns black on washing, yielding cupric oxide.

Cupric Salts. Cupric oxide, even when produced at high temperatures, dissolves in acids much more easily than is the case with most anhydrous oxides, although if the strongly ignited oxide be used, the rate of dissolution is slower than if the hydrated forms described above are employed. Cupric salts may be obtained from the solution by crystallization. The salts of oxidizing acids can also be obtained by the direct action of the acid (e.g. nitric or hot strong sulphuric) on the metal. Many of them, e.g. the **sulphate** and **nitrate,** have bluish solutions; the crystalline salts themselves are in these cases generally blue. **Cupric sulphate,** $CuSO_4.5H_2O$, for instance, crystallizes in beautiful blue triclinic crystals; the anhydrous sulphate obtained by heating the hydrate above 250° C. is colourless.

Some of the salts show interesting colour-changes. The **chloride,** for instance, which is formed by dissolving the hydroxide or carbonate in hydrochloric acid, is pale blue in dilute solution, green in moderately strong solution, and yellowish green when the concentration is very high. Somewhat analogous changes are seen in the solid state; the dihydrate, $CuCl_2.2H_2O$, is green, the monohydrate greenish yellow, and the anhydrous salt brown. The colour also depends on the temperature; a solution which is bluish at low temperatures may become green or even yellow on heating. Further, the passage of hydrogen chloride gas through a green solution turns it yellow or brown; the addition of calcium or magnesium chloride has a similar effect, but the addition of zinc or mercuric chloride tends to cause the colour to return to green or even blue.

The colour-changes are quite analogous to those noticed in a solution of cobalt chloride and (in a less marked manner) in a solution of ferric chloride. The table[1] on the opposite page makes the analogy clear.

If we can depend on analogy, we should expect that the blue colour of ordinary copper solutions would be due to the copper cation (possibly hydrated), whilst the yellowish colour produced on adding hydrochloric acid or calcium chloride would be due to a complex anion containing copper, for instance, $[CuCl_4]''$. There is independent evidence for thinking that this is the case; for,

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[1] F. G. Donnan and H. Bassett, *Trans. Chem. Soc.* 81 (1902), 955.

	Copper Chloride.	Ferric Chloride.	Cobalt Chloride.
Colour of aqueous solution at ordinary temperature	Blue (dilute) Green (concentrated)	Very pale yellow	Red
Colour on heating	Green (dilute) Brown-yellow (concentrated)	Deep brownish-yellow	Blue
On adding calcium chloride, magnesium chloride, concentrated hydrochloric acid or alcohol	Brownish yellow	Deep brownish yellow	Blue
On adding zinc chloride or mercuric chloride	Green or blue	Pale yellow	Red

when a solution of cupric chloride in hydrochloric acid is electrolysed, the yellowish constituent moves towards the anode.[1] The green colour which is characteristic of cupric chloride solutions of ordinary concentration is possibly due to the simultaneous presence of both blue cations and yellow anions. The latter tend to break up when the solution is diluted,

$$[CuCl_4]'' = Cu^{\cdot\cdot} + 4Cl'$$

and thus the solution becomes more bluish.

Recent spectroscopic studies[2] of the solutions appear to confirm the view, put forward some years ago,[3] that the colour of a solution is independent of the actual degree of dissociation into ions. The ions are supposed to have the same absorption for light whether they are moving about independently or are fixed firmly together. Such a state of affairs appears very probable, since it is believed that the ions retain their charge even when united to one another. It is thought that the light blue colour of dilute aqueous solutions is due to a salt of the form $[Cu(H_2O)_4]Cl_2$ (or to the ions of such a salt), analogous to the compound $[Cu(NH_3)_4]Cl_2$, which is the cause of the deep violet-blue colour of ammoniacal solutions. The yellow colour of solutions in hydrochloric acid is supposed to be due to a complex salt $H_2[CuCl_4]$ or to the ions of such a salt. It will be observed that the co-ordination number, four, is assumed in all these compounds.

The chief **insoluble cupric salts** are the basic carbonate, sulphide

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[1] V. Kohlschütter, *Ber.* **37** (1904), 1161.

[2] F. H. Getman, *J. Phys. Chem.* **26** (1922), 217.

[3] By A. Hantzsch, *Ber.* **41** (1908), 1216, 4328; *Zeitsch. Phys. Chem.* **72** (1910), 362.

and ferrocyanide; these may be obtained by precipitation. The green precipitate produced when sodium carbonate is added to a solution of cupric sulphate is apparently a mixture of basic carbonate and basic sulphate; the composition of the precipitate seems to vary with the conditions of precipitation, and it is difficult to assign a definite formula to any of the constituents.[1]

The **sulphide,** CuS, unlike the sulphides of most of the metals hitherto considered, can be produced in faintly acid solution; it is probably the main constituent of the black precipitate which comes down when hydrogen sulphide is bubbled through a solution of a cupric salt containing a little free hydrochloric acid, but it is almost certain that cuprous sulphide and free sulphur are present. Cupric sulphide can be obtained pure by heating cuprous sulphide with flowers of sulphur at the boiling-point of the latter.

The **ferrocyanide** is a brown-red precipitate, which is of considerable interest to the physical chemist, owing to its employment as a *semi-permeable membrane.* When a single drop of copper sulphate is introduced into the interior of a solution of potassium ferrocyanide by means of a pipette, the drop becomes surrounded with a membrane of the brown ferrocyanide, which prevents the salts from mixing further; thus the drop retains its form indefinitely. If a porous vessel is filled with copper sulphate solution and immersed in potassium ferrocyanide solution, copper ferrocyanide is precipitated in the pores of the vessel, and constitutes a membrane pervious to water, but almost impervious to the molecules of substances like sugar. The use of such a semipermeable membrane in measuring the "osmotic pressure" of sugar in aqueous solution has been referred to in the introduction (Vol. I, page 67).

Although the impermeability of the membrane to sugar is nearly complete, this is not true of all dissolved substances; potassium nitrate, for instance, can diffuse through a membrane to an appreciable extent, although less readily than water. Thus the membrane exhibits "selective permeability" rather than "semi-permeability." The cause of selective permeability is still a subject upon which disagreement prevails. The most obvious explanation is that the membrane is threaded by extremely small channels, which let through the small molecules, but which stop the passage of the bigger molecules; thus, according to this view, the membrane acts as a sieve, or ultra-filter.

The sieve theory in the simple form, however, can hardly be

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[1] R. L. Mond and C. Heberlein, *Trans. Chem. Soc.* **115** (1919), 908. Compare S. U. Pickering, *Proc. Chem. Soc.* **25** (1909), 188, and discussion following.

accepted. It has been found by microscopic examination that a thin ferrocyanide membrane consists of a layer of colloidal particles of sizes varying between $50\mu\mu$ and $400\mu\mu$. The diameter of the channels[1] between the particles is believed to be about 10 to $20\mu\mu$. This is much greater than the diameter of the molecule. On the other hand, the pores are small enough to make it likely that all the molecules within the pores are under the influence of capillary forces, which may prevent the molecules of certain substances from entering the channels, whilst favouring the entrance of others. In this modified form, the sieve theory is at least worthy of consideration.

Another possible explanation of selective permeability assumes that the membrane may dissolve different substances to a different extent. Thus a ferrocyanide membrane placed between a sugar solution and pure water will absorb water on each side, but the concentration of water in the membrane will be greatest on the side where the water is pure and undiluted with sugar. Water will then diffuse through the membrane from the side where the concentration of water is greatest to the side where the concentration is less (i.e. the side with the sugar solution), and since the membrane will thus become supersaturated with water on this side, water will pass out into the sugar solution. Thus a steady flow of water through the membrane will proceed in a direction which tends to render the sugar solution more dilute. The sugar which is not appreciably dissolved by the membrane cannot pass through.

Two varieties of this latter theory can be distinguished, since it may be supposed that either " true solution " or alternatively " surface adsorption " of water by the membrane is the important factor.[2] In the second case, the theory becomes practically identical with the " modified sieve theory " suggested above, in which capillary forces—rather than mechanical obstruction—allows the molecules of certain substances to enter the pores, whilst preventing others.

Ammonia Compounds.[3] When ammonia is added to cupric sulphate, a light blue precipitate first appears, which is presumably the hydroxide. This dissolves in excess of ammonia to give a deep violet-blue solution. By adding alcohol it is possible to obtain deep blue needles of the compound, $CuSO_4.4NH_3.H_2O$. Other cupric salts yield a deep blue colour with ammonia, and a solution

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[1] F. Tinker, *Proc. Roy. Soc.* **92** [A] (1916), 357; *Trans. Faraday Soc.* **13** (1917), 133.

[2] E. J. Hartung, *Trams. Faraday Soc.* **15** (1920), iii, 160.

[3] H. M. Dawson and J. McCrae, *Trans. Chem. Soc.* **77** (1900), 1239; H. M. Dawson, *Trans Chem. Soc.* **89** (1906), 1666; **95** (1909), 370.

of similar appearance is obtained by dissolving pure cupric hydroxide (free from sulphates) in aqueous ammonia. The ammoniacal solution of cupric hydroxide has the singular property of acting as a solvent for cellulose.[1] Reducing agents, like sulphur dioxide or potassium cyanide, destroy the deep blue coloration, cuprous compounds being produced.

The ammoniacal solutions of cupric hydroxide and cupric salts are supposed to contain such ammines as $[Cu(NH_3)_4](OH)_2$ and $[Cu(NH_3)_4]SO_4$, and the deep blue colour of the cupric ammines has been ascribed to the complex cation $[Cu(NH_3)_4]^{\cdot\cdot}$ which is present in all the solutions.

It is interesting to note that in the ammines of divalent copper, as in the ammines of divalent palladium and platinum, the co-ordination number is four. On the other hand, complex salts of copper are known in which the co-ordination number is six; as an example the complex nitrite $K_4[Cu(NO_2)_6]$ may be mentioned.[2]

B. Compounds of Monovalent Copper (Cuprous Salts).

Cuprous oxide, Cu_2O, can—as already stated—be produced by heating cupric oxide at a high temperature, and cooling out of contact with air. It is more convenient to prepare it in a wet way, by the action of a reducing agent, such as hydroxylamine or glucose, on a cupric salt in the presence of alkali. The precipitate first thrown down when a solution containing copper sulphate and hydroxylamine hydrochloride is rendered alkaline with potassium hydroxide is light yellow, and is probably a hydroxide. But it soon becomes orange or brick-red, and when dried *in vacuo* over calcium chloride, is found to be nearly anhydrous.[3] The dry oxide usually possesses a bright red colour, although its tint—and still more that of the hydroxide—varies somewhat with the method of preparation, being probably affected both by the size of the particles and also by the water-content.[4] Cuprous oxide can also be obtained by the electrolysis of a sodium chloride solution in a cell fitted with a copper anode; the oxide produced is usually yellow if formed at temperatures below 60° C., but is scarlet if formed at 100° C.

The **cuprous salts** are less stable than the cupric salts. When, for instance, sulphuric acid is allowed to act on cuprous oxide, the main product is not cuprous sulphate, but cupric sulphate along with metallic copper. Nevertheless, cuprous sulphate can

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[1] For details regarding the solubility of cellulose in these solutions, see E. Connerade, *Bull. Soc. Chim. Belg.* **28** (1914), 176.

[2] F. H. Jeffery, *Trans. Faraday Soc.* **16** (1921), 453.

[3] L. Moser, *Zeitsch. Anorg. Chem.* **105** (1919), 112.

[4] H. W. Gillett, *J. Phys. Chem.* **13** (1909), 332.

exist to a small extent in aqueous solution, as can be shown by boiling finely-divided copper with cupric sulphate. A small portion of the copper is attacked, forming cuprous sulphate, according to the balanced reaction.[1]

$$CuSO_4 + Cu \rightleftharpoons Cu_2SO_4$$

The amount of cuprous salt formed is very small, but it is larger at 100° C. than at ordinary temperatures. If the solution is filtered hot, the filtrate on cooling deposits a visible amount of metallic copper, which shows that cuprous sulphate must have existed in considerable quantity in the hot solution, but has partly decomposed on cooling. At ordinary temperatures, in a normal solution of copper sulphate in equilibrium with metallic copper the ratio of cupric ions ($Cu^{\cdot\cdot}$) to cuprous ($Cu^{\cdot}$) is about 100 : 1.

It is not surprising that solid cuprous sulphate cannot be isolated from an aqueous solution. It has, however, been obtained through the action of methyl sulphate upon cuprous oxide at 160° C., water and oxygen being excluded.[2] It is a grey powder which is decomposed by water with the production of cupric sulphate and copper.

The view has been advanced that cuprous sulphate is actually the primary product formed when sulphuric acid acts upon metallic copper.[3]

The halogen salts of monovalent copper are more stable than the sulphate, and can easily be prepared in the solid form. These are almost insoluble in water, like the corresponding silver compounds, which they resemble in many other respects, notably in being sensitive to light. **Cuprous chloride,** CuCl, is formed when a solution of cupric chloride in hydrochloric acid is boiled with metallic copper.

$$Cu + CuCl_2 = 2CuCl.$$

The cuprous chloride produced is soluble in strong hydrochloric acid, but when the solution is diluted with water, it is thrown down as a heavy white crystalline precipitate, insoluble in pure water. On exposure to the light, the white colour turns bluish-grey. Cuprous chloride is soluble in ammonia, producing a colourless solution, which is easily oxidized by the air, yielding the deep blue ammoniacal cupric solution referred to above. A solution of cuprous chloride in hydrochloric acid readily absorbs carbon monoxide gas, doubtless forming a compound. The power of the lower salts of copper to absorb the lower (unsaturated) oxide of

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[1] For further discussion of this equilibrium, and the effect of cuprous salts on the deposition of copper, see A. J. Allmand, "Applied Electrochemistry" (Arnold), Chapter XVII.

[2] A. Recoura, *Comptes Rend.* **148** (1909), 1105.

[3] J. T. Cundall, *Trans. Chem. Soc.* **105** (1914), 60.

carbon may be compared to the power of the lower salts of iron and ruthenium to unite with nitric oxide.

Cuprous bromide is less soluble than the chloride, but resembles it in being sensitive to light. **Cuprous iodide** can be formed from cupric salts without the addition of a reducing agent. On the addition of potassium iodide to cupric sulphate, cuprous iodide is formed; no doubt cupric iodide is first produced,

$$CuSO_4 + 2KI = CuI_2 + K_2SO_4,$$

but it is unstable, and splits up spontaneously,

$$CuI_2 = CuI + I,$$

the cuprous iodide being thrown down as a precipitate. However, since the decomposition of the cupric body is not quite complete, it is best to add a reducing agent, such as sulphur dioxide: this removes the free iodine, and leaves cuprous iodide as a white precipitate, which is even more insoluble than the bromide or chloride.

Cuprous sulphide is formed as a black substance when cupric sulphide is heated in hydrogen. Solid solutions, having a composition between that of cuprous sulphide and cupric sulphide,[1] exist; they can be formed by fusing copper and sulphur together, or by heating cuprous sulphide in hydrogen sulphide. The sulphur content in the latter case depends on the temperature employed. It increases as the temperature falls, until at 358° C. the product is pure cupric sulphide.

Cuprous sulphite is probably the only oxy-salt of monovalent copper easily produced from an aqueous solution. It is obtained as a white precipitate by passing sulphur dioxide into a hot solution of cupric acetate in acetic acid. Sulphur dioxide is here made to function, first as the reducing agent, and then as the precipitant.

Cuprous cyanide, $CuCN$, is formed when potassium cyanide is heated with cupric sulphate; a red precipitate of cupric cyanide is first produced, but loses cyanogen on boiling, yielding white cuprous cyanide. Excess of potassium cyanide redissolves the precipitate to give a colourless solution containing the complex cyanide $KCN.CuCN$, which probably ionizes in the mode expressed by the formula, $K[Cu(CN)_2]$.

C. Miscellaneous Compounds.

Copper peroxide.[2] When hydrogen peroxide is added to an alcoholic solution of cupric chloride at —40° C., and alcoholic

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[1] E. Posnjak and E. T. Allen, *Econ. Geol.* **10** (1915), 491.

[2] L. Moser, *Zeitsch. Anorg. Chem.* **86** (1914), 380. Compare J. Aldridge and M. P. Applebey, *Trans. Chem. Soc.* **121** (1922), 238.

potash is then added, a dark brown unstable peroxide is obtained. It can be washed with alcohol and ether at — 50° C. The same compound can be obtained in the dry state, by the action of ethereal hydrogen peroxide on cupric hydroxide at about 0° C. and is then found to have the composition $CuO_2.H_2O$. *If touched with a* warm glass rod, it explodes.

Action of Light of Copper Salts. It has already been mentioned that cuprous chloride and bromide, like the corresponding silver salts, undergo a change of colour when exposed to light. The substance becomes first greyish blue (or dark green in the case of the bromide) and finally dark copper-coloured ; the change does not occur if the compounds are quite dry.[1] There seems to be little doubt that, as in the case of the silver compounds, partial decomposition occurs, metallic copper and free halogen being produced ; the copper appears first in particles of " colloidal " size. In the dark, the reverse changes occur. In the case of the iodide there is no appreciable change of colour on exposure, but it is fairly certain that some change occurs, since the electrical conductivity of cuprous iodide increases considerably when it is exposed to light, and falls again when the light is shut off.[2] The increased conductivity is ascribed to the free iodine ; its disappearance in the dark is due to the recombination of the two elements. It has been found by independent work that cuprous iodide containing a trace of free iodine is a good conductor, but that it loses practically all its conductivity when the free iodine is driven off.

The action of light upon copper compounds may be exhibited in a different way, by means of an electric cell in which both poles are of copper, being essentially similar except that one is exposed to light and the other is not. The light causes changes which involve an alteration in the potential. The cell

Copper unilluminated	Copper formate solution containing formic acid	Copper illuminated

is capable of developing an E.M.F. of over 0·1 volt.[3] The illuminated plate acts as the negative (attackable) pole.

Analytical

The various reactions of copper salts given above serve to characterize the compounds of the metal. Particularly striking is the intense blue coloration obtained by adding excess of ammonia ;

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[1] G. Singh, *Trans. Chem. Soc.* **121** (1922), 782.

[2] G. Rudert, *Ann. Phys.* **31** (1910), 559. Compare K. Bädeker and E. Pauli, *Phys. Zeitsch.* **9** (1908), 431.

[3] T. W. Case, *Trans. Amer. Electrochem. Soc.* **31** (1917), 351.

nickel, however, gives a similar reaction. The blue precipitate produced by sodium hydroxide also serves as a useful test; it turns black on warming. Copper salts moistened with hydrochloric acid impart a green colour to a Bunsen flame.

Copper is separated from most of the metals hitherto described by the passage of sulphuretted hydrogen through a faintly acidified solution. The sulphides of several other metals (mostly belonging to the "B" groups of the Periodic Table) such as tin, antimony, arsenic, mercury, cadmium, lead and bismuth are precipitated at the same time, if these metals happen to be present in the solution. The separation of these metals by purely chemical means is a rather long operation, and cannot here be described in detail.[1] The separation from tin, antimony and arsenic depends on the fact that the sulphides of these metals are soluble in yellow ammonium sulphide. The separation from the other metals depends on the fact that copper forms a stable complex cyanide. Thus from a solution containing excess of potassium cyanide, it is possible to precipitate lead and bismuth by means of sodium carbonate, or mercury and cadmium by means of hydrogen sulphide, copper remaining in each case in the solution.

Having obtained the whole of the copper in a solution free from all other metals, and having driven off cyanides, if present, by evaporation with sulphuric acid, we can proceed to convert the copper into some form in which it can be weighed. A rough method is to precipitate with sodium hydroxide, and weigh as cupric oxide; but the precipitate thrown down usually contains traces of soda, which cannot easily be washed out. Copper may be precipitated as sulphide by passing sulphuretted hydrogen through the acidulated salt solution; but cupric sulphide, CuS, cannot be ignited in the air, as this would convert it to oxide or to sulphate. If gently ignited in a current of hydrogen, cupric sulphide is converted wholly to cuprous sulphide (Cu_2S), a substance of very constant composition, which can then be weighed. The estimation of copper as sulphide properly conducted is very accurate, but the ignition in hydrogen is a little troublesome.

Copper is, however, most conveniently estimated, as metallic copper, by the *electrolysis* of the sulphate solution in any of the forms of apparatus described in Chapter XI (Vol. I). The precipitation of the metal upon the cathode can be completed in ten to fifteen minutes if the solution is rapidly stirred; the electro-analytical apparatus designed by Sand and by Fischer allow excellent

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[1] For details see F. P. Treadwell, "Quantitative Analysis"; translation by W. T. Hall (Chapman and Hall). R. Fresenius, "Anleitung zur quantitativen chemischen Analyse" (Vieweg).

deposits of copper to be obtained in this time. Neutral copper sulphate solutions do not yield very satisfactory deposits upon the cathode. But from solutions containing a little nitric acid (or, alternatively, sufficient potassium cyanide or ammonium oxalate to form a complex salt) very smooth bright coatings of copper may be obtained ; after deposition is complete, the electrode can be dried quickly by washing with alcohol and heating in the steam oven.

One advantage of the electrolytic method of separating copper is that it largely obviates the tedious chemical separation of copper from most of the other metals referred to above. The addition of nitric acid to the bath is usually sufficient to prevent the co-deposition of lead, zinc, cadmium, nickel and cobalt from solutions containing salts of these metals. On the other hand, if a metal like bismuth, which falls near to copper in the Potential Series, be present in the solution, it is necessary to regulate the cathode potential carefully if the separation of the two methods is desired ; the electrolytic separation of copper and bismuth is conducted from a tartrate solution, in which bismuth exists as a stable complex tartrate.[1] If metals like silver, distinctly more noble than copper, be present in solution, they should be removed (by graded electrolysis, or otherwise) before the quantitative precipitation of the copper is carried out.

Copper may also be estimated by a *volumetric* method, advantage being taken of the fact that cupric salts are oxidizing agents. If copper is present as sulphate in neutral solution, and is warmed with excess of potassium iodide in a stoppered bottle, iodine will be liberated owing to the fact that cupric iodide decomposes spontaneously into cuprous iodide and iodine. The amount of iodine liberated can quickly be found by titration with a solution of thiosulphate of known strength ; the destruction of the iodine is seen by the disappearance of the yellow colour from the solution. Just before the end-point of the titration is reached, a little starch solution is added to the liquid ; starch gives a blue colour with free iodine, and the disappearance of this colour marks the removal of the last trace of iodine from the solution. The amount of thiosulphate used shows the amount of iodine liberated by the copper sulphate, and this gives a measure of the amount of copper present.

The changes involved may be expressed thus :—

$$\begin{aligned} &(1)\ 2CuSO_4 + 4KI = 2K_2SO_4 + 2CuI + I_2 \\ &(2)\ 2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6 \end{aligned}$$

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[1] A. Fischer, " Elektro-analytische Schnellmethoden " (Enke).

The liberation of iodine according to equation (1) is not at first quite complete; however, as the iodine is removed by change (2), the remainder of the cupric salt reacts, setting free iodine, so that the amount of thiosulphate finally consumed corresponds to the quantity of copper present.

TERRESTRIAL OCCURRENCE

Copper is only a minor constituent of rock-magma. It occurs in many ordinary igneous rocks, but the copper-content of most of these rocks is very small, being generally of the order of 0·01 per cent. In a few cases, sulphides of iron, copper, and often nickel, have separated out in the ultra-basic portions of the intrusive masses, and valuable ores have been produced; the nickel-copper ores of Ontario may be of this character. In most cases, however, the copper appears to have accumulated, during the process of solidification of an intrusive mass, in the portion which remains liquid to the last, and the thermal waters which have been given off in the final stages of the process are often comparatively rich in copper. It can be regarded as being present in the water (at least potentially) as a sulphide, which is kept in solution—for the moment—on account of the high temperature and pressure, and possibly also on account of the presence of acid substances such as hydrogen sulphide and carbon dioxide. But copper is by no means the only metal which becomes concentrated in this way; the waters as they leave the intrusive mass contain a very much larger amount of iron sulphide; frequently notable amounts of lead, zinc, and possibly antimony and arsenic are present, and commonly traces of silver and gold. The chief non-metallic substance dissolved in the water is silica, which is probably present in large amount.

As the waters ascend towards the surface, the lowering of temperature and pressure cause the deposition of part of the dissolved substances on the walls of the fissures through which the waters are rising. In the early stages of the ascent, quartz is deposited in the veins, together with

Iron pyrites . . . FeS_2

The iron pyrites itself may contain traces of copper, but where the copper concentration in the thermal waters is sufficient, the double sulphides

Copper pyrites (Chalcopyrite) $CuFeS_2$
and Bornite[1] . . . . Cu_3FeS_3 or perhaps Cu_5FeS_4

soon begin to be deposited along with it. Some of the most

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[1] For the question of formula see B. J. Harrington, *Amer. J. Sci.* **16** (1903) 151.

important copper deposits were formed in this way; it should be noted that iron is almost always present in quantities greatly exceeding the copper.

Copper pyrites is a mineral with brass-yellow metallic lustre, although it is sometimes found tarnished and iridescent. Where there has been sufficient freedom of growth to allow it to assume a proper crystalline form, it crystallizes in the tetragonal system. Bornite is sometimes known as "purple copper ore," but its colour varies from purplish brown to red. It has a metallic lustre when fresh, and when tarnished is iridescent.

The deposition of these sulphides from thermal waters is especially to be expected where the waters have to pass through rocks which will remove the acid gases; it is a fact that many of the veins are richest in copper where they cut limestone. But copper ore is not dependent on the presence of limestone in the same way as the ores of zinc and lead. One of the richest copper deposits in the world, that of Butte (Montana) is found in a granitic rock (quartz-monzonite).

Where the waters are rich in arsenic or antimony, we may also get such minerals as,

	Enargite	Cu_3AsS_4
and	Tetrahedrite . . .	$Cu_8Sb_2S_7$

Both of these are black minerals with metallic lustre. Tetrahedrite sometimes occurs as remarkable tetrahedral crystals, coating, or coated with, crystals of chalcopyrite.

It may be advantageous to point out here that if the ascending waters contain zinc and lead, these metals will—in a similar manner—be deposited as the sulphides,

	Zinc blende . .	ZnS
and	Galena . . .	PbS

The deposition of these two sulphides is particularly likely to occur where the waters pass through limestone. The zinc and lead minerals have rarely been deposited at exactly the same points as the copper ores, and indeed the main zinc-lead ores are found in different localities to the main copper ores. Silver is commonly found in small quantities both in the copper ores, and also in the lead ores, and is accompanied by even smaller traces of gold. Bismuth is frequently found in copper ores—a matter of some technical importance, owing to the fact that bismuth adversely affects the quality of copper.

In the upper portions of old copper-bearing veins, where air, carbon dioxide and water have long had opportunity of reacting with the sulphides, the sulphide ores have been oxidized to sulphates and basic carbonates, such as

	Chalcanthite	$CuSO_4.5H_2O$
	Brochantite	$CuSO_4.3Cu(OH)_2$
	Malachite	$Cu(OH)_2.CuCO_3$
and	Azurite	$Cu(OH)_2.2CuCO_3$

Of these minerals, brochantite and malachite are green, whilst azurite and chalcanthite are blue. Sometimes, as the result of further changes, the oxides

	Cuprite	Cu_2O
and	Tenorite	CuO

appear in the upper zone.

The normal sulphate of copper is soluble in water, and often will pass down in solution from the oxidized zone to the unchanged sulphide zone below. As soon as it enters the latter, however, it will react with the iron sulphides which are usually present in large quantities. Double decomposition will occur; copper sulphate and iron sulphide will produce iron sulphate and copper sulphide, which is considerably less soluble than the sulphide of iron. Thus at the junction of the oxidized and unchanged zone of the deposit, we get a very noteworthy amount of the "secondary" minerals,

	Chalcocite (copper glance)	Cu_2S
and	Covellite	CuS.

This rich region at the junction of the oxidized and unchanged portion of the ore is known as the *Zone of Secondary Enrichment.*[1]

The main copper ores of the world occur at points upon the Pacific Ore-circle. At Chuquicamata (Chili), high up in the Andes, occurs "what is probably the largest copper deposit known to-day."[2] The lower portions of the ore consists of sulphides, but the upper portions of the ore—the parts which are now being mined—have become entirely oxidized, mainly to the basic-sulphate (brochantite). Chlorides also occur in this part of the ore.

Passing northwards, we find extensive ores of copper in Arizona, where a low-grade sulphide ore is largely oxidized to carbonate and oxide in the upper portions; this oxidized ore only contains about 1·6 per cent. of copper, but the aggregate copper-production of the state is quite large. Copper ores occur again in Utah and in the Rocky Mountains near Butte (Montana); the famous Anaconda

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[1] J. F. Kemp, *Econ. Geol.* **1** (1906), 11; E. G. Zies, E. T. Allen, and H. E. Merwin, *Econ. Geol.* **11** (1916), 407; W. F. A. Thomas, *Trans. Inst. Min. Met.* **23** (1913–14), 55.

[2] According to E. A. Cappelin Smith, *Trans. Amer. Electrochem. Soc.* **25** (1914), 193.

mines occur in the latter region. The Montana ores were evidently originally deposited by waters ascending through fissures from an igneous mass, but there has been much secondary enrichment; the secondary sulphides (chalcocite and covellite) are the most important minerals. A great deal of the sulpharsenide, enargite, is found in Montana, and is apparently a primary mineral since it exists in greatest quantities in the lower, unchanged, part of the ore, although, according to some geologists, it is of secondary origin.

Further round the circle, copper ores are found in Alaska. The metal occurs again in Japan, and very important ores are met with in Australia (mainly in Queensland, New South Wales and South Australia) and lastly in Tasmania.

Outside the Pacific Ore-circle, copper deposits of considerable importance occur in the Huelva district of Spain, notably at Rio Tinto.[1] Here the ores consist essentially of iron pyrites, but in many parts it is mixed with a small quantity of copper pyrites. The copper-content is about 2–3 per cent. Secondary enrichment due to descending water has occurred, and in the enriched zone the ores may contain 4–7 per cent. of copper.

The deposit of "kupfer-schiefer" at Mansfeld (Germany) is of interest owing to its mode of origin. The stratum is essentially a blackish, bituminous shale of marine origin, 1–2 feet thick, containing remains of the bones of fish, shells and much organic matter derived from the life which existed in the sea in which the sediments were deposited. The shale now contains, however, 1–3 per cent. of copper, which has evidentially been brought into it later by the agency of waters percolating through the rocks of the district, since the copper-content always increases near to certain fissures through which the copper-bearing waters must have arrived. The organic matter of the shale has apparently reduced the copper—which possibly existed in the water as sulphate—to an insoluble sulphide, and consequently the shale contains a notable amount of copper, whilst the rocks above and below it, which are free from organic remains, contain little or none.

The extensive deposits of the Lake Superior region are of great interest, since the copper here occurs in the metallic state.[2] The rocks of the district include some conglomerates and sandstones (i.e. the shingle and sands of an old beach); an old lava is also met with having a spongy or "vesicular" structure, caused by the escape of imprisoned gases at the moment of solidification. Long after the formation of these rocks, copper-bearing waters, possibly

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[1] A. M. Finlayson, *Econ. Geol.* **5** (1910), 403.

[2] H. C. H. Carpenter, *J. Inst. Met.* **12** (1914), 230.

of igneous origin, have deposited metallic copper in the interstices between the pebbles of the conglomerate and between the sand-grains of the sandstone; likewise the waters have left metallic copper within the vesicules of the lava, where we find "amygdules" (kernels), often consisting of some common mineral (calcite or a zeolite) coated with metallic copper. Fissures also penetrate the rocks and these contain metallic copper, which in exceptional cases may occur in very large lumps; a lump was found in 1857, weighing 420 tons. The copper occurring in the conglomerates and sandstones is found in small particles in the cement which binds together the pebbles or grains, and renders the whole of the red rock tough and difficult to break up.

One naturally inquires what the reducing agent was which caused the reduction to the metallic condition. Probably it was some iron compound occurring in the lava or elsewhere; many ferrous salts—and also iron pyrites—are capable under certain conditions of reducing copper to the metallic state. If we imagine that hot waters containing cupric sulphate enter a bed containing such a reducing agent, much cuprous sulphate will be formed; cuprous salts can exist at high temperatures in considerable concentration. However, as the waters cool, the cuprous sulphate will decompose to cupric sulphate and metallic copper, which will be deposited in the cavities of the rocks through which the waters are percolating.[1]

The important copper-nickel ores of Sudbury (Ontario) have already been discussed in the section dealing with nickel, and need not be described a second time. The ores of Cornwall (England) deserve a passing mention, although the remunerative ores are now completely worked out. The principal minerals were chalcopyrite, bornite and chalcocite, the latter occurring in splendid crystals, known locally as "redruthite."

METALLURGY[2] AND USES

Preliminary Considerations. It will be evident—after reading the preceding section—that unoxidized copper ores, as

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[1] H. N. Stokes, *Econ. Geol.* **1** (1906), 648. Compare S. Croasdale, *Eng. Min. J.* **97** (1914), 745.

[2] Reference should be made to the papers on copper metallurgy by H. C. H. Carpenter, *J. Roy. Soc. Arts*, **66** (1918), 114, 128, 141, and H. O. Hofman, *J. Franklin Inst.* **181** (1916), 83, and to the portions of W. Gowland's "Metallurgy of Non-ferrous Metals" (Griffin) dealing with copper. In consulting textbooks on copper, care should be taken to obtain the most recent edition of the works, as the position is rapidly changing. Standard works include D. M. Levy, "Modern Copper Smelting" (Griffin); E. D. Peters, "Practice of Copper Smelting" (McGraw Hill); H. O. Hofman, "Metallurgy of Copper" (McGraw Hill). A small book by H. K. Pickard, "Copper" (Pitman), gives much useful information.

mined, usually contain comparatively small amounts of copper sulphides accompanied by larger amounts of iron sulphides and by a very large amount of gangue, usually of a siliceous character, and having a high melting-point. The oxidized ores are similar, but the place of sulphides is taken by sulphates, carbonates and oxides.

Owing to the comparatively large amount of valueless material in all copper ore, it is clearly necessary to avoid cost of transport by smelting the ores close to the mines. Thus most of the world's copper is now produced in regions like Arizona, Montana and Chili, where the ores occur, and only the final stages (refining) are conducted at any considerable distance from the mines. Centres like South Wales, which depend upon a supply of ore or concentrate from a distance, have ceased to be of the first importance.

The copper-content of the ore will vary considerably, and sulphide ore arriving at a given smelting works is generally classified at once into "first-class" and "second-class" ore. The former (usually containing more than about 5 per cent. of copper) is considered fit for direct smelting, and the only preliminary treatment needed —apart from drying—is to pass it over screens and thus separate the coarse and fine portions, which usually require to be smelted separately. The second-grade sulphide ore is usually subjected to preliminary concentration so as to produce a high-grade concentrate, which is then passed to the smelter. Oxidized ores are not usually subjected to the same sort of preliminary concentration as a sulphide ore, partly because they are not specially suited for flotation, but mainly because they are nearly always treated by wet methods, and the leaching is itself a form of concentration.

The limit, below which a copper ore ceases to be worth handling, will vary with many local conditions, and with the state of the copper market. In Montana, the average content of second-class ore is about 3 per cent.; but, in Germany during the war, when the demand for copper was very great, Mansfeld ore with only 0·7 per cent. of copper is said to have been treated. At Rio Tinto, the content of those ores which are regarded primarily as copper ores is usually about 3 per cent., but poorer ores are worth treating, on account of the value of the sulphur and iron.

Sizing. Before the particles of copper minerals may be separated from the worthless gangue, it is clearly necessary to reduce the ore to a fairly fine state of division. It is broken up with rock-crushers, and is usually then ground in mills. No method of grinding gives a product of uniform grain-size, and since the concentration of very fine powder is a different problem from that of a coarsely crushed material, it is necessary to classify the product according to the size of the particles. **Screens** or cylindrical "**trommels**" can be employed to separate all particles exceeding a certain size; the particles below this size drop out through the perforations into receptacles placed below.

But for grading the finest particles, screens and sieves are not suitable, and advantage is taken of the fact that coarse particles sink in water more quickly than fine particles. In the most primitive form of the settling process, the powdered ore is stirred with water, and the mixture is allowed to stand in a tank. After a time, the coarse particles will be found at the bottom, whilst most of the fine particles, having a low "settling velocity," will still be in suspension. In modern practice, a continuous system is employed.[1] One form of classifier (see Fig. 1) consists of a funnel-shaped vessel, provided with a perforated plate C. The pulp of ore and water is run in continuously through A; fresh water is also introduced at a carefully regulated rate through B, and rises through the perforated plate C, finally overflowing at D. When the classifier is working the plate C is always covered with a layer of ore particles, and the velocity of the rising water is necessarily greatest where it has to thread through the narrow channels between these ore-particles. The velocity at this point should be less than the normal "settling velocity" of the coarsest particles, but greater than that of the lighter particles. Consequently the coarser particles are able to pass downwards through the plate, and come out through E, whilst the smaller particles are carried upwards, and pass out by the overflow as "**slimes.**" As a rule, the term "slimes" is applied to a product the particles of which are able to pass through a "200-mesh" screen (of which the average opening is 0·07 mm. diameter).

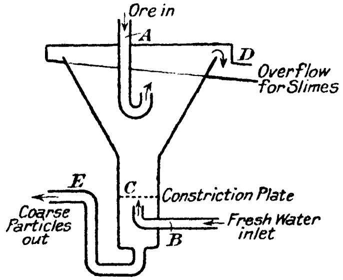

FIG. 1.—Classifier.

Concentration of Sulphide Ores. Having thus "classified" the particles according to size, it is possible to proceed to "concentrate" the valuable copper minerals occurring in each of the fractions obtained. The main methods of concentration depend upon two factors, namely:—

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[1] E. S. Bardwell, *Trans. Amer. Inst. Min. Eng.* **46** (1913), 266; R. Ammon, *Trans. Amer. Inst. Min. Eng.* **46** (1913), 277.

(1) *Gravity.* The metallic sulphides are heavier than the silicates. This is the principle of **Gravity Separation.**

(2) *Surface tension.* The sulphides will often cling to the oil-films surrounding the bubbles of a suitable "froth," whilst the silicates will sink to the bottom. This is the principle of **Flotation.**

(1) **Gravity Separation.** Wilfley tables, and other similar patterns of shaking table, are particularly suited for the concentration of "sands," that is for material containing particles of diameter between 1·5 and 0·07 mm. For coarser material, the device known as the "jig" is generally used, whilst for finer material, a "vanner" is employed in some places. These forms of concentrating plant have all been described in the introduction (Vol. I, pp. 122–124).

The worst feature of all separation methods depending on gravity is that the coarser particles of gangue tend to appear in the concentrate along with the copper grains—simply owing to their size—whilst to some extent the smallest ore-particles may remain suspended, occasionally clinging to the surface of the water; in the latter case the very principle which is usefully employed in flotation is a cause of waste in gravity-separation.

(2) **Flotation.** Separation by flotation is free from many of the disadvantages of gravity separation. Its recent introduction at Anaconda appears to have been a distinct success, and the employment of flotation is likely to become general, not perhaps as a substitute for the older methods, but rather as a supplementary method for treating the portions for which gravity separation has proved a failure. The plant used at Anaconda is known as the "Minerals Separation" type,[1] the principle being shown in Fig. 2. A pulp consisting of the finest ore-particles (slimes), sulphuric acid, "kerosene sludge-acid,"[2] and wood creosote, flows into the compartment A and thence through B into C. In each compartment it is churned up by means of the rotating paddles P. During the churning in each compartment much air is sucked into the mixture, and the liquid passing out into D separates into a liquid layer (which flows out through G) and a froth above it (which passes over the lip E and out through F). If the proportions of oils have been regulated in a manner suited to the ore, most of the valuable

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[1] See T. J. Hoover, "Concentrating Ores by Flotation" (published by the *Mining Magazine*), Chapter IX (1916 edition).

For the operation of the plant at Anaconda, see H. C. H. Carpenter, *J. Roy. Soc. Arts*, **66** (1918), 146.

[2] "Sludge acid is refuse from the refining of oil. It contains sulphuric acid and some greasy material from petroleum."—E. P. Mathewson, *Trans. Amer. Inst. Min. Eng.* **55** (1916), 519.

sulphide particles are found to have adhered to the walls of the froth, whilst most of the worthless silicates pass out with the liquid portions through G. The latter portions are treated again in a similar apparatus for the recovery of the sulphides which have failed to " float " on the first occasion.

One function (possibly not the only function) of the sulphuric acid commonly added in the flotation of copper pyrites ores is that it removes the film of tarnish which generally exists upon the pyrites particles, and which would tend to prevent the flotation of these particles.[1]

Various other forms of flotation plant[2] have been employed with good results. The Elmore Vacuum process, already mentioned in the section on molybdenum (Vol. II), has been in operation for tin-copper ores in this country.

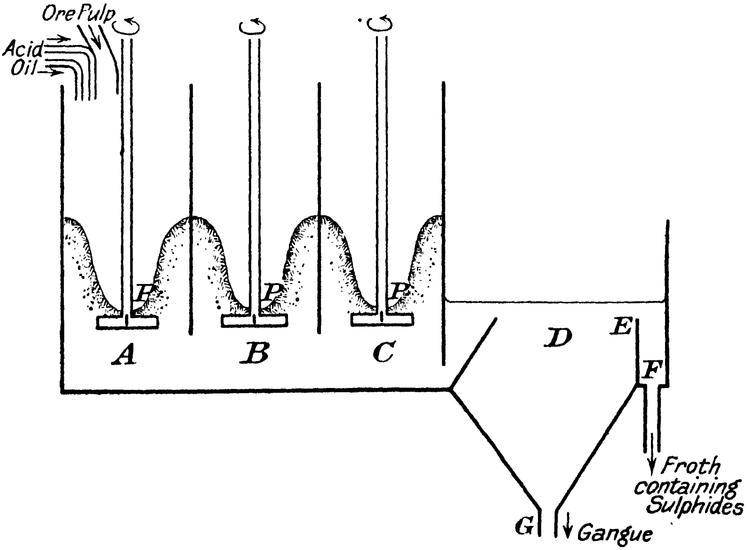

FIG. 2.—" Mineral Separations " type of Flotation Plant.

Smelting Processes. The rough table given below may help the reader to follow the various alternative processes and their different stages. The more usual methods of procedure are indicated by full lines ; those which are rather less common by dotted lines. But he should not regard the table as giving more than a very

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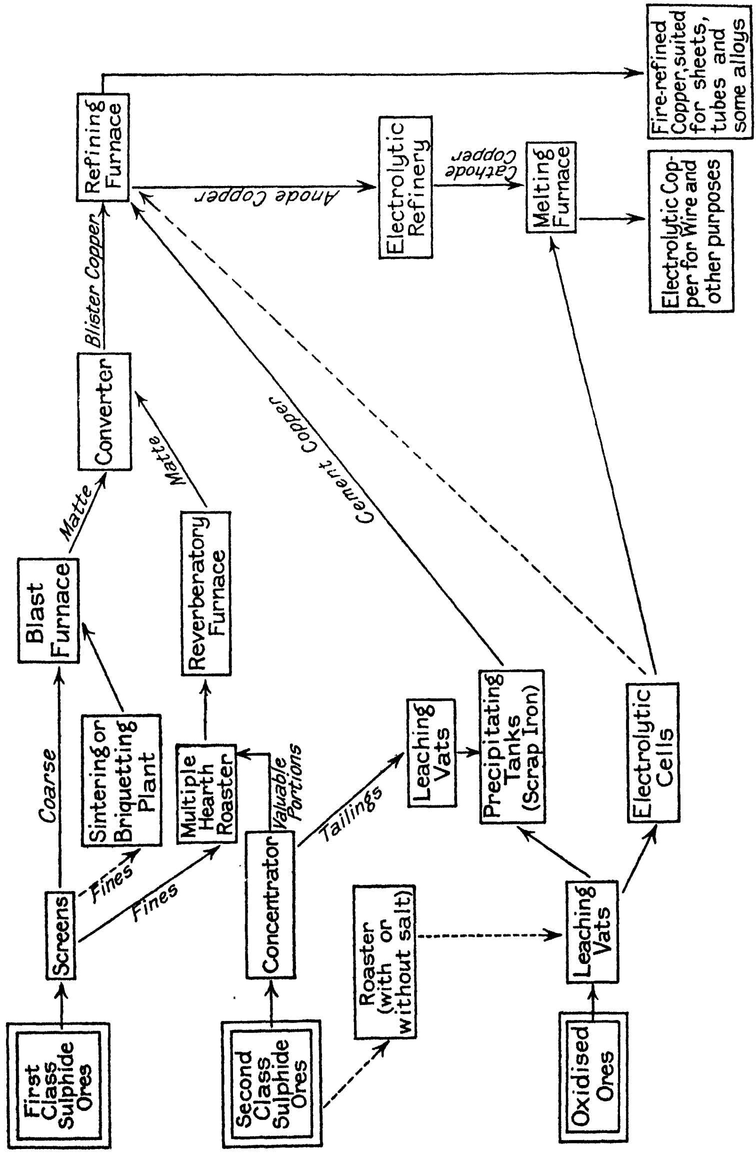
[1] W. S. Morley, *Min. Met.* **176** (1921), 32.

[2] F. Laist and A. E. Wiggin, *Trans. Amer. Inst. Min. Eng.* **55** (1916), 486, describe trials made with several types at Anaconda.

crude indication of the general lines upon which the world's copper industry is carried on.



The possible means of obtaining copper from copper ores are very numerous, but they may be classified into :—

(A) **Dry** (or thermal) processes ; most suitable for sulphide ores.

(B) **Wet** processes ; suited for oxidized ores, and also sometimes used for the certain varieties of sulphide—notably portions which are either poor in copper (as at Rio Tinto) or are in a very fine state of division.

(A) Dry Processes of Copper Production.

There are two main stages in the smelting of copper by thermal methods :—

I. The production of a "**matte,**" a mixture of iron and copper sulphides fairly rich in copper.

II. The production of **metallic copper** from the matte.

I. The Production of Matte.

This may be conducted—

(1) By a *blast-furnace method*, suitable for rich lump ore ;

(2) By a *reverberatory furnace* method, suitable for fine ore; it is also largely used for all poor ore—whether it arrives in lumps or otherwise—because, as already stated, it is usually necessary to grind it, and subject it to concentration before it is fit for furnace treatment.

(1) **Blast-furnace Smelting.** Since the amount of high-grade lump sulphide ore tends gradually to diminish, blast-furnace treatment is tending to give way to reverberatory processes.[1] In some of the important American copper works (e.g. in Montana), the blast-furnaces have actually been closed down. Nevertheless blast-furnace treatment is still of great importance in many districts. The object in blast-furnace smelting is to burn off a portion of the sulphur, and, at the same time, to convert part of the iron to iron oxide, which will then combine with the siliceous matter in the ore to form a fusible slag, consisting mainly of iron silicate ; this will leave a **matte** or mixture of iron and copper sulphides, having a far higher copper-content than the original ore. By the formation of slag, two separate results are achieved ; part of the iron is removed into the slag, and simultaneously the siliceous matter which in itself would be difficult to melt is brought into a state of fusion. Under favourable circumstances, it may be unnecessary to add limestone to the charge, since the iron oxide is a sufficient flux for the silica ; but where the ores are very siliceous—as in the case in some of the Montana ores—the presence of limestone in the charge is highly desirable.

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[1] Compare *Min. Sci. Press,* **119** (1919), 428.

In the simplest system of blast-furnace treatment, the ore is merely mixed with a very little fuel, and charged into the blast-furnace; the heat-evolution attending the oxidation of the sulphur and iron, as well as the formation of iron silicate, is relied upon to maintain the temperature of the furnace. This process, which is known as the "**pyritic process,**" is highly economical of fuel, but only works well in ores rich in sulphur, iron and free silica. If the ore contains a large amount of inert silicate minerals (as opposed to free silica) a considerable amount of carbonaceous fuel must be added to assist in maintaining the temperature; the process is then known as the "partial pyrite" process.

The criticism has been raised against pyritic smelting that it gives a matte of low copper-content. The elimination of iron from the matte is often accelerated if part of the ore has been previously *roasted.* The removal of the sulphur and the oxidation of the iron in this roasted portion being well advanced before the ore enters the blast-furnace, the passage of iron into the slag phase is very rapid, and a matte containing less iron and sulphur and much more copper than is possible in the smelting of unroasted ore is obtained at the bottom of the furnace. On the other hand, the proportion of fuel must clearly be increased if roasted ore is included in the charge.

The true pyritic process is rarely used at present, although in Tasmania it has proved very successful, only ½ per cent. of coke being needed in the charge. But in numerous places, partial pyritic smelting (involving the use of over 3 per cent. of fuel) has given good results, notably in Montana, Tennessee, and South Wales. As an example of the blast-furnace treatment of ore after preliminary roasting, the smelting of the copper-nickel ores of Sudbury may be recalled to memory; this was discussed in the section on nickel (Vol. III).

Whichever variation of the process is adopted, the furnaces are almost invariably water-jacketed blast-furnaces similar to those in use at Sudbury (see Fig. 3). They are commonly rectangular in form, and are usually about 25 × 5 feet at the tuyeres and about 15 feet high. In a few districts where the amount of copper ore to be treated is large, much bigger furnaces are employed; one of the Anaconda furnaces (no longer in use) measured 87 feet × 5 feet at the tuyeres. The tuyeres consist of a large number of iron-pipes about 4 inches in diameter. In Europe round and elliptical furnaces have been used with success.

The charge consisting of ore, some fuel, and, if necessary, limestone, is fed into the top of the furnace. The products are allowed to run out continuously from the bottom of the furnace through a spout into a settler—a large vessel sometimes mounted on wheels—in which they separate into two layers; the lower layer is the *matte*, and the upper one is the *slag*. As the copper has much less affinity for oxygen than iron, the slag should contain but little copper; in practice, the slag is usually found to contain a certain amount of the valuable metal, which is largely present as drops of matte that have clung to air-bubbles entangled in the slag; this loss can be greatly reduced by careful working.

The matte—if allowed to solidify—is a bluish-grey or brown opaque substance having a sub-metallic lustre; at a fracture it often has a "bronzy" appearance. In some works, however, the matte is not allowed to solidify, being conveyed whilst still molten in ladles to the converter.

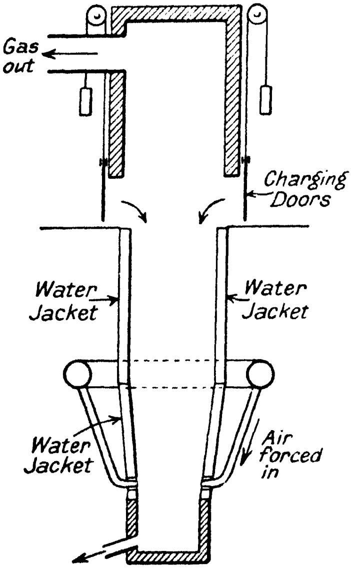

FIG. 3.—Water-Jacketed Blast-Furnace.

The dust carried off by the gases leaving the blast-furnaces contains a considerable quantity of copper and much more arsenic. It is commonly caught by electrostatic or other means, and is treated afresh.

Although for lump ore of high quality, blast-furnace smelting is satisfactory, fines cannot be smelted in this way without previous treatment, as they would either choke the shaft or else be blown out of the furnace. They are commonly treated by a reverberatory furnace, but in some districts good results have been obtained by *sintering* the fines by the Dwight-Lloyd process, such as has been described in the section on iron (Vol. III); the sinter can then be used in the blast-furnace charge. In other places, briquetting is used.

(2) **Reverberatory smelting** is, however, the process commonly adopted to deal with all fine ore, and is largely applied to the concentrates obtained by the preliminary treatment of second-grade sulphide ores. The whole of the ore receives a partial roasting, which is generally carried out in a multiple-hearth furnace, and the roasted product is then melted up in a reverberatory furnace in

which the atmosphere is non-oxidizing, matte and slag being thus produced.

A **multiple-hearth roaster** is shown in Fig. 4. The roaster is usually 18–23 feet high, and may contain five, six, or seven hearths. Rabbles attached to a revolving central shaft move round each hearth, and work the ore from the centre to the periphery or vice versa. The ore is charged into the top hearth through a hopper at the centre and is worked to the periphery, where it falls to the second hearth, and thus traverses all the hearths in turn, emerging roasted from the bottom hearth. The central shaft and rabble arms are usually hollow, and are cooled either by air or water.

In roasting ordinary ores, the heat of combustion of the sulphur is often sufficient to maintain the temperature of the furnace; but where the sulphur-content of the ore is low, it may be necessary to instal an outside grate; the grate usually delivers a flame to the second, third or fourth hearth from the top, and thus raises the charge to the temperature necessary for roasting.

In the roaster, a considerable amount of sulphur is burnt away, the sulphides being in part converted to oxides. Since the ore does not become fused in the roaster, it is probable that only the outer portions of each grain of mineral become changed; very likely in this outer portion the copper becomes converted to oxide just as much as the iron. When, however, the roasted ore is afterwards fused in the **reverberatory furnace,** any copper oxide that may be present reacts with the iron sulphide according to some such equation as,

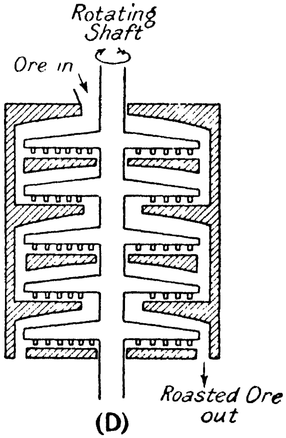

FIG. 4.—Multiple-Hearth Roaster.

$$Cu_2O + FeS = Cu_2S + FeO,$$

and the iron oxide combines with the siliceous matter, and forms a slag. Thus we are left with exactly the same result as in the blast-furnace process; but whereas in the latter process the oxidation and melting are more or less simultaneous, in the reverberatory process the roasting and melting take place in separate stages.

In Montana, where the reverberatory process has developed on progressive lines, extremely long reverberatory furnaces are used;

100 feet is quite usual, and one Anaconda furnace is 112 feet in length. The width is often about 20 feet. The furnaces are fairly low, the form being shown in Fig. 5. The flames pass from the end G over the charge spread over the floor F, and pass out at the end E; the waste heat of the emergent gases is utilized in raising steam in boilers. Originally these furnaces were fired by ordinary coal burnt on a grate (not shown) placed at the end G; now they are generally fired by pulverized coal,[1] a mixture of coal dust and air being forced into the furnace, through a series of tubes T; the coal-dust is supplied to the furnace by an ingenious system of screw conveyers. In Arizona[2] and in other States, reverberatory furnaces are fired by oil, which is injected through nozzles placed at the end G.

The furnaces are charged with roasted ore, which is introduced through hoppers H into the hottest part of the furnace, close to the firing end. Commonly it is added in small quantities, but at frequent intervals; each small charge quickly melts and subsides, mingling with the already molten material on the hearth; when the whole is molten, the furnace is ready for another small charge. By adding the roasted ore in small quantities, it is possible to avoid serious lowering of the furnace temperature during the melting process. In some furnaces, slag is skimmed from the end E every four hours, whilst in others it is allowed to flow out continuously. Portions of the matte are run out into ladles at infrequent intervals, and are taken still molten to the converters. The furnace is, however, never completely emptied, except on occasions when extensive repairs to the lining may be necessary. The process is thus practically continuous.

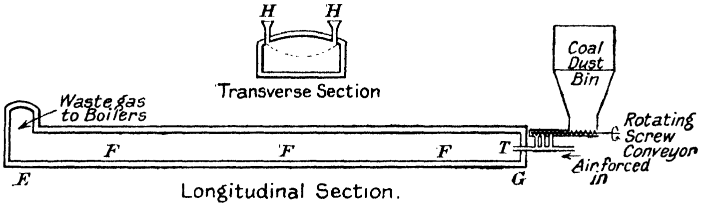

FIG. 5.—Long Reverberatory Furnace fired with Pulverized Coal.

The advantage of keeping the furnace always partly full of matte is that the life of the siliceous lining is greatly prolonged. The

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[1] R. E. H. Pomeroy, *Met. Chem. Eng.* **22** (1920), 347; E. P. Mathewson, *Eng. Min. J.* **100** (1915), 45; G. de Venancourt, *Rev. Met.* **17** (1920), 2; W. Borchers, "Metallhütten betriebe," Vol. II (1917 edition), p. 48 (Knapp).

[2] F. N. Flynn, *Trans. Amer. Inst. Min. Eng.* **55** (1916), 805.

fused matte has no corrosive action upon the lining, but freshly roasted ore, if heaped directly upon the furnace-bottom, would rapidly attack it. Furthermore, if the furnace were to be completely emptied whenever it is tapped, the considerable changes of temperature would be likely to cause serious disintegration to the brick-work.

II. Production of Metallic Copper from Matte.

The matte, whether produced in a blast-furnace or a reverberatory furnace, contains only about 40–45 per cent. of copper, with 30–35 per cent. iron, and about 25 per cent. sulphur. The next step is to eliminate most of the sulphur and iron by oxidation, leaving the less oxidizable copper in the metallic state. This operation is generally carried out in a **converter.** Converters of many different shapes have been designed for use in copper works, but they can be assigned to two main types, namely, the *horizontal* type[1] (Fig. 6) and the *vertical* type[2] (Fig. 7). In both forms, the converters are mounted so that they can be tilted at will into the positions suitable

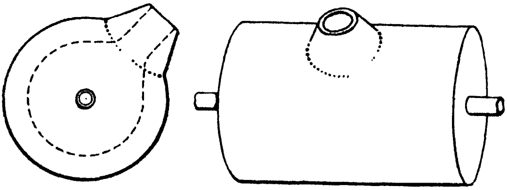

FIG. 6.—Horizontal Converter.

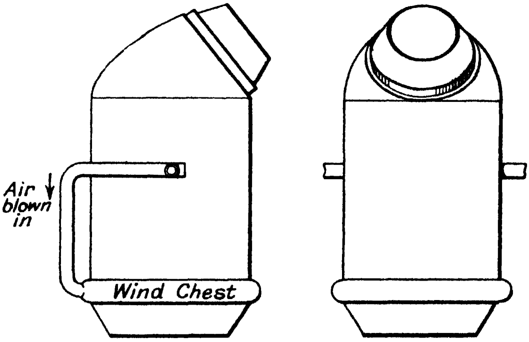

FIG. 7.—Vertical Converter.

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[1] B. de Saint-Seine, *Rev. Met.* **11** (1914), 145.
[2] M. W. Krejci, *Eng. Min. J.* **104** (1917), 669.

respectively for charging, blowing and pouring the charge, and are fitted with a series of tuyeres by means of which air can be forced through the molten matte.

At one time, the converters were lined with silica, but this material was found to be quickly attacked by the iron oxide produced in the "blow," and required frequent replacing. About 1909, the magnesite-lined converter was introduced, but magnesite proved liable to rapid mechanical wear at the temperature of the converter. However, it has been found possible to produce upon the magnesite lining, a coat of magnetic iron oxide, which protects the magnesite itself from abrasion.[1] This coating is obtained very simply by omitting to add any siliceous flux to the charge on the occasion when a freshly lined converter is used for the first time; in the absence of silica, the iron present in the matte does not form a fusible slag, but is deposited as a coating of infusible magnetic oxide on the lining. The coating, once produced, will last for a long time, and even if it wears thin, it can be renewed when desired by blowing a single charge of matte without silica. By these means, the difficulties connected with the lining of a converter have been overcome completely.

The procedure of "converting" is as follows. The converter is filled with molten matte, and the blast is turned on; the oxidation of both sulphur and iron commences at once, and the heat produced is more than sufficient to maintain the temperature of the vessel. The sulphur burns away as sulphur dioxide gas, whilst the iron passes to iron oxide, and is slagged away by siliceous material which is also added (except—as explained above—in the case of a freshly-lined converter). As in the Bessemer process of steel-making, the colour of the flame affords valuable information regarding the progress of the oxidation process.[2] So long as the flame is green, the elimination of iron is continuing. When the green colour begins to fail, the slag is poured away; the contents of the converter now consist mainly of cuprous sulphide, and it is necessary to continue the blowing until the sulphur is mostly burnt off. The colour of the flame is now reddish purple, tending to become bluish as the operation approaches completion. The progress of the operation is also judged by the character of the particles of metal shot out from the mouth. As soon as the furnace-man judges that the process is complete, the converter is tipped up and the charge poured. The copper produced contains much sulphur dioxide,

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[1] A. E. Wheeler and M. W. Krejci, *Trans. Amer. Inst. Min. Eng.* **46** (1913), 562.

[2] D. M. Levy, *Trans. Inst. Min. Met.* **20** (1910–11), 117, gives colour photographs illustrating the flame at different stages.

which is liberated at the moment of solidification, the evolution causing a blistered appearance on the solid metal, which is known as "**blister-copper.**"

Blister-copper is still too impure to be of any practical use, and is generally further **refined** in a small reverberatory furnace.[1] The essential refining operation consists in blowing a blast of air through the molten copper, by means of an iron pipe, the open end of which is pushed just below the surface of the molten metal. It is likely that the copper itself is momentarily oxidized, but since cuprous oxide is soluble in molten copper, it remains in the metallic phase, and serves to oxidize the more reactive elements. The chief impurities, iron and sulphur, are oxidized fairly readily; the former, being non-volatile, collects on the surface as a slag and is skimmed off; other impurities, like arsenic, are only partially removed. When the oxidation of the main impurities is sufficiently complete, the copper contains a great deal of dissolved cuprous oxide, and if it were allowed to solidify without further treatment, it would be very brittle—owing to the production of a copper-cuprous oxide eutectic between the grains. Therefore some deoxidizing treatment is always needed. The method known as **poling,** which is still largely employed, consists in plunging poles of green wood (preferably beech or oak) into the molten metal. This causes a vigorous evolution of gases with strong reducing properties, which convert the dissolved cuprous oxide to the metallic state. Poling must not be continued too long, since excessive poling will again render the metal unsound ("*overpoled*"). The progress of the poling operation is controlled by a man who takes a small sample of the metal from time to time in a ladle, and notes the kind of surface produced when the sample solidifies; underpoled copper has a concave surface, correctly poled copper has a "full" round surface slightly wrinkled, whilst overpoled copper is convex, and often "spews" or "throws a worm." The fracture also is an indication of the progress; underpoled copper has a brick-red inter-granular fracture, due to the presence of cuprous oxide between the grains, whilst the fracture of correctly poled copper is bright and silky. Correctly poled copper is said to be at *tough pitch.*

The unsoundness of overpoled copper is probably partly due to the sponginess caused by bubbles of the reducing gases, and partly to the presence of hydrogen dissolved in the metal. It is also fairly certain that traces of sodium occur in overpoled copper, derived of course from the sodium salts of the wood. This has not been shown conclusively to be an important cause of brittleness,

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[1] L. Addicks, *Met. Chem. Eng.* **17** (1917), 579.

but it is an interesting fact that copper which is made a cathode in a bath of fused sodium chloride, becomes quite brittle, apparently owing to the entry of sodium into the metal.[1]

Attempts have been made to use other reducing agents instead of wood for deoxidizing copper. Poling with oil has been tried, but has not proved altogether satisfactory. In view of the growing scarcity of suitable wood in copper districts, such attempts are likely to be renewed. Other deoxidizing agents, which are added to copper just before casting to remove the last traces of cuprous oxide, may also be mentioned at this point. Phosphorus (added as a copper-phosphorus alloy), zinc, manganese and aluminium are the best known deoxidizers for copper; but all of these, if added in slight excess, decrease the electrical conductivity of the material. It is stated that boron is free from this objection. It is usually introduced into copper in the form of the so-called boron suboxide.[2] This material is made by the reduction of boron oxide (B_2O_3) with magnesium, care being taken to have the boron oxide, and not the magnesium, in excess; the "suboxide" probably consists of boron, holding a little boron oxide in solid solution.

Alternative Methods of Converting Matte to Crude Copper. The production of copper from matte in the converter is not, in every respect, ideal. A great deal of the valuable impurities are liable to be lost and the amount of copper shot out of the converter is considerable. In some districts a less violent, and more easily regulated, process is preferred. One old method which has survived in South Wales, and gives good results where a matte rich in copper and low in iron is available, may be referred to. It consists of packing pigs of this matte (locally known as *white metal*) in a reverberatory furnace, where they are heated rather gently in a strongly oxidizing atmosphere. By the time the pigs are beginning to melt and flatten out the surface is covered with a thick blanket of cuprous oxide. The furnace is then heated more strongly, the excess air being shut off, and the whole charge is fused; the sulphide and oxide react, producing metallic copper,

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

It is usual to conduct the operation so that only a portion of the copper is converted to the metallic form on the first melting. The product tapped from the furnace separates into two layers, the top layer consisting of unchanged matte, and the "bottoms" consisting of metallic copper. The advantage of this procedure is that

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[1] H. S. Rawdon and S. C. Langdon, *Min. Met.* **158** (1920), 34.

[2] E. Weintraub, *Electrochem. Ind.* **7** (1909), 509; *Met. Chem. Eng.* **8** (1910), 629.

practically all the valuable impurities, such as gold and silver, collect in the metallic phase. The matte or " tops " can then be subjected to a second treatment, and finally yields a copper which is singularly free from impurities. This is of the quality known as " Best Selected Copper "; it contains about 99·7 per cent. of copper, which is unusually high for a metal which has not been refined electrolytically.

Limitations of Thermally-Refined Copper. The copper produced by refining only in a furnace is pure enough for the manufacture of sheets, tubes, plates, and some alloys, but it still contains many impurities, which lower the electrical conductivity, and modify (not always adversely) the mechanical properties; the effect of different impurities is discussed in a later paragraph. A very large proportion of the thermally-refined copper is sent to the electrolytic refinery.

(B) Wet Processes of Copper Production

In the treatment of poor copper ores (or the tailings obtained after the concentration of richer ores) it is often advantageous to leach the whole mass with a solvent—such as sulphuric acid—with a view to extracting the copper from throughout the mass; the copper can then be obtained from the solution in metallic form either by

(1) Electrolysis
or (2) Precipitation by iron.

In the electrolytic method, the acid is regenerated during electrolysis and can afterwards be employed to leach fresh ore.

Oxidized ores are particularly suited for wet metallurgy, since they can usually be leached without roasting. Sulphide ores generally require a roasting—either with or without salt—so as to convert the copper to a form which is soluble in water or at least in dilute acid. The principles of wet metallurgy are very simple, but there are many practical difficulties. Special problems arise where tailings are being dealt with, owing to the voluminous character of the product to be leached, the difficulty of separating the copper-bearing solution from the slimy mixture produced, and the large amount of water needed to wash out from the slimes the considerable amount of copper-bearing solution which they necessarily retain.

(1) Electrolytic Methods. In the important copper deposits of Chuquicamata (Chili), most of the ores at present being worked are of an oxidized character, the main mineral being the basic sulphate (brochantite); the ore is usually found mixed with soluble salts, such as sodium chloride, and sometimes nitrate. There is a little basic copper chloride (*atacamite*).

The brochantite is readily soluble in dilute sulphuric acid, and can thus be separated from the large amount of insoluble gangue material by leaching. On account of the easy solubility, very fine crushing of the ore is not needed, and the ore is therefore particularly suited for wet extraction. The process described below is conducted in a large plant built at Chuquicamata about 1914, and is understood to work well.[1]

The ore is crushed to give pieces of about $\frac{1}{4}$ inch diameter, and is then leached with 8–9 per cent. acid in tanks of asphalt-lined concrete provided with a false bottom. In this way a solution with 5 per cent. of copper dissolved as sulphate, and still containing 2–3 per cent. of free acid, is produced.

The solution, however, always contains sodium chloride, and if electrolysed directly such a solution would yield copper mixed with insoluble cuprous chloride. It is therefore freed from chlorides by being passed through copper shot, contained in revolving drums; this treatment precipitates the whole of the chloride as cuprous chloride. In order to free the solution from the cuprous chloride and any other matter in suspension, the cloudy liquor is passed into a series of Dorr continuous thickeners (see Fig. 8), which consist of circular tanks provided with inclined revolving rakes. The cloudy liquid is fed in by means of the launder A; the suspended material sinks, and is gradually pushed by the rakes as they slowly revolve to the central discharge point B, whilst the nearly clear liquid overflows through C. The thickened slime discharged through B is filter-pressed, so as to recover as much as possible of the copper-bearing liquid.

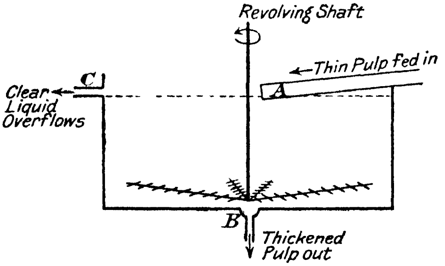

FIG. 8.—Dorr Continuous Thickener.

After removal of the insoluble matter, the clear solution is ready for electrolysis, which takes place in rectangular asphalt-lined concrete tanks (a suitable size is 19 × 3 × 5 feet). The cathodes are thin sheets of copper, which are themselves prepared by electrical

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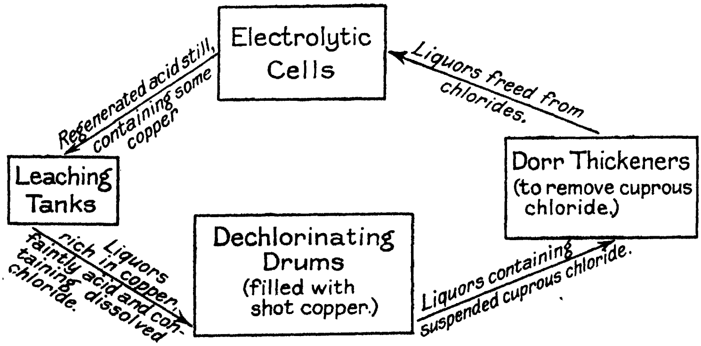
[1] H. C. H. Carpenter, *J. Roy. Soc. Arts*, **66** (1918), 151; C. A. Rose, *Eng. Min. J.* **101** (1916), 321; E. A. Cappelin Smith, *Trans. Amer. Electrochem. Soc.* **25** (1914), 193.

deposition. The anodes in the original plant were of magnetite, made in Germany; but as the war soon shut off the supply, anodes of "duriron" (a cast-iron rich in silicon) were installed in their place.[1] Duriron has proved in many ways a satisfactory anode material, and is said to resist corrosion fairly well; but, owing to its high overpotential, a rather higher E.M.F. is needed for each cell than when magnetite is used; the excess of energy thus supplied reappears as heat, and the solutions may actually require artificial cooling when duriron anodes are employed.

In each cell there may be 37 vertical cathodes separated by 36 anodes. A large number of cells are joined in series, so that a comparatively high E.M.F. can be applied to the whole series. One particular tank-house contains 480 cells arranged in 5 electrical circuits, with 96 cells in series in each circuit. The tanks are also connected with pipes so as to form 30 solution circuits, each consisting of 16 cells. The solution flows continuously through the tanks in a direction at right angles to the electric current (as shown in Fig. 9, p. 47); it enters the tank-house with 5 per cent. of copper and only 2–3 per cent. of free acid, and leaves it with only 1·5 per cent. of copper and as much as 8–9 per cent. of free acid. This spent acid liquor is pumped back into storage tanks, and is subsequently used to leach fresh ore.

The cathodes are removed periodically, being replaced by fresh thin copper sheets; the finished cathodes which have been removed are afterwards melted down.

The process as conducted at Chuquicamata is practically continuous, the solutions being made to flow round the circuit indicated below. The iron pipes joining the tanks are lined with lead, whilst the pumps needed to raise the solution to the storage tanks are of type metal.



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[1] M. de K. Thompson and T. C. Atchison, *Trans. Amer. Electrochem. Soc.* 31 (1917), 213.

As the ore consists of a basic sulphate, not copper oxide, the amount of sulphuric acid regenerated during electrolysis is more than enough to replace any accidental wastage that may occur during the circulation. Consequently it is unnecessary to supply acid for the process after it is once fairly started. Indeed, it is possible periodically to discard a portion of the acid liquor (which may be freed from copper by long-continued electrolysis before being thrown away). This fact is of great importance ; if it were not for the possibility of discarding portions of the liquor from time to time, the solutions would become foul after long use, owing to the continued accumulation of impurities such as iron, which are not precipitated with the copper, but which—if present in large amount—would interfere with the current efficiency. This is one reason why electrolytic reduction in Chili has proved successful whilst many attempts made in other countries have failed.

Large quantities of oxidized ores also occur in Arizona, Utah and Montana ; in these States wet extraction has been practised by methods [1] on the whole similar to those employed in Chili. But many of the ores of the districts mentioned contain copper as sulphide, and require roasting before they can be leached with dilute acid. It is usually more profitable to subject these sulphide ores to a concentration process, and then to smelt the richer portions by the dry metallurgical processes which have been described above; the "slimes tailings," however, still contain a certain amount of copper, and at different times—especially during the recent war when the demand for copper was high—the question of the recovery of this copper by leaching has been investigated. The tailings can be dried, roasted in a multiple hearth furnace, and the roasted portion leached with dilute sulphuric acid, giving a solution which can be electrolysed to yield copper.

Even oxidized ores are sometimes roasted before leaching, so as to convert the iron—as far as possible—to a form of ferric oxide which is undissolved, or only slowly dissolved, by acid. The presence of iron in the electrolytic cell greatly lowers the current efficiency, because the iron is alternately oxidized to the ferric state at the anode and then reduced again to the ferrous state at the cathode, current being thus expended in a manner which produces no copper ; furthermore, the ferric salts have a corrosive action upon the copper already deposited on the cathode. By

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[1] For further details, see J. Irving, *Eng. Min. J.* **103** (1917), 932 ; A. L. Walker, *Eng. Min. J.* **105** (1918), 94 ; L. Addicks, *Trans. Amer. Electrochem. Soc.* **28** (1915), 57 ; R. R. Goodrich, *Trans. Amer. Electrochem. Soc.* **25** (1914), 207 ; L. Addicks, *Met. Chem. Eng.* **15** (1916), 628 ; N. S. Mackay, *Bull. Amer. Inst. Min. Eng.* **153** (1919), 1929. See also general discussion *Trans. Amer. Electrochem. Soc.* **27** (1915), 35–73.

calcining the ore at a fairly high temperature, it is possible to render most of the iron insoluble ; but even if only a small amount of iron is extracted during the leaching of each batch of ore, the iron will gradually accumulate in the liquor, since—unlike copper—it is not deposited on the cathode. Thus, unless it is possible (as at Chuquicamata) to discard periodically a portion of the liquor, the solution will become fouler and fouler, and the current efficiency lower and lower.[1] It is noteworthy that the effect of iron in lowering the current efficiency is very much less pronounced when aluminium salts are present in the solution ; [2] but probably the best way to secure a good current efficiency from a solution containing iron is to saturate it with sulphur dioxide (derived from the roasters), thus reducing the iron to the ferrous condition.

In Arizona, lead appears to be preferred as an anode material ; a lead anode quickly becomes covered with lead peroxide, and after this suffers but little corrosion in a sulphate bath. In some of the earlier American processes, carbon anodes were employed, but were found to become badly disintegrated in a sulphate solution. It is worthy of note, however, that disintegration only occurs when gaseous oxygen is being evolved at the anode. Where a solution containing iron has been treated with sulphur dioxide, and the iron present is consequently in the ferrous state, then—as long as the only anodic action is the reoxidation of the iron to the ferric condition—the disintegration of a good carbon anode is negligible.

The Laszczinski process, which was in operation before the war in a comparatively unimportant copper-field in Poland, appears to have met the difficulties of electrolytic copper-extraction in a way entirely suited to the ores to be treated.[3] The fine ores—which contain iron and copper sulphide—are mixed with 5 per cent. of clay, and made into briquettes which, when dry, are quite porous. They are roasted in a small furnace, at such a temperature that the copper is converted partly to sulphate and partly to oxide, whilst the iron is converted entirely to ferric oxide. Strongly heated ferric oxide is—as is well known—almost undissolved by acid. Consequently when the roasted briquettes are leached with sulphuric acid, a copper solution comparatively low in iron is obtained. This is electrolysed between thin copper cathodes and lead anodes ; the lead anodes are enclosed in close-fitting bags of cotton cloth,

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[1] Interesting curves showing the remarkable effect of iron in reducing the current efficiency are given by P. R. Middleton, *Min. Sci. Press,* **119** (1919), 149.

[2] L. Addicks, *Trans. Amer. Electrochem. Soc.* **28** (1915), 73.

[3] *Times Eng. Supp.* May 13 (1908). W. Stoeger, *Electrochem. Ind.* **4** (1906), 366 ; N. Pittschikoff, *Trans. Faraday Soc.* **4** (1908), 74.

which prevent them from disintegrating, and no doubt reduce to a minimum the diffusion of ferrous iron inwards to the surface of the electrode, and the diffusion of ferric iron outwards into the body of the solution. Thus the current efficiency is quite high—over 90 per cent. The lead becomes covered with peroxide, but is not further attacked.

(2) **Iron Precipitation Processes.** Where a little copper exists in the presence of a very much larger quantity of iron, it is generally preferable to obtain it in the metallic form by precipitation with a less noble metal, such as iron (in the form of scrap or pig-iron), instead of by the application of an externally generated E.M.F. Such processes are used in America mainly for the extraction of copper from tailings and residues.[1] In Europe, however, the iron precipitation process is employed for obtaining copper from the greater portion of the Spanish ores.

In the Rio Tinto mines of Spain, the principal mineral is iron pyrites, but the ores have a copper-content of 2–3 per cent. Some of the ore is treated on the spot, but much is exported to England.

A somewhat primitive process[2] has long been in use in Spain. By mere exposure of the minerals to the combined action of air and water they become oxidized, the sulphides of iron and copper being converted to sulphates. This oxidation, far from requiring the external application of heat, actually develops so much heat that there is a danger of the heaps of wet pyrites catching fire. The production of flames is, however, to be avoided, for it is desirable to convert the copper to the soluble sulphate, whereas if the heating were too strong, an insoluble oxide or basic sulphate would probably be formed. If the soluble salts of iron and copper be periodically extracted with water, it is possible to liberate all the copper in the metallic state as a dark spongy precipitate by the action of scrap-iron or pig-iron. However, the solution obtained from the roasted ore generally contains ferric sulphate, and consequently a certain amount of iron would be consumed in reducing this to the corresponding ferrous salt. For this reason the solution, before the treatment with metallic iron, is treated with fresh ore, which is capable of bringing about the reduction of the iron to the ferrous condition.

The process is conducted in the following way. The ore to be oxidized is piled up in big heaps upon flat ground, rocky or clayey soil being chosen in order that the solution produced may not

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[1] F. Laist and H. W. Aldrich, *Trans. Amer. Inst. Min. Eng.* **55** (1915–16), 866, discuss the process as applied in Montana to tailings.

[2] For further details, see W. E. Greenawalt, "Hydrometallurgy of Copper" (McGraw-Hill).

soak into the ground and be lost. Before the ore is put down, two series of parallel lines of rough stones are laid down, at right angles to each other, so as to form a chess-board pattern on the ground; when the mineral is heaped upon the top, these lines of stone provide clear channels for the passage of air into the centre of the mass, and also for the escape of sulphur dioxide. As the mineral is piled up, vertical flues are also formed at some of the junctions of these lines of stones, by building up at these points with stones, and it is mainly by these vertical "chimneys" that the sulphur dioxide gas escapes into the air. The heaps may contain perhaps 100,000 tons of ore. Distributed over the area of the pyrites-heaps are water-sprinklers, which keep the heaps continually moist with water. Periodically, when it is thought that sufficient soluble copper salt has been formed, a large amount of water is scattered on to the surfaces of the heaps, and this water sinking through the partly-oxidized mineral, dissolves out the copper and iron sulphates, and runs away by trenches at the foot of the heaps, bearing these salts in solution. As already stated, the water runs off through a bed of fresh ore, by which the ferric salts are reduced to the ferrous condition; it then passes into tanks in which the metallic copper is precipitated by pig-iron, or by iron scrap, the complete extraction of the copper requiring many hours. Most of the precipitate of spongy "cement copper" is sent to England, where it is melted down and refined. The method is somewhat crude, but is suited to a region where coal is dear; there is, no doubt, a considerable loss of copper in the process.

A large proportion of the cupriferous pyrites from Spain is sent to this country for treatment. Where the sulphur-content is high, and the copper-content low, it is often sent first to the sulphuric acid works, where it is burnt to yield sulphur dioxide, which is made into acid. The residue left after burning is mainly iron oxide, but still contains sulphur (perhaps 2–6 per cent.); it contains all the copper, as well as any traces of silver, present in the original ore. The copper is not in an easily soluble form, and probably still exists, at least in part, as sulphide. Consequently the ore is almost invariably ground and roasted with salt before leaching; this treatment, known as **chloridizing roasting,** converts the copper to the state of soluble chloride.

The chloridizing roast is usually carried out in a multiple-hearth furnace; the upper hearths are usually heated by means of producer gas, but the combustion of the sulphur existing in the charge generally maintains the temperature in the lower parts. The temperature must not rise too high, since in that case much insoluble cupric oxide will remain in the residue. The exit gases from the roaster contain hydrogen chloride, which is carefully absorbed, the hydrochloric acid produced being utilized in the leaching.

The leaching is conducted in tanks fitted with some sort of false bottom; wooden tanks lined with fire-brick have been recommended. Some of the hydrochloric acid condensed from the gases leaving the roaster is added to the leaching water, so as to dissolve any copper oxide or other compound insoluble in ordinary water. When leaching is complete, the liquid is drawn off from below the false bottom; the residue, mostly iron oxide, can be drained, briquetted and sent to the blast-furnaces for smelting into iron.

The greenish solution drawn off from the leaching vats usually contains—in addition to copper chloride—traces of silver chloride, which is moderately soluble in presence of sodium chloride. It is treated with a requisite small quantity of sodium iodide, which precipitates the silver as the very insoluble salt, silver iodide. The precipitate is separated by settling, or otherwise, and a silver-free solution is finally obtained. This is treated with miscellaneous iron scrap in large tanks, yielding a dark sludge of impure metallic copper, which is periodically collected, drained, and melted up in a furnace, where it usually requires a great deal of refining; the main impurity is arsenic.[1]

Chloridizing roasting is also employed in the American copper districts for the treatment of ores, in cases where it is difficult to obtain a good extraction after ordinary ("sulphating") roasting.

Ammonia Leaching Processes. Various other leaching processes have been used in different parts of the world, in addition to those described above. One of the most interesting methods is that of leaching by ammonia. Ammonia is used especially for the treatment of tailings in Alaska,[2] where acid cannot be employed as a leaching agent on account of the presence of limestone in the ore. Ammonia-leaching has also been utilized for the treatment of tailings obtained in the working up of the Lake Superior native copper.[3] The ammonia serves to extract a considerable proportion of the copper dispersed in small quantities through a large amount of worthless material; on evaporation, the solution yields ammonia, which is carefully condensed, and a copper carbonate, which turns to the black oxide on heating in steam.

Electrolytic Refining and Deposition of Copper

Electrolytic Refining. Commercial copper obtained by any

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[1] D. W. Jones, *J. Soc. Chem. Ind.* **38** (1919), 365T.

[2] H M. Lawrence, *Eng. Min. J.* **104** (1917), 781; L. Eddy, *Met. Chem. Eng.* **20** (1919), 328.

[3] L. S. Austin, *Min. Ind.* **28** (1919), 184.

of the thermal processes discussed above still contains traces of other elements. These may include—

(1) *Non-metallic* bodies, such as sulphur, selenium, tellurium, and either oxygen or hydrogen (according as the copper has been underpoled or overpoled).
(2) Comparatively *noble* metals like gold, silver, bismuth and antimony.
(3) Moderately *reactive* metals like lead, arsenic, iron, zinc, nickel and tin.

The electrical process of copper-refining makes use of the difference in the electro-chemical behaviour of these various elements to secure a separation.

The refining [1] is usually carried out in wooden tanks lined with lead. The copper to be refined is cast into thick slabs (about 3 feet × 2 feet × 1½ inches), which are enclosed in cloth bags, and hung up in a vertical position in the cell. Between them are placed cathodes of the same area, composed of thin pure copper sheet. The electrolyte is a copper sulphate solution (about 16 per cent.) containing 6–13 per cent. of free sulphuric acid, the main function of which is to increase the conductivity of the solution. A trace of hydrochloric acid is usually maintained in the bath, which serves to precipitate any silver which may pass into solution. The anodes and cathodes are placed alternately about 2 inches apart, or less; there may be, perhaps, twenty-three cathodes and twenty-two anodes in a cell; all the cathodes are electrically connected to one another, and likewise all the anodes. Perhaps three hundred or more of these cells are placed in series; the E.M.F. required to force the current through the whole series of cells, which will amount to 100 volts or more (allowing 0·3 volts per cell), can then be provided economically by a dynamo.

Copper enters the solution at the anodes, while a similar amount of the same metal will be deposited on the cathodes. A certain amount of polarization occurs at both electrodes, and the potential at the anode is sufficiently elevated to cause the dissolution, not only of copper and the reactive metals, nickel, iron, lead and arsenic, but also part of the antimony and bismuth. However, the comparatively noble metals, silver and gold, together with the non-metals, selenium and tellurium, are not dissolved anodically; these elements, together with part of the antimony and bismuth, will remain behind as an insoluble slime in the bags. Of the metals anodically soluble, lead is at once precipitated, as lead sulphate, by the sulphuric acid present, whilst antimony and bismuth

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[1] See also A. J. Allmand, "Applied Electrochemistry" (Arnold).

gradually separate out as basic sulphates or hydrated oxides. Of the metals remaining in solution (copper, arsenic, nickel and iron) copper is the most noble. Consequently it is deposited in an almost pure condition upon the cathodes, even when the other three metals have accumulated to a considerable extent in the bath. The potential at the cathode will not—in general practice—become sufficiently depressed for the electrical precipitation of iron and nickel, but the cathode product often contains a little arsenic, together with traces of lead and antimony, the precipitated salts of which are not completely insoluble. It may also contain traces of sulphur, zinc and iron; but this is due to the entrapping of small amounts of solution in the pores of the metallic deposit rather than to true co-deposition.[1]

Since a solution of copper sulphate is heavier than water, it follows that the heavy layer of copper-rich solution produced along the surface of the anodes will tend to sink, whilst the copper-poor layer produced along the cathode will tend to rise; thus unless some steps are taken to counteract this effect, we shall finally get the lower portions of the solution in the tank much stronger in copper than the upper portions, with the result that unevenness of deposition will occur. This is prevented by "circulating" the electrolyte, that is by causing it to flow from one cell to another through pipes joining the different tanks. Where there are several separate rows of cells joined electrically in series in the refinery, it is a common practice to arrange the separate rows in tiers, each row being raised a little above the level of the next. The liquid then flows in pipes in a direction at right angles to that in which the current is passing, as indicated in Fig. 9. Having reached the bottom tier, it is usually pumped up to storage tanks at the highest level, and is thus ready to descend through the various cells once more.[2]

By allowing the liquor to pass through cells in the manner suggested (*at right angles* to the direction of the current), it is possible to avoid the wastage of current by leakage through the pipes, which would inevitably occur if at any point two cells in series were joined by a pipe.

Since the liquid in the cells gradually becomes fouled through the accumulation of arsenic and other impurities, portions are periodically diverted to special "regenerating cells," where the whole of the metal (including the impurities) is deposited on cathodes,

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[1] L. Addicks, *Trans. Amer. Electrochem. Soc.* **26** (1914), 51.

[2] Various devices for allowing the liquid to enter and leave the cells so as to keep the concentration uniform, and also for preventing overflowing are described by B. Blount, "Practical Electrochemistry" (Constable).

insoluble (lead) anodes being employed.[1] The first portions of the copper deposited in the regenerating cells are fairly pure, and it is a not unusual practice to manufacture in the regenerating cells the thin copper cathodes required for the main refining cells. The last part of the metal deposited in the regenerating cells is a very impure sludge, which is returned to the smelter; in this last stage of deposition arsenic is often evolved, to some extent, as the poisonous gas arsine (AsH_3), and it is therefore a good practice to place the regenerating cells in the open air. The liquor is afterwards boiled and evaporated; nickel salts are deposited, and are separated from the hot liquid, whilst sodium salts are usually deposited on cooling. The remaining liquid, now containing little dissolved matter except sulphuric acid, is returned to the electrolytic refining tanks.

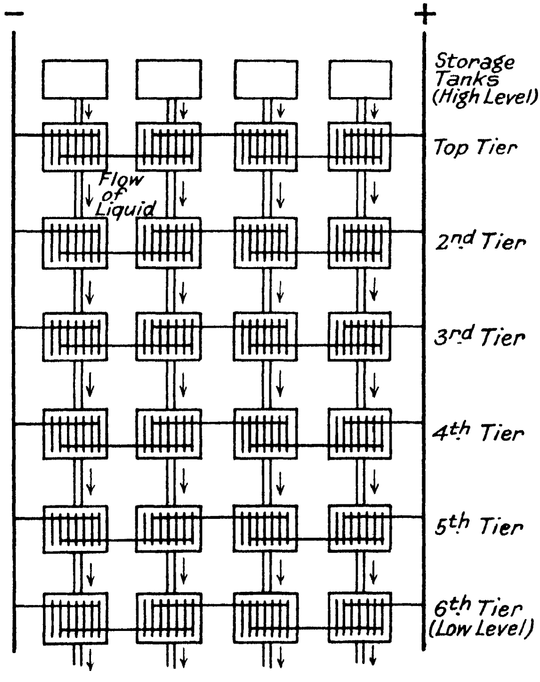

FIG. 9.—Arrangement of Cells.

The current efficiency of copper refining is usually high[2]: 92–95

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[1] L. Addicks, *Met. Chem. Eng.* **16** (1917), 687; F. R. Pyne, *Eng. Min. J.* **98** (1914), 432.

[2] L. Addicks, *Met. Chem. Eng.* **16** (1917), 23. Compare K. S. Guiterman, *Eng. Min. J.* **98** (1914), 338.

per cent. is often obtained. It will, of course, be reduced if much iron is present, or if the evolution of hydrogen is allowed to take place at the cathode. The small value of the E.M.F. needed for each cell is due to the fact that the "critical E.M.F." of the cell

$$\mathrm{Cu} \mid \mathrm{CuSO_4} \mid \mathrm{Cu}$$

is zero. No chemical work is done; the copper is merely transferred from one place to another.

It will generally prove profitable to use the maximum current density consistent with the production of a good deposit, in spite of the extra voltage per cell required to force the high current through the liquid. In America, the current densities employed have risen to nearly 20 amps. per square foot,[1] although in European refineries a slower rate of working is customary. The object for the apparent waste of energy involved by working at high current density may be explained in the following way.[2] With a view to reducing capital expenditure, it is desirable that a small plant should have a large output. It must be remembered that the large amount of valuable copper which has to be put into the cells—as anodes, cathodes and electrolyte—when the refinery is started, represents capital upon which interest is being paid by the refiner. Now although the metal originally put in soon comes out as refined copper, yet it has to be replaced by other crude copper, and the average value of copper locked up permanently in the bath as anode, cathode and dissolved sulphate is constant, and the interest on this capital represents a very serious permanent addition to the cost of running the plant. If a small plant can turn out a large amount of refined copper, the interest charge per ton of refined copper is necessarily reduced. It is therefore advisable to use the highest current density possible. If, however, the current density is unduly increased, the quality of the product suffers, an inconveniently rough deposit of copper being produced. A higher current density is permissible, however, if a hot bath be used, since the rate of diffusion of copper sulphate is facilitated. In modern refineries, heating coils through which exhaust steam may be passed are very commonly laid on to the refining tanks in order that the solution may be kept at about 60° C.

In order to obtain the maximum current density at the minimum E.M.F. (that is to say the lowest power-consumption) the electrodes are placed as close together as possible. This also diminishes the size of tanks needed, and thus reduces the cost of the plant and the amount of copper sulphate solution locked up

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[1] L. Addicks, *Met. Chem. Eng.* **13** (1915), 661.

[2] Compare L. Addicks, *Trans. Amer. Electrochem. Soc.* **25** (1914), 65.

in it. A limit to the nearness of the plates is, however, set by the fact that, if they are close together, the deposit grows irregularly; any small excrescence on the cathode which may occur at any point, will, if the anode be very near, cause a marked increase of the current density at that point, and thus an extra amount of copper is deposited on it. The irregularity therefore will increase as deposition proceeds.

The metal deposited upon the cathodes contains about 99·95 per cent. of copper, and is usually remelted, basic furnaces lined with magnesite or chromite being preferred. Care must be taken to avoid, as far as possible, the reintroduction of impurities. It is poled before being cast into ingots or wire-bars.[1]

The **anode slimes**[2] containing the precious impurities of the anode copper (silver and gold), together with residual copper, lead, arsenic, selenium, tellurium and bismuth, are leached with sulphuric acid containing nitre, so as to remove as much of the copper as possible. They are then dried and "blown" to give a crude bullion containing all the precious metals; this operation is carried out in a small reverberatory furnace, air being forced under the surface of the molten material to promote oxidation of the less valuable elements. The volatile constituents such as arsenic and selenium are carried over with the air-blast, and can be recovered in a dust catcher, whilst other impurities are removed as a slag. The molten bullion is further purified by the action of fused nitre, and is then poured. The product may contain 96 per cent. of silver, about 2 per cent. of copper and about 2 per cent. of gold; it is sent to the silver refinery for further treatment.

An alternative method of arranging the electrodes in copper-refining is known as the **Hayden** or **Series System.** In this process the tanks are lined, not with lead, but with a non-conducting substance such as slate. A number of slabs of impure copper are arranged parallel to one another in the tank; they are large enough to occupy nearly the whole cross-section of the cell, being usually supported in slots at the edges. The outside slabs at the two ends alone are joined to the source of E.M.F.; each of the intermediate slabs acts as an anode on one side and a cathode on the other. Consequently each tank really constitutes a large number of cells in series, and a comparatively high E.M.F. must be applied to the tank (perhaps 15 volts)—a great practical advantage. Furthermore, no specially prepared cathodes are needed. On the other hand, much current leaks round the edges of the slabs, and only on the last plate at the negative end of the tank does the weight

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[1] F. Johnson, *J. Soc. Chem. Ind.* **36** (1917), 803.

[2] L. Addicks, *Met. Chem. Eng.* **17** (1917), 169.

of copper deposited correspond—even approximately—to the current that has passed.

When the amount of pure copper deposited on the cathode side is about equal to the original thickness of the slabs, and consequently when little or none of the original impure copper remains on the anodic side, the slabs are taken out; any remaining portions of impure copper can usually be broken off, especially if the slabs are slightly greasy on the cathodic side when the process starts.

It is obvious that the labour cost will be greater than in the ordinary ("multiple") system of refining. Further, unless the copper of the original slabs is fairly pure and uniform, they will corrode unevenly, a state of affairs which will clearly be fatal to the process. The use of the series system is therefore confined to places where the blister-copper to be treated is moderately pure and uniform, but where electric power is expensive and labour relatively cheap.[1]

Practically all the copper from American sources which requires to be refined electrolytically, is treated at a system of refineries situated around New York Harbour.[2]

Direct Manufacture of Copper Articles by Electro-deposition. Many attempts have been made to deposit copper electrolytically in the form of wire, rods or tubes so as to avoid the expense of remelting, and subsequent drawing, rolling, etc. Electrolytically deposited tubes have the advantage of being seamless. On the other hand, great difficulty is experienced in keeping the deposition smooth and uniform, and in making the metal compact and capable of withstanding pressure. This can only be brought about if the copper is rolled or hammered *continuously throughout its deposition.* In one process copper is deposited upon a revolving "mandrel," of cylindrical form, the mandrel being made the cathode in a bath of copper sulphate in which it is only partly immersed. As it revolves, a polishing tool of special design travels along the length of the tube (first in one direction, then in the other), pressing down any microscopic excrescences that may appear upon the tubular copper deposit whilst these excrescences are still small, and consolidating the copper so as to form a strong, compact non-porous tube. When the deposit is thick enough, it is taken off the mandrel, and constitutes a solid copper tube. The mandrel requires special preliminary preparation, to facilitate the

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[1] For comparison of the processes, see P. L. Gill, *Eng. Min. J.* **101** (1916), 9.

[2] F. L. Antisell and S. Skowronski, *Trans. Amer. Inst. Met.* **10** (1916), 179.

removal. The process presents difficulties and is no longer used in England.[1]

Electrotyping, the art of depositing copper upon a (negative) mould of gutta percha, wax or plaster, the surface of which is made conducting by a covering of graphite, may here be mentioned. After the copper layer is thick enough to possess the necessary rigidity, the mould is removed; the copper deposit, of course, accurately reproduces the form of the negative.

One of the most interesting developments of the direct deposition of copper is the possibility of obtaining in a single piece hollow articles of complicated contour which could not possibly be obtained by casting. These can be made by depositing a copper layer upon a core of fusible metal (e.g. tin) of suitable form; the copper layer is then pierced, and the fusible metal melted out, leaving a copper shell. Interesting attempts on these lines were being made in Italy shortly before the war, for the production of radiator elements and similar articles. Radiator elements have also been made in America in a similar manner, by the deposition of copper on perforated strips of lead, the lead being afterwards removed from within the copper sheath by heat.[2] During the war, copper water-jackets for aeroplane engines were made in this country in a similar manner; the copper was deposited on fusible metal, which was afterwards melted out by boiling in oil—a treatment which was probably responsible for the excellent toughness of the copper composing the jacket.[3]

Copper Plating. The electrolytic deposition of a thin protective layer of copper on another metal—steel for example—is not very frequently carried out. It is not easy to get a thoroughly adherent deposit of copper by plating from a sulphate solution, because at the moment at which the steel article is plunged into the copper solution, a layer of loose copper is produced upon it through simple replacement of the copper in the solution by iron. This unfortunate occurrence, however, can be avoided by commencing the deposition from a bath containing potassium cyanide, towards which copper does not behave as a " noble " metal.[4] After a thin deposit has been obtained from the cyanide solution, the plating may be

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[1] Numerous other processes of this sort are described by W. Pfanhauser, "The Manufacture of Metallic Articles Electrolytically." Translation by J. W. Richards (Chemical Publishing Co.).

[2] *Met. Chem. End.* **12** (1914), 67.

[3] G. Walters, *Trans. Faraday Soc.* **15** (1920), iii, 129.

[4] For details of plating from a cyanide bath, see F. C. Mathers, *Trans. Amer. Electrochem. Soc.* **33** (1918), 147. Another method of obtaining adhesion (a sulphate bath being employed) is advocated by O. P. Watts, *Trans. Amer. Electrochem. Soc.* **35** (1919), 265.

continued from an ordinary sulphate bath containing sulphuric acid.

Two special cases where the electrolytic deposition of copper is useful may be mentioned.[1] Firstly, where it is desired that a steel article should receive case-hardening in certain parts only, the parts which are *not* to be case-hardened are first plated with copper, which serves to protect them from the carburizing agent. Secondly, the radiating fins of engine cylinders are sometimes coated with copper to increase the heat-conductivity.

Much of the copper-protected steel, which is met with in commerce, is not electro-deposited at all. The so-called "copper-clad" steel is obtained by casting copper round a steel billet, and then rolling the whole into sheet.[2]

Recently a new continuous process of covering iron sheets with copper has been put into operation in New Jersey.[3] The sheets are passed between rolls, similar to the inking rolls used by printers, where they are coated with a thick mixture containing a crude oil of an asphaltic character, copper oxide and some precipitated (spongy) copper. The sheets then pass by means of mechanical conveyors through a furnace heated above the melting-point of copper. At this temperature, the copper oxide is reduced by the asphaltic matter to the metallic state, and the sheets come out plated with a good deposit of copper. The portions of the mechanism likely to become most strongly heated are made of nichrome.

Properties and Employment of Commercial Copper

Effect of Impurities and of Cold-working upon Copper. Pure copper is a soft, malleable metal of high electrical conductivity, but its properties are remarkably altered by the presence of quite small quantities of impurities.[4] Impurities can be divided into two groups :—

(1) Those which exist in a state of *solid solution* in the copper

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[1] W. A. Thain, *Trans. Faraday Soc.* **16** (1921), 478.

[2] H. S. Rawdon, M. A. Grossman and A. N. Finn, *Met. Chem. Eng.* **20** (1919), 460, 533. The section (Fig. 14) on p. 536 of that paper shows the formation of a definite layer of iron-copper alloy at the junction of the metals. See also J. O. Handy, *J. Ind. Eng. Chem.* **5** (1913), 884.

[3] J. W. Richards, *Trans. Amer. Inst. Min. Eng.* **60** (1919), 365.

[4] L. Guillet, *Zeitsch. Elektrochem.* **15** (1909), 897 ; A. H. Hiorns, *J. Soc. Chem. Ind.* **25** (1906), 616 ; L. Addicks, *Met. Chem. Eng.* **22** (1920), 449, interprets the results in a rather different way, which is difficult to accept entirely. Compare also the views of F. Johnson, *J. Soc. Chem. Ind.* **36** (1917), 807, who distinguishes three groups of impurities: (1) *insoluble* (Pb, Bi, S, O, Te) ; (2) *soluble*, but *not as compounds* (Ag, Au, Zn, Fe, Sn) ; (3) *soluble as compounds* (Sb, Si, P, As, Al). It is the third group which has the greatest effect on the conductivity.

grains: aluminium, phosphorus, arsenic, silicon. These will greatly reduce the electrical conductivity (as do all substances in solid solution), but will not render the copper unsuitable for mechanical use. On the contrary, they will usually render it stronger and harder.

(2) Those which are almost *insoluble* in solid copper, and collect, often as a eutectic, at the inter-granular boundaries: bismuth, lead, tellurium, oxygen (as cuprous oxide), sulphur (as sulphide). These have but little disturbing effect on the conductivity, but generally render the metal very fragile, giving rise to inter-granular fracture. Bismuth is one of the most detrimental impurities in this respect. In many cases, the inter-granular layer in copper containing impurities of this class can be seen in a micro-section.

It is worthy of note that just those impurities which most seriously affect the mechanical properties of copper have comparatively little effect upon the electrical conductivity. This does not mean, however, that they can be tolerated in electrical conductors, because in actual practice good mechanical properties are just as important in a conductor as good electrical properties. On the other hand, the impurities of class (1), which are, in some cases, looked upon with favour for purely mechanical purposes, are most undesirable for electrical purposes. Arsenic, for instance, is actually a welcome constituent of the copper used for locomotive fire boxes, at any rate in quantities up to 1·0 per cent.;[1] but the smallest trace causes a very serious lowering of the electrical conductivity.

The presence of reducing gases—and especially hydrogen—appears to cause brittleness in copper. Electro-deposited copper—which presumably contains some hydrogen—is rendered much stronger by heating in an oil-bath.[2]

Only less striking than the effect of impurities on copper is the effect of cold work. Cold-worked copper behaves almost like a different metal to hot-worked or annealed copper. The cold-drawn wire, for instance, is very much stronger, although slightly less conductive, than annealed wire. The increase in tensile strength and hardness observed as copper is subjected to progressive drawing or rolling, appears to proceed in a curious discontinuous manner, which is difficult to explain adequately by the ordinary notions of deformation.[3] The matter will require further investigation.

Uses of Copper. The industrial importance of copper depends

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[1] See C. T. Heycock, *Brit. Assoc. Rep.* **88** (1920), 56.

[2] F. S. Spiers, *Trans. Faraday Soc.* **15** (1920), 128.

[3] W. E. Alkins, *J. Inst. Met.* **23** (1920), 381; F. Johnson, *J. Inst. Met.* **23** (1920), 443; **26** (1921), 173. Compare C. H. Desch, *J. Inst. Met.* **26** (1921), 226.

on the high electrical conductivity, the good heat conductivity, the resistance to oxidation even at fairly high temperatures and, to a small extent, on the softness.

The electrical conductivity of pure copper excels that of every other metal, except silver, and copper is used on a very large scale for telegraph and telephone wires, power-lines, etc., and also for electrical machinery. As explained in the section on aluminium (Vol. II), the latter metal may sometimes be cheaper to use ; where the difference in cost is not great, the absence of an almost unremovable oxide-film on copper makes it a far more convenient material. On account of the higher conductivity of pure metals, only electrolytic copper is used for the purpose ; but on account of the greater strength, cold-drawn (or "hard-drawn") copper wire is generally preferred to the annealed wire, in spite of its slightly lower conductivity.

Although the presence of most impurities in copper which is intended for electrical purposes is to be avoided at all costs, the addition of a small amount (1·1 per cent.) of cadmium has many advocates. Wire containing cadmium is said to have been employed considerably in France and Italy. Although the conductivity is reduced by 10 per cent. by the cadmium, the tensile strength is increased by over 50 per cent. ; moreover, the temperature at which cold-drawn copper begins to lose its acquired hardness is raised considerably by the presence of cadmium ; thus in the wire containing cadmium there is less danger of loss of strength through accidental heating.[1]

The manner in which copper withstands corrosion by air and steam at high temperatures, combined with its good heat conductivity, has rendered it useful in locomotive construction.[2] It is the material generally employed for the fire-box (although steel fire-boxes have been used with success in America), and also for the steam-pipes. Copper withstands the action of sea-water well, and was used in the past for ships' bottoms, although it has largely been superseded by such alloys as Muntz metal. Copper is to some extent employed as a roofing material for buildings ; it soon turns green when exposed to the weather, but suffers no serious corrosion. The metal is used for cooking utensils, but they are usually tinned internally. Copper finds employment as a printing surface, and numerous objects of art are made of beaten copper.

The softness of copper is responsible for a few of its minor uses —for instance, in the manufacture of shells. A large proportion

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[1] W. C. Smith, *Met. Chem. Eng.* **25** (1921), 1178 ; *Elect. World*, **79** (1922), 223 ; C. E. Siebenthal, *U.S. Geol. Surv. Min. Res.* (1917), I, 51.

[2] J. W. Hobson, *Mech. World*, **56** (1914), 256; **57** (1915), 22.

of the copper made is devoted to the manufacture of the alloys, which are discussed below.

In casting copper, care should always be taken to avoid access of sulphur dioxide to the molten metal. Copper dissolves the gas, a mixture of sulphide and oxide being probably formed thus,

$$6Cu + SO_2 = Cu_2S + 2Cu_2O.$$

The oxide and sulphide are soluble in the molten copper, but, on cooling, the oxide tends to separate at the inter-granular boundaries, causing fragility.[1] It is usual to add one of the deoxidizers referred to above (e.g. zinc, phosphorus, or boron suboxide) to copper before casting. It is noteworthy that copper containing inter-granular oxide is most likely to fail if heated in hydrogen or other reducing gases. The hydrogen diffuses inwards along the inter-granular boundaries and reacts with the oxide, probably forming steam in the interior. The crystals are thus pushed apart from one another, the metal increases in apparent volume, and inter-granular cracks develop.[2]

Use of Copper Compounds. A certain amount of copper sulphate is obtained as a by-product in the treatment of ores—and especially in the treatment of nickel-copper matte by the Mond process. It is used as the source of the other salts.

Copper salts, even when present in very small amounts, have a poisonous action on some of the lower forms of life. Thus copper sulphate is added to water, especially in bathing-places, to prevent the growth of weeds. It is stated that for this purpose 1 part per million is quite effective, a quantity which has no injurious effect on the fish present in the water.[3]

Likewise, " Burgundy mixture," [4] which is essentially a mixture of basic carbonate and basic sulphate obtained by precipitation, is used by vine-growers to combat plant diseases of a fungoid character. Various copper compounds, including " Emerald green," $Cu(C_2H_3O_2)_2.3Cu(AsO_2)_2$, are employed in anti-fouling preparations for ships' bottoms, as they prevent the growth of marine organisms.[5]

Copper salts are used in glass, and also the ceramic industry, as colouring agents. In the cupric condition, they confer a green or greenish blue colour; but, in presence of reducing agents, a deep ruby glass can be obtained.

Like many other metals which exist in two states of oxidation,

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[1] E. Heyn, *Metallographist*, **6** (1903), 49.

[2] H. Moore and S. Beckinsale, *J. Inst. Met.* **25** (1921), 219.

[3] C. Embrey, *Analyst*, **42** (1917), 264; S. Rideal, *Analyst*, **42** (1917), 268, gives interesting information on the function of copper as a germicide.

[4] R. L. Mond and C. Heberlein, *Trans. Chem. Soc.* **115** (1919), 908.

[5] P. E. Bowles, *J. Soc. Chem. Ind.* **41** (1922), 492R.

copper has been used as an oxygen carrier in organic reactions, for instance, in the manufacture of aniline black.

Copper Alloys [1]

The most important alloys of copper are :—

(1) **Copper-zinc** alloys (**Brasses**).
(2) **Copper-tin** alloys (**Bronzes**).
(3) **Copper-aluminium** alloys (**Aluminium bronzes**).

In addition we have **copper-nickel** alloys (like **Monel metal**) and **copper-manganese** alloys, both of which have been discussed in previous volumes ; alloys with silver and with gold will be dealt with in the sections devoted to silver and gold respectively. Some of the light alloys of aluminium and copper, in which copper is only a minor constituent, were discussed along with the other alloys of aluminium.

The **brasses, bronzes** and **aluminium bronzes** require further consideration at this point. In each case, the equilibrium diagram is somewhat complicated, a large number of different solid solutions being known. A study of the equilibrium diagrams of the three classes of alloys (Figs. 10, 11 and 13) reveals a general similarity between the three systems.

The alloys can be made by melting copper under a layer of charcoal, and adding the second more reactive metal to it. The charcoal is added to prevent the access of oxygen or sulphur dioxide to the alloy. With the same object in view it is advisable to use a crucible furnace, rather than a type of furnace in which the heating gases pass directly over the surface of the alloy. Plumbago crucibles fired by oil or gas are very useful, and for large-scale production are mounted on bearings, so that they can readily be tilted up to pour the alloy. The electric furnace with its neutral atmosphere has also proved suitable for melting the constituent metals in the making of brass castings.[2] Reverberatory furnaces have been used for making large quantities of alloys, but they are likely to allow the introduction of impurities, and in the case of brass cause a considerable loss owing to the volatilization of zinc.

A good deal of heat is evolved when aluminium is added to copper ; this is not so much due to the combination of the two metals as to

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[1] See E. F. Law, "Alloys" (Griffin). A. H. Hiorns, "Mixed Metals" (Macmillan) ; W. T. Brannt, "Metallic Alloys" (Baird) ; G. H. Gulliver, "Metallic Alloys" (Griffin).

[2] For the type of electric furnace used in melting brass, see H. M. St. John, *Trans. Amer. Electrochem. Soc.* **37** (1920), 579 ; G. H. Clamer, *J. Franklin Inst.* **190** (1920), 473 ; H. W. Gillett, *Trans. Amer. Electrochem. Soc.* **39** (1921), 293.

the oxidation of aluminium by cuprous oxide, which is nearly always present in the molten copper.

A large proportion of alloys in technical use contain not merely two metals, but three (or sometimes four). Ternary alloys containing copper, tin and zinc are particularly important.

Copper-zinc Alloys (Brasses). The equilibrium diagram of the copper-zinc alloys, and the general character of the alloys of different compositions, has already been discussed in Chapter IV (Vol. I). But for the sake of completeness the diagram is reproduced here (Fig. 10).

At ordinary temperatures, all the brasses containing less than 36 per cent. of zinc consist of a single solid solution (*α-brass*) ; they show, when annealed, the ordinary polygonal structure characteristic of pure metals, although when quickly cooled they often show the dendritic " coring " so common in mixed crystals ; the coring is well displayed by Fig. A of the frontispiece, which is a micro-photograph of chill-cast brass with 70 per cent. of copper. The time of annealing needed to remove the coring and render the alloy homogeneous varies to a remarkable extent with the temperature. At 650° C. an hour will usually suffice ; but at 600° C. about three hours may be needed.[1]

The colour of the α-brasses varies from pale yellow to yellowish red, the colour becoming redder as the copper-content increases. They have moderate tensile strength, high ductility and are suitable for cold rolling. A section of α-brass which has been cold-rolled and annealed frequently displays twinning ; the same grain is divided into dark and light bands, owing to the orientation being different on each side of the twinning-plane. This phenomenon is shown in Fig. B of the frontispiece.

Alloys containing 36–47 per cent. of zinc are quite different in character ; micro-sections show that they contain two separate kinds of grains. Fig. C of the frontispiece is a micro-photograph of a brass containing 40 per cent. of zinc, etched with ferric chloride. The white grains are the α-solution, whilst the areas which have been darkened by the action of ferric chloride may be called the β_1-solution. The brasses of this character are commonly known as the *αβ-brasses.* They possess a reddish-yellow colour, the reddish tinge being due to the β_1 constituent—a curious fact considering its relatively low copper-content. The *αβ*-brasses have a much greater tensile strength than the α-brasses ; they are suitable for hot rolling. According to Carpenter[2] the β_1-constituent is not

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[1] M. Cook, *Trans. Faraday Soc.* **17** (1922), 522.

[2] H. C. H. Carpenter and C. A. Edwards, *J. Inst. Met.* **5** (1911), 127 ; H. C. H. Carpenter, *J. Inst. Met.* **7** (1912), 70; **8** (1912), 51 ; **12** (1914), 101.

homogeneous, but is a fine mixture of the α-solution and the γ-solution. This is very possibly true; nevertheless the β_1-constituent seems to possess properties of its own, quite different from those of the γ-solution in the structurally free condition; it is therefore convenient, for practical purposes, to regard it as an ultimate constituent of brass (just as pearlite is often treated as an ultimate constituent of steel, having properties quite different from structurally free cementite). αβ-brasses are malleable when hot, but become brittle when over a certain range of temperature. Recent experiments by Prof. Turner show "that the brittleness extends over a considerable range, that the change is gradual,

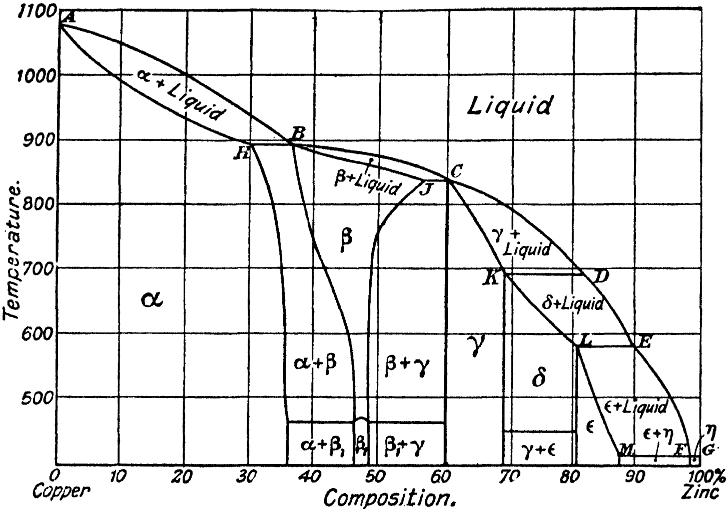

FIG. 10.—The System Copper-zinc (Shepherd's Diagram with Modification suggested by Desch).

and that though it reaches its maximum somewhere in the neighbourhood of 470° C., it extends over more than 200°. The maximum brittleness occurs at a higher temperature at the copper-rich end of the series."[1]

Between about 47 per cent. and 49 per cent. of zinc, the alloys seem to consist of β_1 alone, but when the zinc-content exceeds about 49 per cent., crystals of structurally free γ-brass appear in the alloy.

See, however, O. F. Hudson, *J. Inst. Met.* **12** (1914), 89; C. H. Desch, *J. Inst. Met.* **5** (1911), 171; **12** (1914), 104. Compare L. Guillet, *Rev. Met.* **11** (1914), 1103.

[1] Prof. T. Turner, private communication.

As the γ-solution is very brittle, brasses with more than 50 per cent. of zinc are without mechanical value, and are only employed for castings of a purely ornamental character; they are grey or white in colour. A brass containing about 50 per cent. of zinc is also used for "brazing" purposes.

The question as to whether the various solid solutions met with in brass should or should not be regarded as derived from definite inter-metallic compounds has been discussed in Chapter IV (Vol. I); there is a certain amount of evidence for regarding the brittle γ-solutions as being derived from the compound Cu_2Zn_3, although evidently an excess of zinc atoms are present in the crystal-structure.

Uses of Brass. On account of the ease with which it can be cast, rolled, drawn, stamped, spun and extruded, combined with the manner in which it withstands corrosion, brass is one of the most useful of the non-ferrous alloys. The two types of brass employed in practice are:—

α-Brass. Brass containing about 30 per cent. of zinc (70/30 brass) is much used for condenser tubes. Brass used for castings often contains rather less zinc (20–30 per cent.), whilst that used for cartridge cases has sometimes rather more (33 per cent.).

$\alpha\beta$-Brass. Muntz Metal, an alloy containing about 40 per cent. of zinc (and often some lead), was originally introduced for sheathing ships, but is now used for many other purposes. It is stronger and harder than α-brass; it is capable of being rolled hot, but, as already stated, becomes brittle if cooled to about 470° C. If quenched from above the transformation point, it is considerably hardened. The efficiency of Muntz metal for the sheathing of ships is ascribed in part to the poisonous character of the zinc salts produced by its corrosion; the zinc salts prevent barnacles from attaching themselves to the ship's bottom.

Special Brasses. German silver and similar alloys containing nickel, which can be regarded as nickeliferous brasses, have been referred to in the section devoted to nickel (Vol. III). Several other types of special brasses, however, remain to be described.

"**High tenacity brasses**"[1] are brasses containing small quantities of iron, manganese and aluminium (usually all three elements are present); the strength of these alloys considerably exceeds that of ordinary zinc-copper alloys. They are often described as "**manganese bronzes,**" but the name is unfortunate, since they are brasses, not bronzes (many of these alloys contain

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[1] O. Smalley, *Met. Ind.* **21** (1922), 56, 75, 101, 124, 149; E. J. Davis, *Met. Ind.* **18** (1921), 26.

no tin), and the manganese content is usually very small. The alloys are manufactured on a very large scale, since they combine a strength which sometimes approaches that of steel with the peculiar stability of brass towards sea-water; they are thus used for innumerable purposes connected with shipping and docks. The composition employed usually falls between the following limits:—

	Per cent.
Copper	55–64
Zinc	30–45
Iron	0·5–2·0
Manganese	0·2–4·0
Aluminium	0·2–4·0

"Delta Metal," a hard strong brass of this class, is considerably used for the manufacture of pumps, valves and similar purposes. Some high tenacity brasses contain small quantities of nickel; others contain tin or lead, additions which increase the resistance to corrosion.

High tenacity brass has in recent years been used largely for making the propellers of fast steamships; micro-sections of one alloy which has been employed with success show the $\alpha\beta$-structure, the α-component being in considerable excess of the β-component. Such a material can be used for propellers revolving at speeds which would cause the rapid destruction of most ordinary alloys.[1] It is generally considered that the wear of high-speed propellers is due rather to mechanical erosion than to chemical corrosion, although this matter cannot be regarded as definitely proved.

The exact functions of the three main additions (iron, manganese and aluminium) are still not understood as completely as would be desirable, although recent work by Smalley has thrown much light upon the question. It will be advisable to consider in turn the effect of adding each of these three elements to brass, and at the same time the mode in which the element is added. It should first be pointed out that the presence of the elements (especially aluminium) in brass affects considerably the composition at which a plain α-brass ceases to be possible, and where the β-constituent appears. Thus whilst a brass with 70 per cent. copper, 30 per cent. zinc has the pure α-structure, an alloy containing the same amount of copper with 26 per cent. of zinc and 4 per cent. of aluminium has

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[1] O. Silberrad, *J. Soc. Chem. Ind.* **40** (1921), 38T. See, however, W. Ramsay, *J. Soc. Chem. Ind.* **40** (1921), 65T. Also reply by O. Silberrad, *J. Soc. Chem. Ind.* **40** (1921), 173T.

an $\alpha\beta$-structure similar to that of a plain copper-zinc alloy with 43 per cent. of zinc.[1]

It appears likely that it is the **aluminium** which causes directly the abnormally high yield point and tensile strength of the high tenacity brasses. The alloy just mentioned (containing 4 per cent. of aluminium) has a strength not very different from that of mild steel. The great strength conferred by aluminium upon brass must be considered in connection with the great increase of strength produced when aluminium is added to copper in the manufacture of aluminium bronze. Aluminium is generally added as metal.

The **manganese** may act in part as a deoxidizer and desulphurizer, but probably has also a specific function. Possibly it renders the grain-size finer, in the same way as iron (*see below*). Manganese is commonly added as ferro-manganese, but this alloy —owing to its high melting-point and the presence of carbon— does not readily dissolve in brass ; even if molten ferro-manganese is added to molten brass, it is not unusual to find on cooling that the brass contains hard bluish pellets of undigested ferro-manganese, which are large enough to render the brass quite useless for many purposes ; the machining qualities suffer especially. It is better to use " cupro-manganese " (containing 30 per cent. manganese) as the material for introducing manganese into brass ; this alloy can be prepared by adding ferro-manganese to molten copper.

The effect of **iron**[2] upon brass is a subject upon which many different opinions have been expressed. Many manufacturers of ordinary brass look upon the presence of iron with considerable disfavour. There is no doubt that if iron is introduced into molten brass as ordinary steel scrap, hard nodules of undigested steel are liable to remain in the product, the quality of which will clearly suffer. It is commonly supposed that the presence of manganese or aluminium facilitates, in some way, the alloying of iron with brass.[3] But the fact (mentioned above) that ferro-manganese itself does not readily dissolve in molten brass, renders this view somewhat difficult to accept.

If, however, the iron is introduced into the brass as a copper-iron or zinc-iron alloy, practically free from carbon, the trouble referred to above can be avoided. Small quantities of iron (up to about 0·4 per cent. probably) can exist in brass in solid solution ; if larger

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[1] L. Guillet, *Comptes Rend.* **142** (1906), 1047. But Guillet's principle of the " coefficient of equivalence " must be accepted with caution. See W. Guertler, *Zeitsch. Metallkunde*, **13** (1921), 128.

[2] O. Smalley, *Met. Ind.* **17** (1920), 421 ; F. Johnson and R. E. Rednall, *Met. Ind.* **18** (1921), 101, 125.

[3] C. M. Weld, *U.S. Bur. Mines*, **173** (1920), 25. Compare " C. V." *Machinery*, **13** (1919), 656.

quantities are added, a second phase appears in the brass, and it is at this point that the beneficial effect of the iron begins to be experienced. An α-brass containing 1 per cent. of iron is much more fine-grained than a similar brass free from iron cast under the same circumstances; and accordingly the strength, hardness and shock-resisting qualities of brass containing iron are superior to those of similar brass free from iron. It seems almost certain that the minute particles of the iron-rich phase, which are solid whilst the brass is still molten, act as nuclei for the crystallization of the brass when it passes below its melting-point. Thus a large number of small grains, instead of a few large dendritic crystals, are obtained.

The Effect of Other Elements in Ordinary Brass. In general, elements like lead, cadmium and arsenic—any of which may be introduced accidentally or otherwise with the copper or the zinc—do no harm if present in such small quantities that they remain in solid solution; in fact they may actually increase the toughness. But **arsenic**[1] in quantities exceeding about 0·5 per cent., or **cadmium**[2] in quantities exceeding about 1 per cent., appear between the grains and causes a liability to inter-granular fracture; likewise **lead** above 0·9 per cent. appears as a separate phase, and causes weakness. For many purposes the presence of much lead in brass is not to be tolerated; but where the brass is to be machined, a brass containing lead is actually preferred, since such a brass, just because of its weakness, comes off in chips rather than in long tight rolls which interfere with the work. **Antimony** and **bismuth**,[3] even in very small quantities, are highly deleterious, causing inter-granular weakness; the same is true of **sulphur**, which may be absorbed from the furnace gases.

Tin is added to brass in quantities of about 1 per cent. in order to make the material less corrodible by sea-water; the matter will be referred to again later. In the Navy an α-brass with 29 per cent. zinc, 70 per cent. copper, and 1 per cent. tin is used instead of the old 70/30 brass for condenser tubes, whilst for purposes where a stronger alloy is needed, an $\alpha\beta$-brass with 37 per cent. zinc, 62 per cent. copper and 1 per cent. of tin is employed. More recently non-corroding brasses (both of the α- and $\alpha\beta$-types) containing 2 per cent. of lead, instead of 1 per cent. of tin, have been recommended.

Season-Cracking. Even pure brass, after it has undergone cold deformation, is liable to undergo the type of inter-granular failure known as "season-cracking" when stored for some time;

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[1] O. Smalley, *J. Soc. Chem. Ind.* **36** (1917), 429.

[2] L. Guillet, *Comptes Rend.* **166** (1918), 735.

[3] R. A. Wood, *J. Amer. Inst. Met.* **11** (1917), 181.

it takes place with especial ease at high temperatures and is commonly observed in cartridge cases stored in tropical countries. It is generally connected with the presence of internal strains, such as exist in all metals which have undergone deformation at comparatively low temperatures without subsequent annealing, but which probably exist to a special extent in articles made of "α-brass" just because of the extraordinary aptitude of that metal for being worked into shape. The internal stresses may be nearly equal to the ultimate strength of the material, and if very slightly increased through external causes may come to exceed it.[1] The conception of the inter-granular material as a very viscous liquid has been applied by Rosenhain to account for season-cracking. The grains may slowly part from one another, in the course of months, as a result of internal forces which are too small to pull them apart from one another quickly.[2]

There seems to be little doubt that corrosive agents, such as will selectively attack the inter-granular cement, often play a considerable part in bringing about season-cracking in brass articles, of which the external layer is in tension.[3] As the corrosion penetrates between the grains, the tension existing in the brass pulls the grains apart, thus causing the cracks to open more widely, and allowing the corrosive agent to enter the cavities between the grains. Consequently corrosion proceeds more quickly than would be possible in unstrained brass, and the inter-granular cracks soon come to extend for an appreciable distance into the metal. Recent work has shown that not all corrosive agents produce season-cracking in stressed brass. Only those which cause selective corrosion of the inter-granular material have this action; of these agents, ammonia and ammonium salts are the ones most likely to come into contact with brass under ordinary conditions. Mercury salts also stimulate season-cracking; but nitric and hydrochloric acids, although causing pitting and general corrosion, do not produce cracking. Various corrosive liquids have proved very useful to different investigators, for the detection of internal stresses in worked brass. A solution of mercurous nitrate containing free nitric acid has a distinct solvent action on the inter-granular material in brass and causes inter-granular cracks to develop wherever a

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[1] E. Heyn, *J. Inst. Met.* **12** (1914), 3. See also W. H. Hatfield and G. L. Thirkell, *J. Inst. Met.* **22** (1919), 67.

[2] W. Rosenhain and S. L. Archbutt, *Proc. Roy. Soc.* **96** [A] (1919), 55; W. Rosenhain, *J. Inst. Met.* **22** (1919), 92.

[3] H. Moore, S. Beckinsale and C. E. Mallinson, *J. Inst. Met.* **25** (1921), 35; H. Moore and S. Beckinsale, *Trans. Faraday Soc.* **17** (1921), 162; *J. Inst. Met.* **23** (1920), 223; **27** (1922), 149; C. H. Desch, *Trans. Faraday Soc.* **17** (1921), 17; O. W. Ellis, *Trans. Faraday Soc.* **17** (1921), 193; W. C. Hothersall, *Trans. Faraday Soc.* **17** (1921), 201.

tension exists at the surface. Researches with this solution have demonstrated the fact that by annealing at a fairly low temperature (say 250° C.) it is possible to remove the dangerous internal stresses without materially affecting the hardness. β-brass containing aluminium is particularly prone to inter-granular corrosion; by immersing a piece of this brass in mercury the component grains can be made to part company with one another altogether.[1] An interesting case of the failure of a β-brass containing manganese by the penetration of solder along the grain boundaries has also been recorded.[2]

Corrosion of Brass. Many of the domestic uses of brass are due to its comparatively stable character; in places where unprotected steel would rust badly, brass will remain uncorroded, or only superficially corroded, and if rubbed up occasionally will actually keep bright; brass surfaces are, of course, often protected with a coat of transparent lacquer.

One of the most important properties of brass is that it is but little attacked by salt water: hence the use of brass in the manufacture of tubes for marine condensers. It is, however, well known that condenser tubes are corroded through in time, and occasionally the tubes fail very rapidly. The matter is naturally one of great technical importance, and has been the subject of many investigations. Some years ago a committee was appointed by the Institute of Metals to examine the subject of the corrosion of non-ferrous materials, and the detailed reports[3] published by this committee deal largely with the question of brass condenser tubes, and constitute a mine of most valuable information on the subject.

Condenser tubes are almost invariably covered with an apparently structureless layer, caused by the mechanical working of the surface, and comparable to the "vitreous" film shown by Beilby to be present on the surface of a polished metal.[4] This layer is often distinctly richer in copper than the lower portions of the brass, the richness in copper being mainly the result of the acid-pickling used in cleaning. The presence of such a comparatively uniform layer is no doubt an important factor in preventing

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[1] C. H. Desch, *J. Inst. Met.* **22** (1919), 247, 248.

[2] J. H. S. Dickenson, *J. Inst. Met.* **24** (1920), 315.

[3] Three of the reports which concern brass are:—
W. E. Gibbs, R. H. Smith and G. D. Bengough, *J. Inst. Met.* **15** (1916), 37; G. D. Bengough, and O. F. Hudson, *J. Inst. Met.* **21** (1919), 148; G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 65. Most of the information, including a classification of the corrosion into five distinct types, is in the last of these reports. The results of German experience gained during the war are discussed by Schulz, *Zeitsch. Metallkunde*, **12** (1920), 49.

[4] G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 80.

the initiation of corrosion. Nevertheless, corrosion is not prevented entirely, for in any condenser the failure of a tube does occur from time to time owing to perforation. It is a fact that when once a given tube has begun to corrode in a marked manner at a point, corrosion continues at that point quickly until perforation occurs, although other tubes in the same condenser may remain almost unattacked. The main insoluble products of the corrosion are "*basic chlorides*" *of zinc or copper* (conceivably these are really hydroxides with adsorbed chlorides), *metallic copper* and *cuprous oxide*; a certain amount of soluble chlorides of copper and zinc are probably also produced.

So long as the condenser tubes are kept free of solid matter, and so long as the water flowing through the tube is free from entangled air-bubbles, the only form of corrosion is a slow general attack spread over the whole surface of the tube. This is seldom serious; in sea-water the amount of metal removed will only very slightly reduce the thickness of the tubes even after a long period. In one case a 5 per cent. loss of thickness after eighteen years was observed.[1]

If, however, the solid corrosion-products are allowed to settle on the surface of the tube at any point, the state of affairs is very different. Rapid attack often occurs where the deposit has settled, and this attack may soon lead to failure. Now in the ordinary marine condenser, the corrosion-products (of the kind which produce this effect) are usually swept out of the tube by the current of water. If, however, particles of sand, coke, wood fibre, cotton fibre, seaweed, shells, or colloidal matter of organic origin have access to the tube, they may settle or cling to the surface, and then entrap basic salts. Therefore unless the tubes are kept clear, serious corrosion may occur. It will be obvious that the particles which are capable of causing trouble are most likely to enter the tubes whilst the boat is in harbour. If the tubes could be cleaned out before putting to sea, the trouble—according to the writers of the reports mentioned above—could largely be avoided.

It should be stated that not all or every kind of basic salt is favourable to corrosion. Occasionally, a film of what is described[2] as "white, crystalline zinc oxy-chloride" has been observed upon the brass, which completely protects it from the action of the water. The corrosion product formed upon brass containing tin or lead is generally of a tough, coherent character, and the specially resistant qualities of brass containing these metals is due to this impermeable

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[1] In *fresh-water* condensers fed with acid waters, the rate of attack may be greater, but it is generally capable of control by suitable treatment of the water.

[2] G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 118.

varnish.[1] The type of corrosion-product which is found to be harmful is of a comparatively loose flocculent character, and is generally stained blue or green with copper salts, although this colour may be masked by the presence of iron; it appears almost certain that it is the copper salts which cause the damage.

The writers of the fifth report to the Corrosion Committee of the Institute of Metals prefer to regard the action of the copper salts upon the brass as purely chemical. Supposing the corrosion-product to contain cupric chloride, this will act upon both the zinc and copper of the brass, thus,

$$CuCl_2 + Zn = ZnCl_2 + Cu$$
$$CuCl_2 + Cu = 2CuCl$$

The first reaction produces the metallic copper, which is always found in the corrosion-product, and which the writers of the report regard as being of a secondary nature.[2] The second reaction will produce insoluble cuprous chloride, which will remain *in situ*, until it is reoxidized to cupric chloride by the oxygen dissolved in the sea-water; the cupric chloride will then attack a further quantity of brass. Thus the copper chloride in the adherent matter really acts as an oxygen-carrier.

Of course, whatever the mechanism of the reaction, the rate of corrosion will necessarily be limited by the rate at which oxygen is supplied to the surface. If the water flowing through the tubes contains only dissolved oxygen, an upper limit is set to the rate of corrosion, for the solubility of oxygen in water is but small. However, if entangled air-bubbles are present in the water, the rate of attack is not limited by this cause, and serious pitting may occur at or near the point where they impinge on the brass.

It will be noticed that the writers of the report mentioned have made no use of the conception of corrosion as an electro-chemical phenomenon, which has proved so useful in the study of the corrosion

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[1] C. H. Desch, *Trans. Faraday Soc.* **11** (1915–16), 198; *J. Soc. Chem. Ind.* **34** (1915), 258.

[2] Three types of views have been expressed as to the origin of the copper found in the corrosion product of brass. G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 108, consider that the copper is of a secondary nature, due to *redeposition* by *chemical* agency. The present writer has suggested that it is due to *redeposition* by *electro-chemical* agency; see U. R. Evans, *Trans. Faraday Soc.* **11** (1915–16), 267. C. H. Desch and S. Whyte, *J. Inst. Met.* **10** (1913), 303; **11** (1914), 235; **13** (1915), 80, consider that the copper is *residual* in origin due to removal of the zinc by the corrosive agency, the copper being left behind undissolved. If ordinary corrosion is an electrochemical phenomenon, it is *conceivable* that residual copper might be produced at the *anodic* areas, and redeposited copper at the *cathodic* areas. Desch and Whyte in their experiments made the whole specimen the anode, by applying a current from an external source; if residual copper were ever possible, it would be observed most easily under such conditions.

of many simple metals. Having regard to the object of the report they were probably wise to avoid controversial issues. But it is instructive to consider the subject from the electro-chemical standpoint. In a *new* tube, owing to the uniform character of the surface film, there is little likelihood of the setting up of any corrosion couples with appreciable E.M.F.'s. Hence the corrosion of new tubes is likely to be almost negligible at first—as is indeed found to be the case. But if at any point (owing to unequal stresses, or local variation in composition, or local differences in temperature, or again owing to stray currents from external sources) corrosion should once commence, it will proceed apace. For when once metallic copper and cupric salts have appeared in the corrosion product, opportunities for corrosion couples of the type

$$\text{Brass} \mid \text{NaCl} \mid \text{CuCl}_2 \mid \text{Copper}$$

exist. The brass will function as anode, and the copper as cathode. At the anode, zinc will pass into solution; at the cathode, cupric chloride will act like the cupric sulphate in a Daniell cell, being reduced either to metallic copper (hence the presence of "secondary" copper in the corrosion product), or to cuprous chloride; the cuprous chloride will then be reoxidized by the dissolved oxygen to cupric chloride, and thus the process will continue indefinitely.[1] It is clear that when once corrosion has commenced at a point, it is likely to continue there even if the agency which originally caused it to commence is removed.

It is possible that where the foreign substance which enters a condenser tube is a conducting substance, like coke or iron scale, it may serve as the cathodic member of a corrosion couple[2]; but it is likely that the main reason why foreign particles favour corrosion is that they cause the retention of basic copper salts in the tube.

The electrolytic protection system (see Chapter XIV, Vol. I) has been installed in the condensers of many vessels, and is stated to give fairly good results, at any rate in condensers which have shown a special tendency to corrosion near the ends of the tubes. It does not always afford protection to the middle of the tubes, and it has

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[1] Both W. Ramsay, *Engineering*, **104** (1917), 44, and E. B. Story, *Met. Chem. Eng.* **17** (1917), 653, have expressed views of brass-corrosion with which the present writer finds much to agree. The views of F. von Wurstemberger, *Zeitsch. Metallkunde*, **14** (1922), 23, 59, are essentially not very different from those expressed in this book, but the terms "selective corrosion" and "dezincification" are used in a rather different sense to that in which they are employed by English writers. The views of J. H. Reedy and B. Feuer, *J. Ind. Eng. Chem.* **12** (1920), 541, are less easy to accept.

[2] A. Philip, *J. Inst. Met.* **12** (1914), 133.

usually failed to arrest decay in tubes where corrosion had started before the process was installed.[1]

The corrosion of $\alpha\beta$-brass takes place more readily than that of α-brass, and the zinc-rich β_1-constituent (which may be an α-γ-complex) is always first attacked, its place being taken by a mass of porous copper. " Dezincification " of a Muntz metal article exposed to sea-water often converts it to a reddish material resembling poor copper ; the article retains its original form, but becomes so weak that it can be cut with a knife.[2] The addition of lead (2 per cent.) or tin (1 per cent.) to $\alpha\beta$-brasses is very common, on account of the comparatively resistant qualities of brass containing these metals.

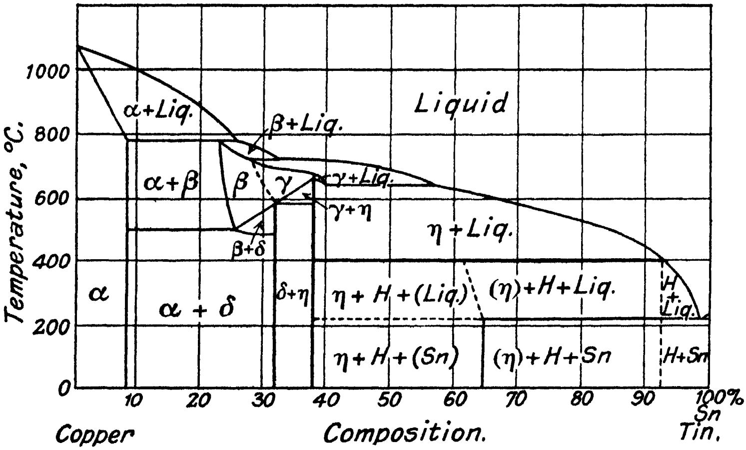

FIG. 11.—The System Copper-Tin (Heycock and Neville).

Copper-tin Alloys (Bronzes). The equilibrium diagram of the copper-tin alloys, as obtained by Heycock and Neville,[3] is shown in

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[1] Compare G. B. Allen, *J. Inst. Met.* **24** (1920), 292.

[2] H. S. Rawdon, *J. Amer. Inst. Met.* **11** (1917–18), 148. See also examples given by S. Whyte, *J. Inst. Met.* **13** (1915), 87, and by L. Belladen, *Gazetta*, **51** (1921), ii, 144.

[3] C. T. Heycock and F. H. Neville, *Proc. Roy. Soc.* **69** (1901), 320 ; *Phil. Trans.* **202** [A] (1904), 1. Compare E. S. Shepherd and E. Blough, *J. Phys. Chem.* **10** (1906), 630. Other diagrams have been put forward by other workers. The different diagrams are reproduced, and compared by J. L. Haughton, *J. Inst. Met.* **13** (1915), 222, **25** (1921), 309, who has carried out extensive fresh researches on the subject. These confirm the work of Heycock and Neville in many respects, but suggest certain modifications—mainly affecting the alloys comparatively rich in tin, which are of no commercial importance. It should be noticed that the solid solutions which Heycock and Neville call " H " are called "ϵ" by later writers (including Haughton).

Fig. 11, whilst Fig. 12 indicates the most important of the modifications proposed recently by Haughton. The diagram recalls that of the copper-zinc alloys, but is more complicated. At ordinary temperatures, alloys containing less than about 8 per cent. of tin consist of a single solid solution (α-brass). Beyond this point (the exact position of which is still a matter of disagreement) the alloys become heterogeneous, and contain, in addition to the α-solution, a second component, the δ-solution; alloys consisting of an $\alpha\delta$-complex undergo a transformation at 500° C., analogous to the transformation in brass at 470° C., and above that temperature we may obtain an $\alpha\beta$-complex. The δ-solutions are often regarded as being derived from a definite compound Cu_4Sn. The α-solutions are yellow and red, whilst the δ-solutions are white; the β-solutions are also white, but may be distinguished in micro-sections both from the α- and δ-solutions by the fact that they are darkened by

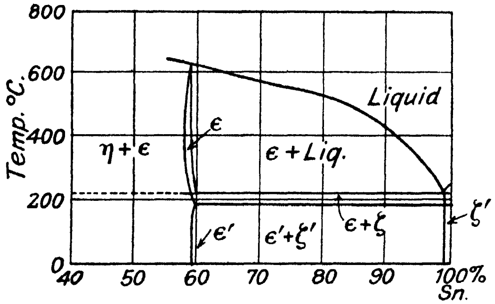

FIG. 12.—The System Copper-Tin. Haughton's Diagram, slightly simplified.

treatment with an acidified solution of ferric chloride. On account of the colour of the α-solutions, bronzes containing less than about 30 per cent. of tin have a yellow or red tinge; those with more tin are white or grey. The mechanical properties of the various solutions also present differences; the α-solution is malleable, whilst the δ-solution is hard, strong, but rather brittle. The structure of the alloys, which depends considerably on the heat treatment, is very interesting, and is best studied by reference to the beautiful micro-photographs of Heycock and Neville.

As in the case of the brasses, nearly all the technically important alloys are those relatively rich in copper. The alloys with 4–16 per cent. of tin are used in machinery, although most of the technically employed gun-metals and bronzes contain a third element, as will be explained below. An increase in the tin-content causes an increase in tensile strength and hardness, but tends to make the alloy brittle. When the tin-content reaches 19–28 per cent., the amount of the hard δ-constituent in the bronzes is sufficient to make the alloys too brittle for any mechanical purpose; such material can undergo a certain amount of elastic deformation, but cannot accommodate itself to a sudden blow by local plastic deformation; if stressed beyond the elastic limit, the material at once fractures. These properties—although rendering the alloys useless for structural purposes—are just what is required for the production of bells and gongs, which must be capable of performing "elastic oscillations" of considerable amplitude without suffering permanent change of shape. Hence alloys of this composition are used as "**bell-metal.**" In order to obtain bell-metal in its hard, brittle and sonorous condition, it must be slowly cooled. Above about 500° C., as is shown by the diagram, the δ-constituent ceases to exist, and if bell-metal be quenched from above this temperature, its properties are quite different; it is then appreciably malleable, and not sonorous.

The only alloy of any practical importance containing more tin than bell-metal, is an alloy with 33 per cent. of tin, which is very hard and white and takes a brilliant polish. It was formerly employed in the making of reflectors for telescopes and other optical instruments under the name of "speculum metal."

Phosphor-bronzes. The introduction of small amounts of phosphorus into bronze is usually effected by the addition of a "phosphor-copper" (copper with 10–15 per cent. of phosphorus), or "phosphor-tin," to the molten bronze. Phosphorus in very small quantities merely acts as a deoxidizer, increasing the soundness of the bronze, and preventing the inter-granular brittleness which is associated with the presence of cuprous oxide. If the alloy is to be rolled or worked, the addition of excess of phosphorus should generally be avoided, since it would reduce the malleability. If, however, the bronze is intended for casting, and especially for the production of machinery parts which have to withstand "wear," the presence of excess of phosphorus is highly beneficial, as it greatly increases the hardness and resistance to abrasion. The good wearing qualities of phosphor-bronze are commonly ascribed to hard particles of copper phosphide (Cu_3P) set in a comparatively plastic matrix. The phosphide particles can be recognized in a *heat-tinted* section, under the microscope, by the blue colour which they assume.

The approximate composition of some of the phosphor-bronzes used for different purposes is suggested below. It will be noticed that both the tin-content and phosphorus-content are increased, when greater hardness is demanded.

	Tin.	Phosphorus.	Copper.
Bolts, springs, screws, wire, rods, tubes	4–5%	< 0·1%	95–96%
Pinions, valves, steam and boiler fittings, pumps	7%	0·2%	93%
Axle-bearings, slide-valves, bushes, cog-wheels	8–12%	0·7 to 1·2%	87–91%

Although its conductivity is much less than that of copper, phosphor-bronze is used for telegraph wires and similar purposes, since the high tensile strength allows a considerably longer " span " than is possible with pure copper.

Zinc Bronzes.[1] Many kinds of bronze, especially those used for casting, contain zinc as well as tin. Amongst other effects, the presence of zinc adds fluidity to the molten bronze. The so-called " Admiralty gun-metal " (no longer used for guns) is an alloy of this character, and contains :—

Copper, 88% ; Tin, 10% ; Zinc, 2%.

Another gun-metal in common use contains :—

Copper, 85% ; Tin, 5% ; Zinc, 10%.

Cast gun-metal (especially when " chill-cast ") generally shows a cored structure ; but annealing removes the coring, and produces a polygonal structure comparable to that of α-brass and containing numerous twin-bands.[2]

On account of the comparative ease with which gun-metal can be cast, it is often used in machinery where a casting is required at short notice, and where it would occupy too much time to make a steel casting. The bronzes, however, lose a great deal of their strength at high temperatures, and they are being replaced more and more by metals and alloys which remain strong when hot, and which in some cases are more resistant to shock than gun-metal. Steel, Monel metal, and aluminium bronze are all now used in many places where bronze was at one time looked upon as the best material, in spite of the manufacturing difficulties met with in all three cases.[3]

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[1] For structure and effect of heat-treatment and annealing, see C. P. Karr and H. S. Rawdon, *U.S. Bur. Standards, Tech. Papers,* **59** and **60** (1916) ; J. Arnott, *Foundry Trade J.* **23** (1921), 2. For influence of impurities see F. Johnson, *J. Inst. Met.* **20** (1918), 167 ; the question of the influence of lead is further discussed by R. T. Rolfe, *J. Inst. Met.* **26** (1921), 85. The question of the best casting temperature is considered by H. C. H. Carpenter and C. F. Elam, *J. Inst. Met.* **19** (1918), 155.

[2] See also O. Smalley, *J. Soc. Chem. Ind.* **37** (1918) 194T.

[3] See Sir H. J. Oram, *J. Inst. Met.* **11** (1914), 26 ; Sir G. Goodwin, *J. Inst. Met.* **23** (1920), 56.

For the so-called "copper" coinage, a bronze with

Copper, 95%; Tin, 4%; Zinc, 1%

has long been used in the country; it shows wonderful resistance to wear. For casting statuary, a very fluid bronze is demanded, and the zinc-content is often increased; the presence of lead is favoured as it is thought to produce an attractive "patina" or oxidation-tint, which appears when the statue is exposed to the weather. Statuary bronze generally varies within the limits,

Copper, 88–91%; Tin, 5–10%; Zinc, 1–5%; Lead, 0–1·5%.

Plastic Bronzes Containing Lead. Although for many mechanical purposes, the presence of lead in bronze is regarded as highly detrimental, bronzes containing 4 to 30 per cent. of lead are very useful as bearing-materials. As in the analogous case of brass, the greater part of the lead fails to dissolve in the molten alloy, and when the metal has solidified, the structure consists of globules of lead distributed uniformly (under favourable conditions of casting) throughout a matrix of bronze. Thus we have a combination of a hard substance and a soft substance, the latter conferring a slight plasticity to the material, which—as will be explained in connection with other bearing-alloys—is desirable in a good bearing-material. Some of these "plastic bronzes" also contain phosphorus, which increases the hardness of the matrix—owing to the presence of copper phosphide; others contain nickel.

Copper-aluminium Alloys (Aluminium Bronzes).[1] Part of the equilibrium diagram of the copper-aluminium system is shown in Fig. 13. The system is very complicated, but we can—for our present purpose—confine our attention to the alloys comparatively rich in copper.

Alloys with less than about 10 per cent. of aluminium consist of a single solid solution (α), at least when annealed. Those with 10–16 per cent. are heterogeneous, and contain α- and δ-solutions when annealed. But there is a transformation point at 537° C. (analogous to the transformation points at 500° C. in the bronzes and at 470° C. in the brasses), and above 537° C. the constitution is different. If the alloys are quenched from a temperature above the transformation point, the structure—and also the hardness—is different from that of the alloys annealed at a temperature below it. The difference is shown by Figs. D and E of the frontispiece, both of which represent an alloy with 11 per cent. of aluminium; such an

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[1] D. Stockdale, *J. Inst. Met.* **28** (1922), 273; H. C. H. Carpenter and C. A. Edwards, *Proc. Inst. Mech. Eng.* (1907), 57; B. E. Curry, *J. Phys. Chem.* **11** (1907), 425; J. H. Andrew, *J. Inst. Met.* **13** (1915), 249; J. N. Greenwood, *J. Inst. Met.* **19** (1918), 55.

alloy consists at 750° C. entirely of β-solution, but if cooled just below 537° C. and annealed, rounded crystals of α-solution separate, which are shown in Fig. D, set in a ground-mass of the $\alpha\delta$-eutectoid. This transformation—if not prevented—is at least modified by quenching, just as the A_{123} change in steel is modified by quenching.

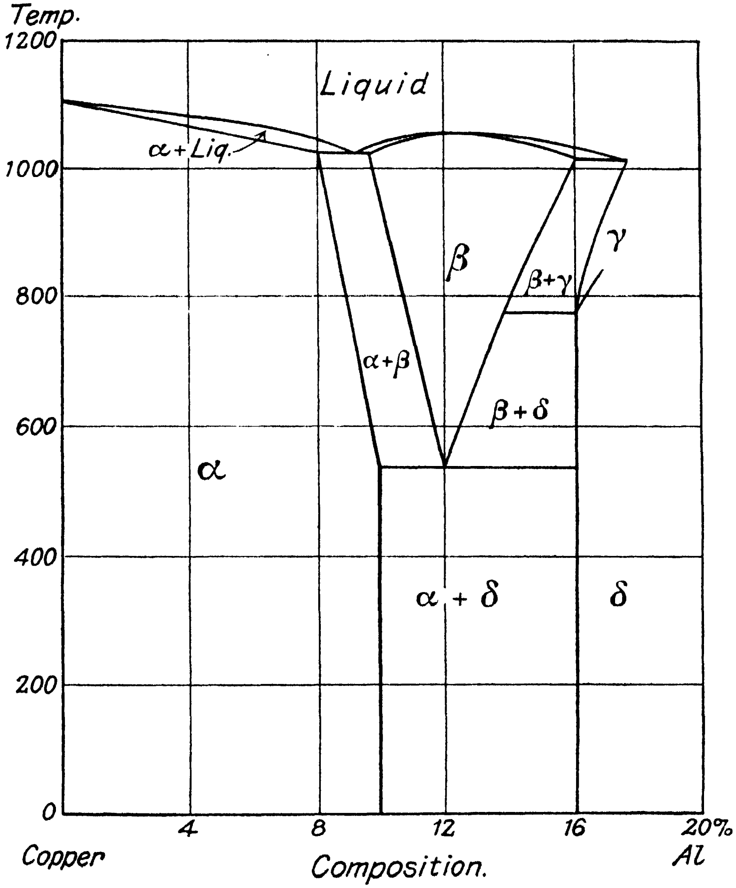

FIG. 13.—The System Copper-Aluminium. Diagram based on the work of Carpenter, Edwards, Curry, Andrew, Greenwood, and Stockdale.

The structure of the quenched alloy shown in Fig. E is "acicular," comparable to the "martensitic" structure of quenched steel. The analogy between the behaviour of steels and aluminium bronzes is interesting, but one difference should be noted; quenched steel is almost invariably harder than slowly cooled steel, whereas in alloys of copper and aluminium, the hardness of samples quenched from above the transformation point is often lower than those cooled from below the transformation point.[1]

The aluminium-copper alloy which is most commonly used contains about 10 per cent. of aluminium. It is a golden-yellow material, which is wonderfully resistant to atmospheric corrosion. Aluminium bronze has about twice the tensile strength of tin bronze and shows better resistance to shock; it is displacing tin bronze for many purposes. Owing to the considerable shrinkage, the casting of aluminium bronze presents many difficulties; but, nevertheless, the use of the alloy, in the cast as well as the rolled forms, is extending.[2] Aluminium bronze has been adopted in France for coinage purposes.[3]

The alloys used for die-castings often contain iron in quantities up to 5 per cent. The iron is very beneficial, rendering the alloy fine-grained, just as in the case of the addition of iron to brass. Very small quantities, such as exist in solid solution, do not affect the grain-size, although they increase the tensile strength. But, if the iron is present in sufficient concentration to involve the presence of a second phase, the minute particles act as nuclei for crystallization and the alloy tends to be much more fine-grained than would otherwise be the case.

An alloy containing 92 per cent. aluminium, 7 per cent. copper and 1 per cent. manganese has also been recommended for die castings.[4]

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[1] The variation of the hardness with the composition and quenching temperature has been examined by J. N. Greenwood, *J. Inst. Met.* **19** (1918), 55. See especially figures on pages 98 and 111. See also the work of A. A. Read and R. H. Greaves, *J. Inst. Met.* **26** (1921), 57, on the ternary alloys of nickel, aluminium and copper, some of which are much softer when quenched from 900° C. than when annealed.

[2] W. M. Cove, *Met. Chem. Eng.* **20** (1919), 162; "C.V." *Machinery*, **13** (1919), 656.

[3] *Engineer*, **134** (1922), 74.

[4] F. A. Livermore, *Met. Ind.* **18** (1921), 109.

SILVER

Atomic weight . . . 107·88

The Metal

Silver falls immediately below copper in the periodic scheme, and a certain analogy may be traced between the properties of the two metals. In the compact state, it is a white metal capable of taking a brilliant polish. The " white " appearance of silver shows that—unlike copper—the metal reflects almost equally well light of all wave-lengths to which the eye is sensitive. The shorter (violet) rays seem, however, to be reflected slightly less completely than the longer rays, since light which has been repeatedly reflected at a silver surface has a perceptible yellow colour. Likewise silver is almost equally opaque to light of all the wave-lengths within the visible portion of the spectrum ; outside the visible range, however, selective absorption does occur, silver being fairly transparent to ultra-violet light of certain wave-lengths.[1]

Silver is harder than copper, but resembles it in being malleable and ductile ; very thin silver leaf and fine silver wire can be obtained. It is a very good conductor of heat and electricity ; in fact, silver and copper surpass all other substances in this respect. Silver melts at a fairly high temperature, 962° C., slightly lower than the melting-point of copper. It is distinctly volatile at high temperatures, and can in fact be purified by distillation at the temperature of the oxy-hydrogen blow-pipe. Silver is heavier than copper, the specific gravity being 10·5.

The metal crystallizes in the cubic system ; native silver is occasionally found in octahedra. The atoms have been shown, by the X-ray method, to be arranged—in silver, as in copper—on a face-centred cubic lattice.[2] The external crystalline form of silver is not infrequently observed in the metallic deposit formed when a solution of silver nitrate is electrolysed, if the conditions are such that the crystals formed at different points on the cathode do not " grow into one another " and thus interfere mutually with the free development. But even under favourable circumstances there is a marked tendency towards arborescent or mossy growths, due to the greater development at the corners where the current

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[1] R. W. Wood, " Physical Optics " (Macmillan).

[2] L. Vegard, *Phil. Mag.* **31** (1916), 83.

density is highest, or where the supply of silver ions in the solution is most readily replenished. The conditions which favour the development at the cathode of a small number of large silver crystals (as opposed to a large number of small crystals) are a high concentration of silver nitrate, a low current density and the absence of free acid.[1]

Silver stands rather at the "noble" end of the Potential Series, and it is not surprising to find that the metal is remarkably stable towards corrosive agents. It retains its brightness indefinitely in ordinary damp air, although it is superficially blackened by air containing traces of hydrogen sulphide—a fact which suggests that silver has a greater affinity for sulphur than for oxygen, as is indeed the case; it is worthy of note that pure hydrogen sulphide in the absence of air does not darken silver.[2] The metal is unattacked by non-oxidizing acids, but dissolves in hot concentrated sulphuric acid with evolution of sulphur dioxide, and also in nitric acid; the action of nitric acid is greatly accelerated by the presence of nitrous acid—as in the case of copper.[3]

Although solid silver—even when heated—withstands the action of oxygen, molten silver has a distinct solvent action upon the gas. When molten silver containing oxygen is cooled, the gas is given off rather violently at the moment of solidification; the sudden evolution of gas may actually cause particles of silver to be shot out from the surface of the metal; the phenomenon, which is known as "spitting," has been aptly described as the "eruption of a miniature volcano." The sudden spitting is accompanied by evolution of light; production of light is commonly attributed to the sharp rise of temperature which may occur at the moment of solidification when the silver has been super-cooled, but it is probably due to another cause; many crystals, such as sugar and uranium nitrate, emit light when crushed in the dark, even at low temperatures, and it seems likely that the lumiscence of solidifying silver is of the same character.[4]

The solubility of oxygen in molten silver is proportional to the square root of the pressure, a fact which shows that oxygen cannot be dissolved as diatomic molecules, but is either dissolved as single oxygen atoms or as molecules of silver oxide (Ag_2O).[5] It seems

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[1] See A. H. W. Aten and L. M. Boerlage, *Rec. Trav. Chim.* **39** (1920), 720, who discuss the various factors that govern crystal-size in an electrolytic deposit.

[2] F. L. Hahn, *Zeitsch. Anorg. Chem.* **99** (1917), 118.

[3] V. H. Veley, *J. Soc. Chem. Ind.* **10** (1891), 204.

[4] W. C. McC. Lewis, "System of Physical Chemistry," Vol. II, p. 407 (1920 edition). (Longmans, Green.)

[5] F. G. Donnan and T. W. A. Shaw, *J. Soc. Chem. Ind.* **29** (1910), 987. See also W. Stahl, *Chem. Zeit.* **39** (1915), 885.

very probable that this oxide, although unstable in the pure state, can exist in dilute solution in molten silver. When molten silver containing silver oxide is cooled down, crystallization occurs in a manner similar to the crystallization of molten copper containing cuprous oxide. In both cases, the crystallites of metal that appear are free from oxygen, and the oxides tend to become concentrated in the still liquid portions. But, in the case of silver, the solution of the oxide will clearly become more unstable as it becomes more concentrated. If the cooling is slow, it is probable that oxygen will be given off from the still liquid portion as the concentration increases, and by the time the whole is solid, the metal is free from gas ; it is noteworthy that if the cooling is very slow, the elimination of oxygen is conducted without serious spurting.[1] On the other hand, if the cooling is rapid, there is very serious over-cooling of the silver ; both the solidification and accompanying gas-production are practically instantaneous, and the spitting out of portions of the solidifying silver is by no means surprising.

Cohen and Helderman[2] have stated that ordinary compact silver contains "at least three allotropes." This view is based on certain slight density changes which occur when silver is annealed. They are probably merely ordinary cases of recrystallization after cold-work.

Laboratory Preparation of Different Forms of Silver. The position of silver in the Potential Series indicates that it is a metal very easy to prepare from its compounds. By the action of almost any reactive metal, such as zinc, upon a solution of a silver salt, metallic silver is obtained. Indeed many silver salts decompose spontaneously at high temperatures with the production of the metal ; thus black spongy silver may be prepared by heating the nitrate, carbonate, or oxide. In some cases the decomposition is accompanied by the evolution of so much heat as to amount to an explosion.

Metallic silver is also conveniently obtained by the electrolysis of an aqueous salt solution. The electrolysis of a solution of the nitrate acidified with nitric acid gives silver in a rugged crystalline form, which will often require remelting before it is put to use. If a compact shining layer of limited thickness is required, a bath of potassium silver cyanide (which will be discussed in the section on electro-plating) can be used.

Where pure silver is to be made from an impure salt, it is best

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[1] C. V. Boys, *Trans. Faraday Soc.* **14** (1919), 227. Compare Sir T. K. Rose, p. 244, and R. E. Slade, p. 248.

[2] W. D. Helderman, *J. Inst. Met.* **16** (1916), 84. See, however, criticism by W. Rosenhain (p. 108), and by C. H. Desch (p. 114).

to precipitate it as insoluble chloride by means of hydrochloric acid, and after washing the precipitate to treat it with zinc and sulphuric acid, a dark precipitate of silver being obtained. This can be washed, and melted under a borax flux to give the compact metal. If necessary the silver can be redissolved in nitric acid, and the whole purification process repeated.

Colloidal Silver. By the action of different reducing agents such as stannous salts, hydrazine, hydroxylamine, tannin, tartaric acid, pyrogallol, formalin, citric acid, dextrin, or phosphorus, upon different silver salts, silver is precipitated in various colloidal forms. The colour of the product varies with the method of preparation; different workers[1] have been able to prepare grey, blue, gold, red, green, black, white and yellow forms of silver, some of the colours being remarkably bright. Many of these preparations contained organic matter and others contained residual silver compounds. The different forms have occasionally been styled "allotropic modifications" of silver, but there is no object in applying the words "allotropy" to such cases.

There is little doubt but that the remarkable variation in the colour of colloidal solutions of silver is largely due to variation in the size of the particles obtained under different conditions. Recent researches[2] have shown that it is possible to obtain a series of "sols" with particles of varying size, which display a gradual change of colour as the particle-size is increased. The sols having the smallest particles ($70\mu\mu$) are orange when viewed by transmitted light; thence we pass through red ($90\mu\mu$), purple ($110\mu\mu$) and blue-violet ($137\mu\mu$) to bluish-green ($180\mu\mu$). The connection between the colour and the size of the particles agrees with that which would be predicted from optical theory.

A comparatively stable colloidal solution of silver is obtained by warming a solution of silver nitrate containing sodium protalbinate, which acts both as a reducing agent and also as a protective colloid.[3] The solution can be purified by dialysis and is yellowish-brown in colour. Fairly stable "sols" can also be obtained by the use of gelatine as protective colloid, hydrazine hydrate being used as reducing agent; these are brown or red by transmitted light, but the scattered light has a greenish hue.[4] Colloidal solutions of silver can be prepared by Bredig's method, namely, by passing an

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[1] M. Carey Lea, *Phil. Mag.* **31** (1891), 238, 320, 497; **32** (1891), 337; J. C. Blake, *Zeitsch. Anorg. Chem.* **37** (1903), 243. Compare F. E. Gallagher, *J. Phys. Chem.* **10** (1906), 701.

[2] K. Schaum and H. Lang, *Koll. Zeitsch.* **28** (1921), 243.

[3] C. Paal, *Ber.* **35** (1902), 2224.

[4] A. Gutbier, J. Huber and A. Zweigle, *Koll. Zeitsch.* **30** (1922), 306.

arc between two silver wires submerged in water; these are more unstable.

Compounds

Only one class of silver compounds is known possessing any degree of stability, namely, those in which the metal is monovalent. They can be regarded as derived from the oxide Ag_2O; the salts, such as AgCl and Ag_2SO_4, are thus analogous in composition to the *cuprous* salts (CuCl and Cu_2SO_4), and are closely akin to them in properties.

Silver oxide, Ag_2O, being distinctly unstable, cannot be prepared by the direct combination of the elements. It may be produced as a precipitate in the wet way, by the addition of sodium hydroxide to a silver salt solution. It will be remembered that, in the analogous case of copper, a "hydroxide" is first precipitated under these conditions, but that this loses part of the combined water on merely heating it in the solution, and changes colour accordingly. In the case of silver the tendency to lose water, which is characteristic of metals of Group IB, is still more marked, for the black precipitate obtained by the action of caustic alkalis on silver salts does not, even at low temperatures, seem to contain any appreciable quantity of combined water. Thus if any hydroxide (AgOH) is first formed, it must at once lose practically the whole of the water yielding the anhydrous oxide (Ag_2O).

Silver oxide is a brown precipitate, which appears almost black when dry. Although difficult to produce in crystals of any size, X-ray examination of the powdery form shows that the atoms are arranged in definite crystal array, and in the same manner as in the crystals of the analogous oxide of copper (Cu_2O).[1] Silver oxide dissolves in acids, yielding the salts of silver. When heated at 250° C., silver oxide decomposes into its elements; it loses a certain amount of oxygen when exposed to light at ordinary temperatures, becoming—it is stated—rather blacker in colour. It is reduced to the metallic state by heating at 100° C. in a current of hydrogen.

Salts. The salts of silver, in contrast with those of copper, are, for the most part, colourless. The comparative absence of colour in silver and silver compounds is quite in accordance with the fact that silver has an almost unchangeable valency; any selective absorption of light which is caused by silver compounds lies—in most cases—beyond the range of the visible spectrum, although in silver iodide it extends into the visible blue region, and the salt has consequently a yellow colour.

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[1] R. W. G. Wyckoff, *Amer. J. Sci.* 3 (1922), 184.

The most striking feature of silver salts is the manner in which they suffer decomposition when exposed to sunlight, especially in the presence of organic matter; this matter will be referred to again in the section on photography. Silver salts are usually preserved in bottles of a yellow brown glass which absorbs the active rays. On account of their action on organic matter silver salts have notable caustic properties. They blacken the skin, precipitating finely-divided silver upon it.

The **soluble salts** of silver may be obtained by the action of acids on the oxide; the sulphate and nitrate may be formed by the oxidizing action of the acids on the metal. The **nitrate,** $AgNO_3$, is the most important salt of silver, as well as one of the most soluble; it crystallizes in colourless rhombic plates. The **sulphate** is much less soluble, and is most conveniently prepared by the action of fairly dilute sulphuric acid, in the presence of an oxidizing agent such as hydrogen peroxide, upon the metal. These salts are both easily reduced to the metallic state by organic matter, especially in the presence of light. The mere access of laboratory dust to a bottle containing them is sufficient to cause a blackening of the salts, due to the formation of metallic silver.

The **insoluble** salts of silver may be obtained most conveniently by precipitation from the soluble salts. The **chloride, bromide,** and **iodide** are, like the corresponding cuprous compounds, highly insoluble substances, the solubility being greatest in the case of the chloride and least in the case of the iodide. Like the cuprous salts, the silver halides darken in the light; the nature of this change will be discussed later. **Silver chloride** is a white curdling precipitate obtained by the action of almost any soluble chloride upon a solution of silver nitrate or sulphate. It is comparatively soluble in excess of concentrated sodium chloride solution. The **bromide** is faintly yellow, whereas the **iodide** is distinctly yellow; both are obtained in analogous ways. The tendency of these precipitates to curdle is very characteristic of the silver halides. When first the precipitating solution is added to the silver salt solution, an ordinary diffuse precipitate is formed. On shaking or heating the liquid, however, the mass coagulates together, leaving the solution free from perceptible suspended matter, but showing a faint opalescence.

The halogen compounds of silver melt at a low temperature, without decomposition, solidifying to a horny mass.

Other insoluble salts of silver include the phosphates, carbonate, chromate and arsenite. They may be obtained by precipitation in the usual manner. The **phosphates** (of which several are known) and the **carbonate** are yellow or white precipitates, darkening in sunlight; the **chromate** and **arsenite** are reddish-brown. Silver

thiocyanate is a white curdling precipitate formed by the action of ammonium thiocyanate on a soluble silver salt. Silver **sulphide** is obtained by the action of sulphuretted hydrogen on a silver salt solution ; it is a brown precipitate, slowly dissolved by nitric acid with the formation of sulphur.

Another important salt is the **nitrite,** which is obtained by mixing together warm concentrated solutions of silver nitrate and potassium nitrite. The silver nitrite separates on cooling as a crystalline precipitate. It decomposes less readily on storage than the other nitrites, and is consequently useful in the preparation of pure sodium nitrite.

Complex Salts of Silver. On the addition of potassium cyanide to a silver nitrate solution, a white precipitate of silver cyanide is at first formed. If, however, excess of potassium cyanide be added, the precipitate redissolves, the soluble double cyanide $KCN.AgCN$ or $K[Ag(CN)_2]$ being formed. This is a complex salt, and ionizes in the manner indicated by the formula $K[Ag(CN)_2]$. The concentration of silver cations in the solution is so low that the addition of a soluble chloride does not produce a precipitate.

Since, in the presence of excess of potassium cyanide, silver is converted to a form which can exist in solution even in the presence of ionized chlorides, it follows that potassium cyanide, added to a solution in which silver chloride has been precipitated, will dissolve the precipitate ; in the same way it acts as a solvent for silver bromide and iodide.

Other salts which cause the formation of complex ions may exert a solvent action upon the silver halides ; for instance, sodium thiosulphate $Na_2S_2O_3$ will dissolve the chloride and bromide of silver, and, to a lesser extent, the more sparingly soluble iodide. Apparently complex sodium silver thiosulphates, such as $2Na_2S_2O_3.Ag_2S_2O_3.2H_2O$ or $Na_4[Ag_2(S_2O_3)_3].2H_2O$, which contain the silver in the anion, are produced. Another substance which will dissolve the silver chloride, as well as silver oxide, is ammonia ; this reagent has only a slight solvent action upon the bromide and iodide.

A complex nitrite can be produced electrolytically in a divided cell containing sodium nitrite solution in the anode compartment and fitted with a silver anode. The anode becomes covered with a crust consisting mainly of nearly colourless silver nitrite ($AgNO_2$) mixed with a small amount of finely-divided silver ; after some hours, this crust begins to interfere with the passage of the current. Meanwhile the solution surrounding the anode has become bright yellow, and from it a complex salt, $Na[Ag(NO_2)_2]$, can be isolated in bright yellow crystals.[1]

Silver Peroxide and Derivatives. Although no well-defined stable compounds corresponding to the cupric salts exist, certain bodies containing silver in a higher state of oxidation have been prepared. When a solution of silver nitrate is electrolysed between platinum electrodes, under such conditions that the anodic current density is fairly high, not only is metallic silver precipitated at the cathode, but a black compound of silver is formed upon the anode. This body, once considered to be a peroxide, has been shown invariably to contain nitrate. Many views have been expressed as to its character, and the composition appears to vary with the conditions.[2] It is now generally assigned the formula $2Ag_3O_4.AgNO_3$. By treatment with water at 60–80° C. for some days, the silver nitrate may be removed, part of the oxygen also being lost; in this way a black oxide, said to have the composition AgO, is arrived at.[3] The oxide when dissolved in concentrated nitric or sulphuric acid, yields a brown liquid, but it loses oxygen on dilution.

A peroxide or mixture of peroxides of silver can also be obtained by the action of potassium persulphate on finely-divided silver (prepared from a silver salt by precipitation with magnesium); the colour of the silver changes from grey to black, and the product contains more oxygen than corresponds to the formula AgO, but less than would be indicated by the formula Ag_3O_4.[4]

Analytical

Silver differs from all other metals in having a chloride insoluble in water but soluble in ammonia. The addition of a soluble chloride to a silver salt solution brings down the whole of the silver as a curdling white precipitate; mercury and lead may also be thrown down, if present, but, when the fresh precipitate is treated with ammonia, the silver alone is dissolved; it may be reprecipitated from the filtrate by adding nitric acid.

The quantitative separation of silver from other metals depends on its precipitation as chloride. In the separation from mercury it is probably best to precipitate both metals as sulphide, and then to treat the precipitate with fairly dilute nitric acid, which dissolves

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[1] F. H. Jeffery, *Trans. Faraday Soc.* **15** (1920), iii, 16.

[2] The older views are summarized, and new investigations are described by M. J. Brown, *Trans. Amer. Electrochem. Soc.* **30** (1916), 326. See also H. C. P. Weber, *Trans. Amer. Electrochem. Soc.* **32** (1917), 391.

[3] E. Mulder, *Rec. Trav. Chim.* **16** (1897), 57; **17** (1898), 129.

[4] G. I. Higson, *Trans. Chem. Soc.* **119** (1921), 2048.

the silver sulphide, but leaves the mercury sulphide undissolved.

Silver is usually weighed as the chloride, a substance of very definite composition which is easy to filter and wash. Alternatively silver can be reduced to the metallic form by electrolysis, and weighed directly. A solution of the nitrate in the presence of free nitric acid gives on electrolysis between gauze-electrodes (for instance, the "Fischer" or "Sand" apparatus) a crystalline deposit of silver ; the solution must be used hot, in order to prevent the formation of "peroxide" derivatives on the anode. Much smoother deposits of silver, which adhere better to the cathode, are obtained if sufficient potassium cyanide be present to form the complex cyanide. Where salts of other metals also occur in the solution, care must be taken that these are not precipitated with the silver and weighed along with it. In the case of most metals, this can be accomplished by the adjustment of the cathodic potential within suitable limits ; the potential must be depressed sufficiently to deposit silver, but not so much as to allow the precipitation of the other metals.[1]

A dry method of assaying silver in an ore, depending upon the use of molten lead as a collector of the metal, is in common use. The ore is heated with a mixture of lead oxide, potassium cyanide, sodium carbonate and iron in a crucible. The lead and silver are reduced by the iron to the metallic state and the whole of the silver is dissolved by the molten lead. On cooling, a button of lead is found at the bottom of the vessel, and this contains all the silver present in the ore.

The separation of the silver and lead depends upon the fact that lead is more easily oxidized. The button of lead is placed upon a "cupel," a saucer-shaped porous vessel composed of bone-ash, and the cupel is placed on the floor of hot muffle furnace. The button soon melts, and the lead is oxidized by the air to lead oxide, which is largely absorbed into the substance of the porous cupel. On the other hand, the more "noble" silver remains in the metallic state ; it dissolves a little oxygen, but this is given up on cooling. The metallic bead left on the cupel at the end of the experiment, therefore, consists of lead-free silver, and may be weighed as such.

The volumetric estimation of silver depends upon the formation of the insoluble chloride. The solution in which silver-content is to be determined is placed in a stoppered flask, and sodium chloride of known strength is added gradually from a burette. After each addition the flask is stoppered and shaken, so as to coagulate the silver chloride. When the further addition of sodium chloride gives

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[1] For details see A. Fischer, "Electroanalytische Schnellmethoden" (Enke).

no fresh cloudiness to the solution, the analyst knows that enough sodium chloride has been added to react exactly with the silver; it is consequently easy to calculate the quantity of silver present. A certain amount of practice is needed to enable the observer to judge whether a "cloud" has been formed or not, but the method, used by a skilful analyst, is extraordinarily accurate.

An alternative volumetric method of determining silver, which is quicker, easier, but rather less accurate, depends on the titration of the silver solution with a standard solution of potassium thiocyanate. A drop of ferric salt is added to the silver solution before the titration commences, and as soon as a red coloration (due to ferric thiocyanate) appears, it indicates that the thiocyanate is present in excess and consequently that the silver has been completely precipitated.

TERRESTRIAL OCCURRENCE

Silver is found only in very small traces in ordinary igneous rocks (usually less than 0·0001 per cent.); but, like copper, it has tended to accumulate in the liquid portion as the igneous magma has solidified, and has been given off in appreciable quantities by the thermal waters which are expelled in the final stages. By the deposition of silver compounds from these waters, as they rose through fissures in the rocks, "silver veins" have been formed. Since copper and lead are also expelled under the same conditions, it is not surprising to find that silver is a minor constituent of many copper and lead ores. But, since silver occurs to a much smaller extent in the average magma than do copper and lead, and, since the conditions needed for the precipitation of the different metals as sulphides are different, many copper and lead ores contain but little silver; in some places, however, veins are found in which silver is present in quite large quantities. Silver veins generally contain a certain amount of gold.

Where the amount of silver in a lead ore or a copper ore is very small, it may occur as a minor constituent of the lead or copper mineral. Thus the important lead mineral, galena (PbS), can hold a small amount of silver—not exceeding 0·2 per cent.—in solid solution.[1] Several copper minerals—notably tetrahedrite—are often distinctly argentiferous. But where the silver-content of the lead or copper ore is considerable, independent minerals containing silver occur to some extent.

The independent silver minerals may include metallic silver itself and the sulphide, which is known as,

Argentite (Silver Glance) . . Ag_2S

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[1] A. E. Nissen and S. L. Hoyt, *Econ. Geol.* **10** (1915), 172.

Argentite is a black or grey mineral with metallic lustre, often found in reticulated or arborescent growths.

Where these ores lie within reach of weathering influences, they may undergo secondary changes. One of the best-known secondary minerals is the chloride,

Horn silver . . . . $AgCl$,

which usually occurs in waxy masses. Silver, like copper, may undergo secondary enrichment, for waters containing soluble silver salts penetrating downwards from the altered zone into the unaltered zone react with sulphides such as pyrites or chalcopyrite, with the reprecipitation of silver sulphide (argentite). But the more common ores of the zone of enrichment are the complex sulphides,

Pyrargyrite (dark red silver ore) $3Ag_2S.Sb_2S_3$ or Ag_3SbS_3
Proustite (light red silver ore) . $3Ag_2S.As_2S_3$ or Ag_3AsS_3
and Polybasite . . . . $9Ag_2S.Sb_2S_3$ or Ag_9SbS_6

By the interaction of silver-bearing waters with reducing agents (perhaps sulphides), native silver may be formed in minute leaves, threads or mossy growths. Thus native silver may be of a primary or a secondary character.

The main silver-mining districts are grouped around the Pacific ore-circle. Starting on the South American side, we find the celebrated silver mines of Bolivia and Peru. In many of these, the silver is associated not only with copper, but also with tin—a somewhat unusual association. In Central America there are some important mines, but the richest series of silver-veins is to be found in Mexico ; in the Pachuca district, which is one of the most important, there are quartz veins containing proustite, pyrargyrite and polybasite, whilst the higher portions contain the sulphide or chloride. The rich silver and gold ores of California and Nevada next call for mention, whilst we find silver-lead ores in Idaho and Colorado.

Passing round to the other side of the Pacific, we find silver in Japan, in Burma, in the Dutch Indies, whilst the lead and zinc mines of Broken Hill in Australia produce a notable quantity of silver.

Outside the Pacific ore-circle there are few deposits of great importance. In Ontario, however, the complex ores of the Cobalt region contain native silver, along with compounds of cobalt, nickel, bismuth and other metals. In Joachimsthal (Bohemia) the same association of silver with cobalt, nickel and bismuth is observed, whilst, on the other side of the Erzgebirge, in the mining district of Freiburg (Saxony), the precious metal is associated with lead and zinc. The copper ores of Spain also contain an appreciable amount of silver. Since, however, out of 187 million ounces of silver produced in 1919, 165 million ounces came from the American Continent, the comparative unimportance of these European sources can easily be appreciated.

METALLURGY AND USES

A large proportion of the world's output of silver is derived from ores which are mined mainly for the copper, lead or zinc which they contain. Even where the ores are so rich in silver that they are worked mainly with a view to the extraction of that metal, the metallurgy of silver is closely interwoven with that of other metals. In order, therefore, to prevent undue repetition, only a short discussion of the treatment of silver ores will be given at this point.

Silver is one of the most easily reducible of metals ; the difficulties which attend the treatment of ordinary silver ore are all connected with the fact that the silver content of the ore is always small ; either the silver minerals are scattered throughout a large amount of worthless material, or the silver may actually occur in traces in solid solution in another mineral, e.g. in galena (PbS).

In order to obtain this sparsely diffused silver from the ore, some agent must be used which will dissolve the silver and leave the worthless material ; two classes of agents are used :

(1) A " **collector** " **of metallic or pseudo-metallic character,** such as

(*a*) molten copper matte
(*b*) molten lead
or (*c*) mercury.

(2) An **aqueous leaching agent,** such as a solution of

(*a*) potassium cyanide
(*b*) sodium thiosulphate
or (*c*) sodium chloride.

(1) **Metallic Collector Processes.** Where silver occurs in a copper ore, practically the whole of the silver will be found in the **matte** produced when the copper is smelted in the ordinary way. In cases where a silver ore is free from copper—or contains too little copper for efficient collection—it is clearly possible to mix it with a further amount of ordinary copper ore and to smelt the mixture. The argentiferous copper matte is " blown " to give an argentiferous " blister-copper," which is then refined electrolytically. The silver remains in the anode slimes, the subsequent treatment of which was described in the section on copper (p. 49). A bullion

consisting of silver and usually a little gold is obtained ; the parting of these two metals is described later.

Copper matte is now commonly regarded as the most efficient collector of silver, but **molten lead** is also largely used. Most of our ordinary lead ores contain silver, which is largely found in the lead produced by ordinary smelting. Silver ores which are comparatively free from lead can be mixed with lead ores and the whole mixture smelted to give an argentiferous lead. The desilverization of this lead will be described in the section on lead. There are three main processes depending respectively on—

(i) The extraction of the silver with molten zinc, in which silver is more soluble than in lead (**Parke's process**).

(ii) The electrolytic refining of argentiferous lead, which leaves silver in the anode slimes (**Betts' process**).

(iii) The fractional crystallization of the lead. The first crystallizing portions contain less silver than the last (**Pattinson's process**).

The use of **mercury** as a collector for silver was formerly important, but may now be regarded as obsolescent, owing to the high price of mercury, and the more complete extraction by other methods.

In the process[1] developed in the United States, a pulp of ore and water is ground up between iron grinders, in an " amalgamation pan " ; mercury is added, together with sodium chloride, crude copper sulphate, and sometimes other chemicals. The silver minerals are reduced to the metallic state by the iron, and the metallic silver is " collected " by the mercury, an amalgam being formed. As a rule the iron of the grinding surfaces actually functions as the reducing agent for the silver, and the " shoes " and " dies " (the pieces which perform the grinding) are generally made renewable. Sometimes scrap-iron, however, is added.

The function of the copper sulphate is probably to set up iron-copper couples which promote the reduction, whilst that of the sodium chloride is probably to keep the iron from becoming passive, and possibly to act as a solvent for silver chloride. Further, chlorides of copper are produced which tend to convert the sulphides of silver into chlorides of silver by some such reaction as

$$CuCl_2 + Ag_2S = CuS + 2AgCl.$$

Since silver chloride is much more easily reduced than silver sulphide, the metallurgical reaction is favoured.

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[1] For further details see W. Gowland, " Metallurgy of the Non-ferrous Metals " (Griffin); C. Schnabel and H. Louis, " Handbook of Metallurgy " (Macmillan).

The pulp and amalgam are separated in settling vats; the amalgam is freed from excess of mercury by filtration through canvas, and is afterwards distilled, to separate the volatile mercury from the non-volatile silver. The mercury is largely recovered, but a small loss occurs each time, and, with the present price of mercury, this loss causes the process—in most places—to compare unfavourably with the leaching processes described below.

The amalgamation process works best if the ores are roasted with salt before the treatment. This roasting converts the sulphides to silver chloride, which—as already stated—is much more readily reduced than the sulphide; it also drives off from the ore any arsenic, the presence of which is prejudicial to amalgamation. But the roasting adds to the cost of the process.

The old "*patio process*,"[1] used until quite recently on a fairly big scale in Mexico, was chiefly remarkable in that mercury was used not merely as a "collector," but also as the reducing agent, no iron being employed. It is now largely replaced by cyanide leaching.

(2) **Leaching Processes.** The system of leaching with a cyanide solution—so successful in the extraction of gold—has been applied with great success in Mexico, and elsewhere, to silver ores.[2] The cyanide has no action on silica and on most other gangue materials, and consequently is able to perform the separation of traces of silver from a very large volume of worthless matter. It is generally found convenient to subject the ore to a preliminary concentration by a gravity method, and then after grinding to leach with cyanide solution in the presence of air. Cyanide acts quickly on silver chloride, but less quickly on the sulphides. The suspension of ore in the cyanide bath is filtered, and the clear solution obtained is treated with aluminium dust or with zinc, which precipitates the silver in a finely-divided form.

In some places, as at Nipissing (Ontario), sodium sulphide has been substituted for aluminium dust as the actual precipitant owing to the high cost of the latter.[3] The silver is thus precipitated as sulphide which is mixed with 8 per cent. sodium hydroxide solution and the mixture is made to circulate through tube mills containing aluminium ingots; the aluminium removes the sulphur, and after the treatment is complete, the precipitate shows a silvery lustre when rubbed on paper. It is then removed by filtration, washed and melted down in a furnace to give bullion. It will be

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[1] C. P. Duarte, *J. Chem. Met. Soc. S. Africa*, **9** (1908), 105.

[2] A. F. J. Bordeaux, *Trans. Amer. Inst. Min. Eng.* **40** (1909), 764; G. A. Tweedy and R. L. Beals, *Trans. Amer. Inst. Min. Eng.* **41** (1910), 324.

[3] R. B. Watson, *Eng. Min. J.* **103** (1917), 378.

noticed that even in this modified form of the process, aluminium is still used as the reducing agent; but the amount consumed is no doubt much less than if aluminium dust were introduced directly into the cyanide solution.

Other solvents for silver, such as sodium *thiosulphate* and sodium chloride, are only effective *if the silver is present as silver chloride.* Before leaching with these reagents, therefore, it is necessary to subject the ore to a preliminary chloridizing roasting, which can be carried out in the same way as described in the treatment of copper ores. Thiosulphate is still used as a solvent in some of the works where the complex cobalt ores are treated (Vol. III, p. 167); the silver is subsequently precipitated as sulphide. Sodium chloride—on the other hand—is only an effective solvent for silver chloride when concentrated, and is now rarely employed for true silver ores. However, in the treatment of Spanish copper ores by the method of "chloridizing-roasting" and leaching—which has already been discussed in the section on copper (page 44)—the silver present in the ore is brought into solution by means of sodium chloride and is then precipitated as silver iodide by the addition of sodium iodide.

The treatment of the complex ores occurring in the Cobalt region has already been discussed in the section on cobalt. It is, however, interesting to note at this point that many of the ores coming from this region are subjected to a concentration process in order to obtain an enrichment of silver in certain portions, and that not only gravity concentration, but also flotation, has been applied with satisfactory results.[1] Attempts made elsewhere to apply flotation to silver ores have not been in every case successful. Some of these attempts were "war measures" caused by the need of economy for cyanide during the war; flotation has been started and abandoned at several places in Nevada and at Cripple Creek (Colorado),[2] but it is said to be practised in Mexico.[3]

A rather interesting example of silver leaching is carried on in Germany for the extraction of silver from the argentiferous copper mattes obtained from the Mansfeld copper ores. The matte is roasted under such conditions that the copper is converted to oxide, and the silver to sulphate. The silver sulphate can be extracted with water and the silver is thrown down with scrap copper. The insoluble copper oxide is mixed with fuel and reduced in water-jacketed blast-furnaces yielding metallic copper.

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[1] R. E. Dye, *Trans. Can. Min. Inst.* **20** (1917), 11; J. M. Callow and E. B. Thornhill, *Trans. Can. Min. Inst.* **20** (1917), 28.

[2] G. H. Clevenger, *Eng. Min. J.* **105** (1918), 743.

[3] H. A. Megraw, *Eng. Min. J.* **105** (1918), 102.

Parting of Gold and Silver. The bullion derived either from silver ores or from gold ores almost invariably contains both metals, and often other less valuable constituents, such as copper and iron. Where the precious metals have been extracted by leaching and precipitated with zinc, the bullion often contains zinc and lead as well; but these easily oxidizable elements can largely be eliminated if the precipitated metal is melted under a flux containing nitre which is occasionally stirred into the fused metal.

The parting of the main valuable constituents, gold and silver, is carried out in different ways, but it is generally necessary to start with an alloy containing not more than about 40 per cent. of gold. If the bullion to be treated is found to contain more gold than this amount, it is melted with some other sample of crude silver containing but little gold, so as to give an alloy with a lower gold-content. Where the sulphuric acid process is to be used the alloy should contain only 18–25 per cent. of gold, but it may be made as rich as 30–40 per cent. if electrolytic refining is contemplated.

The older method of parting consists in the treatment of the alloy with concentrated **sulphuric acid,** which dissolves the silver, but leaves the more noble gold in a brown porous form. The alloy is first granulated by being poured molten into water; the granulated mass is then treated with sulphuric acid in kettles of white cast-iron, which are slowly heated to the boiling-point; sulphur dioxide, which is given off in large quantities, passes off through lead pipes. Special arrangements must be made for absorbing the gas, which is sometimes reconverted into sulphuric acid and sometimes utilized in other ways. When the reaction is over, the whole contents of the pot are siphoned into lead-lined vessels containing water. The sudden diluting of the hot concentrated acid causes a most violent commotion; after this has subsided, the brown gold settles quickly to the bottom. The clear silver sulphate solution is drawn off to another vessel in which the silver is precipitated by means of scrap copper or scrap iron; the precipitated gold and the precipitated silver are separately washed, dried, and melted down. In the melting of gold, an oxidizing flux of nitre is generally advisable to eliminate traces of lead, which would cause brittleness. On the other hand, in silver melting—at any rate in the final stages—oxidizing conditions are disadvantageous, since they would lead to violent "spitting." Sometimes the molten silver is covered with charcoal and stirred with a birch pole before it is allowed to solidify, thus preventing the spitting.[1]

At one time, nitric acid was used, instead of sulphuric acid, for

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[1] W. Stahl, *Met. u. Erz*, **13** (1916), 298.

parting; but it has proved too expensive. Indeed even the sulphuric acid process is tending to be replaced by the electrolytic method, in which the consumption of acid is avoided altogether. **Electrolytic parting** is used almost exclusively in the American refineries, and has been adopted at several of the larger refineries in Europe. In the American Mints,[1] the parting is carried out in two stages, the first stage producing fine silver, and the second stage fine gold. In the *first stage,* ingots consisting of the crude bullion with 30–40 per cent. of gold are wrapped in cloth bags and are made the anodes in a solution containing 2–5 per cent. of silver nitrate with about 2 per cent. of free nitric acid contained in a tank of stoneware. The cathodes are thin sheets of silver, being hung, like the anodes, vertically in the cell. Each cell may contain, perhaps, five cathodes and four bags containing anodes arranged between them. Six to twenty cells may be connected in series, and an E.M.F. of about 0·8 volt per cell is applied; the solution is sometimes kept in motion by means of a glass propeller, arranged in the centre of each cell. Silver is dissolved at the anode, and silver crystals of over 99·9 per cent. purity are formed upon the cathode; the gold remains, however, undissolved in the form of a spongy mass in the anode bags. The cathodes are generally taken out at intervals and the silver crystals are brushed off; in some plants a device is installed for brushing off the silver continuously. The silver crystals after being drained and washed are sent to the melting room, where they are melted down and cast into bars.

At one time it was customary to add a little glue to the electrolyte in order to improve the character of the cathode deposit, but it is stated that this practice is now abandoned.[2]

The solution tends to become weaker in silver, and silver nitrate is periodically added. When impurities have collected in the solution to such an extent that the cathode product is beginning to suffer in quality, the solution is replaced. The silver present in the discarded bath is usually recovered by electrolysis in a cell fitted with an insoluble iron anode; in some refineries, however, it is precipitated by means of scrap copper.

The anode sponge, consisting mainly of gold, is melted down, and used in the production of the anodes for the second stage; these anodes still contain much silver. In the *second stage,* the electrolyte consists of a solution of gold chloride (4–7 per cent. of

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[1] H. J. Slaker, *Eng. Min. J.* **90** (1910), 214; E. B. Durham, *Eng. Min. J.* **92** (1911), 901, 950; G. G. Griswold, *Trans. Amer. Electrochem. Soc.* **35** (1919), 251.

[2] F. C. Mathers and J. R. Kuebler, *Trans. Amer. Electrochem. Soc.* **29** (1916), 417.

gold) with free hydrochloric acid (10 per cent.); the cathodes consist of pure gold. An E.M.F. of 1·1 volts per cell is applied. The bath is heated by steam and is agitated by means of a rapidly revolving propeller. The anodic behaviour of gold and silver in a chloride solution is different to that in a nitrate solution; gold is dissolved anodically, whilst silver remains, as the insoluble chloride, in the slimes. On the cathode, gold of above 99·9 per cent. is obtained (if desired it can be purified still further by a second electrolytic refining). The deposit on the cathode does not readily strip, so that the cathodes are periodically withdrawn to be melted up, their place being taken by fresh cathodes of thin gold. When the electrolyte becomes foul it is renewed; platinum, if present, is usually recovered from the spent electrolyte by the addition of ammonium chloride; the ammonium platinichloride, which is precipitated, yields spongy platinum on ignition.

Other parting methods are used to some extent. The **Miller process** is useful for the refining of bullion in which gold is the main constituent. The process consists in blowing chlorine gas through the molten bullion; a layer of molten silver chloride appears on the surface of the gold, whilst the baser impurities are also eliminated (partly as a fume). The method has long been used in Australia, for treating gold bullion containing 4–11 per cent. of silver and 5 per cent. of base metals. It has recently become usual to blow air and chlorine simultaneously into the molten gold. At the commencement of the process, much air and little chlorine is used, and the base metals, which are easily oxidized, are thus removed. Afterwards the supply of chlorine is increased, and the silver also is attacked. In this way, the complete removal of the base metals like lead (which renders the gold brittle) is brought about without serious loss of precious metals.[1]

The process is now used in South Africa,[2] and in a slightly different form in Canada.[3]

"Parting Limits." It is convenient at this point to refer to the recent investigations of Tammann into the theory of gold-silver parting by means of corrosive acids or by anodic corrosion. Clearly in the parting of an alloy containing little gold, the removal of the atoms of silver will allow the corrosive agency to penetrate into the interior of the alloy, and the corrosion will continue until the whole of the alloy is desilverized and nearly pure gold is left. On the other hand, if the alloy contains but little silver, the removal of silver from the surface will merely cause the formation of a layer

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[1] R. R. Kahan, *Trans. Inst. Min. Met.* 28 (1919), 35.
[2] *S. African Min. Eng. J.* 32 (1921), 467.
[3] M. W. von Bernewitz, *Min. Ind.* 28 (1919), 298.

of almost pure gold, which will stop further penetration. Tammann[1] has investigated the question of the proportion of silver atoms necessary to allow of continued parting, and has determined the limits of composition which are necessary with different kinds of corrosive agencies. Thus he finds that alloys in which less than half the atoms consist of silver are not appreciably attacked by boiling nitric acid, except on the surface, whilst from those in which $\frac{5}{8}$ (or more) of the atoms are silver, practically the whole of the silver is removed by that reagent.

Tammann has studied many other systems of metallic mixed crystals and finds that *for metals crystallizing in the cubic system*, the "parting limit" usually occurs when either $\frac{1}{8}$, $\frac{2}{8}$, $\frac{3}{8}$, $\frac{4}{8}$, $\frac{5}{8}$, $\frac{6}{8}$, or $\frac{7}{8}$ *of the atoms consist of the more attackable component*; he has considered the significance of this fact in connection with the arrangement of the atoms on the space-lattice.

Silver-plating.[2] It is well known that a thin, smooth and adherent coating of silver is frequently applied to articles of less resistant materials, such as German silver, to protect them from attack and to improve their appearance. The plated table-ware now manufactured consists generally of German silver coated with silver; another material used as the basis in silver-plating is Britannia metal, but this is now used much less than German silver. The thickness of the silver-coat applied may vary from the thinnest film up to about 1/50 inch; in special cases thicker deposits are called for. The plating is always brought about by making the object to be coated the cathode in a suitable silver salt solution. Opposite the cathode, anodes consisting of silver plates are suspended, and whilst silver is deposited on the cathode, it is dissolved at the same rate from the anode, the strength of the bath being thus maintained.

A solution of a simple silver salt like silver nitrate cannot be used in electro-plating, since such a solution does not yield a uniform coat of silver, but either a granular crystalline deposit, or a black sponge. It has been found, however, that a very uniform and compact film of silver can be obtained if a solution consisting of the double cyanide of potassium and silver be used as the plating-bath; the bath can be obtained by dissolving either silver chloride or silver cyanide in a solution of potassium cyanide. The current density must not be too high, or the quality of the deposit will suffer. Usually about

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[1] G. Tammann, *Zeitsch. Anorg. Chem.* **107** (1919), 1; **112** (1920), 233; **114** (1920), 281; *Zeitsch. Metallkunde,* **13** (1921), 406.

[2] A complete list of plating bath *recipes* is given by F. C. Frary, *Trans. Amer. Electrochem. Soc.* **23** (1913), 62. The early history of plating is described by R. E. Leader, *J. Inst. Met.* **22** (1919), 305.

0·3 amps per 100 sq. centimetres is allowed. A specially bright deposit may be obtained if the bath is saturated with carbon disulphide, but this brightening bath is usually only employed for the final stages of plating.[1]

The smooth and fine-grained character of the deposit obtained from cyanide baths has been referred to in Chapter XI of Vol. I; it is probably due to the high polarization obtained in baths in which silver cations are only present in very small amount. The brightening action of carbon disulphide may be compared to the action of a protective colloid. A slight excess of potassium cyanide in the solution is usually recommended to ensure the regular dissolution of the silver anodes, and to prevent the formation of a film of insoluble silver cyanide upon the anode surface.

The surfaces of the articles to be plated must be scrupulously free from grease and from any film of oxide, or the silver-coat will not be sufficiently adherent. Oxide must first be removed, as far as possible, mechanically, then grease is dissolved away by immersion in a hot alkaline bath; it is advisable finally to dip the article into an acid bath, in order to dissolve the film of oxide that is generally still present upon the metal. German silver articles—just before being plated—are often dipped into a solution of a mercury salt, preferably potassium mercuric cyanide, so as to obtain upon the surface a coating of metallic mercury or an amalgam, the operation being known as "quicking."

The mode of suspension in the plating-bath varies with the shape of the object to be plated. Objects like spoons are usually hung in a wire loop; where the shape would render this form of attachment difficult, the objects can be placed in a wire basket. In any case, the wire attachment or basket serves to connect the object to the negative pole of the battery furnishing the current.

Frequently the plating is commenced in a rather dilute "striking-bath" at a very high current density; but after a momentary immersion in this, the articles are transferred to the plating-bath proper, where the current density is lower. Usually they are finished in a "brightening" bath containing carbon disulphide. After plating, the articles are washed, burnished and finally polished with rouge, an agent which exerts a very distinct dragging effect upon the silver and produces a smooth (possibly amorphous) film upon the surface, thereby conferring the well-known brilliant lustre. A certain amount of rouge is probably retained on the surface film; silver polished with rouge is perceptibly darker than silver polished with magnesia. Indeed if the rouge is not applied in the most

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[1] Some authorities, including Langbein, consider the addition of carbon disulphide a mistake.

suitable manner (e.g. if it is applied to the surface when overheated) distinct red stains may be produced on the surface.[1]

As in the case of all electro-chemical processes in which there is a considerable quantity of precious metal " locked up " permanently in the plant, a great saving would be effected if the current density could be increased. Under ordinary conditions it is impossible to use a current density exceeding about 3–4 amps. per square foot, since at high current densities the deposit becomes " burnt." Recent experiments with alkaline baths containing potassium carbonate appear to indicate that good deposits can be obtained with current densities as high as 8 amps. per square foot.[2]

Silvering of Glass. It is convenient at this point to refer to the production of mirrors by heating glass when in contact with a solution containing a suitable silver compound. The silvering solution usually contains silver nitrate, excess of ammonia, and some organic reducing agent such as a tartrate, an aldehyde or glucose. One bath which is said to be very successful,[3] when properly manipulated, contains silver nitrate, ammonia, tartaric acid and white sugar. Such a solution—although sufficiently stable at low temperatures—deposits silver as a bright film when warmed in contact with glass.

Alloys of Silver. Apart from the cases of electro-plating and mirror-making just mentioned, and its occasional use for vessels employed in the laboratory for the heating of corrosive substances, such as caustic alkali, pure silver is but little used. The " standard silver " used in the arts is a silver-copper alloy containing 7·5 per cent. of copper or other alloying element. The equilibrium diagram of silver-copper alloys was discussed in Chapter IV (Vol. I) as an example of an alloy-system with metals which form mixed crystals throughout certain limits. It may be recalled that in the annealed state,

Alloys with 0–5 per cent. of copper consist solely of crystals of cupriferous silver.

Alloys with 5–27 per cent. of copper consist of crystals of cupriferous silver in a eutectic.

Alloys with 27–94 per cent. of copper consist of crystals of argentiferous copper in a eutectic.

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[1] A. Jefferson, *J. Inst. Met.* **28** (1922), 447.

[2] F. Mason, *Trans. Faraday Soc.* **16** (1921), 534. Compare G. B. Brook and L. W. Holmes, *Trans. Faraday Soc.* **16** (1921), 524, who suggest that the alleged superiority of " old " plating-baths over newly prepared baths is due to the accumulation of carbonates in the former; the carbonates increase the conductivity.

[3] G. Martin, " Industrial Chemistry " (Crosby Lockwood).

Alloys with 94–100 per cent. of copper consist solely of crystals of argentiferous copper.

The employment of "standard silver" depends on the stability in air, the beauty and good wearing qualities of the alloy. It keeps its lustre well in ordinary air, although the older variety tarnishes in air containing hydrogen sulphide. Recent research at Sheffield has evolved a new "stainless silver," which does not tarnish.

The new British coinage, introduced in 1920, contains only 50 per cent. of silver. The silver-content is fixed by law, but the alloying material is not legally specified; hitherto nickel with a little copper has been employed as the alloying material.

The Use of Silver Salts in Photography

General. A large quantity of silver is consumed in the manufacture of photographic plates, films and papers. It has already been mentioned that the halogen compounds of silver darken in the light, and that many other salts become reduced to the metallic state when exposed to sunlight in the presence of organic matter. The decomposition of the halides also is greatly aided by organic matter; if a suspension of silver chloride in gelatine jelly be exposed to the light, a reddish colour is quickly produced in the jelly. The early chemists ascribed the colour-change produced in silver chloride to the formation of sub-chloride, such as Ag_2Cl. It is now certain, however, that part of the silver chloride is decomposed by the light into chlorine and silver

$$2AgCl = 2Ag + Cl_2$$

and that the silver produced remains dispersed in the silver chloride as particles of colloidal size; the coloration is, of course, due to these colloid particles.[1] The same red colour is formed by the absorption of colloidal silver, separately prepared, into silver chloride. Brightly-coloured bodies can be obtained containing less than 1 per cent. of reduced silver, and the colour varies with the conditions of formation, as is so often the case with colours due to colloid particles. It is unlikely, therefore, that the hypothetical sub-chlorides referred to above have any real existence.

If a clear crystal of silver chloride is exposed to light, the growth of the particles can actually be observed by means of the ultramicroscope. On exposure, the surface becomes brown, and after a time particles become visible under the ultra-microscope; if at this stage the crystal is removed from the light and heated at

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[1] Lüppo-Crämer, *Koll. Zeitsch.* 2 (1908), 103, 135, 360; W. Reinders, *Zeitsch. Phys. Chem.* 77 (1911), 213. A good summary of different theories is given by F. F. Renwick, *J. Soc. Chem. Ind.* 39 (1920), 156T.

350° C., the growth still continues. The cloudiness caused by the particles of silver in the crystals is in every way analogous to the metallic fogs which can be produced in salts of lead.[1]

When silver *bromide* is exposed to the light for a short time, there is no change in its outward appearance, although a long exposure causes the colour to become light grey or brown, bromine being set free in recognizable amounts.[2] However, even a very short exposure to the light is capable of bringing about sufficient reduction to cause a notable change in the behaviour of the silver bromide towards reducing agents. Ordinary silver bromide, prepared in the dark, is not quickly reduced to the metallic state by such reducing agents as pyrogallol made alkaline with sodium carbonate. The bromide, however, after a very short exposure to sunlight, suffers some change which causes it to be readily reduced by alkaline pyrogallol. Apparently the small particles of reduced silver produced by the light act as nuclei which aid the reduction of more silver bromide, somewhat in the same way that the addition of a small crystal of sodium sulphate to a large amount of the supersaturated solution of that salt initiates the crystallization, which when once started proceeds apace.[3]

The action of organic matter in facilitating photolytic changes appears to be an indirect one. Reactions such as

$$2AgCl = 2Ag + Cl_2$$

involve an *increase* of free energy in the system, and cannot occur spontaneously unless light is falling upon the salt, the energy being then supplied by the light. If no organic substance were present, the decomposition would soon be balanced by the opposing change

$$2Ag + Cl_2 = 2AgCl$$

(which involves a *decrease* in free energy); when the light ceased to beat upon the silver salt, the silver and chlorine (if the latter had not diffused away) might recombine completely. But in the presence of organic matter, which will react with the chlorine as quickly as it is liberated, the reverse change is impossible. In a photographic plate or "bromide paper," the gelatine, besides acting as emulsifying agent or vehicle, also acts as an absorbent for the halogen produced; in the "printing-out-papers," as we shall see,

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[1] R. Lorenz and K. Hiege, *Zeitsch. Anorg. Chem.* **92** (1915), 27.

[2] See R. Schwarz and H. Stock, *Ber.* **54** (1921), 2111. The loss of weight due to the loss of halogen on exposure to light can be detected. See E. J. Hartung, *Trans. Chem. Soc.* **121** (1922), 682. Compare P. P. Koch and F. Schrader, *Zeitsch. Phys.* **6** (1921), 127.

[3] Compare S. E. Shephard and C. E. K. Mees, *Proc. Roy. Soc.* **78** [A] (1906), 461; S. E. Shephard, *Trans. Amer. Electrochem. Soc.* **39** (1921), 429; S. E. Shephard and A. P. H. Trivelli, *Photo J.* **61** (1921), 400.

a special halogen-absorbent, usually a citrate, is present in the emulsion.[1]

Manufacture and Use of Plates, Films and Papers.[2] The so-called "emulsion" used in the manufacture of plates, films and "bromide papers" consists essentially of a suspension in gelatine of small crystals of silver bromide (or mixed crystals of silver bromide and iodide). It is prepared in a dark room by mixing a concentrated solution of potassium bromide (and often iodide) containing gelatine, with a concentrated solution of silver nitrate. Owing to the presence of the gelatine, the silver bromide is not precipitated in the ordinary form, but remains as particles of colloidal size. After mixing, the emulsion is subjected to a prolonged heating, or "ripening." The function of the ripening is to cause the growth of comparatively large silver bromide crystals, about 2–3μ in diameter, that is, of a size easily visible under the microscope. Most of the crystals present in the ripened emulsion consist of hexagonal or triangular plates, although here and there a rod-shaped crystal may be seen; it is noteworthy that all the crystals actually belong to the cubic system, their shape being due to the unequal development of the different faces. The increase in the size of the grains during the ripening process causes the emulsion to become increasingly sensitive to light; a reason for this increase of sensitiveness with the coarseness will be suggested later.

After ripening, the emulsion is usually allowed to cool and set to a jelly, which is cut into shreds, washed free from potassium nitrate, and again melted. It may now be used for coating glass plates or paper; in the manufacture of "films," a transparent flexible support such as celluloid, or cellulose acetate, is employed.

If such a plate or film is placed in a camera, and an image of the object to be represented is cast upon it by means of the lens, a small amount of reduction will take place in the parts which are reached by the light. The amount of reduction depends upon the intensity of the light reaching the plate. If the exposed plate is afterwards immersed in a "developing" bath, containing sodium pyrogallate, or some other organic reducing agent, the silver bromide

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[1] For further information regarding the absorption of halogens by gelatine, and the "reversal" consequent upon a *long* exposure to light, see R. E. Crowther, *J. Soc. Chem. Ind.* **35** (1916), 817.

[2] The machinery and methods used in plate-manufacture are described by A. J. Munro, *Photo J.* **60** (1920), 209. The general process is discussed by C. E. K. Mees, *J. Soc. Chem. Ind.* **31** (1912), 307, and the structure of the coating by C. E. K. Mees, *J. Franklin Inst.* **191** (1921), 631. The colloidal chemistry of emulsion-making, with details of crystal-size, is discussed by R. E. Slade, *Brit. Assoc. Rep.* **88** (1920), Appendix, p. 74.

will be reduced in the parts which have been affected by the light, the reduction being most conspicuous where the light has been most intense. This produces a "negative" image on the plate, representing the object photographed, but reversed as regards light and shade. The insoluble silver bromide remaining can now be dissolved out by the action of a solution of sodium thiosulphate, the operation being termed "fixing."

In order to make a reproduction of the picture which shall not be reversed as regards light and shade, a piece of "bromide" or "gaslight" paper coated with a similar but less sensitive emulsion is pressed up against the glass negative, and exposed to the light through the latter. After the paper is developed and fixed, a "positive" image in black finely-divided silver is obtained.

Grain-size and Speed. It is now possible to consider why a coarse-grained emulsion which has been fully "ripened" is generally more sensitive than a fine-grained emulsion. It is fairly certain that if once a "nucleus" of metallic silver appears at any point on a grain, the whole grain becomes "developable," that is, capable of reduction by the developer. This important fact has been ascertained by taking microphotographs of the developed but unfixed plate; these microphotographs show that some of the silver halide crystals become completely blackened whilst others are unchanged. If the time of developing has been very short, we may meet with grains which are blackened only in one part; but in a fully-developed image each grain is either wholly black or else wholly white. Evidently, therefore, if reduction has commenced at any point on a grain, it is able to extend over the whole grain. Now the large grains will offer a larger "target" to the light than the small ones; the "chance" of a large grain becoming effected by light at some point, and thus becoming "developable" is greater—other things being equal—than the "chance" of a small grain. Careful measurements have shown that, in one particular emulsion, an exposure which causes 80 per cent. of the largest grains to become developable will only cause 0·9 per cent. of the smallest ones to become developable.[1] In brief, the larger the grain-size, the greater the amount of metallic silver which will be produced by growth from a single nucleus. In general the growth from a nucleus will not extend outside the grain in which it exists, although where the grains are in contact, one may "infect"

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[1] Th. Svedberg, *Zeitsch. Wiss. Photo.* **20** (1920), 36; *Photo J.* **62** (1922), 183, 186, 310; Th. Svedberg and H. Andersson, *Photo J.* **61** (1921), 325. See, however, S. E. Shephard and A. P. H. Trivelli, *Photo J.* **61** (1921), 400; F. F. Renwick, *Photo J.* **61** (1921), 333. Compare also L. Silberstein, *Phil. Mag.* **44** (1922), 257.

another.[1] The complete consideration of the various factors determining the working "speed" of a plate is too lengthy a matter for inclusion in the present work; reference should be made to the classical work of Hurter and Driffield, to whose labours the existing systems of measuring plate-speeds is due,[2] as well as to later writings on the same subject.[3]

Great interest attached to the manner in which the nuclei are distributed throughout the grains sporadically according to the laws of chance, and especially to the application of the quantum theory to photolysis.[4] Recent researches have made it probable that the nuclei—although they only become effective as such after exposure to the light or some similar treatment—may actually have existed, in some sense, from the moment of the preparation of the emulsion. It is possible to render the grains developable by other treatment than exposure to light—for instance, by treatment with sodium arsenite solution. If after such a treatment, a plate is developed with an ordinary developer, the reduction commences from nuclei which are distributed throughout the grains in exactly the same sporadic manner as the nuclei produced (apparently) by the action of light.[5] It is fairly certain that the true nuclei consist of something in the grain which even before exposure was not silver bromide.[6] Many authorities think that the true light-sensitive material is a small amount of colloidal silver which is inevitably present in the silver halide from the moment of its precipitation. If so, it seems conceivable that the true function of the light is to cause coagulation of the colloid, thus causing at certain points aggregates large enough to act as nuclei for the reducing action of the developer; it is known that light can cause the flocculation of a colloidal solution of a metal in water,[7] although it seems rather less easy to picture the phenomenon occurring in a crystal. An alternative view is that the light striking the colloidal silver may, by the ordinary "photo-electric effect," cause the splitting off of an electron, which may be absorbed by the silver halide around, and cause the decomposition of the latter.

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[1] A. P. H. Trivelli, F. L. Righter and S. E. Shephard, *Photo J.* **46** (1922), 407.

[2] F. Hurter and V. C. Driffield, *J. Soc. Chem. Ind.* **9** (1890), 455. See also C. E. K. Mees, *J. Roy. Soc. Arts.* **68** (1920), 699; A. W. Porter and R. E. Slade, *Phil. Mag.* **38** (1919), 187.

[3] E. P. Wightman and S. E. Shephard, *Brit. J. Photo.* **68** (1921), 169, give a good summary.

[4] J. Eggert and W. Noddack, *Sitzungsber. Preuss. Akad.* (1921), 631.

[5] W. Clark, *Brit. J. Photo.* **69** (1922), 462.

[6] F. C. Toy, *Phil. Mag.* **44** (1922), 352. Compare F. F. Renwick, *J. Soc. Chem. Ind.* **39** (1920), 156T.

[7] E. B. Spear, P. F. Jones, A. S. Neave and M. Schlager, *J. Amer. Chem. Soc.* **43** (1921), 1385.

Such an idea is confirmed by recent work on the darkening of *chloride* emulsions [1] (*see below*); the darkening is slow at first, but afterwards becomes fast, apparently because the freshly-reduced silver itself acts as a light-sensitive substance; finally the action becomes slow again, mainly because the reduced silver begins to obstruct the passage of light to the unchanged portions below.

Printing Papers. As already stated, the ordinary " bromide " paper used for making positives is coated with an emulsion similar to that used for plates or films, although rather slower. " Gaslight " paper is coated with a still slower emulsion, which can be developed with safety in diffused gaslight. Both bromide and gaslight papers receive no visible image during printing and require to be developed like plates.

Amateur photographers often prefer to use a " printing-out-paper," or " P.O.P." This is paper coated with a gelatine emulsion containing silver chloride and silver citrate. If exposed to bright light through a negative, a visible image is produced owing to the reduction of the citrate to form colloidal silver which, adsorbed upon the silver chloride, gives one of the reddish adsorption-products mentioned above. The fact that a visible image is produced is very convenient, since it enables the inexperienced photographer to judge when the printing is complete; it also dispenses with development. On the other hand, the image, if merely freed from unreduced silver salts by " fixing " in thiosulphate, would—in many cases—have an unpleasing yellowish-brown colour. It is therefore " toned " with a solution containing a gold salt in such a way that the silver is in part replaced by the still more noble metal gold. The finely-divided gold is black or bluish in colour, and the image assumes a hue which is pleasing to the eye.

At present, most commercially prepared papers of the " printing-out " type are " self-toning." Either the papers themselves contain sufficient gold to cause the toning reaction to take place when the print is immersed in the fixing bath of sodium thiosulphate, or the composition of the emulsion is adjusted in some other way so as to give an image of pleasing tint. The colour of the image obtained on P.O.P. depends primarily on the size of the silver particles, being (like the colour of silver " sols ") reddish when the particles are small, and bluish when they are large.

Orthochromatic Plates. It is well known that only light of high frequency is capable of affecting silver salts. Ordinary (" unbathed ") photographic plates are practically only sensitive to the ultra-violet (invisible), violet and blue rays; red and yellow

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[1] F. Weigert and W. Schöller, *Sitzungsber. Preuss. Akad.* (1921), 641.

rays have no action upon them. According to the quantum theory, the light energy is taken up by the molecules in definite proportions, probably one quantum for each molecule. Now in the case of the red rays a quantum is a comparatively small parcel of energy, whereas in the ultra-violet rays (which have a much higher frequency) the quantum is a big parcel of energy, which may easily be sufficient to bring about the decomposition of the molecule, where the small parcel provided by the red radiation would fail to do so.

Now for many purposes the fact that plates are insensitive to red light is by no means a disadvantage; it enables the photographer, for instance, to use a ruby lamp for the process of development. It causes, however, a completely wrong representation of colour values in the picture, since the rays which mainly affect the eye are not those which mainly affect the plate. It has been found that if the plate be "bathed" in a solution of a suitable dye-stuff, it often becomes sensitive to light of the colour absorbed by the dye. Thus erythrosine, a dye which absorbs green light (and which possesses therefore a reddish colour) renders a plate sensitive to green. The common "orthochromatic" plate is a plate which has been bathed in some dye of this character, and which has become sensitive to green and possibly to yellow; such plates can still be developed in ruby light. Other dyes, such as pinaverdol and pinacyanol, render the plate sensitive to red rays.

By choosing a suitable combination of dyes, it is possible to obtain a "panchromatic" plate sensitive to all the rays of the visible spectrum. Such a plate is best developed in total darkness. Panchromatic plates are essential for colour photography, and are greatly superior to ordinary plates for long-distance work.[1] Ultra-violet light is so much absorbed by the atmosphere that attempts to take photographs of distant scenery (mountains, etc.) with plates insensitive to the longer waves almost always lead to disappointment. On the other hand, with panchromatic plates excellent results can be obtained.

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[1] Sir W. J. Pope, *J. Soc. Chem. Ind.* **39** (1920), 369R. See also C. E. K. Mees, "The Photography of Coloured Objects" (Wratten and Wainwright).

GOLD

Atomic weight . . . 197·2

The Metal

The remaining element of Group Iʙ is, as is well known, a bright yellow metal, possessing an extraordinary degree of malleability. It can be beaten out to the very thinnest leaf, so thin as to be quite translucent, the light transmitted having a green colour. According to Beilby, gold leaf consists largely of amorphous gold, but still contains granules representing portions of the original crystalline grains present in the cast gold from which the leaf was prepared. Very thin gold wire can also be obtained; gold wire has a fibrous structure; the fibres possibly represent the remains of the elongated crystal grains.[1]

Pure gold is a somewhat soft metal, much softer than those alloys used in jewellery and coinage, which are commonly referred to as "gold." The melting-point, 1,063° C., is not far removed from that of copper. Gold is heavier than silver, just as silver is heavier than copper; the specific gravity (about 19·3) is higher than that of any other metal, outside the platinum group. It is a good conductor of heat and electricity, surpassing all metals except silver and copper in this respect.

Finely-divided or porous gold may have almost any colour, according to the state of division. When an alloy of gold and silver containing excess of the latter is treated with nitric acid, the silver is dissolved, and the gold is left in a brown spongy form. On heating, this brown voluminous gold undergoes spontaneous sintering; a considerable shrinkage takes place and the characteristic golden colour of the metal appears.[2] The change is analogous to that noticed on heating the voluminous form of chromic oxide (see Vol. II, page 305).

The addition of stannous chloride to a gold chloride solution produces first a purple coloration and then a precipitate known as "Purple of Cassius," which consists essentially of finely-divided gold, but also contains tin oxide; when sulphur dioxide or ferrous sulphate is employed as a reducing agent, the precipitated gold is nearly black. Colloidal gold has been discussed in Chapter VII (Vol. I). It is prepared in a ruby-coloured or scarlet form by the

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[1] G. T. Beilby, *Proc. Roy. Soc.* **79** [A] (1907), 463.

[2] Hanriot, *Comptes Rend.* **151** (1910), 1358; **152** (1911), 138.

reduction with formaldehyde of a very dilute gold chloride solution containing a trace of alkali. Small amounts of sodium chloride (or even smaller quantities of calcium or aluminium chlorides) convert the red colour of these solutions to purple or blue, the colour-change being due to the union of the smaller colloid particles to form secondary aggregates. If sufficient salt is added, a dark precipitate of gold appears and settles to the bottom.

Just as silver is more noble than copper, so gold is more noble than silver, standing, in fact, ahead of all the better-known elements in the Potential Series. It is not readily attacked chemically, and such compounds as exist are easily reduced to the metallic state. Gold remains untarnished indefinitely when exposed to the atmosphere, and even when heated in the air. It is not expected, of course, that gold should liberate hydrogen from dilute acids ; but even oxidizing acids, such as nitric or hot concentrated sulphuric acids (either of which will readily dissolve copper or silver) have very little action upon gold. It has, however, been shown that nitric acid, and also hydrochloric acid in the presence of oxygen, have an appreciable solvent action upon brown (spongy) gold.[1] The best solvent for gold is aqua regia, a mixture of nitric and hydrochloric acids. This fuming liquid, which is supposed to contain nascent chlorine, attacks gold readily with the formation of the chloride, $AuCl_3$. Gold is also soluble in potassium cyanide solution in the presence of dissolved oxygen.

The *anodic behaviour*[2] of gold is interesting. If an electrolytic cell is fitted with a gold anode immersed in nitric acid (the concentrated acid diluted with an equal quantity of water), the acid slowly becomes deep green and then yellow-brown, indicating that the gold is passing into solution ; from the solution the compound $H[Au(NO_3)_4].3H_2O$ can be isolated. Sulphuric acid behaves in a similar manner if moderately concentrated. In all cases, however, the current efficiency of the anodic dissolution is very low, rarely exceeding 4 per cent. In dilute sulphuric acid a gold anode becomes covered with a ruby-red crust of auric hydroxide, but very little gold passes into solution. The behaviour of a gold anode in a potassium sulphate solution is similar.

In a chloride solution, gold can be made to dissolve almost quantitatively at a low current density, but if the E.M.F. applied to a cell fitted with a gold anode is allowed to become too high, the gold may become passive, and dissolution practically ceases,

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[1] Hanriot and F. Raoult, *Comptes Rend.* **155** (1912), 1085.

[2] F. H. Jeffery, *Trans. Faraday Soc.* **11** (1915–16), 172. See also V. Lenher, *J. Amer. Chem. Soc.* **26** (1904), 550 ; W. G. Mixter, *J. Amer. Chem. Soc.* **33** (1911), 688.

the current thereafter being used in the production of free chlorine.[1] In a potassium cyanide solution, a gold anode usually dissolves at a high current efficiency, provided the concentration of potassium cyanide is kept between about 1 per cent. and 3 per cent.

Laboratory Preparation. Almost any metal except those of the platinum group, when brought into contact with a gold salt solution, becomes covered with a layer of velvety gold, the more reactive metal passing into solution. A similar reduction of gold to the metallic state can be brought about—as already mentioned —by reducing agents, such as ferrous sulphate, sulphur dioxide, or stannous chloride. Furthermore, most compounds of gold decompose spontaneously upon heating, with the production of the metal in a dark form. Finely-divided gold is converted to the coherent metal by melting in a crucible of clay or plumbago. The metal is difficult to obtain directly from its compounds in the characteristic compact form at low temperatures, although the electrolysis of a cyanide solution, such as is used for plating, may be employed for the purpose.

In making pure gold from the impure material, it is best to dissolve it in aqua regia; the solution of gold chloride obtained, diluted and separated from any insoluble silver chloride that may be present, is reduced with sulphur dioxide. The precipitated gold is washed until free from chlorides, dried and remelted in a crucible. If necessary the process may be repeated.[2]

Compounds

Gold, like copper, but unlike silver, is a metal of variable valency; accordingly it is interesting to note that most of the compounds are coloured. The main compounds are those in which the metal is either monovalent or trivalent, the latter series being the more stable. Gold has a much greater affinity for chlorine and for cyanogen, than for oxygen; in fact, the oxides are unstable and somewhat difficult to prepare. In each case it will be convenient to consider the chloride first.

A. Compounds of Trivalent Gold (Auric Compounds).

Auric chloride (*gold trichloride*), $AuCl_3$, is obtained by the dissolution of gold in aqua regia. The yellow solution obtained can be evaporated on a water-bath, until the excess of acid and water is driven off. The residue obtained is, however, apt to contain a little aurous chloride, formed by partial decomposition

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[1] A. Coehn and C. L. Jacobsen, *Zeitsch. Anorg. Chem.* 55 (1907), 321.

[2] Sir T. K. Rose, "Precious Metals" (Constable).

of the auric chloride. Auric chloride forms orange-red crystals, of the composition $AuCl_3.2H_2O$; the solution has a yellow colour. It may be prepared in the anhydrous state by the action of chlorine gas upon gold powder; the anhydrous chloride is red. By heating to 185° C., auric chloride evolves chlorine, and leaves aurous chloride, AuCl; continued heating at this temperature, however, finally produces metallic gold. Auric chloride combines with the chlorides of the alkali metals to form complex salts, which contain the gold in the anion, and can be compared with the complex cyanides formed by silver and copper. By careful crystallization of gold chloride solutions containing potassium chloride, **potassium auri-chloride,** $KCl.AuCl_3$ or $K[AuCl_4]$, is obtained in yellow crystals. It may be regarded as the potassium salt of **auri-chloric acid,** $H[AuCl_4]$; the acid may itself be prepared by the addition of hydrochloric acid to an auric chloride solution, and by careful evaporation. Auri-chloric acid crystallizes in yellow needles containing three molecules of water of crystallization.

Analogous compounds are known containing bromine and iodine instead of chlorine. **Auric bromide** is best obtained by the direct union of gold and bromine, whereas **auric iodide,** being rather insoluble, is conveniently prepared by double decomposition of the chloride with potassium iodide; it is a dark green, very unstable body, which decomposes even at ordinary temperature into aurous iodide and iodine.

Auric oxide is best obtained from the chloride. When auric chloride is precipitated with magnesium hydroxide, orange **auric hydroxide** is produced; when dried over phosphorus pentoxide for some weeks the product has the composition AuO(OH); on lengthy heating at 140° C., we obtain **auric oxide,** Au_2O_3, a brown powder. This is itself very easily decomposed by further heating to gold and oxygen. When the auric hydroxide is heated at 160° C. it is said to yield an intermediate oxide, AuO, which is also a brown powder.

Auric oxide, unlike the oxides of most metals, is distinctly endothermic—a fact that no doubt explains why it cannot be prepared by the direct union of gold and oxygen.

It is difficult to obtain salts of gold with oxy-acids. Auric hydroxide dissolves in sulphuric and in nitric acids, but the solutions obtained are readily hydrolysed, and auric hydroxide again appears when they are diluted. If the solution of auric hydroxide in nitric acid is evaporated at 60–80° C., and then allowed to stand for some hours over soda-lime, crystals of an **acid nitrate,** $Au(NO_3)_3.HNO_3.3H_2O$ can be obtained; it is generally regarded as **auri-nitric acid,** $H[Au(NO_3)_4].3H_2O$. The same compound is obtained electrolytically in a divided cell fitted with a gold anode surrounded by nitric acid. The solution in the anode compartment becomes deep green, then yellow-brown ; if the yellow-brown solution is placed in a vacuum desiccator over concentrated sulphuric acid with a vessel containing sticks of sodium hydroxide close to it, the free nitric acid evaporates and auri-nitric acid is obtained.[1] When heated at 72° C., auri-nitric acid melts and commences to give off nitric acid ; finally a blackish residue is obtained, which may contain the normal nitrate $Au(NO_3)_3$, although it is clearly partly decomposed.[2]

Auric sulphide, Au_2S_3, is not produced in a pure state when sulphuretted hydrogen is passed through a solution of auric chloride (or auri-chloric acid), since partial reduction always occurs and the black precipitate is mixed with metallic gold, sulphuric acid being formed at the same time.[3] Auric sulphide can, however, be formed by the action of hydrogen sulphide on a dry auric salt at low temperatures. For this purpose dry lithium auri-chloride ($LiCl.AuCl_3.2H_2O$) is convenient ; if exposed to hydrogen sulphide gas at −10° C. it turns brown, auric sulphide being produced. The product can be washed free from lithium chloride by means of alcohol, and any uncombined sulphur present may be removed by means of carbon disulphide.[4] The use of potassium auri-chloride for making the sulphide is unsuitable, since potassium chloride is insoluble in alcohol, and auric sulphide, if washed with water, would decompose. The sulphide is a black body.

Whilst the basic character of auric oxide is most feeble, it has certain acidic properties. For instance, on evaporating auric hydroxide with caustic potash *in vacuo*, potassium aurate $KAuO_2.3H_2O$ (or $K_2O.Au_2O_3.6H_2O$) is formed in yellow needles.

B. Compounds of Monovalent Gold (Aurous Compounds).

Aurous chloride, AuCl, is, as already stated, formed when auric chloride is heated to 185° C. It is a yellow powder, scarcely dissolved by cold water, although by warm water it is slowly decomposed, auric chloride and metallic gold being produced,

$$3AuCl = 2Au + AuCl_3.$$

Like auric chloride, aurous chloride forms a complex salt, $K[AuCl_2]$, with potassium chloride, which can conveniently be obtained by heating potassium auri-chloride, $KAuCl_4$.

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[1] F. H. Jeffery, *Trans. Faraday Soc.* **11** (1915–16), 172.

[2] H. Wohlwill, " Abeggs Handbuch der Anorganischen Chemie," II, 826 (Hirzel).

[3] A. Gutbier and E. Dürrwächter, *Zeitsch. Anorg. Chem.* **121** (1922), 266.

[4] U. Antony and A. Lucchesi, *Gazetta,* **20** (1890), 601.

On precipitation with dilute potassium hydroxide it yields **aurous hydroxide,** AuOH, which if heated at 200° C. loses water, leaving the violet **aurous oxide,** Au_2O. Since this oxide itself decomposes into gold and oxygen at about 250° C., the preparation must obviously be carried out with care.

The most stable of the aurous compounds are the complex cyanides, formed when metallic gold dissolves in a cyanide solution containing dissolved oxygen. Just like copper and silver, gold behaves less like a noble metal towards a solution of a cyanide than to any other reagent, and the explanation is the same, namely that gold passes into the anionic condition in the presence of cyanogen ions. The dissolution of gold by potassium cyanide only proceeds, however, if dissolved oxygen, or some other oxidizing depolarizer, is present to remove the hydrogen as quickly as it is formed. By the reaction of dissolved oxygen on the hydrogen, hydrogen peroxide as well as water may be formed. The reaction may be expressed in *ionic* language thus :—

At the *anodic* areas of the gold surface,

$$Au + 2(CN)' = [Au(CN)_2]' + e$$

At the *cathodic* areas $H^{\cdot} + e = H$
followed by *either* $2H + O_2 = H_2O_2$
or, *alternatively*, $2H + O = H_2O$

On the assumption that all the hydrogen is oxidized to hydrogen peroxide, we can write the *complete* reaction, thus :—

$$2Au + 4(CN)' + 2H^{\cdot} + O_2 = 2[Au(CN)_2]' + H_2O_2$$

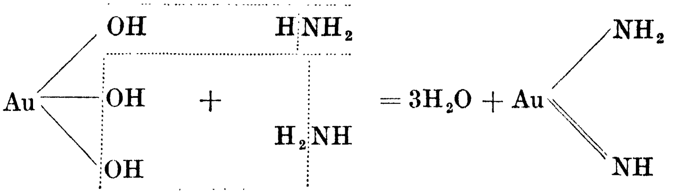
or in *non-ionic* language,

$$2Au + 4KCN + 2H_2O + O_2 = 2K[Au(CN)_2] + 2KOH + H_2O_2$$

Potassium aurocyanide, $K[Au(CN)_2]$, is best prepared by the electrolytic attack of a gold anode immersed in potassium cyanide solution. It can be obtained also by the action of potassium cyanide upon finely-divided gold, in the presence of air, or upon aurous oxide. It may be isolated by crystallization in colourless rhombic octahedra.

C. Miscellanesous Compounds.

Fulminating Gold. When concentrated ammonia is allowed to act upon auric hydroxide it converts the latter into a yellowish or greenish substance ; this substance may be dried without decomposition, but explodes with violence if struck with a hammer or heated. The body has the composition AuN_2H_3. It is probably to be regarded as derived from two molecules of ammonia by the replacement of part of the hydrogen by gold. Thus,



Auric hydroxide. Ammonia. Fulminating gold.

The precipitate obtained by the action of aqueous ammonia upon auric chloride consists of the same substance mixed with its derivative, NH : AuCl.

Analytical

Owing to the exceptional ease with which gold is reduced to the metallic state, it is not surprising that practically all the methods for the detection and estimation of the precious metal depend upon this change. Gold is recognized in solution by the precipitate of finely-divided metal obtained by the addition of stannous chloride or ferrous sulphate. Solid compounds of gold, on heating with charcoal before the blowpipe, give a malleable bead of the yellow metal, which is not affected by heating in the oxidizing flame.

Since the baser metals are not reduced to the metallic state by ferrous sulphate, the separation of gold when present in solution as chloride is easily accomplished by the addition of that reagent. Conversely, a rapid separation of the gold present in an alloy from the other metals is often possible, owing to the fact that metallic gold remains unchanged under conditions which cause other metals to become oxidized. When an alloy of gold and silver is treated with nitric acid, " parting " occurs, the gold being left behind as a brownish residue, whilst the silver passes into solution. The estimation of gold in a lead-gold alloy may be determined by roasting the material on a bone-ash cupel; under these conditions all the lead is oxidized, while the gold is left as metal.

The dry assay of gold[1] in an ore is brought about by the use of lead as a collector, as in the dry assay of silver. A weighed quantity of ore is mixed with lead oxide, potassium cyanide, sodium carbonate and iron, and the whole is heated. The iron reduces the lead to the metallic state, and the molten metal dis-

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[1] For full details of different variations of the method, see Sir T. K. Rose, " Metallurgy of Gold " (Griffin).

solves all the silver and gold present. The button of lead obtained is then cupelled, which brings about the oxidation of the more reactive metal, and leaves a silver-gold alloy. This is "parted" by the continued action of boiling nitric acid, and the undissolved gold is weighed. Most gold ores contain enough silver to bring the silver content of the alloy obtained up to the proportion needed for successful parting; but if the necessary amount of silver is not already present, it must be added.

In the assay of gold bullion, a cupellation method is often used. A weighed sample of the bullion—along with sufficient silver to ensure successful parting—is wrapped up in lead foil, and subjected to cupellation, and then to parting. Recently another method has been worked out, in which the weighed sample of bullion is melted down with excess of copper, giving a copper-gold alloy, which is "parted" with acid, leaving the gold undissolved.[1]

Gold can also be estimated electrolytically. Potassium cyanide is usually added to the solution containing gold before the operation, to form a complex cyanide, and by electrolysis the whole of the gold may be deposited as a smooth coating upon a platinum gauze cathode.

The separation of gold from platinum was discussed in connection with the latter metal (Vol. III).

TERRESTRIAL OCCURRENCE

Gold must have been present only in very minute traces in the original rock-magma, but during the consolidation of igneous intrusions it has, like so many metals, become to some extent concentrated in particular portions. The metal is found in appreciable quantities in certain veins of quartz and pegmatite which are connected with intrusive rocks of sub-acidic character such as grano-diorite. Probably most gold-bearing quartz-veins were actually deposited by the hot waters expelled from the igneous mass in the final stages of the consolidation.[2] Since gold is one of the vein-metals which is deposited deep down in the earth's crust close to the intrusive mass from which it is derived, many of the important gold-fields of the world are connected with earth-movements of the very earliest (pre-Cambrian) times.[3]

The gold sparsely dispersed throughout the quartz veins is mainly in the metallic state—a fact by no means surprising in

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[1] A. Westwood, *J. Inst. Met.* **27** (1922), 307.

[2] Compare J. E. Spurr, *Econ. Geol.* **1** (1906), 369; H. C. Cooke, *Econ. Geol.* **14** (1919), 281.

[3] J. W. Gregory, *Trans. Chem. Soc.* **121** (1922), 771.

view of the chemical character of the element. But it also appears to be present in particles of pyrites possibly in solid solution, or perhaps in intimate intergrowth. The close association of gold and pyrites in nature is certainly very remarkable.

The grains of metal found in nature are, however, in no case pure gold, but almost always contain silver, or in some cases mercury, copper, bismuth, or palladium. In addition to grains of metallic gold, certain so-called "tellurides" of gold and silver are found in nature; some of these, like

Calaverite . . . $(Au,Ag)Te_2$,

have been assigned definite formulæ, although it is a disputed question as to whether they are really chemical compounds, or whether they should not be regarded as gold-tellurium alloys.[1]

By the weathering and breaking up of auriferous veins and rocks, gold-grains are washed into the rivers that flow from hills composed of such rocks; but owing to the high specific gravity of gold, the particles are dropped—along with the heavier sand particles—as soon as the velocity of the stream becomes slightly reduced. Thus placers and gold-gravels are formed. Sometimes the rich gold-bearing sand is to be found within the present bed of the stream; sometimes the course of the stream may have changed since the placers were formed, and the gold beds are no longer below the surface of the water. Perhaps, as a result of climatic changes, or of earth movements, the rivers which deposited the gold-bearing alluvium have ceased to exist. The older placers are often covered up with more recent material, sometimes of volcanic origin, which is free from gold.

Whilst, however, a very large number of gold beds have been formed by the simple *mechanical* transport of gold-grains from the original veins to the present position through the agency of running water, yet in several important cases it is clear that the gold has been dissolved *chemically* at one point and precipitated afresh at another. Thus secondary enrichment has occurred. Ferric chloride, which may be found where saline waters have access to weathered iron minerals, has an appreciable solvent action on gold. It is likely that the presence of manganese has also been an important factor in causing the dissolution of the metal.[2] Minerals like pyrolusite will react with sodium chloride to produce a certain amount of free chlorine, which has a very marked action

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[1] V. Lenher, *J. Amer. Chem. Soc.* **24** (1902), 355; B. Brauner, *Trans. Chem. Soc.* **55** (1889), 391.

[2] W. H. Emmons, *Trans. Amer. Inst. Min. Eng.* **42** (1911), 4. A different view of the function of manganese in producing enrichment is given by V. Lenher, *Econ. Geol.* **9** (1914), 523.

on gold. Whatever the nature of the solvent, there seems little doubt but that gold has been dissolved at certain places and precipitated, often in crystalline or dendritic growths, at points originally free from gold. The usual precipitants appear to be pyrites, or ferrous compounds obtained from the weathering of pyrites, which are able to effect the reduction of the gold to the metallic state. But basic minerals, such as calcium carbonate, may favour the precipitation of gold, the compounds of which are more stable in the presence of acid than in the presence of alkali.[1]

The origin of the rich gold-reefs of the Witwatersrand in South Africa has led to much discussion.[2] The reefs are a series of conglomerates, which occur at numerous different horizons, being separated by softer beds; the gold is practically confined to the conglomerates. The whole series is of very early geological origin, being possibly of pre-Cambrian age. The material of the conglomerate ("Banket") consists of quartz pebbles set in a finer matrix; in the matrix, especially at certain horizons, there are numerous grains of gold. As a rule, conglomerates represent old consolidated beach-shingles, and the Rand conglomerate may be of this character; there is some evidence that the shingles accumulated in or near the delta of a large river. It is probable that the same river brought down the gold-grains derived from the weathering of gold-bearing rocks in the hills where the river rose, and dropped them along with the other heavy particles in the delta or round the coast of the sea into which it flowed. It is noteworthy that primary quartz veins are known to occur in the Transvaal, although their commercial importance is small compared to that of the conglomerate.

According to the view just expressed, which is now widely held, the Rand deposits must be regarded as marine or estuarine placers. Some geologists, however, have expressed the opinion that the conglomerates were free from gold when they accumulated, and that the metal has *subsequently* been introduced by means of water percolating through the beds. Certainly some of the gold, which is of an arborescent character, would seem to have been deposited from solution, and bears no signs of mechanical transport. But this does not necessarily mean that the "placer theory" is incorrect, because—in view of the age of the deposits—it is quite to be expected that at some points the original gold-grains should have been attacked by infiltering waters, the gold being reprecipi-

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[1] Compare V. Lenher, *Econ. Geol.* **13** (1918), 161.

[2] E. T. Mellor, *Trans. Inst. Min. Met.* **25** (1916), 226; J. W. Gregory, *Econ. Geol.* **4** (1909), 118; *Trans. Inst. Min. Met.* **17** (1907–8), 2; *Trans. Chem. Soc.* **121** (1922), 766; G. F. Becker, *Econ. Geol.* **4** (1909), 373; G. A. Denny, *Econ. Geol.* **4** (1909), 470.

tated at other points where the conditions were favourable. On the whole, the placer theory may be accepted, at least provisionally.

The richness of the Rand deposits may be judged by the fact that the Transvaal contributed in 1919 about two-fifths of the world's output. Apart from the Rand, the main gold areas are to be found around the Pacific ore-circle. Starting as usual on the South American side, we find gold in Peru, and also, along with platinum, in Columbia. There are rich deposits in California, Colorado, Nevada, and British Columbia; the deposits become especially rich in Alaska. Gold occurs in Korea, in Japan, and in the Dutch Indies; it becomes extremely important in Australia, and appears also in New Zealand.

Other important gold-producing regions include the Porcupine district in Ontario, various places in West Africa (notably the Gold Coast where gold-bearing conglomerates are found), and the Kolar Gold-field of Mysore (India). In normal times the Ural Mountains, besides being a producer of platinum, yield a considerable amount of gold.

METALLURGY [1] AND USES

The difficulties connected with the winning of metallic gold from gold ore are simply due to the fact that the gold occurs sparsely disseminated through a great volume of worthless material. Since the gold is generally, in the first instance, in the metallic state, there is no metallurgy in the stricter sense of the word, and the winning of gold may be regarded as somewhat analogous to the "concentration" of the ores of other metals.

The separation of the gold particles from the rocky matter with which it occurs depends upon three distinct differentiating properties:—

(1) Gold is *heavier* than all the materials occurring with it. If the finely-powdered gold-bearing matter be suspended in a flowing stream of water, running with a carefully adjusted velocity, the stream will "drop" the gold-grains, but carry off the lighter particles.

(2) Gold is *soluble in mercury*, and grains of the metal when brought in contact with mercury, or with an amalgamated surface, will stick to it, whereas the rocky matter will pass over the mercury without adhering.

(3) Gold is *soluble in a solution of a cyanide solution* in presence of air, whereas the siliceous constituents are not. Therefore traces of metallic gold may be leached out chemically by cyanide, and the solution obtained can afterwards be treated with zinc, aluminium

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[1] Sir T. K. Rose, "The Metallurgy of Gold" (Griffin).

or even carbon, to give metallic gold. Chlorine was at once time also used as a leaching agent, but its employment has largely been abandoned in favour of that of potassium or sodium cyanide.

Sometimes these three methods are applied in turn in the treatment of the same auriferous material, but the procedure will clearly vary very much according as the material to be treated is—

(*a*) A gravel or sand situated at the edge of an existing river or creek ;
(*b*) a gravel or sand existing in the centre of the bed of an existing river ;
(*c*) an old placer deposit situated far away from existing rivers ;
(*d*) the original veins of hard auriferous quartz, or other hard deposits of a secondary character (such as the " banket " of the Rand).

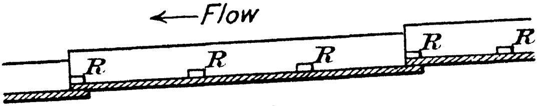
(*a*) **Where the rich sands exist at the edge of an existing river,** comparatively primitive methods suffice to extract a considerable proportion of the valuable constituent. The simplest method of all is " panning," used mainly by the prospector. A circular iron pan, about a foot in diameter, is partly filled with the " pay-dirt " and covered with water ; the dirt is then broken up by the hands as far as possible, and a peculiar swirling motion is imparted to the pan whereby the lighter constituents pass over the edge, and the gold—along with the stones and heavier sand-grains—remain in the pan.

When the workings become developed, more elaborate methods are introduced, **sluices** usually being installed. In these a suspension of " dirt " and water is made to flow down a narrow channel formed by a series of long narrow boxes of wood planking, arranged at a slight gradient (see Fig. 14). The bottom of the boxes is crossed by a series of wood strips or " riffle bars," R, set at right angles to the direction in which the dirt is travelling; occasionally they are arranged in a zig-zag fashion. As the dirt passes along the channel, the heavy particles of gold tend to sink, and get caught behind the riffle bars, whilst the lighter constituents are carried over the riffle bars, and pass out at the end of the series of boxes.

Although " sluicing " is primarily a method of gravity separation, mercury is often introduced into the riffles, and undoubtedly serves to catch many of the finer particles of gold, which would otherwise be carried away by the water. Periodically (perhaps once a week) the sluices are " cleaned up " ; the contents of the riffles containing mercury are strained, skimmed, and then distilled in retorts, so as to separate the gold from the mercury, which should largely be recovered and used again.

The dirt passing out from the end of the sluices still contains fine particles of gold, and is sometimes passed over a series of "amalgamated plates," which serve to catch a further quantity of the precious metal. The plates consist of copper or Muntz metal; they are prepared for use by cleaning with acid or cyanide, and are then amalgamated by being rubbed with mercury, and afterwards, as a rule, with an amalgam of mercury and gold: they are then ready for use for the catching of gold.

A large proportion of the gold particles which have escaped through the sluice-box system are caught upon these plates, if the mercury surface is kept clean. There is, however, a tendency for the mercury surface to "foul" or "sicken" by becoming covered with a film of oxide or sulphide (or sometimes grease). The precautions taken to prevent mercury from fouling resemble those taken to protect common metals (steel or brass) from corrosion. If strips of a more reactive metal like iron be placed in contact with the mercury, both being under the stream of aqueous ore-pulp, the mercury surface will be kept cathodically polarized, which will prevent the formation of an oxide-film. Any oxidation which occurs will proceed at the expense of the iron, and the mercury surface will remain bright or "quick."



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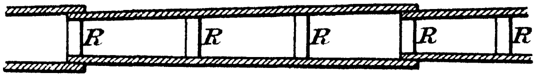

Plan.

FIG. 14.—Sluice-Box System.

Another plan is to dissolve a little sodium in the mercury. If any oxidation occurs to a sodium amalgam, it is certain that it will be the reactive sodium which is first attacked, and since sodium hydroxide is soluble this will not in any way block or render less active the mercury surface. It is found that amalgams of mercury with zinc or cadmium are also useful, being less liable to fouling than pure mercury.[1] Where Muntz metal plates are employed, the mercury is likely to absorb a little zinc, and possibly the advantage of Muntz metal plates for the purpose may depend upon this fact.

The gold-amalgam which collects on the plates is scraped off from time to time, strained and distilled in iron retorts. The gold remains in a porous form and requires remelting to yield ingots.

The amalgamation process does not usually extract the last traces of gold from the ore. For part may survive as fine "float-gold" which remains in suspension in the water, or more often clinging to the air-water interface. Again, it does not extract grains of "rusty" gold, which have their surfaces covered with a film of grease or sulphide—a condition that will hinder the adhesion to the mercury. Finally, amalgamation clearly cannot extract any gold which may exist within the grains of pyrites or other mineral. These forms of gold are generally lost, unless the material issuing from the sluices is treated by means of cyanide or other chemical leaching agent.

It should be pointed out that the actual "catching" of gold grains by amalgamated plates is a process of surface adhesion; the dissolution of the adhering gold in the mercury to form an amalgam occurs slowly *after* the grains have been caught. However, the surface adhesion and solubility of substances are so closely connected that it is unnecessary to distinguish further between the two stages in the process.

(*b*) **Where the gold-bearing deposit to be worked lies at the bottom of a river,** the only profitable method in most cases is by **dredging.** Gold dredges are square-ended boats, some of which are designed to float freely in the stream which is being dredged, but others ("paddock dredges") are able to cut their way through the bed of a partially dried stream. The curious feature of paddock dredging is "that the dredge floats in an artificially-made pond, and then carries the pond along with it."[2] Paddock dredges are most useful for working gravels in river-beds where there is not a sufficient gradient for sluicing.

Most dredges are worked on the familiar "bucket" system, which is so often seen upon dredges used for keeping navigable the channels of ordinary rivers and harbours. An endless chain of buckets is carried on rollers resting on a steel ladder, and serves to scoop up the gravel from the river bottom, and to convey it to screens situated in the centre of the vessel. The coarse material

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[1] C. H. Aaron, *Eng. Min. J.* 48 (1889), 118.

[2] C. C. Longridge, "Gold and Tin Dredging," Third Edition (*Mining Journal*), p. 78.

which fails to pass through these screens passes to another bucket-conveyer which dumps this worthless matter well to the stern of the dredge, so that it will not be scooped up a second time. The finer material passing through the screens, runs over a series of gold-saving tables; these are similar in principle to the sluice-boxes referred to above, but are more elaborate, and produce a more efficient extraction. Riffles may be used to catch the larger particles of gold, but finer particles are usually caught by passing the material over tables covered with coco-nut matting, calico, or plush. Mercury is used with some kinds of gravels, but, in many cases, is found to become "foul" quickly, and is less efficient than matting. The discharge from the tables is either returned to the river at the stern of the boat, or is in some cases piled up on the bank.

The system of dredging was largely developed in New Zealand, and was also applied early in California; it has since been adopted on the rivers of British Columbia and Alaska, where it is considered to have an important future.

(*c*) **Where the position of the gold deposit is far from a river** at the present time, the chief difficulties are concerned with the necessary supply of water. Often pipe-lines have been laid for considerable distances in order to bring an adequate supply of water to the gold-fields.[1] Since the brackish or bitter waters of desert regions commonly contain magnesium and sodium chlorides in considerable quantities, there is likely to be trouble owing to the corrosion of the pipe-lines in such places; this trouble has been experienced particularly in Western Australia. In California, where there is in most parts a considerable local rainfall during certain parts of the year, the water-supply has been obtained by the construction of reservoirs. When once the adequate supply of water, preferably at a moderately high pressure, is at hand, the washing of the old placer deposit presents no special difficulty. A jet of water may be directed upon the gold-bearing material, and the water, carrying the sand in suspension, runs off through a series of sluice-boxes; if the supply of water is restricted, they should be designed in such a way as to use the minimum quantity.

Often in working old dry placer deposits it will be found that the beds which are now on the surface contain little or no gold. Where the supply of water and the pressure is sufficient, it is convenient to remove this top layer of comparatively worthless matter by the disintegrating action of a water-jet, until the richer bed below is reached; this method, known as *hydraulic mining*, was largely developed in California.

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[1] See N. A. Loggin, *Trans. Inst. Min. Met.* 20 (1910–11), 170.

(*d*) **Treatment of hard deposits.** Wherever in a gold-district the comparatively soft placer deposits are approaching exhaustion, attempts are made to extract gold from the original veins of hard quartz. Moreover, in certain places, and notably the Transvaal, deposits, although of a secondary character, are so hard as to call for similar treatment. In such cases the first part of the process consists in crushing the rock between the jaws of rock-breakers and then stamping it to a small size in a **stamp battery**;[1] often the grinding is completed in tube mills. A stamp battery (Fig. 15) consists essentially of a row of giant pestles and mortars made of iron or steel, the pestles being raised by mechanical means and then allowed to fall by gravity into the mortar. Generally there are about five "stamps" or pestles to each mortar, which may be a rectangular box 5 ft. long and 1 ft. wide. The ore is fed into the mortar at A in pieces of about 1½–2 in. diameter, and the fine particles produced by the stamping are carried off by a current of water through the screens S in the front of the battery; the screens, which have holes of $\frac{1}{20}$–$\frac{1}{40}$ in. diameter, serve to prevent the uncrushed material from being swept or splashed out of the mortar. Often mercury is introduced into the stamps, and a great deal of the gold is thus extracted before the pulp leaves the battery. The pulp flowing from the battery sometimes passes over a system of amalgamated plates, which retain a further quantity of gold.

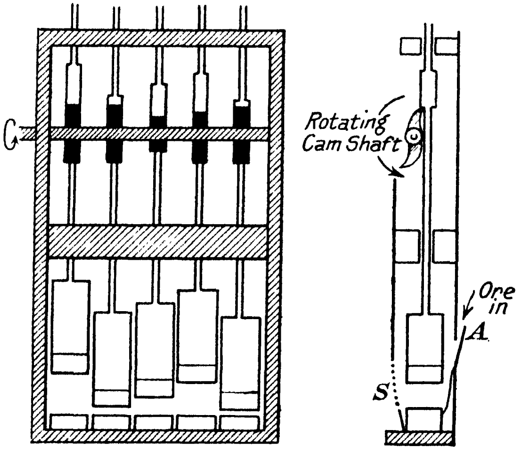

FIG. 15.—Stamp Battery.

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[1] See F. A. Thomson, "Stamp Milling and Cyaniding" (McGraw Hill). Also W. A. Caldecott, *Trans. Inst. Min. Met.* **19** (1909–10), 57, for the development of the heavy stamps on the Rand.

In other cases, gravity, rather than amalgamation, is relied upon to extract the gold, and after the larger particles have been caught by an ordinary sluice-box system, the crushed matter is further treated on Wilfley tables, whilst for the more finely ground material a vanner has been used to recover the gold. Both of these devices have been mentioned in connection with the concentration of the ores of other metals.

Cyaniding of Gold Ores and Tailings. It has already been stated that neither gravity nor amalgamation succeed in extracting the whole of the gold. Consequently, in the more highly developed gold-fields the tailings are invariably leached with a solution of potassium or sodium cyanide (commercial cyanide is frequently a mixture of the two salts).

In the Witwatersrand gold-field of South Africa,[1] the ore, powdered by treatment first in rock-crushers, then in stamp batteries, and finally in tube mills, is allowed to flow over amalgamated plates so as to collect as much gold as possible ; it is then separated into sands and slimes in some form of classifier, in which the sands settle and pass out below, whilst the slimes overflow from the top ; the principle of classification into sands and slimes has already been discussed in connection with copper (page 24).

The treatment of the *sands* is fairly simple, they are charged into circular vats, fitted with a filter bottom of coco-nut matting covered with canvas, and cyanide solution is introduced from above and allowed to percolate downwards through the mass. The liquid drawn from below the filter-bottom contains gold in solution, and is allowed to flow through a series of boxes containing zinc shavings upon which the gold is precipitated. The zinc is rendered much more active as a reducing agent if it is previously treated with a little lead acetate solution ; lead is deposited on the zinc, and the zinc-lead couple produced brings about rapid precipitation of gold, the lead acting as the cathodic member of the couple.

The treatment of the *slimes* is less easy owing to the fact that they tend to settle and form a mass which is almost impervious to water. They are usually thickened as far as possible in a mechanical thickener, and are then run into leaching tanks, in which the cyanide solution is introduced and the whole is agitated together, either by mechanical means or by compressed air. Since oxygen is absolutely necessary for the dissolution of gold by cyanide, the latter method would appear to be advantageous.

The separation of the clear liquid from the slimes is a problem of some difficulty. At one time a process of settling and decanta-

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[1] H. Louis, *J. Soc. Chem. Ind.* **37** (1918), 209T ; W. Cullen, *J. Soc. Chem. Ind.* **41** (1922), 316T.

tion was the common one, but obviously this process is wasteful, since the slimes are difficult to wash and will certainly retain much gold-bearing solution when they are thrown away. Most of the pulp is now clarified by filtration, the so-called " leaf-filter " being largely employed. A " leaf " consists of a rectangular frame of wood or metal on both sides of which is stretched a filter-cloth. The narrow space between the filter-cloths on either side (which are about 2 in. apart) is connected by a pipe to a suction pump. About forty of these leaves (L) may be placed parallel to one another in a tank (Fig. 16), which is filled alternatively with the cyanide pulp and water. When the tank is full of pulp, the suction pump draws clear auriferous cyanide solution through the filter, a solid cake of pulp being formed on the outside of each leaf. Then the tank is emptied and filled with wash-water, and a certain amount is sucked through, so as to recover the gold still present in the cake. Finally the cake of slime is washed off the outside of the leaf by water-pressure into the tank, which may then be emptied, and used for the filtration of a fresh quantity of pulp. The auriferous solution, drawn through the filter, passes to the tank, where it is treated with zinc for the recovery of gold.

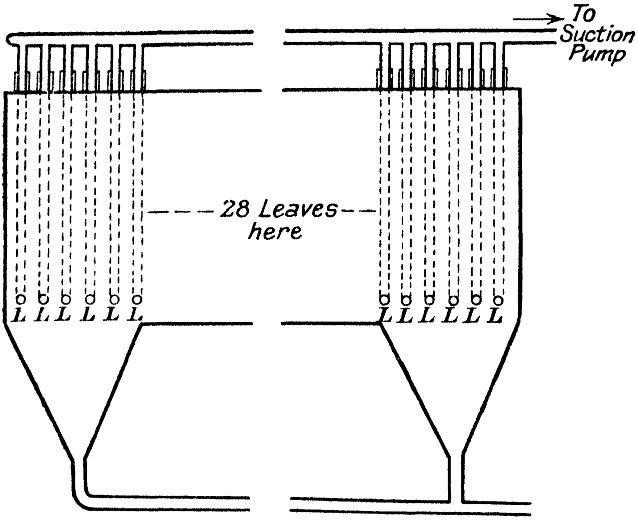

FIG. 16.—Principle of the Leaf Filter.

An alternative method of treatment, which has long been carried out in America, is now being introduced into some of the mines of the " Far East Rand," where the ore does not readily give up its gold unless finely ground. In such a case, the stamp batteries, amalgamation plant and sand-treatment plant may be omitted; the *whole* of the ore is ground in tube mills to a fine state of division, and is then subjected to the "slime-treatment" described above.[1]

In South Africa shavings are still the usual form in which zinc is used as the reducing agent for gold. But in America, zinc dust (often the "blue powder" which is a by-product at zinc smelting works) is largely used in the place of shavings.[2] This is a far more rapid precipitant, and gives a remarkably high recovery of gold, 98 per cent. of the precious metal in the solution being precipitated in a few minutes. The dust is generally introduced into the gold-bearing liquid in the form of an emulsion; the requisite quantity of this emulsion is run into the tank containing the gold-bearing solution, and the whole is at once pumped into filter-presses where the precipitated gold is retained.

The use of so active a reagent as zinc dust is not without its disadvantages. It requires careful storage, since otherwise it may oxidize and deteriorate, and possibly fires or explosions may be caused. Furthermore, if it is introduced into cyanide liquors containing dissolved oxygen, it may be quickly attacked and brought into solution, in a way which contributes nothing to the precipitation of gold. It is stated that about half the zinc actually added to the precipitation vat is generally wasted in this way, unless precautions are taken to reduce the amount of dissolved oxygen present. Thus, whilst in the *dissolution* of gold by cyanide dissolved oxygen is absolutely necessary, in the subsequent *precipitation* of that gold by zinc, oxygen is highly detrimental. It is very advantageous to remove oxygen from the clear solution before the treatment with zinc.[3] This is commonly done in practice by treatment in a vacuum vessel, as in the Crowe process, which at one American establishment has apparently reduced the zinc consumption by one-half. The Crowe process has also been used with success in South Africa. Many alternative methods of removing dissolved oxygen are available; treatment with tannin has been considered.

Aluminium dust has been tried in the place of zinc dust, but has not given universal satisfaction. The high price of zinc has, however, led to many attempts to find a substitute, and charcoal is in use in many places, originally in Western Australia, but now,

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[1] M. W. von Bernewitz, *Min. Ind.* **30** (1921), 308, 309, 311.

[2] A. M. Merton, *Eng. Min. World,* **39** (1913), 429.

[3] H. A. White, *J. Chem. Met. Soc. S. Africa* **20** (1919), 1, 97; **21** (1920), 105. T. B. Crowe, *Trans. Amer. Inst. Min. Eng.* **60** (1919), 111; O. P. Watts, *Met. Chem. Eng.* **19** (1918), 652; S. Newton and L. L. Fewster, *J. Chem. Met. Soc. S. Africa,* **22** (1922), 249.

to some extent, in South Africa.[1] The gold-bearing liquor usually passes through a bed of charcoal, and when sufficient gold has accumulated the charcoal is burnt to recover the precious metal. The carbon is clearly not the true reducing agent, but it is probable that reducing gases present in the charcoal, such as carbon monoxide and possibly hydrogen, bring about the reduction of the gold. According to another view, the potassium gold cyanide $K[Au(CN)_2]$ is retained by physical adsorption, no reduction taking place until the charcoal is burnt. The fact that charcoal usually requires to be heated to a red heat and quenched in water before it becomes "active" as an absorbent for gold is quite consistent with this view, although it can also be explained on the theory that carbon monoxide or hydrogen is the reducing agent.

At different times, the deposition of gold by electrolysis of the cyanide extract has been practised.[2] In the method used in South Africa for several years (1887–1898), lead cathodes and iron anodes were employed, the latter being hung in sacks; a good deal of cyanide was regenerated as a result of the electrolysis, and could be used to leach more tailings. Normally, however, the zinc precipitation process is cheaper, but owing to the shortage of zinc during the war, fresh experiments were made with electrolytic precipitation.

One former objection to the electrolytic process, namely, the difficulties of removing the deposited gold from the cathode, has been avoided by the use of a higher current density (0·3–0·5 amps. per sq. ft.), under which circumstances the gold is deposited as a non-adherent slime. Iron has proved more suitable than lead as a cathode material. An alternative suggestion to deposit the gold upon cathodes of waxed paper coated with flake graphite is of some interest; when the gold deposit has reached a suitable thickness the cathode is removed, and the paper backing is burnt off from the gold.[3]

Purification of Gold. Whether obtained by gravity separation, amalgamation, or by the cyanide process, the crude product does not yield pure gold when melted up. The bullion nearly always contains silver and other metals originally present in the gold-grains of the ore; further, when the cyanide process has been used, it often contains zinc and lead. The gold is often melted with silver

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[1] H. R. Edmands, *Trans. Inst. Min. Met.* **27** (1918), 277; A. W. Allen, *Met. Chem. Eng.* **18** (1918), 642; M. Green, *Trans. Inst. Min. Met.* **23** (1913), 65.

[2] G. H. Clevenger, *Trans. Amer. Electrochem. Soc.* **28** (1915), 263; H. A. Megraw, *Eng. Min. J.* **97** (1914), 1232.

[3] D. Lay, *Eng. Min. J.* **100** (1915), 276.

to give an alloy suitable for parting, and is then parted by the acid process or by the electrolytic process, both of which were discussed in the section on silver. Where the gold is in great excess in the original material, other methods, such as the Miller chlorine process, may be preferred; the Miller process is used on the Rand.

Uses of Gold. The uses to which gold is put in ordinary life are too well known to merit a lengthy description. Gold possesses special importance as a "standard of value," although since the war few countries have been able to retain the gold basis for their currency. The metal is used extensively in the manufacture of jewellery, watches, gold plate, and the like. A certain quantity is required in dentistry, while the salts find application in the toning of photographs; but the use of gold for both these purposes is probably declining. A great deal of gold-leaf is used for lettering and decoration, whilst the metal is used in the "gilding" of pottery. For this latter purpose the gold is often applied to the pottery as an organic salt suspended in an oily medium, which also contains a mixture of substances (such as borax and bismuth nitrate) which vitrify at a low temperature. After application the pottery is fired at a comparatively low temperature. It is stated that the gold should contain about 1 per cent. of other metals, otherwise the desired lustre cannot easily be obtained.[1] Gold is also used in some kinds of ruby glaze and glass.

The employment of gold as a standard of value is, of course, primarily dependent upon the comparative scarcity of the metal; and it is probable that the popularity of gold jewellery is due quite as much to the value of the material as to the intrinsic beauty of the articles. Gold forms, therefore, an exception to the general economic rule that the high price of a substance tends to reduce its employment. Undoubtedly, however, gold has one practical advantage over other materials, namely, that it is less prone to corrosion or tarnishing than the less noble metals; its lustre is almost unaffected by exposure to any ordinary atmosphere. The mechanical properties of pure gold, on the other hand, are not favourable to its use; the metal is too soft and malleable for general employment. Gold used for jewellery and coinage is always therefore alloyed with a little copper. British gold coins—now so rarely seen—contained 8·33 per cent. of copper; this alloy, which consists of a single solid solution of gold and copper, is much harder than pure gold.

Gold-plating. If an article made of a less valuable metal be covered with a thin coherent film of gold, this lends to the object

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[1] H. K. Pickard, *Trans. Inst. Min. Met.* **28** (1919), xlix.

the colour of gold and at the same time affords protection from corrosion. A gold-plated article thus combines the cheapness and mechanical strength of the common material with the beauty and permanence of the noble metal. "Gilding" is now chiefly brought about by electrolysis. The article to be plated is made the cathode in a solution of a gold compound. In order to obtain a smooth deposit of the metal, it is best, as in the case of silver, to use a salt in which gold exists chiefly in the anion. Thus a solution of potassium aurocyanide is usually employed. Another good plating bath is made by dissolving fulminating gold in potassium cyanide. Gold anodes are placed in the solution, and, if these are dissolved by the current as quickly as metal is deposited at the cathode, the strength of the bath can be maintained. The danger of passivity is largely avoided by keeping the anodic current density low and it is therefore advisable to make the area of the anodes as large as possible in order that the current may be distributed over a wide surface. Nevertheless, gold-plating baths do tend to lose strength during use; they must occasionally be replenished by the addition of gold salts. Silver objects can be plated with gold direct; but the more reactive metals are usually covered with silver before gilding, since if immersed directly in a gold bath they would be likely to cause the precipitation of gold in a spongy form by simple replacement.

By varying the composition of the gilding bath and the conditions of deposition, a considerable range of colours can be obtained.[1] A comparatively cool bath (32° C.) gives a pale colour, whilst a warmer bath (50° C.) confers a deposit with a reddish tinge; a low current density produces a paler deposit than a high current density. By using a bath containing silver as well as gold, a deposit with a green tinge is obtained,[2] whilst a reddish tone is given by baths containing copper.

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[1] A complete list of gilding baths is given by F. C. Frary, *Trans. Amer. Electrochem. Soc.* **23** (1913), 25.

[2] The deposition of the "green" gold-silver alloys is discussed by S. Field, *Trans. Faraday Soc.* **16** (1921), 502.

GROUP IIB

	Atomic Weight.	**Normal Electrode Potential (Hydrogen Scale).**
Zinc	65·37	−0·770 volts
Cadmium . . .	112·40	−0·420 ,,
Mercury . . .	200·6	+0·7928 ,,

The metals of Group IIB differ from those of Group IB in possessing a relatively low melting-point and a low boiling-point. The melting-points fall as the atomic weight rises, and mercury is a liquid at ordinary temperatures ; all the metals volatilize appreciably when heated in a non-oxidizing atmosphere.

Unlike most of the metals previously considered, zinc and cadmium crystallize in the hexagonal system. Most of the metals hitherto described have been cubic, but it is noteworthy that certain divalent metals of Group IIA, beryllium and magnesium, also crystallize in the hexagonal system.

The metals are less " noble " than those of the previous group, but here again the noble character rises with the atomic weight. Thus, whilst zinc is a highly reactive metal, displacing hydrogen from dilute acids, and oxidizing quickly when heated in air, mercury is an extremely stable substance.

The metals are for the most part divalent in their principal compounds. In zinc the valency is almost invariable and practically all the salts are colourless. In mercury, there is a second class of salts in which the metal would appear to be monovalent ; coloured compounds are met with in the case of mercury. Although the normal salts of all the metals are well developed, there is a marked tendency in the group towards the formation of complex salts, especially complex chlorides and iodides, in which the metal appears in the anion.

It is noteworthy that the anodic dissolution and the cathodic deposition of the metals of this group are in general processes which take place smoothly and without complicated secondary effects. Passivity and valve-action are less frequently met with in metals of Group IIB than in those of most other groups. The general employment of zinc in primary cells, and of cadmium and mercury in standard " cells " and " half-cells " (e.g. in the " cadmium standard cell " and the " calomel electrode ") depends largely on this fact.

ZINC

Atomic weight . . . 65·37

Zinc is the first metal of Group IIB which we shall consider; lying next to copper in the periodic classification, it has certain points of resemblance to that element, many of the salts of the two metals being isomorphous. On the other hand, there is also a distinct similarity between the compounds of zinc and those of magnesium, a metal which we have placed in Group IIA.

The Metal

Zinc is a whitish-grey substance, capable of taking a good lustre when polished.[1] It conducts heat and electricity well, but by no means so well as copper or silver. At ordinary temperatures cast zinc is slightly brittle, and specimens can often be broken on sharp bending. The fracture usually displays the crystalline structure of the metal; an ordinary rod of cast zinc, for instance, shows a fine radial structure, due to the existence of long thin crystallites which have commenced to grow at the periphery and which have met one another at the centre. At higher temperatures (about 150° C.) zinc is ductile and malleable; at this temperature it is readily rolled into sheet, or even drawn into wire. It commonly becomes brittle again when heated to about 180° C. The sudden drop in ductility at about 180° C. has been ascribed to an allotropic change, and it is significant that many of the other properties of zinc, including the density and hardness, appear similarly to show an abrupt change between 170 and 180° C.[2] Certain investigators,[3] however, state that the change of properties is not found in pure hot-rolled zinc, and consider that the change at 170° C. in zinc which has undergone cold deformation may be simply due to the commencement of grain growth or recrystallization. Evidence[4] of

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[1] The reflection spectrum of zinc presents some exceptional features, especially in the infra-red region. See *U.S. Bur. Stand. Sci. Paper*, **379** (1920), 251.

[2] K. E. Bingham, *J. Inst. Met.* **24** (1920), 333. These views are supported by C. A. F. Benedicks, *J. Inst. Met.* **24** (1920), 354.

[3] W. Pierce, *J. Inst. Met.* **24** (1920), 358. Compare G. Masing, *Zeitsch. Metallkunde*, **13** (1921), 425.

[4] H. Le Chatelier, *Comptes Rend.* **111** (1896), 454; M. Werner, *Zeitsch. Anorg. Chem.* **83** (1913), 275. Compare E. Cohen and W. D. Helderman, *Proc. Amst. Acad.* **16** (1913), 565; **17** (1914), 59.

another allotropic change about 300° or 360° C. has been put forward, but the matter is still in doubt.

Whatever view is taken of the question of *the alleged allotropic change at 170–180° C., the consideration of the mechanical properties of zinc is undoubtedly complicated by the fact that zinc which has suffered slight deformation undergoes great coarsening of grain when annealed a little below 200° C.*[1] The coarsely crystalline metal is apt to be very brittle at low temperatures, but the mechanical working of the coarsened metal at about 150° C. tends to break up the big grains and thus to refine the structure; such treatment renders the material comparatively workable even at low temperatures.[2]

The effect of mechanical work on the properties of pure zinc is somewhat exceptional, apparently owing to the fact that deformed zinc undergoes self-annealing at quite low temperatures. A sheet of rolled zinc when viewed in a micro-section does not display grains elongated in the direction of rolling; the structure is generally equi-axed.[3] Likewise, although cold-rolling is able to bring about a considerable increase in the hardness of pure zinc (if the reduction of thickness is sufficient), yet the added hardness is not permanent, and tends to disappear in the course of a few days at ordinary temperature.[4]

Whilst, however, the temperature at which pure zinc undergoes marked self-annealing is quite low, it is greatly raised by the presence of impurities in solid solution, especially copper. Thus whilst pure zinc can scarcely be maintained in a work-hardened condition, commercial zinc is considerably hardened by deformation at ordinary temperatures, and the hardening appears to be fairly permanent.[5]

Zinc is a much more easily fusible metal than copper, silver, or gold; it melts at 419° C. It is distinctly volatile even at the melting-point and boils at about 918° C. The density of the vapour has been determined, and seems to show that zinc in the vaporous state exists in monatomic molecules.

Zinc is a highly reactive metal. Thin foil, when strongly heated in air, may be made to burn with a bluish-white flame, zinc oxide being formed in the combustion. A good deal of heat is liberated during the combination with oxygen. At ordinary temperatures oxidation proceeds only superficially upon a fresh zinc surface,

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[1] G. Timoféef, *Rev. Met.* **11** (1914), 127.

[2] Z. Jeffries, *Bull. Amer. Inst. Min. Eng.* **138** (1918), 1043.

[3] D. H. Ingall, *J. Inst. Met.* **26** (1921), 281.

[4] H. W. Brownsdon, *J. Inst. Met.* **26** (1921), 397–399.

[5] Compare C. H. Mathewson, C. S. Trewin and W. B. Finkeldey, *Bull. Amer. Inst. Min. Eng.* **153** (1919), 2775.

which soon becomes somewhat dulled if exposed to moist air. But here the oxide film produced protects the metal from further oxidation. In the case of finely-divided zinc, the oxidation is much more marked, and fires have been caused at places where zinc dust has been stored owing to the heat generated by the oxidation. Zinc dust suspended in air may constitute an explosive mixture. Compact zinc exposed to damp air containing hydrogen chloride quickly becomes visibly wet, owing to the hygroscopic character of zinc chloride, and corrosion then proceeds very rapidly.[1]

When a piece of zinc is placed in contact with the solution of a salt of a distinctly more noble metal, such as lead, copper or gold, zinc enters the solution and the other metal is precipitated usually in the spongy state. This replacement of a less reactive metal by zinc is all the more rapid if the zinc is not uniformly pure, or where there is already another more noble metal in contact with the zinc. For instance, as has already been pointed out, the precipitation of gold from very dilute cyanide solutions by zinc is a slow process ; but if the zinc be first covered with lead particles by immersion in a concentrated lead salt solution, the reduction of gold proceeds apace. Facts of this kind show that the replacement of other metals by zinc is not a direct chemical interchange, but proceeds electro-chemically, a number of little short-circuited electric batteries being formed, as explained in Vol. I, Chapter XIII.

Zinc, standing on the reactive side of hydrogen in the Potential Series, will dissolve in dilute acids with the evolution of that gas, if brought in contact with a noble metal of low "overpotential" value, such as copper or platinum. Commercial zinc always has sufficient noble particles embedded in it to evolve hydrogen freely with dilute acids, and actually the most convenient method of preparing hydrogen in the laboratory is by the action of dilute sulphuric acid upon granulated zinc. But *pure* zinc will not dissolve readily in dilute sulphuric acid, unless brought into contact with a "noble" substance. The best method of obtaining a rapid dissolution of zinc in this acid is the addition of a few drops of copper sulphate solution. Copper is precipitated upon the zinc, and acts as the cathode of the corrosion couple.

It is noteworthy that when moderately pure zinc is immersed in an acid, the rate of attack is slow at first, but after an interval (known as the *period of induction*) the evolution of hydrogen becomes rapid and the corrosion proceeds apace. A moment's consideration will show the significance of the period of induction. The traces of foreign metals exist partly in solid solution

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[1] U. R. Evans, *Trans. Faraday Soc.* (1923).

in the zinc crystals, and therefore cannot serve as the cathodic elements of the corrosion couples. As, however, the initial slow corrosion proceeds, the zinc begins to pass into the ionic state, and traces of the second metal pass also into the acid solution. This second metal is immediately reprecipitated in the metallic condition, as a separate phase, and then begins to function as the cathode of the corrosion couple. Likewise the impurities which exist as a separate phase at the crystal-boundaries can play but little part in promoting corrosion when the zinc is first immersed in the acid, being inaccessible to the solution; as the zinc is eaten away, however, these insoluble impurities become exposed and gradually accumulate. When corrosion has been proceeding for some time a black scum can usually be seen on the zinc which consists of the metallic impurities (e.g. lead and cadmium); if the black scum be wiped off from the metal, corrosion is greatly retarded, and a fresh period of induction is observed.[1]

The effect of the presence of various elements in aiding the dissolution of zinc in acids is very different. The presence of only 0·01 per cent. of gold or platinum has a most marked influence, but the effect of other elements, such as arsenic and cadmium is less great. The comparative efficiency of different impurities in aiding the elimination of hydrogen in gaseous form by zinc, is naturally connected with the different overpotential values of the foreign metals in question,[2] the overpotential of the metal being, in fact, of far more importance in determining whether hydrogen can be eliminated than is the position of the metal in the Potential Series. Thus the presence of arsenic has comparatively little influence in accelerating the corrosion of zinc by acids.[3] This fact, which appears to have puzzled some chemists, is quite to be expected in view of the fact that the overpotential value of arsenic is high.[4]

The liability of zinc to corrosion by acids is greatly reduced by rubbing the surface with mercury. Not only is the amalgamated surface uniform in composition, and hence free from corrosion couples, but the high overpotential value of the mercury-rich surface militates against the evolution of hydrogen in gaseous form.

Zinc is attacked by solutions of caustic alkalis, hydrogen being

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[1] M. Centnerszwer and J. Sachs, *Zeitsch. Phys. Chem.* **87** (1914), 742. The theoretical views of these two experimenters are not held by the present writer. See U. R. Evans, *J. Inst. Met.* **28** (1922), 120.

[2] See A. Thiel, *Zeitsch. Elektrochem.* **20** (1914), 460.

[3] M. Centnerszwer, *Zeitsch. Phys. Chem.* **92** (1918), 563.

[4] Compare O. P. Watts and N. D. Whipple, *Trans. Amer. Electrochem. Soc.* **32** (1917), 259.

evolved, and soluble zincates being produced. In a solution of a neutral salt, such as sodium chloride, compact zinc is less readily dissolved; any corrosion leads to the formation of the insoluble hydroxide, which under certain circumstances forms a slimy, moderately adherent layer upon the zinc, and obstructs to a considerable extent the corrosive action.[1]

Zinc powder is naturally much more readily attacked than compact zinc. If the powder is merely wetted with water, hydrogen is evolved. It is noteworthy that if air is present, a certain amount of hydrogen peroxide is formed at the same time.[2]

When zinc is used as the anode in an electrolytic cell containing a chloride or sulphate solution, it is attacked with a current efficiency of approximately 100 per cent.[3] A familiar example of the nearly quantitative anodic dissolution of zinc is afforded by the employment of zinc as the attackable element of a primary cell.

Laboratory Preparation. In view of the reactive character of zinc, it is to be expected that difficulty will be experienced in reducing the compounds to the metallic state. The only convenient laboratory method of preparing the metal from its salts is by the electrolysis of a pure zinc salt in aqueous solution. Upon the electrolysis of a pure zinc sulphate solution acidified only very weakly, the metal is deposited on the cathode at a good current efficiency; but if the solution contains traces of more noble metals, corrosion couples will be set up and the zinc will be dissolved away almost as quickly as it is deposited. The electrochemical precipitation of zinc requires therefore considerable care in the preparation of a zinc salt solution quite free from all other metals, and especially from lead and copper. If a solution of pure zinc sulphate containing a trace of free acid is electrolysed, a compact, if somewhat rugged, coating of zinc is obtained. In order to obtain a good current efficiency, the solution must be kept cool, and the acidity must be kept low: otherwise much of the current is wasted on the production of hydrogen. Sulphuric acid in regulated quantity can be used, but it is preferable to use a weaker acid; with a bath containing acetic acid along with sodium acetate, a current efficiency of nearly 100 per cent. is possible.[4]

The preparation of pure zinc from impure materials can be carried out by a distillation process, and an electric furnace intended for use in a laboratory equipped with a suitable power installation

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[1] E. Prost, *Bull. Soc. Chim. Belg.* **28** (1914), 98. Compare G. D. Bengough and O. F. Hudson, *J. Inst. Met.* **21** (1919), 84.

[2] M. Kernbaum, *Comptes Rend.* **152** (1911), 1668.

[3] G. R. White, *J. Phys. Chem.* **15** (1911), 727.

[4] J. W. Richards, *Trans. Amer. Electrochem. Soc.* **25** (1914), 284.

has been designed to carry out refining by this method.[1] In the ordinary laboratory, however, it would prove easier to dissolve the crude material in acid, eliminate foreign metals from the solution by chemical means, and regenerate the zinc by electrolysis.

Compounds

Zinc forms only one series of compounds, in which the metal is apparently divalent.

The **oxide,** ZnO, can be obtained, as has already been stated, from the metal by combustion in air ; it may also be prepared by heating the carbonate, nitrate or hydroxide. It is a white substance, but becomes yellow at high temperatures—a fact which is interesting in view of the circumstance that cadmium and mercury, the other metals in the group, have oxides which are coloured even when cold. The **hydroxide** [2] is obtained by careful precipitation of zinc chloride or nitrate with sodium hydroxide (if too much alkali is added, the precipitate redissolves). The hydroxide as thus produced is a white gelatinous precipitate, which cannot be washed free from chlorides (or nitrates) by cold water. Treatment with boiling water does succeed in removing chlorides (or nitrates), but at 100° C. the hydroxide loses water, anhydrous zinc oxide (ZnO) being formed ; the change is not characterized by an alteration in colour—as in the analogous case of copper—but is rendered visible by the disappearance of the gelatinous character in the precipitate, which becomes " gritty."

A crystalline form of the hydroxide can be produced by adding zinc sulphate to normal potassium hydroxide cautiously until the liquid is just turbid. On violent shaking, or by scratching the walls of the containing vessel, a sandy precipitate consisting of tiny bar-shaped crystals comes down. This has a composition accurately expressed by the formula $Zn(OH)_2$. It is, however, metastable, and if kept in contact with a solution containing a trace of alkali, it is converted to the stable anhydrous oxide, which is less soluble in alkali than the hydroxide.

Zinc oxide is amphoteric ; that is to say, it possesses both a basic and acidic character. It dissolves in acids to form the normal zinc salts, but also dissolves in the caustic alkalis, to form the so-called " **zincates.**" [3] Zinc hydroxide is also soluble in ammonia. The dissolution both in acid and in alkali proceeds most quickly

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[1] F. A. J. FitzGerald, *Trans. Amer. Electrochem. Soc.* **36** (1919), 319.

[2] F. Goudriaan, *Proc. Amst. Acad.* **22** (1919), 184.

[3] F. Goudriaan, *Proc. Amst. Acad.* **22** (1919), 179. Compare the earlier work of J. H. Hildebrand and W. G. Bowers, *J. Amer. Chem. Soc.* **38** (1916), 785 ; also A. Hantzsch, *Zeitsch. Anorg. Chem.* **30** (1902), 298.

in the case of the gelatinous hydroxide; but it takes place also, although more slowly, even if the anhydrous oxide is used, so long as this has not been too strongly ignited.

The liquid obtained on shaking zinc hydroxide with alkali has been regarded by some chemists as a colloidal solution of the zinc hydroxide, the alkali acting merely as peptizing agent. It is now certain that the solutions contain, in addition to colloid particles, molecules of a true zincate. Until recently, there was no certain information regarding the composition of the zincates, but Goudriaan has not only isolated sodium zincate, but has worked out the equilibrium diagram of the system "Zinc oxide-sodium oxide-water." He finds sodium zincate to have the formula

$$Na_2O.ZnO.4H_2O.$$

The isolation of the body is rendered a little difficult by the fact that it is unstable in the presence of pure water, which causes immediate hydrolysis to sodium hydroxide and zinc oxide. Solid sodium zincate can only exist in contact with a very strongly alkaline solution. When, for instance, 50 grams of sodium hydroxide are added to 50 grams of water, and 17 grams of zinc oxide are introduced in small quantities, sodium zincate crystallizes out from the solution, and can be separated and dried on porous earthenware, precautions being taken to prevent access of air or carbon dioxide.

Zinc Salts. All the zinc salts are colourless, except in the case of the salts of coloured acids. The *soluble salts* may be obtained by the action of the corresponding acids upon metallic zinc, or by the dissolution of the hydroxide or carbonate in the acids in question. The **sulphate,** $ZnSO_4.7H_2O$, crystallizes in fine rhombic prisms, and is a member of that large class of isomorphous sulphates which is characteristic of divalent metals, and which includes the sulphates of zinc, cadmium, magnesium, divalent iron, nickel, cobalt, manganese, and chromium.

Zinc **chloride** may be obtained in solution by the action of hydrochloric acid on the metal or hydroxide. On crystallization, this solution yields a hydrate $ZnCl_2.H_2O$. The hydrate has its water of crystallization firmly attached to the molecule; it is somewhat difficult to drive off the water by heating, without raising the substance to such a temperature that the salt loses hydrogen chloride. The anhydrous chloride, however, may be obtained by the action of dry chlorine upon metallic zinc. It is a white solid, with a great affinity for water; it is deliquescent, and, when exposed to damp air, absorbs so much water that it becomes dissolved in it, and the solid salt gradually turns to a syrupy liquid. The combination of zinc chloride with water is attended with the evolution of heat. It will be remembered that the lighter members of Groups IIA, magnesium and calcium, have also deliquescent chlorides. Anhydrous zinc chloride is volatile at a red heat, and can be purified by sublimation; the vapour density corresponds to the formula $ZnCl_2$.

Solutions of zinc chloride readily lose hydrogen chloride when boiled, and on the subsequent addition of water, a precipitate is generally formed. This is often described as a basic chloride or "oxychloride," and is sometimes said to contain the compound $Zn(OH)Cl$, mixed with zinc chloride. Possibly, however, it consists merely of zinc hydroxide with adsorbed zinc chloride.

Complex salts are formed between zinc chloride and ammonium chloride, and it seems likely that even in an ordinary acidified solution of zinc chloride complex salts of the type $H[ZnCl_3]$, containing the zinc in the anion, exist.[1] The tendency of zinc to enter the anionic condition is shown by the fact that zinc chloride, added to a blue cobalt chloride solution, restores the red colour by forcing the cobalt from the anionic to the cationic state.

The *insoluble salts* of zinc are formed through the precipitation of soluble zinc salts by the sodium salts of the acids in question. Thus the addition of sodium carbonate to zinc sulphate solution gives a precipitate of **zinc carbonate,** $ZnCO_3$, which soon loses carbon dioxide, and passes into a basic carbonate. Similarly, the addition of sodium sulphide to a solution of zinc sulphate gives a white precipitate of **zinc sulphide**; this is decomposed by mineral acids, with the production of a soluble zinc salt and the evolution of hydrogen sulphide gas, but is undissolved by dilute acetic acid.

Zinc sulphide, ZnS, is a compound of some little interest owing to the fact that it often shows *phosphorescent* properties. It will be remembered that the sulphides of certain other divalent metals, such as magnesium, calcium, strontium, and barium, acquire phosphorescent properties when heated with minute traces of a compound of a heavy metal, such as copper, together with a suitable fluxing agent. Many of the older investigators[2] declared that zinc sulphide may be phosphorescent even when quite pure, but recent careful work has shown that, if prepared in a perfectly pure condition, zinc sulphide does not become phosphorescent on heating.[3] The presence, however, of a minute trace of copper is sufficient to cause marked phosphorescence.

As in the case of the sulphides of other metals, the presence of a fluxing agent is very beneficial to obtaining a strongly phos-

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[1] J. H. Hildebrand and W. G. Bowers, *J. Amer. Chem. Soc.* **38** (1916), 785.

[2] C. Henry, *Comptes Rend.* **115** (1892), 505.

[3] R. Tomaschek, *Ann. Phys.* **65** (1921), 189.

phorescent material, although if the temperature employed is sufficient to melt the zinc sulphide itself, fluxing agents can be dispensed with[1]; chlorides appear to be most beneficial as fluxing agents. If precipitated zinc sulphide, containing a suitable proportion of potassium chloride and a trace of a heavy metal (such as copper or manganese) is heated in a crucible at about 1,000° C. for half an hour, a strongly phosphorescent product is obtained. The proportion of fluxing agent may be perhaps one-fifth of that of the zinc sulphide, but only very small amounts of the heavy metal (about $\frac{1}{10,000}$ of the sulphide) are desirable. The conditions governing the phosphorescence of zinc sulphide are thus closely analogous to those governing the phosphorescence of calcium sulphide.

The temperature at which the material is heated has a most important influence on the phosphorescence of the product.[2] Thus, heating at below 650° C. produces only feeble phosphorescence, presumably because at this temperature there is but little fusion, and the zinc sulphide and the heavy metal are not brought together into a single phase; this is confirmed by the appearance of the product, which is described as being "viscous and amorphous." Heating between 650° and 900° C. yields a highly phosphorescent product, which is described as having a "semi-crystalline" appearance when viewed under the microscope; this appearance probably indicates that partial or superficial fusion has occurred. If heated to a very high temperature (1,100° C.), the phosphorescent qualities of the product again decline, the product being now "purely crystalline" in appearance. Some investigators have sought to connect phosphorescence with the existence of a skin of non-crystalline matter tightly stretched over the surface of the zinc sulphide crystals, which are supposed to be kept thereby in a state of strain. It appears to the present writer that other explanations might be suggested; for instance, the comparatively weak activity of the sulphide obtained by heating at a high temperature may be due to the comparatively small radiating surface presented by this more compact variety. It seems unlikely that the crystalline character of the substance has anything to do with its phosphorescence, since zinc sulphide is known in two separate crystalline forms (cubic and hexagonal), and both have been prepared in the phosphorescent condition.[3]

The colour of the light emitted by phosphorescent zinc sulphide

[1] E. Tiede and A. Schleede, *Ber.* **53** (1920), 1721.

[2] E. MacDougall, A. W. Stewart, and R. Wright, *Trans. Chem. Soc.* **111** (1917), 663.

[3] E. Tiede and A. Schleede, *Ber.* **53** (1920), 1721; A. A. Guntz, *Comptes Rend.* **174** (1922), 1356.

varies with the conditions between blue and green. In the presence of manganese it is described as golden yellow.[1]

The close connection between fluorescence and phosphorescence is well shown by certain researches on zinc sulphide. The spectrum of the fluorescent light given off by zinc sulphide during illumination by a mercury arc lamp was compared with that of the phosphorescent light which it continues to emit after the exciting light is shut off; it is found that the distribution of energy in the fluorescent and phosphorescent spectra was the same.[2]

Like uranium nitrate (another fluorescent substance) many forms of zinc sulphide containing a heavy metal impurity (e.g. manganese) show the phenomenon of "triboluminescence" and emit light when crushed. At the same time pressing or crushing causes a marked decrease in the phosphorescent properties, and a distinct change in colour, which becomes brownish.[3] It is noteworthy that the amount of impurity required to produce strong triboluminescence is generally much greater than that suited for the production of strong phosphorescence; many samples which show strong triboluminescence are only weakly phosphorescent.[4]

Zinc cyanide is a white precipitate obtained by the addition of potassium cyanide to a zinc sulphate solution; it is soluble in excess of potassium cyanide, giving a complex potassium zinc cyanide; a similar phenomenon has been already noticed in the case of the corresponding copper, silver, and gold compounds. The **ferrocyanide** may also be obtained by precipitation in dilute acid solutions, and is properly a white substance; but it is readily oxidized, the colour becoming yellowish during the change. Other insoluble zinc salts are the **phosphates** and **oxalates**, prepared by precipitation with the corresponding sodium salts; they are white precipitates.

Zinc Peroxide.[5] When hydrogen peroxide is added to zinc hydroxide a white body of indefinite composition is formed; this is apparently a mixture of compounds, but is believed to contain bodies of the state of oxidation represented by the formula $ZnO_2.nH_2O$. It loses the active oxygen on heating.

Organic Compounds of Zinc. Very important to the organic chemist are certain compounds of zinc with "alkyl groups." When

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[1] K. A. Hofmann and W. Ducca, *Ber.* **37** (1904), 3410.

[2] C. A. Pierce, *Phys. Rev.* **30** (1910), 663.

[3] P. Lenard and V. Klatt, *Ann. Phys.* **12** (1903), 439; R. Tomaschek, *Ann. Phys.* **65** (1921), 195.

[4] A. Karl, *Comptes Rend.* **144** (1907), 841; **146** (1908), 1104.

[5] A recent study of the peroxide which leads to various suggestions regarding structural formulæ is due to F. W. Sjöström, *Zeitsch. Anorg. Chem.* **100** (1917), 237.

excess of ethyl iodide (C_2H_5I) is heated with zinc, a white crystalline compound C_2H_5ZnI is produced; on stronger heating, this yields zinc iodide and zinc ethide, the latter being obtained by distillation in a current of an inert gas,

$$2C_2H_5ZnI = ZnI_2 + Zn(C_2H_5)_2.$$

Zinc ethide, $Zn(C_2H_5)_2$, is a heavy colourless liquid, boiling at 118° C., which usually takes fire spontaneously when exposed to the air. The analogous compound, **zinc methide,** $Zn(CH_3)_2$, is similar but more volatile. Both compounds are used in the synthesis of several organic compounds.

Analytical

When compounds of zinc are mixed with sodium carbonate and heated on charcoal in the blowpipe flame, an incrustation of zinc oxide is formed round the mixture; this incrustation is yellow when hot and white when cold. The phenomenon, which is characteristic of zinc, depends upon the volatility of the metal; the zinc compound is reduced to the metallic state by the carbon, and the metallic vapour travels out into the oxidizing zone of the flame, where it becomes reoxidized, and the oxide is deposited upon the charcoal. Another dry test may be used to recognize zinc compounds; if any zinc salt be ignited upon charcoal before the blowpipe, then moistened with cobalt nitrate solution and re-ignited, a green coloration may be observed; this coloration is due to bodies of the nature of "Rinmann's green" referred to in the section on cobalt pigments (Vol. III).

As all the ordinary zinc salts are colourless, there are no very striking reactions which would help in the recognition of zinc in aqueous solutions. The fact, however, that sodium hydroxide produces in zinc salt solutions a white precipitate which redissolves in excess of the precipitant distinguishes the metal from many others; the salts of aluminium, lead, and tin, however, also show this phenomenon. The white precipitate obtained when hydrogen sulphide is bubbled through a solution which is ammoniacal, neutral, or acidified only with acetic acid, is also characteristic. The precipitate obtained with potassium ferrocyanide is sometimes recommended as a test.

The separation of zinc from other metals depends upon the peculiar conditions under which the sulphide is precipitated. The solution is first acidified with hydrochloric acid and hydrogen sulphide is bubbled through the hot solution, in order to precipitate the metals whose sulphides are insoluble in mineral acids; after filtration, and boiling to remove excess of hydrogen sulphide, certain other metals, iron, aluminium, and chromium, are removed, as hydroxides, by the addition of ammonium chloride and ammonia. If ammonium sulphide is added to the filtrate, zinc sulphide will be precipitated; but if nickel, cobalt, and manganese are present these metals also will be precipitated as sulphides. The separation of zinc from these three metals depends upon the fact that zinc alone can be precipitated as sulphide by the rapid passage of hydrogen sulphide through a cold solution containing a trace of free sulphuric acid; it has been stated that the precipitation of zinc is complete even if the concentration of acid be as high as $\frac{N}{100}$, a strength which is quite sufficient to prevent the precipitation of any cobalt, nickel, or manganese.[1]

When the zinc is completely precipitated as sulphide, this may at once be filtered off through asbestos fibre in a weighed Gooch crucible, dried at 100° C., and the weight determined. Or the sulphide may be redissolved by heating in dilute sulphuric acid and the solution precipitated with sodium carbonate; zinc carbonate is converted to oxide on gentle ignition, and zinc may be weighed as the latter compound. A difficulty always arises, however, if an attempt is made to filter a zinc precipitate through ordinary filter-paper. It is impossible to remove the precipitate completely from the filter-paper, and if an attempt were made to obtain the residue by burning the filter, reduction of zinc to the metallic state would occur during the combustion, and, owing to its volatility, the metal would pass off as vapour and be lost. Therefore zinc precipitates should either be filtered through asbestos, or alternately through a filter-paper which is dried and weighed before use, and can be weighed again afterwards with the dry precipitate.

Another plan is to estimate zinc as the metal, which is obtained as a smooth deposit by electrolysis.[2] If the zinc is present in the solution as sulphate, it should be run into a solution containing sufficient excess of potassium oxalate to avoid the precipitation of zinc oxalate; the clear solution obtained contains the soluble salt, potassium zinc oxalate. From this complex salt solution the zinc can be precipitated completely, as a smooth bluish-white deposit, upon a weighed cathode. The solution must be free from metals more noble than zinc; nitrates and most oxidizing agents interfere with the deposition, and the presence of ammonium salts is said to be disadvantageous.

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[1] See W. W. Scott, "Standard Methods of Chemical Analysis" (Crosby Lockwood), 1917 edition, pp. 479, 483, 485, 486.

[2] H. E. Medway, *Amer. J. Sci.* 18 (1904), 56.

It is not advisable to deposit zinc directly upon a platinum cathode, since zinc alloys easily with platinum, and it is difficult to remove the zinc-deposit from the platinum basis without loss of the precious metal or damage to the electrode. It is preferable therefore to cover the platinum electrolytically with a layer of bright copper, and after drying to re-weigh the electrode; the zinc may then be deposited on the copper, and the gain in weight shows the amount of zinc obtained from the solution.

Various volumetric methods for the estimation of zinc have been described.[1] The method usually recommended depends on the insolubility of zinc sulphide. An ammoniacal zinc salt solution is titrated with sodium sulphide solution, which is added in small quantities from a burette. After each addition, a drop of the liquid is taken out on a stirring-rod, and brought into contact with a drop of lead acetate solution on a filter-paper; so soon as sodium sulphide is in excess, the drop produces a black precipitate with the lead salt. When this black colour is seen for the first time, it is obvious that enough sodium sulphide has been added to precipitate the whole of the zinc. If the strength of the sodium sulphide solution be known, the zinc content of the solution under examination is easily calculated. Unfortunately sodium sulphide does not keep well in solution and the strength must be determined frequently by titration against a standard zinc sulphate solution.

Apart from this objection, methods of titration which make use of a " side-indicator " are never very rapid. A modification of the method, which is practised at various zinc-smelting works, consists in adding a drop of ferric chloride to the warm ammoniacal zinc solution; red flakes of ferric hydroxide appear and sink to the bottom of the beaker. Sodium sulphide is now run in until these flakes change their colour from red to black, due to the formation of iron sulphide. This change indicates that all the zinc has been precipitated.

Another volumetric method for the determination of zinc depends upon titration with potassium ferrocyanide; it is considered to be inferior to the sulphide method.[2]

TERRESTRIAL OCCURRENCE OF ZINC AND LEAD

The geo-chemistry of zinc is so closely connected to that of lead that it will be convenient to consider the two metals together.

Zinc and lead, like copper, must have been minor constituents

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[1] For details see F. Sutton, " Volumetric Analysis " (Churchill).

[2] See E. Olivier, *J. Soc. Chem. Ind.* **40** (1921), 107T.

of the original rock-magma. Judging from the analyses of the different igneous rocks accessible to us, the content of each of those three elements was probably under 0·01 per cent. But, as already frequently explained, they have become concentrated in the thermal waters evolved in the later stages of the consolidation of an intrusive mass, and have been carried upwards, probably in the form of sulphides held in solution by the water, which contained hydrogen sulphide under pressure. As the waters rose, the various metallic sulphides were liberated, but not at the same points, since the conditions favourable for deposition of the three metals are not identical. Copper, as already stated, is deposited readily along with iron, as some highly insoluble double sulphide, such as copper pyrites ($CuFeS_2$) ; but the sulphide of zinc is probably more soluble, and will generally remain in solution after all the copper has been thrown down. The principal factor which will determine whether or not the precipitation of zinc sulphide can occur is the hydrion concentration ; it is well known in the analytical laboratory that zinc sulphide can readily be thrown down from a neutral or alkaline solution, but not from a highly acid solution. Hence the zinc-bearing waters are likely to throw down zinc sulphide wherever they pass upwards through a basic formation such as limestone, which will greatly reduce the hydrion content ; but they will not deposit it to the same extent at other points. We find, therefore, the sulphide of zinc

Zinc blende (sphalerite) . . ZnS

often associated with limestone. The same is true of the corresponding lead sulphide

Galena . . . . . . PbS.

In the case of lead, however, the limiting value of the hydrion concentration (above which precipitation of sulphide cannot occur) lies higher than in the case of zinc.

It is, for instance, noteworthy that in the Western States of America the copper veins occur in all sorts of formations, whilst the lead and zinc minerals occur together practically only in limestone (as in Nevada and Arizona).[1] Moreover, whilst the copper occurs largely in veins, along with quartz and other typical vein-minerals, lead and zinc—although also found in veins—occur largely in chambers in the limestone, often filling in the cavities where the limestone has been eaten away in neutralizing the acid waters. Further, the calcite of the limestone is often changed locally by " metasomatic replacement " to the ore-mineral, which

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[1] Compare W. Lindgren, " Mineral Deposits " (McGraw-Hill), 1919 edition, p. 921.

in some cases reproduces faithfully the structure of the limestone as it existed before the change. In fact, we sometimes find, in the limestone, fossil remains of organisms that existed in the sea in which the limestone was originally formed; but the fossils now consist no longer of calcium carbonate but of compounds of lead or zinc. Where a lode with zinc and lead ores passes from limestone into some other formation, it usually becomes almost "barren." Numerous examples may be found in this country of a lode ceasing to be productive where it passes from carboniferous limestone into the overlying "millstone grit."

Of the two minerals mentioned above, zinc blende is a mineral varying in colour from yellowish white through brown to black, according to the content of iron; it may indeed be colourless when pure. Where freedom of growth has been allowed, it is often found to have crystallized in tetrahedra; more often it is massive, or occurs in fibrous growths. A second crystalline form of zinc sulphide, known as wurtzite, is also found in nature; it belongs to the hexagonal system. The sulphide of lead (galena) is a heavy lead-coloured mineral with bright metallic lustre, often occurring in remarkably perfect cubes or cube-octahedra. As a rule, neither mineral is pure; zinc blende generally contains, besides iron, a considerable quantity of cadmium; galena usually contains silver, and sometimes other metals.

By the weathering of primary zinc-lead sulphides, carbonates and sulphates are formed. The carbonate of lead is known as

Cerussite . . . . $PbCO_3$

and the sulphate as

Anglesite . . . . $PbSO_4$.

Both are insoluble, and are common constituents of the upper (oxidized) portions of zinc-lead deposits. On the other hand, zinc sulphate is soluble, and, where formed, is usually carried away by meteoric waters; thus the upper portions of zinc-lead deposits are often comparatively free from zinc. In general the zinc sulphate will react with limestone before it has been carried far, forming the insoluble carbonate which is known as

Smithsonite . . . . $ZnCO_3$.

It is possible that, by the action of descending and percolating waters, both zinc and lead may be dissolved at certain points, and re-deposited at others. Consequently, many of the zinc-lead ores occurring in limestones in different countries are probably not primary ores at all, but have been formed by the reaction of the limestone with descending waters of meteoric origin which have become zinc-bearing or lead-bearing through the leaching of older ore-deposits. In other cases, pyrites or other sulphides may have acted as the precipitant for the zinc held in solution in percolating waters, secondary deposits of zinc blende being produced. It is often very difficult to decide whether the lead-zinc ores found in limestone are of *primary* origin (deposited from *ascending thermal* waters), or of *secondary* origin (deposited from *descending meteoric* waters), and a great deal of controversy has arisen amongst geologists as to the origin of the ores in different districts. In a typical series of ores deposited from descending waters, the ores are likely to die out gradually as we follow them deeper into the earth's interior. Zinc sulphide, which is more soluble than lead sulphide, and which is therefore less easily deposited, may persist to a greater depth, and thus in the deeper portions we get zinc ores comparatively free from lead ; but if we go low enough zinc also will fail. Perhaps in the upper parts we may get lead ores comparatively free from zinc. In ores deposited by ascending waters—in so far as there is any separation of the two metals—the lead is likely to be richer in the deeper parts and the zinc in the upper parts.

Amongst other oxidized ores of zinc

	Willemite	Zn_2SiO_4
and	*Hemimorphite* (“ Electric calamine ”)	$Zn_2H_2SiO_5$

deserve mention. In addition the oxide

Zincite	ZnO

and the zinc spinel

Franklinite	$ZnO.Fe_2O_3$

are found in New Jersey in a crystalline limestone, pierced by granitic dykes and in contact with a gneiss. It was probably an ordinary limestone containing zinc ore, but the limestone has been “ baked ” at a later date by contact with the igneous rocks. The heat has caused recrystallization of the limestone, and has converted the original zinc compound (probably the carbonate) to the state of oxide. Franklinite usually contains manganese.

Amongst the less common oxidized lead minerals we find the chromate, molybdate, and tungstate ; they are known as

Crocoite.	$PbCrO_4$
Wulfenite	$PbMoO_4$
Stolzite	$PbWO_4$.

A large proportion of the world's rich zinc and lead ores are to be found in the United States and in Mexico. Some of the most important deposits occur in Idaho, Montana, Utah, Colorado, and also in the well-known Joplin district of Missouri and Kansas.

Many of the ores—notably those of Idaho—contain a highly argentiferous galena and are regarded rather as silver ores than as ores of lead and zinc. In many cases distinct silver minerals also occur in the ore, intimately mixed with the compounds of lead and zinc. The well-known ores of Leadville (Colorado) occur in limestone of carboniferous age, between the limestone and an impervious porphyry rock above. The lead has here probably been brought up by waters ascending from an igneous mass below, although some authors assert that it has been deposited by descending (meteoric) waters, which have derived their lead-content from some primary ores which have since disappeared. The zinc and lead ores of the Joplin district are probably of secondary origin.[1] In contrast with most American lead ores, many of those occurring in the Mississippi and Missouri region are comparatively free from silver.

Zinc and lead minerals occur in various limestone formations in Europe. In the British Isles,[2] the carboniferous limestone of Derbyshire, Flintshire, Cumberland, and the South of Scotland, contains both lead and zinc minerals; the zinc, for the reasons already explained, is often found mainly in the lower parts of the ore-bodies. Some of the Flintshire lead-ores are nearly free from zinc. The galena, especially in Derbyshire, is associated with fine crystals of fluorspar. The ores of Belgium and the adjacent parts of Germany also occur mainly in a limestone of carboniferous age, now largely dolomitized. The ores are partly in veins, partly in cavities in the limestone, and are partly found replacing the limestone itself. The minerals are sulphides (zinc blende, etc.) below, and are oxidized substances (calamine, etc.) in the higher portions. The extensive ores of Silesia, which contain—in addition to lead and zinc—an appreciable quantity of silver, occur in a limestone of triassic age; here again we find sulphides below, and carbonates and silicates above. Another country rich in ores of lead and zinc is Spain; the zinc ores, consisting of blende in the lower portions and oxidized minerals in the upper portions, occur in various limestones—some of carboniferous age, but others of a much later date. Much zinc ore is now mined in Algeria.

The remarkable ores of lead, zinc, and silver which occur at Broken Hill, Australia, call for special remark. Here there are two big lodes; the main one measures 60–100 ft. across, and traverses a gneissic rock. It contains zinc blende and highly argentiferous galena, along with quartz, fluorite, garnet, and other minerals. The upper part is largely oxidized, the lead being

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[1] C. E. Siebenthal, *U.S. Geol. Surv., Bull.* **606** (1915).

[2] See also A. M. Finlayson, *Quart. J. Geol. Soc.* **66** (1910), 299.

present as carbonate, whilst at the junction of the oxidized and unoxidized portions, there is a zone of secondary enrichment containing abundant silver as sulphide.

METALLURGY AND USES [1]

Zinc—unlike most other metals—is a volatile substance, and the method of metallurgy is essentially a process of distillation. This process serves to separate zinc from the non-volatile metals such as iron, which is almost invariably present in zinc ores, and to some extent from lead, but not from other volatile metals, like cadmium. It is possible to treat the ores containing intimately mixed zinc and lead minerals, without previous separation, if the lead-content is not too large. Nevertheless it is very much better to subject the ores to a preliminary **concentration process,** so as to produce

(1) *a zinc concentrate,* and
(2) *a lead-silver concentrate,*

and, at the same time, to eliminate to some extent the less valuable minerals, such as quartz, calcite, pyrites, barytes, and fluorspar. The removal of the latter mineral is particularly important if it is intended to use the gases obtained during the roasting of the ore for making sulphuric acid, since fluorine would attack the lead chamber in which the acid is produced.

Various methods have been employed for the separation of the different minerals. **Gravity separation** on jigs and Wilfley tables gives fairly good results. Galena is much heavier than zinc blende, which in turn is heavier than quartz and calcite. **Magnetic separation** has also been employed; usually the ore is first given a short roast to convert pyrites to the magnetic oxide of iron. Treatment in the Weatherill separator (described in Vol. I, page 126) with a comparatively weak magnetic field serves to eliminate the magnetite. A magnetic process is used in America, for the elimination of iron from zinc ore.[2] Magnetic separation was also used at Broken Hill some years ago, where garnet and other iron minerals were separated by a preliminary treatment, and then, by subjecting the ore to a more powerful field, the blende was pulled out from the galena.[3] However, the process has there been superseded by **flotation,** which is found to be cheaper.

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[1] H. O. Hofman, "Metallurgy of Zinc and Cadmium" (McGraw-Hill); W. R. Ingalls, "The Metallurgy of Zinc and Cadmium" (*Engineering and Mining Journal*); E. A. Smith, "Zinc Industry" (Longmans, Green); T. E. Lones, "Zinc and its Alloys" (Pitman); R. G. M. Liebig, "Zink und Cadmium" (Spamer).

[2] E. G. Deutman, *Eng. Min. J.* **107** (1919), 1107.

[3] H. M. Ridge, *J. Soc. Chem. Ind.* **36** (1917), 676.

At first flotation was used simply to separate the zinc blende from the gangue, after the galena had been removed by gravity. Later it was found that galena adheres to the froth more easily than zinc blende, and that by carefully adjusting the conditions it is possible to separate, by flotation, first the easily flotable galena, and afterwards the less easily flotable blende. The differential flotation of zinc and lead has proved successful at Broken Hill, Australia.[1] More than one process is used there. In one method now practised,[2] the ore is subjected to a preliminary concentration by gravity. The heavier portions are ground and mixed with water; the pulp is then made weakly acid and is churned up with the addition of just enough eucalyptus oil to "lift" the galena, but not to "lift" the blende. In this way a "lead concentrate" is obtained. Then, after most of the lead has been taken out, the pulp is made rather more acid, and further oil is added—factors which are favourable to flotation—so that the blende also rises into the froth, and a "zinc concentrate" is obtained, the gangue remaining in the tailings. The zinc concentrate is usually further treated on Wilfley tables to take out part of the remaining galena.

Various devices have been tried for aiding the flotation of the "difficultly flotable" zinc blende. In many places, the zinc-flotation is carried out at a slightly elevated temperature, which is favourable to flotation. In one process, the pulp is saturated with sulphur dioxide gas during the flotation of the zinc blende.[3] This gas has a specific action upon the blende, facilitating adhesion to the oil in the froth. Various explanations have been offered for the action of sulphur dioxide, but further research is required before it is possible to decide between them.

The final zinc concentrates contain 47–50 per cent. of zinc and 4–5 per cent. lead, whilst the final lead concentrates have 60–63 per cent. lead and 8–13 per cent. zinc.

A process of "**concentration by volatilization,**" which has lately become important for obtaining a crude zinc oxide from low-grade ores, is described later in connection with zinc pigments. Although originally applied to the manufacture of pigments, it has lately been used as the first stage in the making of metallic zinc.[4]

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[1] V. F. S. Low, *Min. Mag.* **20** (1919), 211, 276; *Trans. Inst. Min. Met.* **28** (1919), 29.

[2] R. J. Harvey, *Trans. Inst. Min. Met.* **28** (1919), 5; H. K. Pickard, *Trans. Inst. Min. Met.* **28** (1919), 22.

[3] R. S. Dean, *Met. Chem. Eng.* **20** (1919), 372; G. C. Riddell, *Met. Chem. Eng.* **19** (1918), 822.

[4] W. R. Ingalls, *Eng. Min. J.* **104** (1917), 457; **105** (1918), 96.

The concentration of the ore is usually carried out—for obvious reasons—close to the place where it is mined. But the concentrate is then often shipped over a very considerable distance to one of the smelting centres, where the subsequent metallurgical operations are carried out. The chief smelting centres in Europe are Silesia, Westphalia, Belgium, and South Wales; Europe now depends mainly on imported ore or concentrate, although the industries originally grew up owing to the occurrence of local ore, or owing to the special suitability of some local clay for making the retorts used in the distillation. At present most British smelters use a clay imported from the Continent, but experiments with British clays have given good results.[1] The American smelters have both ores and fire-clay in their own country.

Previous to the war, most of the Australian concentrates had been under German control, and had been smelted in Germany or Belgium. With the outbreak of war, a sudden shortage of zinc in this country arose, and arrangements were made for treating the Australian supplies in England, a large amount being smelted at Seton Carew (Durham).[2] Provision was afterwards made in Australia to smelt an increased quantity of zinc in that country.[3]

Roasting of the Ore or Concentrate. When an ore or concentrate containing zinc as sulphide is to be used, it must first be roasted to convert the zinc to the state of oxide, which is then reduced with some form of carbon to metallic zinc in a separate operation. Where the ore is present as carbonate, roasting (as such) is not needed, but the ore must be calcined to drive off carbon dioxide and moisture. Owing to the partial exhaustion of the carbonate ores, the greater portion of the world's zinc supply now depends upon sulphide ores.

The roasting of the concentrates [4] is nearly always carried out in a multiple-hearth furnace, similar in some respects to those used for the roasting of copper ores. It is often desired that the sulphur dioxide produced in the roasting should be utilized for making sulphuric acid, and in such cases it is desirable that the sulphur dioxide should not be diluted more than is absolutely necessary with other gases. Sometimes a muffle furnace is employed, in which the hot gases from the fireplace do not pass directly over the concentrate, but around the outside of muffles within which

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[1] H. M. Ridge, *J. Soc. Chem. Ind.* **39** (1920), 6R.

[2] *Bull. Imp. Inst.* **13** (1915), 611; **14** (1916), 44.

[3] *Cham. Comm. J.* **36** (1917), 44.

[4] H. M. Ridge, *J. Soc. Chem. Ind.* **36** (1917), 676; J. C. Moulden, *J. Soc. Chem. Ind.* **38** (1919), 177R; M. de Lummen, *Chem. Trade J.* **58** (1916), 255; M. Hutin, *Mon. Sci.* **7** (1917), 25; M. F. Chase, *Eng. Min. J.* **104** (1917), 698.

the concentrate is roasted. Various forms of the multi-hearth furnace (both of the muffle-type and direct-heating type) are used. Furnaces rabbled by hand are still employed at many European works; in fact, even during the war—when manual labour was scarce—hand-rabbled furnaces were erected in this country.[1] In America a mechanical furnace, known as the Hegeler furnace, is largely used; it consists of seven hearths, one above the other, the lower hearths being heated by hot gases which pass along chambers between the various hearths. Periodically the ore is shifted from one hearth to the one below by means of a sort of plough which is dragged along the length of the hearth. The Hegeler furnace occupies a great deal of ground-space. The types of roaster furnished with revolving rabbles are more compact and are perhaps preferable. The Ridge furnace, which has proved very successful for the treatment of Broken Hill concentrates, is shown in Figs. 17 and 18. The ore is introduced on to the top hearth, which is used for the purpose of "drying" it. It is then worked by means of rabbles attached to rotating shafts through the three "roasting" hearths, and finally falls into the cooling hearth below, where it serves, whilst cooling, to preheat the air used in the roasting. The furnace is heated by gas which is burnt below the bottom roasting hearth only. The revolving shafts are water-cooled, and it is arranged that the rabble-parts which actually stir the ore, and which tend to wear out most quickly, can easily be detached and renewed, whenever this is required.

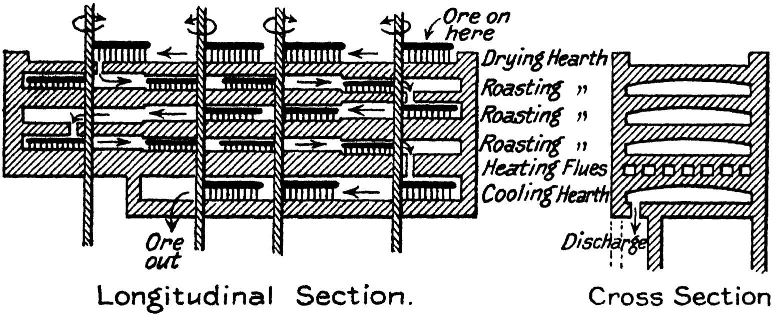

FIG. 17. FIG. 18.

Ridge Roaster.

In some countries—notably the United States[2] and Germany—a considerable proportion of the sulphur dioxide eliminated in the

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[1] H. K. Picard, *Trans. Inst. Min. Met.* **28** (1919), xxxviii.
[2] L. B. Skinner, *Met. Chem. Eng.* **18** (1918), 82.

roasters is used for acid-making ; in this country, the manufacture of sulphuric acid has been practised only to a comparatively small extent.[1]

One modification in the procedure for roasting zinc-ores which is being made at several spelter works may be mentioned. There has always been a difficulty in obtaining the complete elimination of the sulphur ; in order to effect this a rather high temperature is needed in the last roasting hearth. In the modified method, the ore is roasted in the multi-hearth roaster until the sulphur-content is reduced to 9 per cent., and then the remainder of the sulphur is eliminated in a Dwight-Lloyd sintering machine (see Vol. III, page 62). At the same time, if a powdery ore, or concentrate is being used, it becomes consolidated to a good porous sinter.

Reduction of the Roasted Ore. The reduction of zinc oxide by means of carbonaceous fuel is in principle a very simple process ; when zinc oxide and carbon are heated together strongly, the main reaction is probably

$$ZnO + C = Zn + CO.$$

The zinc will be carried off as vapour in the stream of carbon monoxide, and under favourable conditions can be condensed as molten zinc.[2] However, zinc in the vaporous condition is an easily oxidizable substance, and if the carbon monoxide were to become mixed with any considerable amount of carbon dioxide the zinc would be oxidized again ; moreover, the dilution of the carbon monoxide even with an inert gas would militate against efficient condensation. For these and other reasons, the charge of zinc ore and fuel cannot be heated by the direct passage of hot flames over the mixture—as in a reverberatory furnace. The mixture must be placed in some form of closed retort, and be heated through the walls of the retort. Usually the retorts are set in a gas-fired furnace, so designed that a flame of burning producer gas plays around the outside of the retorts. The furnaces are generally built on the " regenerative " principle, which was explained in connection with the manufacture of glass (Vol. II, page 60). In some recent furnaces, the " recuperative " system of heat economy has been employed, especially in Silesia.[3]

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[1] Compare *Rep. Insp. Alkali Works*, **56** (1919), 17 ; **57** (1920), 14.

[2] For considerations regarding the conditions of equilibrium, see E. Jänecke, *Met. u. Erz*, **16** (1919), 247. M. Lemarchands, *Rev. Met.* **17** (1920), 803 ; *Comptes Rend.* **170** (1920), 805, discusses the question as to whether carbon, or carbon monoxide, constitutes the effective reducing agent for zinc.

[3] H. M. Ridge, *J. Inst. Met.* **16** (1916), 188.

The retorts in which the charge is heated require to be made of a specially selected variety of fire-clay ; only the best fire-clay will withstand the very high temperature without softening. It is necessary, as far as possible, to choose a clay which will withstand the fluxing action of the hot ferrous oxide and other bases contained in the charge.[1] But however excellent the material and manufacture, the retorts only have a limited life, which has been estimated as being—on the average—four to six weeks.[2] Consequently arrangements must be made for the manufacture of new retorts ; retorts are now usually made by means of a specially designed hydraulic press ; a ball of plastic clay mixture is pressed into the necessary form, and, after drying, is burnt at a very high temperature in a furnace. The retorts formerly varied considerably in shape and size, and were classified as **Silesian** (large D-shaped muffles), **Rhenish** (medium, D-shaped), and **Belgian** (small, circular tubes). But now the intermediate (Rhenish) size of retort is tending to displace the others throughout all the European smelting districts (including this country), although some American works still adhere to the use of smaller retorts. The average size of a retort may now be taken as 6 in. in breadth, 12 in. in height, and 5 ft. in length. The large (Silesian) muffles are now but little used.[3]

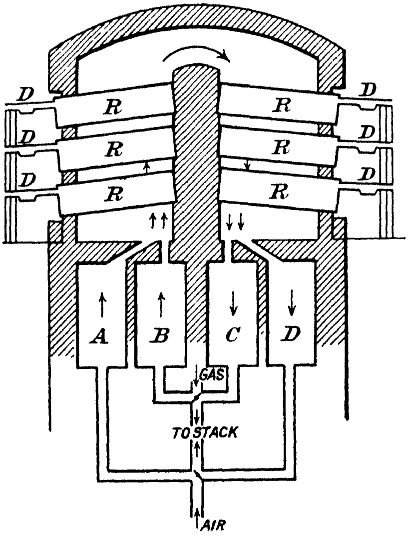

FIG. 19.—Principle of the Regenerative Zinc-distillation Furnace (Cross-section).

The retorts R are set in the furnace in the manner indicated in Figs. 19 and 20. They are placed parallel to one another in rows, so that they lie horizontally, or (more usually) are made to slope gently downwards towards the mouth. There may be three to seven rows in a furnace, each containing six to forty retorts. Often,

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[1] O. Proske, *Met. u. Erz*, **11** (1914), 333, 377, 412, 553, discusses the action of slag, vapour, etc., on different kinds of retorts.

[2] G. C. Stone, *Trans. Amer. Electrochem. Soc.* **25** (1914), 161. Other authorities give similar estimates.

[3] A. Rzehulka, *Zeitsch. Angew. Chem.* **27** (1914), i, 327.

as shown in Fig. 19, the furnaces are double, having two series of retorts on either side of a central partition. The open mouths of the retorts are accessible from the outside of the furnace. To these mouths can be fitted the tubular or conical "adapters," D, open at both ends. The adapters, which are composed of a clay-mixture similar to that used in retort-making, serve as condensers for the zinc vapour. Usually an iron nozzle—or "prolong"—is fitted to the further end of each adapter, to catch particles of metal carried by the gases through the adapters, or to condense a further portion of the vapour.

The producer gas which serves as fuel is formed in an external "producer." If the furnace is built on the regenerative principle, both producer gas and air are drawn in through hot regenerators (B and A), and are thus extremely hot when they enter the furnace. Their combination produces an intensely high temperature around the outside of the retorts; for successful zinc-smelting a temperature of about 1325–1350° C. should be reached. The hot products of combustion pass out through two other regenerators, C and D, to which they give up much of their heat. The course of the gases through the regenerators is periodically changed, just as in the working of the regenerative glass-furnaces and steel-furnaces.

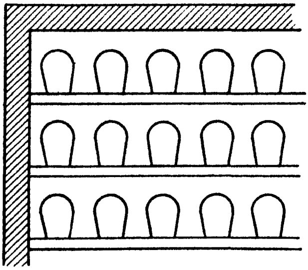

FIG. 20.—Zinc Distillation Furnace (Longitudinal Section), showing Arrangement of Retorts in Rows.

The smelting operation is conducted as follows. The roasted ore or concentrate is mixed with coal (preferably anthracite) and the retorts are charged with this mixture, either by hand or by machine, the furnace being comparatively mildly heated during the charging; sometimes salt is also introduced into the retort, as it is found to diminish the amount of "blue powder" produced. When the retort is filled, the adapters are put into position at the mouth of the retorts, the heating is increased, and distillation begins. At first the zinc vapour passing through the adapters is oxidized by the oxygen or carbon dioxide therein contained. Later, when carbon monoxide has largely displaced the dioxide from the adapter, metallic zinc begins to condense. The first portions of zinc metal, however, condense to minute liquid globules, which, becoming slightly oxidized on the surface, do not coalesce to form molten zinc; they remain as a "fume" and are carried into the nozzle, where they cool to a "blue powder." These first condensed portions of the zinc contain nearly all the cadmium present in the ore ; for this metal, being more easily reduced and also more volatile than zinc, distils over in the early stages.

After some time, zinc vapour begins to come over in increased quantity, and, the proportion of carbon dioxide being now so low that little further oxidation of zinc can occur within the adapter, molten zinc begins to form. Once, twice, or three times a day the molten metal is drawn out from the condensers (usually by means of a tool shaped rather like a gardener's hoe) and is allowed to fall into a kettle placed to catch it ; after skimming, it is poured into moulds and allowed to solidify. As stated above, however, it is difficult to bring about complete condensation of the zinc vapour, and there is still a certain production of powder, consisting of zinc particles coated with oxide, often mixed with a portion of the charge carried over mechanically from the retorts, and nearly always containing a good deal of lead. This powder will be found in the nozzle, and on the ground in front of the furnaces ; it can be collected and returned to the retort during the next charge ; but about 10 to 20 per cent. of the zinc is usually lost, presumably by passage into the open air, and by absorption into the material of the retort and adapter.[1] In the old Silesian muffles the loss was higher. An important cause of loss—not always fully appreciated—is due to the zinc vapour which remains in the retort after the distillation is complete.[2] The amount lost by combination of zinc oxide with the retort material is very serious in new retorts, but practically negligible in old ones.[3]

The residue left in the retorts usually contains much lead, and is often sold to the lead smelter. The silver present in the ore is also largely preserved in this " leady residue."

Electrothermal Smelting.[4] The wastage inherent in the ordinary zinc-furnace practice depends ultimately upon the fact that heat has to be conveyed to the charge *through the walls* of the retorts. In the first place, this involves the exposure of the materials of these walls to a white heat, and is particularly disastrous in view of the corrosive nature of the bodies present in the retorts ; in actual practice, whether the retorts become worn out by chemical corrosion or through thermal softening, the retorts have frequently to be replaced. Secondly, in order to maintain the materials within the retorts at the required temperature, an even higher temperature must be produced outside the retorts. The amount of heat lost

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[1] H. L. Sulman, *Trans. Inst. Min. Met.* **20** (1910), xxxv.
[2] A. Rzehulka, *Chem. Zeit.* **38** (1914), 895.
[3] O. Mühlhaeuser, *Met. u. Erz*, **18** (1921), 1, 45.
[4] W. R. Ingalls, *Trans. Amer. Electrochem. Soc.* **25** (1914), 169.

by radiation and carried off by the hot gases leaving the furnace is greater, therefore, than in a reverberatory furnace, where the heating gases are allowed to play directly upon the charge. The losses are reduced, but are not eliminated, by the use of the regenerative or recuperative system.

Now the electrothermal method of zinc-smelting provides a means of heating the mixture of zinc oxide and coal, without unduly heating the containing walls, and without introducing a stream of hot gases. A strong current of electricity is made to pass through the charge, producing the very high temperature needed for the reduction of zinc oxide and the distillation of the zinc ; the electricity is only used as the means of maintaining the high temperature, and the reduction is not to be looked upon as electrolytic. In an electrothermally heated charge, the walls and floor may be kept comparatively cool ; it is only the part of the charge between the electrodes that is heated, and the corrosion and heat-loss by radiation is reduced to a minimum. One authority[1] stated in 1914 that the calorific efficiency of the " most modern " retort furnaces of the gas-fired type was only 8 per cent., whilst that of the electric furnace was 60 per cent. Electrothermal smelting, therefore, would seem to have many advantages in places where electric power is cheap.

Nevertheless the first Swedish attempts to distil from an electric furnace were by no means successful, owing to the large amount of blue powder produced ; and although the troubles due to this cause, which are further discussed below, have to a large extent been overcome, yet the difficulties seem to have acted as a deterrent to the employment of electrothermal methods elsewhere. At any rate, the use of such methods has been confined hitherto to a few localities.

The type of furnaces used in the De Laval process at Trollhätten, Sweden,[2] are of the resistance type ; there is no arc, the heat being developed by the passage of the electricity through the charge. A large vertical electrode of carbon passes through the roof, whilst the other electrode is a carbon block set at the bottom of the furnace. The charge is a mixture of partly roasted ore (containing a great deal of lead and as much as 7 per cent. of sulphur still uneliminated) with coke (or anthracite) and flux. It is introduced through a hopper. Zinc and lead are reduced to the metallic condition and the zinc is volatilized and passes to the condenser ; molten lead and slag collect at the bottom of the furnace, and also a certain amount

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[1] C. V. Lordier, *Met. et Alliages*, 7 (1914), No. 12, 1.

[2] See report by Mr. F. W. Harbord : Abstract, *Eng. Min. J.* **93** (1912), 314. See also E. A. Smith, *J. Inst. Met.* **16** (1916), 156.

of matte (a fused mixture of sulphides). These are run out together from a tapping-hole. The silver present in the ore is found partly in the metallic lead, and partly in the matte.

The main difficulty experienced at first was that at least two-thirds of the zinc condensed in the state of blue powder ; only one-third condensed as ordinary liquid zinc. The type of blue powder obtained there was of no commercial value ; it contained only about 54 per cent. of zinc, with much lead, as well as dust from the furnace charge. The powder was simply returned to another electric furnace, mixed with some fresh roasted ore, and distilled again. Thus, on an average, each atom of zinc passed through the furnaces three times before it reached the commercially useful condition.

This state of affairs was clearly unfavourable to the success of the process, and led, for the first time, to a scientific consideration of the conditions of condensation, which determine whether the metal shall condense in the valuable form of " liquid zinc " or as comparatively worthless " blue powder." It will be noticed that the De Laval process differs from the classical process of retort-smelting in much more than the substitution of electrical heating for gas heating. It is a highly ambitious attempt : (1) to substitute one large still in the place of numerous small retorts ; (2) to substitute semi-continuous hopper-charging for the intermittent charging of retorts ; (3) to treat complex ores containing much lead, and only partly freed from sulphur ; and (4) to make metallic lead at the same time as metallic zinc, and to tap the former in the molten state. Thus the process departed in four important respects from the old method of distillation and condensation, which represented the experience of nearly a century ; the fact that difficulties were experienced at first is scarcely surprising.

The main factor which causes the condensation of zinc as blue powder [1] is the presence of carbon dioxide or moisture—the former being dependent on the introduction of air when the furnace or retort is charged. In the Rhenish retort process, where small retorts are used, and the content of zinc in the charge is high, the fraction of the total zinc oxidized is small ; moreover, in the Rhenish process the heating is slow, and most of the carbon dioxide and moisture are driven off before ever the distillation of zinc begins. In the electric furnace, the state of affairs is different ; the amount of air introduced in hopper-charging is much larger ; and, since in Sweden a low-grade ore is used, the ratio of air to zinc is greater than if a high-grade ore were employed. Further, the heating is rapid, and the carbon dioxide, moisture, and zinc pass over practically simul-

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[1] A. Stansfeld, *J. Inst. Met.* **15** (1916), 289 ; G. C. Stone, *Trans. Amer. Electrochem. Soc.* **25** (1914), 162.

taneously. The fact that two-thirds of the zinc is condensed as blue powder is easily understood.

Various means have been suggested to reduce the amount of carbon dioxide in the "exit gases," one being the increase of coke in the charge. Experiments have shown that by passing the vapours through a space filled with incandescent carbon, the formation of blue powder can largely be avoided.

There is, however, another important cause of the formation of powder, namely, an unduly low temperature in the condenser.[1] If the condenser is only slightly below the *boiling-point* of zinc, the metal will condense only on the walls, and the drops of liquid first formed may grow, and coalesce. If, however, the temperature of the whole vessel is below the *melting-point* of zinc, small globules of zinc will appear in suspension in the gas as it passes through the condenser; these globules will have no chance to coalesce before they become solid. Thus a powder is produced instead of compact zinc. Evidently the temperature should be kept between the boiling-point and the melting-point of zinc. In some experimental plants,[2] the artificial heating of the condenser has been applied, but in a manufacturing plant this ought not to be necessary.[3]

The type of blue powder due to an abnormally cool condenser can usually be melted up to form ordinary compact zinc, whereas the oxide-coated powder due to the presence of carbon dioxide cannot be melted.

By maintaining proper conditions of working the special technical difficulties met with in Scandinavian smelting have—it is understood—largely been overcome. Outside Scandinavia, several attempts have been made to distil zinc by electrothermal methods, but it seems unlikely that the industry will become established except where power is very cheap. Towards the end of the war, zinc was being manufactured near Cologne in an electric furnace of a cylindrical form, which revolved about a horizontal axis.[4] Another interesting process[5] has been worked out in France, in which an unroasted sulphide ore of zinc and lead is heated with metallic iron. The iron removes the sulphur from both lead and zinc; the former is tapped molten and the latter volatilizes. The zinc vapour passes through a chamber filled with incandescent coal, before entering the condenser, and thus carbon dioxide is removed, and the production of blue powder is avoided. In one

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[1] Compare F. L. Clerc, *Met. Chem. Eng.* **11** (1913), 637.

[2] For instance, that described by T. M. Bains, *Met. Chem. Eng.* **26** (1922), 894.

[3] F. T. Snyder, *Trans. Amer. Electrochem. Soc.* **19** (1911), 328.

[4] A. J. Allmand and E. R. Williams, *J. Soc. Chem. Ind.* **38** (1919), 303R.

[5] C. V. Lordier, *Met. et Alliages,* **7** (1914), No. 12, p. 1.

modification of this process, the unroasted ore is heated with lime and fuel, no iron being added to the charge.

Effect of Impurities. The zinc produced at the smelting works is usually impure, containing lead, iron, and generally cadmium. A great deal of purification can be effected by carefully remelting it, at a regulated temperature in a small furnace. Most of the lead (which is only slightly soluble in molten zinc) forms a separate layer at the bottom, whilst a zinc-iron alloy sometimes separates just above the lead. Obviously, however, the zinc is not completely purified in this way. A good deal of zinc is now purified in the United States by redistillation ; a product containing only 0·1 per cent. of lead is obtained.[1] Where, as in Sweden, complex ores containing much lead have been used as raw material without preliminary concentration, a very " leady " zinc is obtained, and redistillation becomes an essential part of the smelting process.

At many zinc-works it is customary to collect separately the distillate coming over at different stages of the operation. The first portions contain most cadmium, the latter most lead. The " brass-special " spelter made at American works consists of the earlier (lead-free) portions, which are most satisfactory for brass-making.

The effect of different impurities on zinc has been the subject of some discussion.[2] Most impurities increase the susceptibility to corrosion ; lead in small quantities has but little effect on the mechanical properties of zinc itself, but renders it unsuited for brass-making ; iron up to 0·1 per cent. has no effect, but large quantities make it hard and brittle. Cadmium renders zinc hard, and to some extent brittle ; the hardness of commercial spelter is dependent largely on its cadmium content. Zinc containing cadmium is unsuited for making galvanized wire, as the coating would soon peel off, but—in the amounts usually met with—cadmium does not render zinc unsuited for brass-making.

The difference in hardness between pure zinc and commercial spelter is much more marked in the worked state than in the cast state, because, whilst the pure metal undergoes self-annealing at quite low temperatures, the commercial metal can be obtained, and preserved, in the work-hardened condition.[3] For the manufacture of zinc sheet, a metal with about 1·25 per cent. of lead and 0·25 per cent. of cadmium is preferred ; the addition of 1 per cent.

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[1] W. R. Ingalls, *Eng. Min. J.* **105** (1918), 96.

[2] G. C. Stone, *J. Amer. Inst. Met.* **12** (1918), 11. W. R. Ingalls, *J. Inst. Met.* **16** (1916), 196 ; G. Rigg and G. M. Williams, *Proc. Amer. Test. Mat.* **13** (1913), 669.

[3] C. H. Mathewson, C. S. Trewin, and W. B. Finkeldey, *Bull. Amer. Inst. Min. Eng.* **153** (1919), 2775.

of copper to zinc is said to improve the rolling properties considerably.[1]

Electrolytic Reduction of Zinc. Although the electrolytic deposition of zinc has been carried out at intervals for a long time in different parts of the world, it has only recently become of considerable importance. It is especially suited for the extraction of zinc from certain complex ores. Many American lead-silver ores containing a certain amount of zinc are concentrated to give a product rich in lead and silver, but the portion containing the zinc has until recently often been wasted.[2] In such cases, it may prove profitable to roast the zinc-concentrate, leach with sulphuric acid, and, after purification of the solution, to electrolyse it, thus producing metallic zinc of great purity (which commands a high price), the acid being, at the same time, regenerated. The process, however, will only prove remunerative where power is cheap, and electrolytic zinc-production on a large scale is confined to a few localities, the most important being Trail (British Columbia),[3] Great Falls (Montana),[4] and certain places in Tasmania and Australia.[5]

The main requirements for successful electrolytic zinc-production are that the roasting should be conducted at a low temperature, and that the solution should be scrupulously freed from other metals before electrolysis. If the roasting is conducted much above 700° C., a very stable zinc ferrite, $ZnO.Fe_2O_3$ (probably identical with the mineral franklinite), is formed by combination of zinc oxide with the oxide of iron present in the material. This stable compound is almost insoluble in sulphuric acid, and when the roasted material is afterwards leached, the extraction of zinc will be very poor.[6] Cases of extraordinarily poor yields of zinc obtained by electrolytic methods, which have been reported from time to time, have almost always been due to an unduly high roasting temperature. Both at Trail and at Great Falls the roasting of the material is carried out in a multiple-hearth furnace. At Trail the temperature is said to be kept below 600° C.; at Great Falls, below

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[1] J. L. Haughton, *Met. Ind.* **18** (1921), 4; Hanszel, *Zeitsch. Metallkunde*, **13** (1921), 209.

[2] T. French, *Trans. Amer. Electrochem. Soc.* **32** (1917), 321.

[3] E. H. Hamilton, *Trans. Amer. Electrochem. Soc.* **32** (1917), 317.

[4] O. C. Ralston, "Electrolytic Deposition and Hydrometallurgy of Zinc" (McGraw-Hill); W. R. Ingalls, *Trans. Amer. Electrochem. Soc.* **29** (1916), 347; W. N. Ingalls, *Met. Ind.* **11** (1917), 345. Compare H. O. Hofman, *Eng. Min. J.* **105** (1918), 93.

[5] *J. Soc. Chem. Ind.* **40** (1921), 48R; J. A. Zook, *Min. Ind.* **28** (1919), 734.

[6] E. H. Hamilton, G. Murray, and D. McIntosh, *Trans. Can. Min. Inst.* **20** (1917), 168, gives details of the conditions of formation of zinc ferrite on roasting.

730° C. The leaching of the calcined ore by acid presents a problem rather similar to that involved in the leaching of copper ores or the cyaniding of gold tailings. The counter-current principle is commonly used, so that the fresh "calcine" comes in contact with practically neutral solutions, whilst the nearly exhausted calcine containing but little soluble zinc is acted upon by fresh and highly acid liquors.

The zinc sulphate solution—before it is suitable for electrolysis—must be free from all metals more noble than zinc; for if a solution containing such a metal as copper were electrolysed, corrosion couples would be set up on the cathode, and the resultant current efficiency of zinc-deposition would prove to be very low.[1] Of the different impurities likely to be present, iron is usually removed during the leaching by blowing air into the tanks, which serves to bring the whole of the iron to the ferric state. In the final leaching tank, where the acidity of the liquor is completely removed through the presence of excess of calcined ore, hydrolysis occurs, and the whole of the iron is precipitated as ferric hydroxide, which is separated—along with the insoluble part of the ore—in a series of classifiers, thickeners, and filter-presses. At some works the precipitation of the iron is carried out by means of limestone. From the clear iron-free solution of zinc sulphate, copper and cadmium are precipitated in metallic form by the addition of zinc dust. The solution is then ready for electrolysis, which is often conducted between lead anodes and aluminium cathodes. An E.M.F. of about 3·4–3·8 volts per cell is commonly employed. The cathodes are periodically taken out and the zinc deposit stripped off. When a large fraction of the zinc has been deposited, and the bath is becoming distinctly acid, it is drawn off and used to leach a further quantity of calcine. The solution leaving the cells may contain 6–10 per cent. of free sulphuric acid and 2–4 per cent. of zinc as sulphate; after the next leaching the zinc content will be as high as 6–8 per cent. and the free acid will have disappeared.

The current efficiency of deposition naturally depends greatly on the purity of the bath; with ordinary precautions it can be kept as high as 93–94 per cent. The deposit of zinc is quite sufficiently good, if impurities such as copper and nickel are absent; but it will contain pin-holes, due to minute corrosion couples, if the solution is foul. It is impossible to obtain satisfactory deposits of zinc in the presence of appreciable quantities of the metals mentioned. In some cases, where an impure solution is used,

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[1] C. A. Hansen, *Bull. Amer. Inst. Min. Eng.* **135** (1918), 615; S. Field, *Trans. Faraday Soc.* **16** (1921), 492; G. D. Scholl, *Met. Chem. Eng.* **26** (1922), 595.

" beards " of zinc may be formed, the deposition proceeding rapidly where the current density is high (i.e. at the tips of the beards), whilst elsewhere zinc is actually being corroded away; sometimes the impurities "eat holes" right through the deposit. Of the objectionable impurities, copper and iron are easily removed, as stated above; but nickel, if present in the ore even in small quantities, will tend to accumulate in the bath—not being co-deposited with the zinc. Ores containing nickel are therefore unlikely to be suitable for electrolytic treatment. Minute traces of cobalt or antimony cause very serious corrosion to the deposit; arsenic is also objectionable.

Manganese, which is present in many zinc-ores, is not harmful, and its presence is stated by some writers[1] to be essential to good working. Probably the principal benefit derived from the presence of manganese is that manganese dioxide is deposited on the lead anode, and reduces the danger of the lead sulphate passing into suspension in the bath, which would be highly undesirable.

Many authorities recommend the addition of organic substances,[2] such as glue or naphthol, in order to improve the deposit obtained, and to increase the current efficiency; others say that the bath works best without doctoring.[3] It seems probable that some of the additions advocated are very distinctly beneficial; but it is certain that no addition will cause a good zinc deposit to be obtained from a really foul bath. Glue is said also to aid the adhesion of manganese dioxide to the anode, and prevents the "sulphating" of the lead.

The zinc obtained by these electrolytic methods is extraordinarily pure, 99·95 per cent. purity having been reached in Australia. Until a few years ago electrolytic zinc was produced in this country (at Winnington, Cheshire). Here a zinc chloride bath was obtained by the leaching of zinc oxide with waste calcium chloride solution in the presence of carbon dioxide; the calcium chloride was a by-product of the ammonia-soda alkali process. The method is now abandoned. Recently, however, the employment of electrolytic methods of zinc production or recovery in this country has found several advocates.[4] A German authority suggests the electrolytic recovery of zinc from the dusty mixture of zinc and zinc oxide, obtained

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[1] F. D. James, *Univ. Miss. Bull.* **4** (1917), No. 1, p. 24. Compare T. French, *Trans. Amer. Electrochem. Soc.* **32** (1917), 326.

[2] O. P. Watts and A. C. Shape, *Trans. Amer. Electrochem. Soc.* **25** (1914), 291. Compare C. A. Hansen, *Bull. Amer. Inst. Min. Eng.* **135** (1918), 642, 643.

[3] D. McIntosh, *Trans. Roy. Soc. Canada,* **11** (1917–18), 113.

[4] S. Field, *Trans. Faraday Soc.* **17** (1922), 400. Compare S. C. Bullock, *Met. Ind.* **16** (1920), 121.

when brass-scrap is " blown " in a converter for the recovery of the copper.[1]

Uses of Zinc.[2] The main uses of zinc are founded upon the fact that it is—under ordinary conditions and in the absence of free acid—remarkably resistant to corrosion. Zinc sheet, made by rolling the metal between 100° and 150° C., is itself used for domestic articles, such as bath-tubs, pails, etc., as well as for roofing and for lining boxes ; it can be stamped with ornamental designs for ceilings, and the like ; zinc castings also have been made for ornamental purposes. For use on a large scale, however, the so-called " galvanized iron," which consists of steel covered with zinc, is employed, as it combines the cheapness, strength, and comparative rigidity of steel with the non-rusting character of zinc ; both galvanized sheet and galvanized wire are made on a large scale, the methods being discussed below.

Other uses for zinc depend, on the contrary, on its electromotively " active " character. Zinc is used almost universally as the attackable material of primary batteries. Of these the Leclanché cell in the " dry " form is by far the most important ; it has been described in the section devoted to manganese (Vol. II, page 380). The employment of zinc to precipitate more noble metals, just as gold and silver, from their solutions has been referred to in connection with those metals ; zinc dust is tending to replace zinc shavings for this purpose, and many varieties of " blue powder " can be used with good effect. At different times during recent years, the amount of by-product dust suited for this and other purposes has not been equal to the demand, and in 1916 atomized zinc was being purposely manufactured in the United States.[3]

Another industry which accounts for the consumption of a large proportion of the world's zinc production is the manufacture of **alloys**. Of these, brass is the most important, although others, such as German silver, zinc-bronze, and the light alloys of zinc with aluminium and other metals, may be referred to ; they have all been discussed earlier in this work.

Galvanized Iron

For the protective coating of iron against rust, zinc is probably used more extensively than any other metal. It is more useful than tin and nickel, for instance, owing to its cheapness and owing to the

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[1] Compare H. Paweck, *Zeitsch. Elektrochem.* **27** (1921), 16.

[2] E. A. Smith, *J. Inst. Met.* **16** (1916), 164 ; J. C. Moulden, *J. Roy. Soc. Arts*, **64** 1916), 519.

[3] H. J. Morgan and O. C. Ralston, *Trans. Amer. Electrochem. Soc.* **30** (1917), 230.

fact that zinc—being less " noble " than iron—continues to protect it to some extent, even if the covering contains pin-holes or is otherwise discontinuous. In certain manufacturing towns, however, where acid substances, like sulphur dioxide, occur in large quantities in the air, galvanized iron is quickly attacked.[1] Moreover, owing to the poisonous character of zinc salts, zinc-covered iron cannot be used for the canning of food-stuffs.

There are four distinct methods used for producing a layer of zinc upon iron. These are :

(1) Dipping the article in a bath of molten zinc (**hot galvanizing**).
(2) Heating the article in zinc dust (**Sherardizing**).
(3) **Electro-deposition** from an aqueous solution of a zinc salt.
(4) **Spraying** the article with zinc globules by means of a special gas-jet (**Schoop process**).

Hot galvanizing[2] is the oldest process, and has long retained its popularity in this country. In 1913 practically the whole of the British production of galvanized sheets and wire were still produced by the hot method.

Before dipping into molten zinc the articles must be scrupulously cleaned. Sand-blasting is useful, but it must usually be followed by chemical cleaning. Pickling in hydrochloric acid is quick and effective, but leaves the metal super-saturated with hydrogen, and consequently hard and somewhat brittle. In low-carbon steels, such as are used for galvanized sheets and for fencing wire, this brittleness is not serious ; but for high-carbon steel of high tensile strength, such as is used for colliery-windings, the danger of such brittleness must not be overlooked.

The molten zinc to be used in the galvanizing is usually contained in tanks of steel, which may be heated by gas, by oil, or by coke. Often there is a layer of molten lead at the bottom of the tank, below the molten zinc ; the lead serves to protect the bottom, and facilitates the removal of the dross (see below). A little aluminium is often dissolved in the zinc to increase the fluidity ; this practice appears to be more common in America than in this country. Ammonium chloride is thrown on to the surface of the molten metal from time to time to prevent undue oxidation, and to take up any zinc oxide that may be formed. If it is omitted the zinc oxide formed upon

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[1] H. Wislicenus, *Zeitsch. Angew. Chem.* **33** (1920), i, 204.

[2] N. K. Turnbull, *Iron Coal Trades Rev.* **88** (1914), 783, 829 ; *J. West Scotland Iron Steel Inst.* **21** (1913–14) 192. M. Sang, *Rev. Met.* **9** (1912), 78. J. R. Wemlinger, *Met. Ind.* **18** (1921), 388.

the surface tends to encase the articles as they pass through it, and interferes with the adhesion of the zinc. It is considered advantageous to have a voluminous foamy covering upon the surface, where the articles enter the bath, as it serves to remove any last traces of oxide which may remain on the articles. Glycerine is commonly added, as it is found to facilitate the formation of a covering having the desired character. The zinc bath should be kept as cool as is consistent with complete fusion, so as to avoid undue loss by volatilization.

The iron articles, previously cleansed, are then introduced, and are kept in the bath long enough to reach the temperature of the zinc ; they should not be immersed for longer than is necessary, or brittleness may result. Where wire is being galvanized, it is allowed to pass continuously through the bath. Where sheets are to be galvanized, the bath is sometimes equipped with a pair of internal rolls between which the sheets pass ; these internal rolls pass the sheets on to the " exit rolls," through which the sheet leaves the molten metal.

The article on being withdrawn is found to be covered with a layer of zinc, and when the article has cooled down, the zinc will be observed to have crystallized out from centres, producing the familiar " spangled " patterns which are characteristic of hot-galvanized iron. Owing to the extreme thinness of the coating, the number of nuclei produced per unit area is generally small, and the individual spangles are of considerable size. At the edge of a sheet where the zinc layer is generally thicker, the area of the crystal-grain is often smaller. The size of the spangles depends also on the composition of the molten zinc and of the steel. In America, " large-spangled " sheets are said to be favoured, being believed to be less liable to corrosion ; some manufacturers are stated to use a steel containing titanium, in order to obtain the spangles of the size desired.[1]

It must not be supposed, however, that the coating produced on galvanized iron consists of pure zinc throughout. Only the surface itself consists of anything like pure zinc, and below it are layers of zinc containing iron, the iron-content increasing as we go lower into the metal.[2] In the intermediate layers, the inter-metallic compounds $FeZn_3$ and $FeZn_7$ are present. The existence of these

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[1] *J. Soc. Chem. Ind.* **39** (1920), 14R.

[2] H. S. Rawdon, M. A. Grossman, and A. N. Finn, *Met. Chem. Eng.* **20** (1919), 530 ; H. S. Rawdon, *Proc. Amer. Soc. Test. Mat.* **18** (1918), 216 ; W. Guertler, *Int. Zeitsch. Met.* **1** (1911), 353 ; Y. Taji, *Engineering*, **109** (1920), 327 ; H. Winter, *Rev. Met.* **7** (1910), 1064. Compare U. Raydt and G. Tammann, *Zeitsch. Anorg. Chem.* **83** (1913), 257, who discuss the equilibrium diagram of zinc-iron alloys.

intermediate layers increases, no doubt, the adhesion of the zinc to the iron, but some of the zinc-iron compounds are very brittle, and, if the intermediate layer is too thick—which will be the case if the immersion in the liquid zinc has been lengthy—the coating may tend to crack. Sometimes the intermediate layer cracks, whilst the comparatively pure zinc on the surface remains intact.

The hot-galvanizing process is extravagant of zinc. Not only is the layer produced thicker than in the other processes, but a considerable amount of zinc is lost through the formation of oxide upon the surface, as well as through the formation of solid iron-zinc alloys (dross) within the bath ; the dross sinks to the bottom of the tank and is periodically removed with a perforated scoop. As regards the thickness of the layer, experience is teaching the manufacturers how to reduce it ; but it is stated that the new, thin-coated, galvanized iron is less durable, under adverse climatic conditions, than the old material.[1] Conservative buyers will probably continue to demand hot-galvanized iron for some time to come, owing to the absence of the familiar " spangles " on the products of the other processes.

The second method of producing galvanized iron, namely, by heating in zinc-dust, is called "**Sherardizing,**" after the inventor.[2] The articles are packed in zinc dust contained in air-tight drums which are placed in a furnace heated by gas or by electricity, and kept for a few hours at 250°–400° C. Many types of the by-product " blue powder " can be used as zinc dust, but it should preferably contain as much as 85–90 per cent. of zinc ; the presence of a certain amount of zinc oxide on the particles is actually beneficial, in order that the powder may be heated above the melting-point of zinc without running.

It is commonly stated that the layer of zinc—or rather of zinc-iron alloy—produced by sherardizing is due to the action of zinc vapour on the iron. This may be true at the higher temperatures, but at 250° C., a temperature actually employed for the sherardizing of steel springs, the vapour pressure of zinc is extremely small. Under these conditions, it is probably a contact action between solid zinc and iron.[3] It is noteworthy that if certain parts of the article are not in close contact with the zinc dust, they escape galvanizing.

The third method of producing a zinc deposit is by **plating the**

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[1] A. S. Arguelles, *Philippine J. Sci.* **11** (1916), 177 ; J. C. Witt, *Philippine J. Sci.* **11** (1916), 147.

[2] Sherard Cowper-Coles, *J. Soc. Chem. Ind.* **28** (1909), 399. See also *Machinery*, **5** (1915), 613 ; M. Sang, *Rev. Met.* **9** (1912), 275, 343.

[3] J. W. Hinchley, *Trans. Faraday Soc.* **6** (1911), 133 ; O. W. Storey, *Met. Chem. Eng.* **14** (1916), 683.

article electrically from an aqueous solution of a zinc salt. Sometimes a solution of the sulphate is employed for this purpose,[1] the solution being generally kept faintly acid; some of the baths recommended contain acetic acid. Various addition agents are frequently included in the bath in order to improve the deposit; aluminium sulphate is often added, whilst the presence of glucose is said to cause brilliance in the coating. Recently a cyanide bath has come into favour, as it is said to have a better " striking power "; that is, it allows zinc to be deposited in the depressions of irregularly shaped objects. The bath can be prepared by stirring zinc oxide into a solution containing sodium cyanide and sodium hydroxide.[2]

A zinc-plating bath must obviously be free from other more noble metals, and, since the very conditions needed for a good current efficiency depend on the absence of corrosion, it may be expected that the deposit formed electrolytically will protect the underlying metal extremely well. Naturally the articles, before plating, must be freed most scrupulously from all grease and oxide. The current density employed is about 2–3 amps. per sq. dm. with the cyanide bath, but may often be rather higher with a sulphate bath. The articles are usually kept in motion; small articles can be placed in perforated drums which are rotated during the operation, whilst wire is reeled through the bath continuously and comes out with a covering of zinc.

The electrolytic deposition of zinc has been advocated for the galvanizing of the cables used for the suspension of the cages in mines, where some authorities regard hot galvanizing as dangerous, owing to the possible formation of brittle iron-zinc compounds.[3] The intermediate layer of iron-zinc alloy which is present on hot-galvanized articles is absent—or at least is very thin—on electro-galvanized iron.

A method of applying a protective coating of zinc by spraying (**Schoop's process**) has recently become very popular in Germany and elsewhere, since it has proved useful for treating large objects which are difficult to galvanize in other ways. The " spray " of zinc is applied by means of a " pistol " which is held in the hand and is directed at the part of the surface to be coated. The pistol[4] contains mechanism which causes a zinc wire to be fed forward towards the mouth, where the zinc is melted by a jet of coal-gas or acetylene, which blows out a spray of fine zinc globules from the mouth of the pistol upon the surface to be galvanized. The wires

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[1] M. Sang, *Rev. Met.* 9 (1912), 160.

[2] W. Blum, F. J. Liscomb, and C. M. Carson, *U.S. Bur. Stand. Tech. Paper* **195** (1921).

[3] K. Arndt, *Zeitsch. Angew. Chem.* **29** (1916), iii, 77.

[4] M. V. Schoop, *Met. Ind.* **16** (1920), 41. *Amer. Machinist,* **55** (1921), 647.

are fed forward at the same rate as they are consumed. Various modifications of the process have been introduced ; in some forms the heat is produced electrically.[1]

Technically important Compounds of Zinc

Manufacture of Zinc Oxide. It has been repeatedly stated above that it is very difficult in zinc-distillation to prevent a certain amount of the zinc being burnt to oxide. If we conduct the process with free access of carbon dioxide, it is easy to obtain the whole of the zinc as oxide. Various ores and concentrates which are unsuited for making metallic zinc can profitably be employed as the source of zinc oxide, which is a valuable white pigment. For instance, the complex ores of New Jersey contains both franklinite and willemite, and a partial separation of these two minerals by a magnetic process is possible. The fraction containing mainly willemite can be smelted for metallic zinc, but the fractions containing the franklinite are somewhat unsuited for this purpose, owing to their high content of iron and manganese. They are therefore used for oxide-production, the Wetherill process being employed.[2] The furnace is a brick kiln, provided with a grate through which an upward blast of air can be forced ; a charge of ore and anthracite rests upon the grate, and the anthracite is burnt by means of the air blast. The zinc is for the moment reduced to the metallic state, and begins to distil off as vapour ; but immediately it rises out of the layer of incandescent coal, it is at once burnt by the excess of air to zinc oxide, which, however, being in a finely divided form, is carried over as a fume ; the gases pass first through a cooling-tower, and then to a bag-house, where they are filtered through a series of bags which serve to collect the zinc oxide.

Most of the zinc oxide of commerce is prepared in this way. In the case of zinc ores containing much lead, the product is by no means pure zinc oxide, but is a mixture containing basic lead sulphate and is styled " leaded zinc " or " zincy lead," according to the predominant metal. It forms, however, a satisfactory pigment.

The residues left in the retorts of the ordinary zinc-smelting furnaces are also used as raw material for the Wetherill process. The residues contain both zinc and lead, and give a leaded zinc oxide on treatment on the grate.

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[1] W. Kasperowicz, *Zeitsch. Angew. Chem.* **31** (1918), i, 144.

[2] *Oil, Paint and Drug Rep.* Nov. 2, 1914 ; Abstract, *J. Soc. Chem. Ind.* **33** (1914), 1092. E. A. Smith, *J. Inst. Met.* **16** (1916), 154 ; S. J. Cook, *J. Soc. Chem. Ind.* **38** (1919), 138T.

As already mentioned, the Wetherill process can be used as a method of concentrating complex zinc ores, the crude oxide obtained being employed for the production of metallic zinc.[1]

Zinc oxide is a most valuable pigment, and is the basis of many of the best white enamels.[2] It has an advantage over white lead in that it does not blacken in the presence of hydrogen sulphide. It is often considered superior to white lead for indoor use, but inferior for employment in the open air.

Other Zinc Pigments. Several other pigments containing zinc have already been mentioned in former volumes of this book. These include "**lithopone,**" the important pigment consisting of zinc sulphide and co-precipitated barium sulphate, which has the unfortunate habit of darkening when exposed to light, owing to the formation of metallic zinc. The green pigment consisting of mixed crystals of zinc and cobalt oxides may also be recalled in this point, whilst the employment of the chromate (*zinc yellow*) is worthy of mention.

Other Uses of Zinc Compounds. The zinc compounds have poisonous properties, and prevent the development of certain objectionable forms of life; thus the sulphate is used as a preservative in glue, and the chloride as a preservative for timber, as well as an antiseptic in surgery; zinc oxide is used considerably in the preparation of ointments. The oxide also finds employment on a large scale in the linoleum and rubber manufactures.

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[1] W. R. Ingalls, *Eng. Min. J.* **104** (1917), 457; **105** (1918), 96; P. C. Choate, *Met. Chem. Eng.* **19** (1918), 20.

[2] S. J. Cook, *J. Soc. Chem. Ind.* **38** (1919), 138T.

CADMIUM

Atomic weight . . . 112·40

Cadmium occupies a position in the Group IIB intermediate between zinc and mercury, and its properties are, on the whole, intermediate between the properties of those two metals, although it has perhaps more in common with zinc than with mercury.

The Metal

Cadmium is rather whiter than zinc and resembles tin somewhat in appearance. It is more easily fusible and more volatile than zinc, the melting-point being 322° and the boiling-point 778° C.; the vapour-density indicates that the molecules consist of single atoms—as in the case of zinc. When molten cadmium is allowed to solidify in a crucible, fine six-rayed stars may be seen in relief on the free surface, indicating that cadmium crystallizes in the hexagonal system.[1] Cadmium is fairly soft, and sufficiently malleable and ductile for the making of foil and wire. According to some authorities, more than one allotropic modification of cadmium exists.[2]

A considerable part of the traces of impurities which are present in ordinary cadmium exist not in solid solution, but in the space between the grains, presumably as a eutectic. The existence of this inter-granular network of impurities, which must be of some importance in determining the mechanical character of ordinary cadmium, can be made visible by dissolving the cadmium in a concentrated solution of ammonium nitrate—a reagent which dissolves the metal without gas-evolution, and thus leaves the films of insoluble impurities undisturbed.[3] It is noteworthy that cadmium which has been purified by distillation *in vacuo* leaves a much smaller quantity of this inter-granular impurity.

Although less reactive than zinc, cadmium can evolve hydrogen gas from dilute hydrochloric acid, when brought into contact with a metal like nickel; it will precipitate more noble metals, such

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[1] W. Campbell, *Metallurgie*, **4** (1907), 801.

[2] F. H. Getman, *J. Amer. Chem. Soc.* **39** (1917), 1806. E. Cohen and W. D. Helderman, *Proc. Amst. Acad.* **16** (1913), 485; J. N. Greenwood, *Trans. Faraday Soc.* **17** (1922), 681. However, M. Cook, *Trans. Faraday Soc.* (1923), attributes the changes of properties obtained on annealing cadmium to recrystallization.

[3] G. Tammann, *Zeitsch. Anorg. Chem.* **121** (1922), 275.

as lead, copper, silver, or gold, from solutions of their salts. These replacements proceed best when the cadmium is not quite pure. As is to be expected, cadmium is less easily oxidized and more easily reduced to the metallic condition than zinc. The superficial oxidation of cadmium on exposure to hot air is, however, possibly more noticeable than that of zinc ; but in considering this fact the dark colour of cadmium oxide should be remembered. The metal can be " burnt " to the brown oxide, when heated in the air.

Laboratory Preparation. Cadmium can be prepared comparatively readily by the electrolysis of the salts. The difficulties connected with the efficient electrolysis of zinc solutions do not so seriously affect the treatment of cadmium salts, on account of the less reactive character of the latter metal ; but nevertheless the deposition is more efficient and the deposit is more regular if the *solution employed is pure.* If a concentrated solution of cadmium sulphate containing a trace of free acid is electrolysed, metallic cadmium is deposited on the cathode. An alternative method of obtaining metallic cadmium is to treat a solution of the sulphate with metallic zinc, which brings down the cadmium in a dark spongy form.

Compounds

Cadmium is, like zinc, divalent in its stable compounds, but, unlike zinc, forms a few highly unstable compounds in which it is monovalent.

A. Compounds of Divalent Cadmium (Cadmic Compounds).

Cadmic oxide, CdO, is a brown body formed by heating the metal in air ; it may also be obtained by igniting the nitrate or carbonate. When prepared in the hydrated condition by the precipitation of cadmium salts with sodium hydroxide, the " hydroxide " produced is white. The anhydrous oxide can be obtained by heating this hydroxide. Cadmium hydroxide is soluble in ammonia, but not in sodium hydroxide, thereby differing from the corresponding zinc compound.

Cadmic Salts. The *soluble* cadmic salts are formed by the action of the acids on the metal, the hydroxide, or the carbonate. They are white crystalline bodies, on the whole resembling the zinc salts. The **sulphate**, $3CdSO_4.8H_2O$, crystallizes in monoclinic prisms, although under certain circumstances a heptahydrate, $CdSO_4.7H_2O$, which is rhombic and isomorphous with zinc sulphate, can be isolated.[1] The chloride has not the same affinity for water

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[1] F. Mylius and R. Funk, *Ber.* 30 (1897), 827.

as zinc chloride, and the anhydrous chloride can be obtained by heating the hydrated chloride without serious loss of hydrogen chloride; like the chloride of the zinc, it is volatile, and may be purified by sublimation.

Even more pronounced than in the case of zinc is the tendency to the formation of complex anions containing cadmium and halogen elements. Thus the double iodide of potassium and cadmium appears to ionize in the manner indicated by the formula, $K[CdI_3]$; on electrolysis of the solution, the cadmium moves, not towards the cathode, but towards the anode. Even in a solution of the simple iodide, the cadmium tends to move to the anode rather than to the cathode when the concentration is high, and the facts are best explained by assuming the formation of some complex salt such as $Cd[CdI_3]_2$. When the solution is diluted, the complex begins to break up, and the cadmium begins to move towards the cathode.[1]

As in the case of zinc, the carbonate, phosphate, oxalate, and sulphide are *insoluble*. The first three mentioned are white precipitates obtained by the addition of the corresponding sodium salts to a cadmium sulphate solution. The **sulphide** is, however, a golden yellow precipitate. It differs from zinc sulphide in being insoluble in dilute hydrochloric acid, and may be prepared therefore by passing hydrogen sulphide gas through a hot solution of a cadmium salt containing that acid.

B. Compounds of Monovalent Cadmium (Cadmous Compounds).[2]

When anhydrous cadmic chloride, $CdCl_2$, is fused with metallic cadmium, a mixture is obtained which contains **cadmous chloride,** $CdCl$, mixed with residual cadmic chloride. When treated with water, the product gives cadmous hydroxide, which can be dehydrated to give the yellow **cadmous oxide,** Cd_2O. The yield obtained by this method is small. A green mixture consisting of the same oxide mixed with globules of metallic cadmium is obtained by heating cadmium oxalate in a stream of carbon dioxide at 300° C.; it is possible to remove the metallic cadmium by volatilization if the powder is heated *in vacuo* at about 350° C.

Analytical

Cadmium is distinguished and separated from zinc by the fact that it gives a yellow precipitate of cadmium sulphide when hydrogen sulphide is passed through a solution acidified with hydrochloric

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[1] Compare J. W. McBain, *Zeitsch. Elektrochem.* **11** (1905), 215. See also R. G. van Name and W. G. Brown, *Amer. J. Sci.* **44** (1917), 453.

[2] H. G. Denham, *Trans. Chem. Soc.* **115** (1919), 556.

acid. Various other metals, however, under these conditions also give precipitates, which in some cases are yellow. Cadmium sulphide is separated from the sulphides of arsenic, antimony, and tin through its insolubility in ammonium sulphide, and from sulphide of copper by virtue of its insolubility in potassium cyanide. The separation of lead depends on the precipitation of the latter as sulphate. The separation of cadmium from mercury depends on the behaviour of the sulphides towards hot dilute nitric acid, which dissolves the cadmium sulphide, together with that of bismuth, if present, but leaves mercury sulphide undissolved. From the solution bismuth may be precipitated as basic carbonate, leaving cadmium in solution.[1]

In this way the separation of cadmium from all other metals is brought about. It may then be precipitated as carbonate and weighed as oxide. As in the case of zinc, cadmium compounds must not be ignited in contact with the filter-paper, or they will suffer serious loss of weight through the reduction and volatilization of the metal.

Cadmium may be estimated as metal[2] by the electrolysis of a solution containing potassium cyanide, a bright silver-white deposit being obtainable under these conditions. Solutions of cadmium sulphate containing free sulphuric acid may also be used, but the deposit obtained is in this case darker and not quite so smooth and coherent.

A volumetric method of estimating cadmium depends on its precipitation as sulphide, and the titration of the cadmium sulphide with iodine in the presence of hydrochloric acid.[3] The reaction is:

$$CdS + 2HCl + I_2 = CdCl_2 + 2HI + S.$$

TERRESTRIAL OCCURRENCE

Cadmium occurs to a very much smaller extent than zinc in rock-magma, but the conditions favourable to the concentration of zinc are likewise favourable to the concentration of cadmium. Consequently small amounts of cadmium are found in many zinc ores, whether primary ores like blende, or oxidized ores like calamine. The cadmium probably exists, in most cases, in solid solution in the zinc minerals, the cadmium atoms no doubt replacing a certain number of zinc atoms in the crystal-structure. The

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[1] For further details of methods, see W. W. Scott, "Standard Methods of Chemical Analysis" (Crosby Lockwood).

[2] See A. Classen, "Quantitative Analysis by Electrolysis." Translation by W. T. Hall (Chapman & Hall).

[3] S. Pile and R. Johnston, "Tested Methods of Metallurgical Analysis" (Witherby).

cadmium content of the zinc minerals rarely exceeds 3 per cent. and is generally much less. The occurrence of small amounts of cadmium in what are regarded as ores of lead or of copper will also readily be understood. Minerals which contain cadmium as the main metallic constituent are very rare, although the yellowish sulphide

Greenockite . . . . CdS

has been found in Scotland.

TECHNOLOGY AND USES

When cadmiferous zinc-ores are smelted, the cadmium, being not only more easily reducible than zinc but also more volatile, comes over almost entirely with the first portions of the distilled metal. These first portions of zinc-vapour, as has been remarked already, do not collect as liquid zinc in the adapter, because the condensed globules become at once oxidized on their surface, and will not coalesce. The cadmium-rich portion of the zinc is therefore found after the distillation as a partly-oxidized powder in the nozzle or prolong attached at the end of the adapter, and for this reason it is obtained separately from the bulk of the metal.

A quantity of cadmium oxide is also present in the dust carried out by the gases from the preliminary roasting of the zinc ores.[1] In addition, a great deal of the dust obtained in the bag-houses at certain American copper-works and lead-works, is a valuable source of cadmium.[2]

If the cadmiferous dust—whatever its origin—is mixed with fresh coal, and distilled at a low red heat, the first portion of the distillate will be found to be still richer in cadmium, the content of which may now reach 75 per cent. If this rich distillate be then mixed with coal and distilled carefully a third time, at a low temperature, moderately pure cadmium metal may be obtained.

It is, however, more usual to dissolve the dust containing cadmium in acid, the cadmium and copper being thrown down from the solution as a " mud " by means of zinc. The mud is then treated with dilute sulphuric acid which dissolves the cadmium, and leaves the copper. The cadmium is again thrown down by zinc and once more redissolved in acid; the solution is purified chemically from iron, thallium, etc., and the cadmium is finally deposited by electrolysis.[3]

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[1] A. T. Ward, *Min. Ind.* 28 (1919), 64.

[2] H. R. Hanley, *Met. Chem. Eng.* 23 (1920), 1257. See also C. E. Siebenthal, *U.S. Geol. Surv. Min. Res.* (1917), I, 49.

[3] H. R. Hanley, *Chem. Trade J.* 68 (1921), 67.

A little cadmium is produced as a by-product of the lithopone manufacture. If the zinc salts intended for the preparation of lithopone have been made from cadmiferous ore, the cadmium should be removed by means of zinc dust, or the pigment will be yellowish owing to cadmium sulphide.

Uses of Cadmium. Although cadmium-plating has been used occasionally, instead of galvanizing, for special purposes, the greater part of the metal manufactured is consumed in the preparation of alloys. Cadmium has itself a low melting-point, and, by admixture with other metals of low melting-points, very easily **fusible alloys** can be made. For instance, Wood's metal is composed of lead, bismuth, tin, and cadmium, and melts at about 60° C. It is used for automatic electrical cut-outs and thermometric alarms, as well as for the "setting" of crystals in the "detectors" of wireless-telephone apparatus. Other fusible alloys which melt at rather higher temperatures are known. An alloy of lead with about 10 per cent. of cadmium and about 10 per cent. of tin was used as a solder during the war, especially in Germany, where there was a shortage of tin.

The question of adding cadmium to the copper used for electrical purposes has been referred to in the section on copper (page 54).

Cadmium sulphide is a valuable yellow pigment, whilst cadmium is also used as a colouring agent in the glass and ceramic industries.

MERCURY

Atomic weight . . . 200·6

The Metal

Mercury is the remaining member of group IIB. The change of properties which was noted in passing from zinc to cadmium is observed again in passing from cadmium to mercury. Just as the boiling-point and melting-point of cadmium were lower than those of zinc, so the boiling-point and melting-point of mercury are lower than those of cadmium. In fact mercury is a liquid at ordinary temperatures, and only becomes solid at —39° C.; it is, moreover, appreciably volatile at ordinary temperatures, and boils at 357° C. Mercury vapour consists of monatomic molecules. Mercury is heavier than cadmium, just as cadmium is heavier than zinc, the specific gravity of mercury being as high as 13·6; it is, in fact, the heaviest liquid known.

Mercury is a silver-white liquid, which possesses a high surface tension; a mass of mercury displays a marked tendency to gather itself into such a form that the surface area is a minimum. For this reason, in spite of the high specific gravity of the metal, small globules preserve an almost completely spherical form, the sphere being the shape in which the ratio of surface area to volume is a minimum. Larger masses of mercury assume the form of flattened spheroids, as the result of a compromise between the opposing forces of surface tension and gravity. Surface forces of a similar character are responsible for the shape taken up by the surface of mercury placed in a glass vessel; the surface of the mercury droops downwards at the edges of the vessel where it approaches the glass. Again, if a U-tube with two limbs of unequal bore be partly filled with mercury, the level of the liquid will be found to be lower in the narrow limb than in the wide limb; with water, and most ordinary liquids, the level is highest in the narrow limb.

Another effect of the same surface forces is that two globules of clean mercury when brought into contact at once coalesce into a large globule, the combined surface area being greatly diminished by the change. If, however, the surfaces of the globules be covered with the least scum, no such coalescence will occur. If, for instance, mercury be rubbed up with fat, it becomes divided into minute globules which do not reunite, and a mercurial " ointment " results.

Similarly mercury treated with sulphur becomes changed to what appears to be a grey powder composed of solid particles; really it consists of liquid globules, prevented from uniting by the film of sulphur or sulphide on their surface. These phenomena, which can be observed in the case of mercury at the ordinary temperature, help to elucidate some of the facts mentioned in the section dealing with zinc (see page 149). It was there stated that the superficially oxidized globules of molten zinc obtained during the first stage of the distillation in zinc-smelting fail to coalesce together, but remain as separate particles, which finally pass into the solid state without uniting; the formation of "blue powder" in zinc-distillation finds an analogy in the formation of powder when mercury is rubbed up with sulphur.

Mercury drops exposed to an atmosphere containing ozone or hydrogen peroxide lose their characteristic mobility, and tend to stick to the glass, or when they are made to run over it leave streaks or "tails" behind them; this is also due to superficial oxidation.

The increase in "nobility" which was noticed in passing from zinc to cadmium is very marked when we pass on to mercury. The latter metal falls close to silver in the Potential Series. Mercury is very easily reduced to the metallic state, and is not easily oxidized. By heating mercury to the neighbourhood of its boiling-point in air or oxygen a certain amount of mercuric oxide is certainly formed, but this oxide is itself decomposed by heating at a higher temperature.

Since mercury falls on the "noble" side of hydrogen in the Potential Series, it is unattacked by dilute sulphuric or hydrochloric acids. When treated, however, with hot concentrated sulphuric acid or with nitric acid, it reacts with the formation of mercury salts. Sulphuric acid is reduced to sulphur dioxide, and nitric acid—under ordinary conditions—to oxides of nitrogen. Nitric acid free from nitrous acid has practically no action upon mercury.[1]

Laboratory Preparation. Most mercury compounds, e.g. mercuric chloride, when mixed with excess of lime and heated in a glass retort, yield the metal, which distils over and can be condensed in a vessel containing water. It is likely that the oxide is produced first, which then decomposes into mercury and oxygen.

Mercury compounds are also easily reduced to the metallic state in a wet manner, e.g. by adding stannous chloride to the solution of a salt; but the mercury is brought down as a black finely-divided form, which is only converted to the familiar silvery liquid upon boiling with hydrochloric acid.

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[1] V. H. Veley, *J. Soc. Chem. Ind.* **10** (1891), 204.

Mercury is very apt to become impure by attacking other metals with which it may come in contact, and also to become foul owing to the formation of a superficial film of grease or oxide which prevents ready coalescence of the particles. The purification of mercury is therefore a familiar laboratory operation. A great deal of scum can usually be removed by pressing the liquid through leather or fabric, whilst many of the less noble metallic impurities can be dissolved out by treatment of the metal with dilute nitric acid.

The only completely satisfactory method of purification is, however, by distillation, preferably under reduced pressure. Innumerable forms of apparatus have been designed for "distillation *in vacuo*" in the laboratory.[1]

Colloidal solutions of mercury can be obtained by striking an arc below water between a platinum negative pole and a mercury positive pole, 110–220 volts being employed,[2] or by the action of hydrazine or other reducing agent on a solution of mercurous nitrate.[3] In both methods—especially the second—the preparation is extremely unstable, unless a protective colloid is present; gum arabic is recommended in the first method and sodium protalbinate in the second.

Alloys of Mercury. Mercury forms with other metals a series of alloys, known as **amalgams.** These are usually liquid when only a small quantity of the second metal is present, but are otherwise generally solid.

Many amalgams are formed by the direct union of the component metals. Thus on adding sodium to mercury it dissolves readily with a great evolution of heat, yielding sodium amalgam; in fact, if mercury is poured on to sodium an explosion usually occurs. This heat-evolution would seem to point to some chemical combination, and the melting-point curve of the sodium-mercury alloys[4] actually suggests the existence of several inter-metallic compounds. There is evidence of the individuality of the following compounds:

$$NaHg_4, NaHg_2, NaHg, Na_5Hg_2 \text{ and } Na_3Hg;$$

whilst there are less certain indications that others, such as $Na_{12}Hg_{13}$ and Na_3Hg_2, may exist. Amalgams containing more than about 0·8 per cent. of sodium (by weight) are solid at ordinary temperatures; the amalgam having the composition $NaHg_2$ consists simply of

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[1] A. W. Wright, *Amer. J. Sci.* **22** (1881), 479, describes a form which maintains its own vacuum.

[2] A. Gutbier and G. L. Weise, *Koll. Zeitsch.* **25** (1919), 97.

[3] C. Amberger, *Koll. Zeitsch.* **8** (1911), 88.

[4] A. Schüller, *Zeitsch. Anorg. Chem.* **40** (1904), 385.

this one inter-metallic compound and has a maximum melting-point 360° C. On the other hand, alloys in which the atomic percentage of sodium is 85·2 per cent. consist of a eutectic mixture of sodium and the compound Na_3Hg, and have a melting-point as low as 21·4° C.

Sodium amalgam decomposes water giving sodium hydroxide, the reaction being aided by a substance like iron or carbon which acts as the cathode of the corrosion couple. But even under such circumstances, sodium amalgam reacts with water much less violently than pure sodium, since part of the energy inherent in sodium has already been expended in its combination with mercury.

Amalgams weak in sodium can actually be prepared by electrolysis of a sodium salt solution, using a mercury cathode, but only the liquid amalgams are readily prepared in this way.

Sodium amalgam is used in organic chemistry as a reducing agent.

The **amalgams** of **zinc, cadmium, bismuth, lead** and **tin** can be prepared readily either by the addition of the second metal to gently heated mercury—or by the action of mercury upon the molten metal. In preparing the alloys the molten metallic mixture should be covered with a layer of vaseline or paraffin to prevent oxidation. According to Puschin,[1] the melting-point curves in all cases afford no indication of any definite intermetallic compound. The alloys of mercury with cadmium and zinc appear to consist of mixed crystals, and the beautiful six-rayed stars which appear on the upper surface of these alloys when they are allowed to solidify in a crucible seem to indicate that the mixed crystals belong to the hexagonal system. Copper also reacts slowly with mercury, becoming converted into a brittle **copper amalgam.**

Silver amalgams can be obtained either by the action of silver nitrate on mercury, or by the action of mercurous nitrate on silver; the alloy-system appears to include three inter-metallic compounds, namely, Ag_3Hg_4, Ag_3Hg_2, and probably Ag_3Hg; as to which of these will be produced depends on the proportions of silver and mercury salts in the solution. The compound Ag_3Hg_4 is the best-known; it usually appears in fine four-sided needles, and is stable in contact with all solutions in which between 2·5 and 18 per cent. of the total quantity of the two dissolved salts consists of silver nitrate.[2]

The **amalgams of gold** have also been studied in detail; three inter-metallic compounds Au_2Hg, Au_2Hg_5 and $AuHg_4$ exist.[3]

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[1] N. A. Puschin, *Zeitsch. Anorg. Chem.* **36** (1903), 201.

[2] W. Reinders, *Zeitsch. Phys. Chem.* **54** (1906), 609. Compare A. Ogg, *Zeitsch. Phys. Chem.* **27** (1898), 285. See also Vol. I, page 398.

[3] S. A. Braley and R. F. Schneider, *J. Amer. Chem. Soc.* **43** (1921), 740.

Several of the amalgams can be obtained in a plastic form which is capable of "setting" slowly to a hard mass. This matter, which is of great importance in dentistry, is considered in the technical section. Metals like iron and platinum which have very high melting-points are not readily attacked by mercury, at any rate at low temperatures; mercury can be preserved in an iron bottle without undue fouling.

Compounds

Mercury forms two series of compounds. Besides the **mercuric** salts, in which mercury is divalent, and which are analogous to the zinc and cadmic salts, there is also a lower series of **mercurous** salts, in which the metal is apparently monovalent. No zinc compounds of this type are known, although unstable bodies of similar composition (the "cadmous" salts) have already been described in the case of cadmium. In mercury, however, the lower series of salts are very well developed.

When mercury is *heated* with an *excess of strong nitric acid*, *mercuric* nitrate is formed; if any mercurous compound is formed in the first instance, it is soon converted by the oxidizing acid present into the mercuric salt. On the other hand, if *excess of mercury* be acted upon by *dilute nitric acid* at *ordinary temperatures*, *mercurous* nitrate is the product; any mercuric salt which may be formed temporarily is almost completely reduced by the excess of metallic mercury present. From the two nitrates, the oxides and other salts of the two series may be prepared.

A. Compounds of Monovalent Mercury (Mercurous Compounds).

The mercurous compounds closely resemble the silver compounds in properties—a circumstance that is not surprising, since the formulæ of the two classes are analogous. The **oxide,** Hg_2O, as prepared by precipitation of a mercurous salt with caustic alkali is a brown-black precipitate containing apparently no combined water; in this respect it resembles silver oxide. But, when precipitated at a very low temperature (e.g. by the action of potash dissolved in 70 per cent. alcohol upon alcoholic mercurous nitrate at − 42° C.), a yellow precipitate is obtained, which may be a hydroxide [1]; if the temperature is allowed to rise, the precipitate at once darkens. Mercurous oxide absorbs oxygen when exposed to the air, but decomposes to mercury and oxygen upon gentle heating. The **nitrate,** $HgNO_3.H_2O$, is—as already stated—prepared by the action of dilute nitric acid on the metal, and when isolated by evaporation

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[1] G. B. Bird, *Amer. Chem. J.* **8** (1886), 426.

is a white crystalline body; the **sulphate** is, like silver sulphate, a much less soluble substance than the nitrate, and is prepared by the action of sulphuric acid on excess of mercury. The **chloride,** HgCl (*calomel*) and **bromide,** HgBr, are, like the corresponding silver compounds, heavy curdling precipitates, very insoluble in water, the bromide being more insoluble than the chloride; they are produced by the addition of any soluble chloride or bromide to a mercurous nitrate solution. To complete the analogy with silver, they darken when exposed to light, metallic mercury being formed. Both these compounds are volatile, and distil *apparently* unchanged (*see, however, below*).

Mercurous iodide, HgI, is rather unstable, and partially decomposes to mercuric iodide and mercury; consequently when potassium iodide is added to a mercurous salt, a greenish mixture is precipitated, containing finely-divided mercury as well as mercurous iodide. Similarly when sulphuretted hydrogen is passed through a mercurous salt solution, instead of the precipitation of mercurous sulphide, a black mixture of mercuric sulphide and mercury is obtained.

Solutions of all soluble mercurous salts readily hydrolyse, basic salts being precipitated. Basic nitrates and sulphates of various compositions are known. Mercurous nitrate, for instance, can only be kept permanently as a clear solution if a little free nitric acid is added. In this respect mercurous salts differ from silver salts, which do not undergo hydrolysis, being derived from a more strongly basic oxide.

Molecular Formulæ of Mercurous Salts. The question of the vapour density of mercurous chloride is one which has aroused a great deal of controversy among chemists. It is now known [1] that if mercurous chloride is vaporized in the complete absence of water, the vapour consists of double molecules Hg_2Cl_2. If the smallest trace of water is present, the vapour density is halved. However, this is probably not due to the splitting of Hg_2Cl_2 into two HgCl molecules, but into mercury and mercuric chloride, thus,

$$Hg_2Cl_2 = Hg + HgCl_2.$$

The mercury and mercuric chloride recombine when the substance condenses, and hence mercurous chloride *appears* to sublime unchanged.[2]

The molecular formula of undecomposed mercurous chloride in the gaseous condition must therefore be regarded as Hg_2Cl_2. It

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[1] H. B. Baker, *Trans. Chem. Soc.* **77** (1900), 646.

[2] W. Harris and V. Meyer, *Ber.* **27** (1894), 1482; V. Meyer, *Ber.* **28** (1895), 364.

is worthy of notice that in aqueous solution also the mercurous salts show a tendency to yield ions containing two atoms of mercury; thus there is evidence[1] that in solutions of mercurous nitrate and mercurous perchlorate the principal cation is not $Hg^{\cdot}$, but $[Hg_2]^{\cdot\cdot}$. This evidence is derived from measurements of the variation of the potential of the electrode

$$\text{Hg} \;\Big|\; \begin{array}{l}\text{Mercurous}\\ \text{salt solution}\end{array}$$

with the concentration of the solution. If the solution contains monovalent $Hg^{\cdot}$ ions, then it follows from electrochemical principles (see Vol. I, page 324) that a tenfold decrease in the concentration should shift the potential by 0·058 volts; if the solution contains divalent $[Hg_2]^{\cdot\cdot}$ ions it should alter it by only half this amount, namely, 0·029 volts. Experiment has shown that the potential is shifted through about 0·029 volts, and we conclude that the principal ion is $[Hg_2]^{\cdot\cdot}$.

But although, both in the *gaseous* state and in *solution*, mercurous compounds show a marked tendency to form double molecules or double ions, this does not appear to necessitate the practice—adopted by many authors—of writing the formulæ of the *solid* salts as Hg_2Cl_2, $Hg_2(NO_3)_2$, etc. Probably $Hg_{\infty}Cl_{\infty}$ would more accurately represent the state of aggregation of solid calomel. In this volume, the simplest formulæ, such as HgCl, will be employed.

B. Compounds of Divalent Mercury (Mercuric Compounds).

The mercuric salts resemble the zinc and cadmic salts more than any others, although the resemblance is not so close as that between the mercurous and silver salts.

Mercuric oxide, HgO, can be obtained by heating mercury in air at temperatures close to the boiling-point. But this is too slow a method of preparation for practical use. It may be formed more conveniently by gently heating mercuric nitrate. As prepared in the dry way it is red; but, by precipitation of a mercuric salt with sodium hydroxide in the cold, a yellow form, apparently free from combined water, is obtained; even when obtained by the "wet" method, the precipitate is orange when brought down in warm solution, and is stated to be red when boiling barium hydroxide is the precipitant. The yellow and red forms are apparently identical, as they have the same dissociation pressure curve.[2] The

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[1] A. Ogg, *Zeitsch. Phys. Chem.* **27** (1898), 295; G. A. Linhardt, *J. Amer. Chem. Soc.* **38** (1916), 2356.

[2] G. B. Taylor and G. A. Hulett, *J. Phys. Chem.* **17** (1913), 565.

difference in colour is probably due to the yellow form being in a finer state of division. A somewhat interesting jelly-form of mercuric oxide is obtained under certain conditions when mercuric chloride and potassium hydroxide interact in the presence of acetone.[1]

If strongly heated in a glass tube, mercuric oxide decomposes into mercury and oxygen, the mercury distilling away as vapour at the temperature in question, and condensing upon the cooler parts of the tube.

Mercuric oxide is generally stated to be insoluble in sodium hydroxide. It is found, however, that it is soluble to a small extent, especially in a concentrated solution of the alkali. Apparently a body analogous to sodium zincate is formed.[2]

The **soluble** mercuric salts are in general colourless crystalline solids. The nitrate, $Hg(NO_3)_2.nH_2O$, is obtained by the action of excess of strong nitric acid upon mercury; the **sulphate,** $HgSO_4$, is likewise formed when excess of concentrated sulphuric acid acts on mercury. Solutions of both these salts readily deposit insoluble basic salts, owing to hydrolysis; they can only be kept in solution when free acid is present.

Mercuric chloride, $HgCl_2$, may be prepared by the action of chlorine on mercury, or by dissolving mercuric oxide in hydrochloric acid. It is a white crystalline body. Being more volatile than the chlorides of zinc and cadmium, it may be sublimed with ease; hence the common name, *corrosive sublimate.* Various dry methods of preparing the salt are founded on this fact; the simplest method is to heat sodium chloride and mercuric sulphate in a large glass vessel; mercuric chloride sublimes, and condenses in fine transparent crystals on the cooler parts of the vessel. Like most soluble salts of mercury, mercuric chloride is extremely poisonous.

It is noteworthy that a mercuric nitrate solution has an appreciable solvent action upon silver chloride.[3] This shows that mercuric chloride is capable of existing in the same solution as silver nitrate under certain circumstances without the precipitation of silver chloride, a fact which would suggest that mercuric chloride yields but few chlorine ions when dissolved in water. Probably mercuric chloride should be regarded as a complex salt, $Hg[HgCl_4]$, or possibly $Hg[HgCl_3]_2$, analogous to cadmium iodide, $Cd[CdI_4]$ or $Cd[CdI_3]_2$. Mercuric chloride is more soluble in potassium chloride solution than in pure water, a fact which suggests that a complex

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[1] E. H. Bunce. *J. Phys. Chem.* **18** (1914), 269.

[2] G. Fuseya, *J. Amer. Chem. Soc.* **42** (1920), 368.

[3] H. Morse, *Zeitsch. Phys. Chem.* **41** (1902), 709.

chloride may be produced, possibly $K_2[HgCl_4]$ or $K[HgCl_3]$ containing mercury in the anion.[1]

The **insoluble** mercuric salts include the iodide ; in this respect, mercury differs from zinc and cadmium, which have soluble iodides. **Mercuric iodide,** HgI_2, is a scarlet precipitate, obtained by adding potassium iodide to a mercuric salt ; it redissolves in excess of potassium iodide, forming a yellowish liquid which contains complex potassium mercuric iodides such as $K_2[HgI_4]$ and $K[HgI_3]$, both of which are known in the solid state. These complex salts are so soluble that very heavy solutions can be obtained ; solutions having a specific gravity of 2·8, a remarkably high value for an aqueous solution, are easily produced. Mercuric iodide can be obtained in well-formed crystals, by crystallization from a hot solution of potassium iodide. The compound exists in more than one form. When potassium iodide is added to a mercuric chloride solution the precipitate is momentarily yellow, but almost immediately becomes red. If, however, the solution contains 1 per cent. of gelatine, the change is retarded, and the precipitate may retain a canary-yellow colour for half an hour or more. Finally, however, it becomes red.[2]

The red variety is thus the form stable at ordinary temperatures. But when it is heated above 127° C. it changes suddenly to a yellow variety, which, however, returns to the red form on cooling. Here we seem to be dealing with two separate crystallographic varieties, since the red form is tetragonal and the yellow form rhombic. The yellow rhombic form grows gradually redder when heated above 180° C. and melts about 255° C. to a blood-red liquid.[3] It is quite volatile, the vapour being yellow. The vapour, whether it condenses above or below 127° C., usually yields the yellow form, but if the condensation is very sudden a colourless product may be obtained. This may be prepared by heating the iodide at 300–500° C. in a long tube connected to an exhausted apparatus, arranged so that the pressure can suddenly be reduced from 1 atmosphere to $\frac{1}{50}$ atmosphere ; the rapid reduction of the pressure causes a sudden condensation of the iodide vapour as a white snow, which in a few seconds becomes pink, and, after some minutes, red.[4] The possibility that this apparently colourless form may perhaps consist of very small particles of the yellow form, does not appear to be completely excluded by the facts as they are known at present.

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[1] Compare M. S. Sherrill, *Zeitsch. Phys. Chem.* **43** (1903), 705.

[2] J. N. Friend, *Nature*, **109** (1922), 341.

[3] The colour-changes are considered by A. Smits and S. C. Bokhorst, *Zeitsch. Phys. Chem.* **89** (1915), 365, 374, in connection with a special theory of allotropy.

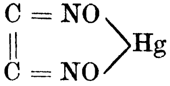
[4] G. Tammann, *Zeitsch. Anorg. Chem.* **109** (1920), 213.

Another interesting property of mercuric iodide is that its electrical conductivity increases when it is exposed to the light.[1]

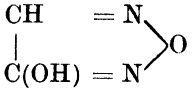
Mercuric sulphide, as obtained in aqueous solutions by the action of hydrogen sulphide on a mercuric salt, is a black precipitate. It differs from all other freshly precipitated sulphides by being insoluble in hot dilute nitric acid, a fact utilized in the separation of mercury from other metals. Like most other mercury compounds, it is volatile, but passes on sublimation into a red crystalline variety, which is usually known as " vermilion."

C. Miscellaneous Compounds.

The interesting and extremely dangerous substance known as " **mercury fulminate** " will be discussed further in the technical section. It is a white, crystalline, explosive substance, which is formed by the action of mercuric nitrate on alcohol. It has the same empyrical composition as mercuric cyanate ($HgC_2N_2O_2$), but the constitution is still a little uncertain. One authority[2] states that it should be expressed



whilst another[3] considers it the mercury salt of the acid



Mercuric fulminate detonates with violence when struck with a hammer, or when heated suddenly. By cautious heating *in vacuo* at about 80° C. it can be made to decompose slowly with evolution of carbon dioxide ; the velocity of decomposition is extremely slow at first, but after a time it becomes quicker, apparently owing to the formation of some substance which catalytically accelerates the change.[4]

Action of Ammonia on Compounds of Mercury.[5] When ammonia is added to precipitated mercurous chloride, the white precipitate turns black ; this is due to conversion of the mercurous compound to a mixture of a mercuric compound and metallic

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[1] F. Kämpf, *Ann. Phys.* **66** (1921), 463.

[2] G. S. Heaven, *J. Soc. Chem. Ind.* **37** (1918), 143T.

[3] W. R. Hodgkinson, *J. Soc. Chem. Ind.* **37** (1918), 190T.

[4] R. C. Farmer, *Trans. Chem. Soc.* **121** (1922), 174.

[5] E. C. Franklin, *Amer. Chem. J.* **47** (1912), 361 ; M. C. C. Holmes, *Trans. Chem. Soc.* **113** (1918), 74 ; H. Saha and K. N. Choudbury, *Zeitsch. Anorg. Chem.* **86** (1914), 225 ; D. Strömholm, *Zeitsch. Anorg. Chem.* **57** (1908), 72.

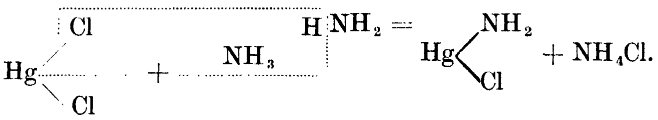
mercury, which appears black in the finely-divided state. The reaction is important in analysis because it serves to distinguish mercurous chloride from silver chloride.

The ammoniacal compounds of divalent mercury received much attention from the early chemists. As a result they are usually still known by old-fashioned names.

There are three separate classes of compounds ; these are—

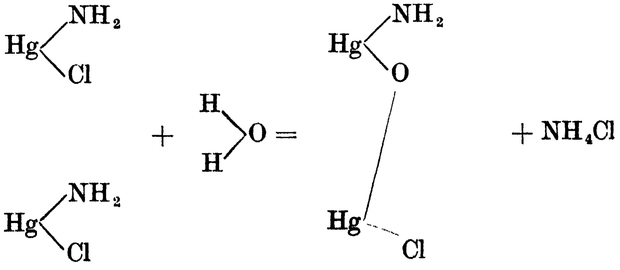
(1) **Additive compounds,** such as "**fusible white precipitate,**" $HgCl_2.2NH_3$, which can be made by the direct action of gaseous ammonia on mercuric chloride, but is more easily obtained by the adding mercuric chloride to a boiling solution containing both ammonia and ammonium chloride ; the precipitate comes down on cooling. Other additive compounds, such as $3HgCl_2.2NH_3$ and $HgCl_2.12NH_3$, have been described.

(2) "**Ammonolysed**" **Compounds.** If in the method just described the ammonium chloride is omitted, "ammonolysis" of the mercuric chloride occurs,



The product, $\mathrm{Hg}\langle^{NH_2}_{Cl}$, known as "**infusible white precipitate**" differs from the product obtained in presence of ammonium chloride in volatilizing without fusion when heated. When boiled with ammonium chloride, it gives the fusible precipitate.

(3) "**Hydrolysed ammonolysed**" **Compounds.** When the infusible precipitate is digested with a large amount of water for twelve hours at 60–70° C., hydrolysis occurs, and we get the so-called "Chloride of Millon's base."



The same chloride can also be produced by the interaction of ammonia and mercuric chloride in very dilute solution. The corresponding hydroxide (**Millon's base**) is formed on warming mercuric oxide with dilute ammonia.

The connection between the three classes of compounds just described can be summarized by the two equations,

$$HgCl_2.2NH_3 \rightleftharpoons NH_2.HgCl + NH_4Cl$$
$$2NH_2.HgCl + H_2O \rightleftharpoons NH_2.Hg.O.HgCl + NH_4Cl.$$

Both these equations are reversible. Any increase in the concentration of ammonium chloride tends to favour the reactions in the " right-to-left " direction, whilst dilution with water has the opposite effect.

Neither Millon's base nor its chloride are in themselves of any special interest, but if a soluble iodide be brought into contact with them, we get a yellow or brown precipitate of the corresponding iodide, $NH_2.Hg.OHgI$. The production of a yellow precipitate (or in very dilute solutions a yellow coloration) when a mercuric salt, potassium iodide and ammonia are brought together, provides a very delicate means of detecting ammonia. Upon this fact depends the use of "**Nessler solution**" as a method of estimating ammonia or ammonium salts. Nessler solution consists of a solution of the complex potassium mercuric iodide made strongly alkaline with potassium hydroxide. If a trace of ammonium salt be present in a drinking water, for instance, its amount may be determined by the addition of a drop of Nessler solution. The caustic alkali present liberates free ammonia, and this reacts to form the iodide of Millon's base. The depth of the yellow coloration produced, carefully compared with those formed, under similar conditions, by standard solutions of ammonium chloride of known strength, gives an indication of the amount of ammonia present.

Analytical

Nearly all mercury compounds when heated with lime or sodium carbonate at the bottom of a hard glass tube are reduced to mercury, which volatilizes from the heated portion, and globules of the metal appear further up the tube. The aqueous solutions of the salts mostly give a bright film of mercury when copper is immersed in the acidified solution, but this test does not apply to all the complex salts.

The mercurous salts give with sodium chloride a white precipitate which is turned black by ammonia ; with potassium iodide they give a muddy green precipitate, and with caustic soda a black precipitate. The mercuric salts, on the other hand, give a red precipitate with the iodide, and a yellow one with caustic soda. The action of stannous chloride on mercuric compounds is also characteristic ; this reducing agent first converts the mercury to the mercurous state, which results in the precipitation of white mercurous chloride ; then a further partial reduction to metallic mercury *occurs, and so the precipitate darkens. Sulphuretted hydrogen gives with mercuric solutions a black precipitate, insoluble in hot* dilute nitric acid.

The estimation of mercury depends on the volatility of the metal. In most cases when a substance containing mercury is distilled with lime in a combustion tube, the whole of the mercury passes off as metallic vapour. But some mercury compounds, like mercuric iodide, would under these conditions distil away unchanged ; in these cases, a reducing agent, such as copper filings, should be added to the mixture.

The quantitative distillation of mercury is conducted as follows. At the closed end of a combustion tube is placed some dry sodium bicarbonate ; next to it is put the mixture of the substance under examination with lime, and, if necessary, copper ; next comes pure lime, and finally, towards the open end of the tube, asbestos fibre. The open end of the tube is now drawn out to a point, and bent down so that the opening dips below the surface of water in a beaker. Before the distillation starts, the asbestos and lime must be brought to a high temperature ; then the mercury mixture also may be heated, so that reduction occurs. Finally the bicarbonate at the closed end of the tube is also warmed, and a gentle stream of carbon dioxide is thus produced which carries the metallic vapour along the tube and out at the constricted end, where the mercury is condensed beneath the surface of the water. If any mercury salt commences to distil unchanged, it is decomposed when passing over the red-hot line. The metal globule obtained is collected, dried with filter-paper and weighed.[1]

Since other metals will not be volatilized under these conditions, their presence does not interfere with the process ; and this method affords, therefore, a means not only of estimating mercury in its pure salts, but also of separating it from other metals. Difficulty is occasionally experienced in causing the minute beads of mercury which are obtained to coalesce to form a single globule. In one variation of the method, which is used in the assay of ores, the mercury is not weighed as a globule, but is collected as an amalgam upon balls of metallic gold. The balls are weighed, and are then ignited to eliminate mercury and re-weighed.[2]

There is also a method for the separation of mercury in a " wet "

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[1] Sir W. Crookes, " Select Methods of Chemical Analysis " (Longmans).

[2] R. G. Place, *Eng. Min. J.* **109** (1920), 1313. Other technical methods are given in the same paper.

way. Mercuric salt solutions, in the presence of dilute hydrochloric acid, give a black precipitate when hydrogen sulphide is passed through them. Several other metals give sulphide precipitates under these circumstances, but the sulphide of mercury alone is undissolved by heating with dilute nitric acid; thus the other sulphides, if present, may be removed. It is not, however, advisable to weigh mercury directly as sulphide, since the precipitate frequently contains sulphur produced through the oxidizing action of the mercuric salt—or of nitric acid—on the hydrogen sulphide. The precipitate may be redissolved in aqua regia, and re-precipitated in the presence of excess of potassium cyanide, which prevents the formation of sulphur. The sulphide may be dried at 100° C. and weighed; it is, of course, impossible to dry it by ignition.

Mercury, when present in a salt solution free from other metals, may be estimated electrolytically as the metal. It is best to add nitric acid, and to deposit the metal upon a dish of roughened platinum which is made the cathode. In this way a lustrous deposit of mercury, consisting really of minute drops adhering to the rough surface, is produced, which may be washed with alcohol, dried in a vacuum desiccator and weighed. Owing to the volatility of the metal, it is impossible to dry the dish at 100° C. In fact, in the case of a mercury deposit spread out over a large surface on a platinum dish, there is a danger of a loss by volatilization even at ordinary temperatures. Hence it is necessary, to saturate with mercury the air of the desiccator in which the dish is to be dried, by placing therein a globule of mercury on a glass pan.[1]

A fairly rapid volumetric method of estimating mercury in a neutral solution depends on the addition of an ammonium salt to the liquid followed by the addition of a known amount of standard alkali, which should be more than sufficient to bring down the whole of the mercury as fusible white precipitate. The liquid is filtered, and the residual alkali estimated by titration with acid; the amount of acid required gives an indication of the amount of alkali used up in precipitating the mercury.[2]

TERRESTRIAL OCCURRENCE

Mercury is rarely found in appreciable quantities in solid igneous rocks, and it is likely that, in most cases, the small amount of mercury contained in the original molten magma has largely been expelled with the thermal waters in the last stages of the consolidation of the rocks. The waters probably contained the mercury

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[1] V. Borelli, *Zeitsch. Elektrochem.* **12** (1906), 889.

[2] A. A. Hall, *J. Soc. Chem. Ind.* **40** (1921), 85R.

as mercuric sulphide; this may have been held in solution by sodium sulphide, or by hydrogen sulphide, in the presence of which mercuric sulphide is appreciably soluble.[1] As the waters rose, changes in the temperature and pressure, or the removal of hydrogen sulphide by passage through limestone, may have caused —in certain places—the throwing down of the mercuric sulphide, either in the red crystalline form known as

Cinnabar . . . . HgS

or the black amorphous form known as

Metacinnabarite . . . HgS

Both of these are found in nature, but crystalline cinnabar is the more important of the two. Laboratory experiments would seem to show that red cinnabar is produced by the slow deposition of the sulphide, the dark amorphous form being thrown down where the conditions allow of rapid precipitation. It is noteworthy that bituminous substances are associated with mercury ores, and have probably played a considerable part in the precipitation. Very frequently mercury occurs in the ores in the metallic state, as well as in the form of sulphide.

Whatever be the exact conditions that determine the throwing down of mercury sulphide from thermal waters, the formation of the ore only occurs when the waters have reached a much higher part of the crust than that at which the ores of copper, lead and zinc are thrown down. The primary ores of mercury have been deposited quite close to the earth's surface. Sometimes they are actually produced above the surface; certain Californian thermal springs are depositing cinnabar at the present time. Consequently, the ores of mercury are restricted to areas which have been affected by folding-movements of comparatively recent (Tertiary) times; if mercury ores were produced in connection with the earlier movements, they have since been removed by the forces of denudation.[2] Three European localities, namely, Almaden (Spain), Idria, and Tuscany, produce the greater part of the world's output; there are also quicksilver deposits in California, Texas, and Mexico. The mercury minerals occur sometimes—as in California—along with various vein-minerals in definite lodes, which probably represent the original fissures through which the mercury-bearing waters ascended. More often the greater part of the mercury sulphide is found dispersed through the country rock as an impregnation, or in cavities. In contrast with the ores of zinc, which are largely

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[1] S. B. Christy, *Amer. J. Sci.* **17** (1879), 453. Compare G. F. Becker, *U.S. Geol. Surv. Monograph,* **13** (1888).

[2] J. W. Gregory, *Trans. Chem. Soc.* **121** (1922), 769, 771.

confined to limestone, the mercury ores do not appear to be confined to any one kind of stratified rock. At Almaden (Spain) the cinnabar, with some free mercury and pyrites, occurs in quartzite lodes piercing sandstone and clay-slate; in California, cinnabar occurs as an impregnation in sandstone. On the other hand, the passage of the thermal waters through limestone often does appear to have been favourable to the throwing down of the mercury. In Tuscany, the main deposits are found in limestone or in a clay which is the residual deposit of certain marly limestones; probably the cinnabar has been deposited where the limestone has been dissolved away. The Idrian deposits include some veins, but consist largely of dolomitic limestones, and other common rocks, impregnated with cinnabar.

Massive cinnabar—especially when weathered—has not the bright red colour of freshly sublimed artificial vermilion. It is often a darkish brown-red substance, but the "streak" obtained when the mineral is rubbed over an unglazed porcelain surface is usually scarlet. Occasionally well-formed tabular crystals, belonging to the rhombohedral system, are found, whilst a bright-red earthy variety is not uncommon. Cinnabar is very heavy, the specific gravity being about 8·6.

METALLURGY AND USES

The metallurgy of mercury—like that of zinc and cadmium—is essentially a distillation-process, but owing to the fact that mercury is much more easily reduced and much more volatile than zinc or cadmium, a less hot furnace is needed. Moreover, previous roasting of the ore is not necessary; roasting and reduction can be effected in one operation. When hot oxidizing gases are passed over a charge containing mercury sulphide, the metal is carried off in the vaporous form. If any mercury oxide is momentarily formed, it decomposes at once into mercury and oxygen.

On the other hand, the treatment of mercury ore is rendered less easy by the fact that the cinnabar generally occurs disseminated throughout a great volume of worthless material; American mercury ores contain usually under 1 per cent. of the metal. Further, the fact that mercury is appreciably volatile even at low temperatures renders efficient condensation difficult, and some of the earlier furnaces allowed at least a quarter of the mercury to escape; this state of affairs was not merely wasteful, but extremely dangerous, owing to the poisonous character of mercury. Much of the loss was occasioned by leakage through the walls of the distillation plant; this loss can be reduced in several ways, partly by maintaining a suction rather than a pressure in the apparatus, and partly by improving the construction of furnaces and condensers. Further difficulties occur owing to the *mercury condensing in the form known as "soot," consisting of fine globules which will not coalesce; this form corresponds to the "blue powder" obtained in zinc-production.* The presence of carbonaceous matter in the distillate—due to the bituminous substances in the charge—appears favourable to the production of "soot."

In America, where the ores are very poor, preliminary wet concentration upon shaking-tables has been practised to some extent,[1] but it is by no means general. The Californian ores mined in 1916 and 1917 contained only 0·38 per cent. of mercury on the average, although the Texas ores were richer.[2] For the treatment of these American ores the Scott shaft furnace has proved most economical; with this furnace, fitted with proper condensers, the amount of mercury lost can be made extremely small.[3]

The furnace consists of four rectangular shafts built in a single block; along the sides of the shafts are fixed a series of sloping tiles as shown in Fig. 21. The ore to be treated passes down the shafts, sliding down from one tile to the next in zigzag fashion. The openings between the tiles may vary from 3 to 8 in. according to the coarseness of the ore to be treated. The hot gases from a fire-place common to all four shafts are made to pass in a horizontal direction along the channels between the tiles, as indicated in Fig. 21, and finally leave the furnace at the top, carrying off the mercury from the ore in the vaporous condition.

The mercurial vapours pass to the condensing plant, usually consisting of a series of large brick, wooden, or cement chambers, which may have a capacity of 20,000 cu. ft. Where bricks are used they should have smooth surfaces, and should be laid very carefully so as to prevent absorption of mercury vapour or retention of "soot" at the joints. Redwood is said to have proved a better material than brick for the construction of the condensers, since at the temperature in question it "sweats" out pitch, which forms an impermeable layer on the surface.[4] Air-cooling is generally relied on to keep down the temperature of the walls, but in some furnaces water-cooling is installed. Sometimes the final condensing chamber is of glass.

The portion of the mercury which condenses to liquid quick-

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[1] W. H. Landers, *Eng. Min. J.* **102** (1916), 630.

[2] F. L. Ransome, *U.S. Geol. Surv. Min. Res.* (1918), I, 157.

[3] M. Innes, *Eng. Min. J.* **105** (1918), 110. The furnace is described in *California Min. Bur. Bull.* **27** (1903), 218.

[4] C. A. Heberlein, *Trans. Amer. Inst. Min. Eng.* **51** (1915), 110.

silver collects on the floor, the surface of which slopes down towards certain openings so that the mercury can be drawn off; after filtration through canvas, the mercury is bottled in iron flasks. The "soot" collects on the side and is periodically scraped off, openings in the side wall of the condenser being provided to allow of this operation. It is removed to a trough, mixed with lime or alkali, and worked up with hoes—a treatment which causes part of the mercury to coalesce to the familiar liquid form. The residue which resists this treatment requires redistillation.

Shaft furnaces are less suited for very fine ores than for coarse ores. The briquetting of fine ores and concentrates naturally suggests itself, but difficulty is experienced in finding a suitable binder. Binders containing volatile hydrocarbons are unsuitable as they interfere with the satisfactory condensation of the mercury. Retort furnaces have been used to some small extent for distilling the richer "fines," but they are very wasteful of mercury. They are, however, still employed to some extent for the redistillation of the "sooty" residue referred to above; also for rich concentrates obtained by wet processes, as well as in the recovery of mercury from the "amalgam" obtained in the extraction of gold and silver by "amalgamation." The retorts may be tubes of iron, 1 ft. in diameter, set in a brick furnace. The condensers should be cooled by water, otherwise the loss is apt to be high.

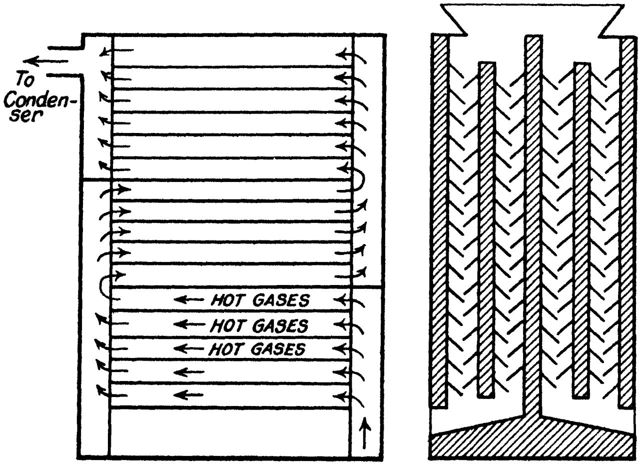

Fig. 21.—Scott Furnace.

In Europe the ores are much richer than in America; in Spain the mercury-content often reaches 7 per cent. Rather different types of furnace are used, but the general principle is the same as in America. In Tuscany,[1] the coarser ore is stated to be heated with charcoal in simple tank ovens, but for the finer ores a rather more elaborate furnace is needed. The Czermak-Spirek furnace (Fig. 22) has given good results in Tuscany and in Spain, whilst similar furnaces have long been in operation in Idria; it works upon the same principle as the Scott furnace, but the shafts, instead of being tall and narrow, are low and broad. Across the furnace pass a series of ʌ-shaped "ridges" in four to eight rows, one above the other; these ridges fulfil the same *rôle* as the sloping tiles in the Scott furnace. The ore is charged in at the top and falls on to the upper row of ridges, where, resting in the funnel-shaped grooves between the ridges, it forms a layer 3–5 in. thick. Periodically ore slips through the openings on to the row of ridges below; finally the spent ore falls out into boxes below, whence it is usually washed away by water. The charge during the descent is heated by hot gases, which are introduced at the bottom, and pass in turn along the diamond-shaped channels between the different rows of ridges, finally leaving the furnace at the top charged with mercury vapour. The gases then pass into the condensers, which usually consist of vertical air-cooled pipes of cast-iron or stoneware. The former material conducts best, but is apt to be attacked by the sulphurous gases; it is sometimes lined with concrete. After passing through the pipe-condenser, the gases are generally taken through a chamber condenser before being discharged.

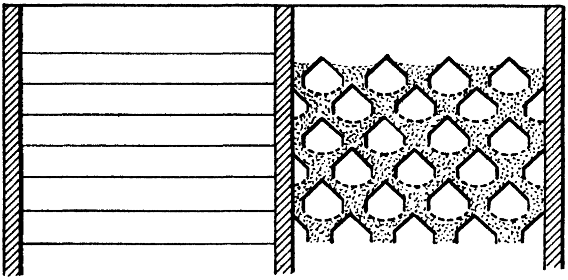

FIG. 22.—Principle of the Czermak-Spirek Furnaces.

Rotary furnaces—similar to those in use at cement works—have been used in Italy, and also in the United States.

Uses of Mercury. In many ways quicksilver is a unique substance; it is the heaviest liquid known, and it expands more

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[1] *J. Roy. Soc. Arts*, 68 (1920), 705.

when heated than any other liquid. It is the only metal which is liquid at ordinary temperatures, and is a good solvent for most other metals, a property which is used—as we have seen—in the "**amalgamation processes**" of extracting gold and silver, and also in the **electrolytic preparation of alkali.**

The great weight of mercury makes it convenient for employment in the barometer and in pressure-gauges. The weight of a column of mercury of a quite manageable length (about 30 in.) is sufficient to balance the pressure of the atmosphere, and thus to give a measure of the latter. If water were employed in a barometer, the tube would require to be 13½ times as high; the height needed would thus be about 34 ft. The high density of mercury is also made use of in the Sprengel pump, which serves to evacuate a vessel by carrying out the air between small drops of falling mercury.

The considerable expansion of mercury with changes of temperature is the reason for the employment of mercury in the thermometer, and in thermostats. Since a given rise of temperature causes a greater relative expansion in mercury than in any other liquid, it is clear that a thermometer tube filled with mercury will be more sensitive than a similar one filled with another liquid. It is, of course, well known that glycerine thermometers have either larger bulbs or stems with narrower bores than mercury thermometers of equal sensitiveness. The commonly employed scales of temperature are *defined* in such a way that a rise of one degree in any part of the scale represents an equal increase of volume of mercury. Other liquids do not necessarily expand to an equal extent in different parts of the "mercury" scale; for instance, water expands much more when heated from 18° C. to 19° C. than when heated from 4° C. to 5° C.; it actually *contracts* if heated from 3° C. to 4° C. It happens, however, that the "mercury" scale of temperature accords well with the so-called "absolute" or "thermo-dynamic" scale of temperature, which is independent of the properties of any one substance. Thus mercury may be regarded as a liquid which—in the strictest sense—"expands uniformly with rise of temperature."

Among the minor uses of mercury may be mentioned its employment in electrical contact-breakers, keys, and so on. The end of an amalgamated wire, if dipped into mercury makes an almost perfect electrical contact with it, without any screwing up of terminals. A "mercury contact" carries none of the uncertainty that is felt in the case of contacts made by pressing two solid metals together, an uncertainty due to the possibility of an oxide-film upon the metals; therefore mercury contacts are always used in " conductivity cells," and in other instances where it is important to have a contact of negligible resistance.

Use of Amalgams. A great deal of mercury is used by dentists in compounding the amalgams employed in stopping teeth. An amalgam suitable to this purpose must be plastic when freshly prepared, but must " set " to a hard mass within a few hours of the time of the " filling " of the tooth. Amalgams of copper, palladium and cadmium have all been employed, but of these copper amalgam, at least, is no longer used, as it tends to blacken. An amalgam containing both tin and silver is regarded as being the best for general purposes.[1] The alloys of tin and silver contain the intermetallic compound Ag_3Sn. When the powdered alloy is mixed with mercury, a mass is obtained which is plastic at first, but which sets to a hard mass as the mercury displaces tin from combination with the silver

$$Ag_3Sn + 4Hg = Ag_3Hg_4 + Sn.$$

It has been shown that the filings of tin-silver alloy used by dentists undergo a change when stored, the power of taking up mercury being considerably retarded. This change, which is known as " ageing," is attributed to a polymorphic transformation in the intermetallic compound Ag_3Sn. It does not occur in pure tin or pure silver.[2]

Tin amalgam was at one time employed largely for coating glass in the manufacture of mirrors, but the silvering of glass has now practically displaced the old amalgam process, which involved considerable risks of mercury-poisoning to those engaged in it.

Technically Important Compounds. Of the mercury salts, the two chlorides are employed in medicine, while mercuric chloride (*corrosive sublimate*) is also used in surgery as an antiseptic, and in the hide-industries for purposes of sterilization. It is one of the most efficient killers of anthrax-spores, which are very liable to be present in hides and which are a source of considerable danger to tanners. Mercurous chloride (*calomel*) if pure is a safe medicine on account of its very low solubility ; a saturated solution of the substance contains only ·0004 per cent. of mercury ; so, even if an overdose be taken internally, a greater concentration of the poisonous metal is not produced. Abnormal cases of poisoning with calomel have usually been attributed to the presence of soluble mercuric salt in the sample, owing to careless preparation.

Mercuric chloride is prepared commercially from metallic mercury through the sulphate. By dissolving mercury in excess

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[1] T. M. Lowry and S. Wilding, *J. Soc. Chem. Ind.* 39 (1920), 110T.

[2] J. W. McBain and W. A. Knight, *Dental Cosmos*, 57 (1915), 630.

of hot concentrated sulphuric acid, a crystalline crust containing both mercuric and mercurous sulphates—mainly the former—is obtained; when these sulphates are dried and heated with sodium chloride, the corresponding chlorides, which are volatile, are evolved, and may be condensed by suitable means. Since it is desired to prepare mercuric chloride quite free from calomel, it is best to mix a little manganese dioxide with the mixture before the sublimation is carried out.

Mercurous chloride (calomel) can also be prepared from mercury by first converting the metal to the sulphate. If excess of mercury is treated with sulphuric acid, the main product is mercurous sulphate. When this salt is heated with sodium chloride, mercurous chloride sublimes. But, in this case, in order to avoid the presence of mercuric chloride, a little mercury should be mixed with the charge before distillation. Furthermore, the calomel should be washed thoroughly with water before being packed, so as to ensure that the poisonous mercuric chloride is completely removed. An alternative method of preparing calomel is to heat mercuric chloride with mercury.

Another technically important compound is the pigment, **vermilion,** which is merely mercuric sulphide prepared under such conditions as yield the brightest red colour. Mercury and sulphur are mixed together in a revolving drum yielding a dark powder consisting probably of tiny globules of mercury prevented from coalescing by a film of sulphur. This powder is then heated in special earthenware retorts. At about 150° C., the mercury and sulphur combine; and at a rather higher temperature, the mercuric sulphide begins to volatilize, a scarlet sublimate being obtained, which is afterwards ground, washed, and dried. Very careful attention to details is needed in order to obtain the finest vermilion.

Wet processes can also be used. If mercury is digested with sodium polysulphide at 40–50° C. for some hours, mercuric sulphide is formed, which is at first brown, but finally becomes red. When the desired colour is obtained, the pigment is separated from the liquid, which can then be boiled with sulphur to regenerate polysulphides and used to convert a fresh quantity of mercury to vermilion. In the wet process, as in the dry process, careful attention must be paid to the time, temperature, and other factors.

Vermilion is highly valued as a pigment; it possesses a fine colour, but tends to blacken when exposed to light.

An important use of vermilion—as well as for the oxide and iodide of mercury—is in the manufacture of anti-fouling preparations for ships' bottoms: this depends on the poisonous action of mercury compounds upon the forms of life responsible for "fouling."

Like those of many metals which exist in more than one state of oxidation, compounds of mercury can function as catalysts in certain oxidation processes. For instance, in the oxidation of naphthalene to phthallic acid, by means of sulphuric acid, mercury can be used as an oxygen-carrier; the conversion of naphthalene to phthallic acid is the first step in the production of artificial indigo.

A very large amount of mercury was required during the war for the manufacture of the highly unstable "**mercury fulminate,**" which was used largely as a detonator. In the usual process of manufacture a cooled solution of mercuric nitrate containing nitric acid is poured into 94 per cent. alcohol at 25° C.[1] After 20 minutes, crystals begin to separate, and the mixture is poured into water. The fine crystalline precipitate of fulminate is washed by decantation, sifted through a net to separate large crystals and again washed free from acid. Owing to its dangerously explosive properties, fulminate is always stored below water, and before it is dried for use, it is again washed, and tested for acidity; it is dried at 63° C., the temperature being regulated with great care.

The peculiar value of fulminate lies in the fact that it decomposes explosively on impact or when heated. Although not actually used as an explosive, a small percussion cap of fulminate is used in cartridges or shell. When a rifle is fired, the impact of the striker upon the percussion cap causes the explosion of the fulminate, which in turn causes the explosion of the explosive proper. Coarse fulminate is more sensitive to impact than fine powder, and hence more dangerous to handle.

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[1] G. S. Heaven, *J. Soc. Chem. Ind.* **37** (1918), 143T.

GROUP IIIB

	Atomic Weight.	Normal Electrode Potential (Hydrogen Scale).
Gallium . . .	70·1	—0·53 volts (approx.)
Indium . . .	114·8	—0·38 ,,
Thallium . . .	204·0	—0·34 ,,

The metals of the group IIIB are all comparatively rare and unimportant elements, and a brief description will suffice. They are soft metals characterized by low melting-points, but comparatively high boiling-points. They have a certain general relation to the members of the previous group, but form compounds in which the metal is trivalent, and which closely resemble the corresponding derivatives of aluminium. There is also a tendency to form lower salts, which is best developed in thallium, the last member of the group.

GALLIUM

Atomic weight . . . 70·1

The Metal [1]

Gallium is a bluish-white metal, about 5·9 times as heavy as water; when pure, it is soft enough to be cut with a knife. The chief physical peculiarity is the unusually low melting-point; gallium fuses when heated above 29·8° C., and—so great is the tendency to supercooling—that the liquid metal may be cooled to ordinary temperatures and preserved for an indefinite period without solidifying. But the liquid is metastable, and, if a nucleus of solid gallium be introduced into it, the whole crystallizes out. Liquid gallium possesses a high surface tension, only a little lower than that of mercury; consequently gallium shows the same disposition to gather into spherical globules as does mercury.

Gallium, like water, but unlike many metals, expands on freezing; the density of liquid gallium (6·0947) exceeds that of solid gallium (5·9037). The boiling-point of gallium is high, far above 1,600° C.[2] The electrode potential of gallium towards a normal solution has been shown recently to be —0·25 volts on the absolute scale, which is equal to —0·53 volts on the hydrogen scale. Hence gallium lies slightly on the "noble" side of zinc in the Potential Series. The metal dissolves in hydrochloric acid or in sodium hydroxide with evolution of hydrogen. It is stated that solid gallium is more readily attacked by hydrochloric acid than the liquid metal, a difference which will be easily understood in view of the increased likelihood of the existence of corrosion couples on the solid surface. With cold dilute nitric acid there is little action upon the solid metal, which becomes passive. The tendency of gallium to become passive is noticeable in other cases. When pure gallium is placed in a solution of copper sulphate there is practically no deposition of metallic copper; if the metal is placed in a solution of copper chloride, the replacement commences slowly, but becomes more rapid as it proceeds. Gallium oxidizes only superficially when exposed to the air; the oxide film produced is of a protective character.

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[1] T. W. Richards and S. Boyer, *J. Amer. Chem. Soc.* **41** (1919), 133; **43** (1921), 274.

[2] P. E. Browning and H. S. Uhler, *Amer. J. Sci.* **41** (1916), 353.

Laboratory Preparation. Gallium can be obtained from its salts by electrolysis of an aqueous solution made alkaline with caustic potash[1]; bright globules of gallium appear on the cathode and drop off as they grow larger. If desired, electrolysis can be conducted in weakly acid solution,[2] but this is a somewhat less suitable condition; a rather high current density is needed, since otherwise the only product at the cathode is hydrogen. If electrolysis in a nearly neutral bath is attempted, the deposit of gallium is liable to contain basic salts, and will be spongy and incoherent. As cathode material for use in the deposition of gallium, platinum, or iron—metals which only slowly alloy with gallium—should be employed. Silver, for instance, is unsuited as a cathode material, since it alloys readily with gallium.

The recovery of gallium from the residues left in the zinc retorts after distillation is dealt with in connection with the extraction of indium, thallium, and germanium (page 206).

Compounds

The stable salts correspond to the oxide Ga_2O_3, and contain trivalent gallium. They closely resemble the aluminium compounds. The **chloride** $GaCl_3$ is obtained in the hydrated condition by dissolving the metal in hydrochloric acid, or aqua regia. The anhydrous chloride can be prepared by heating the metal in chlorine; like so many anhydrous chlorides, it is deliquescent. The chloride melts at 75° C., and boils at 215–220° C.; the vapour density corresponds to the simple formula $GaCl_3$ at high temperatures, but just above the boiling-point there is evidence of the existence of Ga_2Cl_6 molecules. The volatility of gallium chloride gives a convenient method of obtaining it in a state of high purity. It may be distilled, first in a current of chlorine, then in nitrogen, and finally *in vacuo*.[3] Having obtained the chloride in a state of purity, other pure gallium compounds can be made from it.

From the chloride the "**hydroxide**" is obtained by precipitation with ammonia in the presence of ammonium chloride. This body is a gelatinous precipitate, very similar to aluminium hydroxide. It gives the white **oxide**, Ga_2O_3, on ignition, and, like aluminium hydroxide, dissolves in alkalis to form "gallates,"

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[1] H. C. Fogg and C. James, *J. Amer. Chem. Soc.* **41** (1919), 949; L. M. Dennis and J. A. Bridgman, *J. Amer. Chem. Soc.* **40** (1918), 1540.

[2] Compare T. W. Richards and S. Boyer, *J. Amer. Chem. Soc.* **43** (1921), 279.

[3] T. W. Richards, W. M. Craig, and J. Sameshima, *J. Amer. Chem. Soc.* **41** (1919), 131. Compare L. M. Dennis and J. A. Bridgman, *J. Amer. Chem. Soc.* **40** (1918), 1540.

as well as in acids to form gallium salts. Unlike the aluminium compound, it is fairly soluble in excess of ammonia.

The **gallium salts** closely resemble those of aluminium. The soluble salts are colourless crystalline bodies, readily hydrolysing in solution. For instance, **gallium sulphate,** $Ga_2(SO_4)_3$, is obtained by dissolving the hydroxide in dilute sulphuric acid, but the solution, on boiling, gives a white precipitate of a basic sulphate. Gallium sulphate combines with ammonium sulphate to form a true **gallium alum,** $Ga_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, isomorphous with all the other alums, and crystallizing in cube-octahedra. Like aluminium, gallium may be precipitated from its solutions by the addition of the carbonate, phosphate and oxalate of ammonium; the insoluble compounds of gallium produced are white precipitates resembling the analogous compounds of aluminium. But gallium differs from aluminium and resembles zinc, in giving a white precipitate of the sulphide when ammonium sulphide is added, even in the presence of acetic acid; moreover, it is precipitated by potassium ferrocyanide.

The tendency to form lower salts is exhibited by the formation of a **dichloride** when gallium and the trichloride are heated together. This is a white substance, stable enough to be volatilized without apparent decomposition; the vapour density corresponds to the formula $GaCl_2$.

Analytical

Traces of gallium are often detected by means of the spark-spectrum, which shows two lines in the violet region. The precipitate thrown down when potassium ferrocyanide is added to a gallium solution containing hydrochloric acid forms a sensitive wet test for the metal. The gallium is usually precipitated as hydroxide, and, after ignition, weighed as oxide.

Details of methods of separation from the associated elements must be sought elsewhere.[1] The common method of separation from zinc depends on the fact that, if a solution of the chlorides containing hydrochloric acid in excess is made ammoniacal, and then boiled to expel ammonia until it once more reddens litmus, gallium hydroxide remains precipitated, whilst the zinc is found in the solution. The separation from thallium—previously reduced to the lowest state of oxidation—is somewhat similar. The separation from indium depends on the fact that indium is precipitated by excess of boiling potash, whilst gallium remains in solution.

[1] Full particulars in Sir W. Crookes' "Select Methods of Chemical Analysis" (Longmans).

Most of these separation processes are incomplete, and usually double precipitation is needed. The separation from aluminium and chromium depends on the precipitation of gallium by ferrocyanide in presence of acid; the filtration of gallium ferrocyanide presents difficulties unless special precautions are observed.[1] The separation from cadmium depends on the fact that, under correct conditions of acidity, nearly all the cadmium is precipitated by hydrogen sulphide, but little or no gallium. In this latter case, however, each fraction must be treated a second time before the separation is even approximately quantitative.

Various alternative methods have been proposed. For instance, the separation of moderate quantities of zinc from gallium in a neutral or weakly acid solution can be effected by boiling for a few minutes with ammonium bisulphite.[2] This reagent precipitates all the gallium as a sulphite which forms a granular precipitate, and filters much more readily than the gelatinous hydroxide; zinc remains in solution.

Historical

Gallium—like scandium and germanium—is of special interest to the chemical historian—in that the properties of the element were foretold before it was actually discovered.

When the periodic table was worked out in 1869–1871, certain places in the table were left unfilled; Mendeléeff ventured to offer an opinion, that these places corresponded to elements which actually existed, but which had hitherto not been discovered. He even went as far as to predict the properties of the three missing metals; these properties he inferred from those of the known elements which fall near the "gaps" in the table. In each of the three cases, the missing metal has since been discovered, and, in every instance, Mendeléeff's predictions have been found to be substantially accurate. Gallium was actually discovered in 1875 by Lecoq de Boisbaudran in a French zinc-ore (hence the name "gallium").

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[1] Details given by L. E. Porter and P. E. Browning, *J. Amer. Chem. Soc.* **43** (1921), 111.

[2] L. E. Porter and P. E. Browning, *J. Amer. Chem. Soc.* **41** (1919), 1491.

INDIUM

Atomic weight . . . 114·8

The Metal

Indium is a whitish metal, considerably softer and more malleable than gallium ; it is somewhat softer than lead. It is also heavier than gallium, and melts at a higher temperature (155° C.), although still among the more fusible of metals. It is often stated to crystallize in the cubic system, but X-ray analysis shows that the atoms are probably arranged on a face-centred tetragonal space-lattice, although the dimensions of the lattice are such that it comes very near to being a face-centred cubic lattice.[1]

Indium is distinctly more " noble " than gallium, but dissolves in dilute acids, evolving hydrogen. It is less readily oxidized than gallium, and keeps bright when exposed to the air.

Laboratory Preparation.[2] The metal can be obtained by the electrolysis of a solution of the sulphate containing free sulphuric acid, but containing also ammonium sulphate which serves to reduce the acidity. The electrolysis can be conducted from a solution of an acidity which would prevent almost entirely the deposition of the more reactive metal gallium.[3]

Compounds

Indium forms salts corresponding to and resembling the gallium salts ; they are mostly colourless compounds obtainable by the action of the acids on the metal or the oxide. The anhydrous **chloride,** $InCl_3$, which, like gallium chloride, is highly deliquescent, is prepared by the action of chlorine on the metal. From solutions of the chloride, ammonia precipitates the "**hydroxide,**" a white heavy gelatinous mass, which gives the anhydrous **oxide,** In_2O_3, on ignition. This body is yellow when cold and brown when hot, a property recalling the oxide of cadmium, the metal which falls alongside of indium in the Periodic Table. Indium hydroxide is soluble in acids ; it is usually described as being insoluble in

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[1] A. W. Hull, *Phys. Rev.* **17** (1921), 587.

[2] A. Thiel, *Zeitsch. Anorg. Chem.* **40** (1904), 280.

[3] Compare T. W. Richards and S. Boyer, *J. Amer. Chem. Soc.* **43** (1921), 278.

ammonia or in caustic alkali, although the hydroxide, when freshly precipitated, seemed to be dissolved freely by *concentrated* ammonia.[1]

Indium salt solutions hydrolyse very readily. The **sulphate,** obtained on dissolving the oxide in sulphuric acid, deposits an insoluble white basic salt on heating. Another highly insoluble basic salt is the **basic sulphite,** which is produced when an indium solution containing sodium bisulphite is boiled. As few other metals are precipitated under the same conditions, the basic sulphite can be obtained pure, and used as the material for the preparation of other indium compounds. The **sulphide** of indium is a yellow precipitate insoluble in dilute acids ; it may therefore be obtained by passing hydrogen sulphide through a weakly acidified solution of an indium salt. The other insoluble salts of indium are in most cases white bodies, obtained by precipitation.

The power of forming lower chlorides is well developed in indium. Besides the **trichloride** ($InCl_3$) described above, obtained by the action of chlorine on the metal, two others are known. The **dichloride,** $InCl_2$, is formed when hydrogen chloride is passed over hot indium, and the **monochloride,** InCl, when the vapour of the dichloride is itself passed over the heated metal. All three chlorides are volatile and in all cases the vapour densities are found, at high temperatures, to correspond to simple formulæ, InCl, $InCl_2$, $InCl_3$.

Analytical

When indium compounds (moistened, if necessary, with hydrochloric acid) are introduced into a flame, the spectrum produced consists of a brilliant indigo-blue line and a less intense violet one ; the blue colour imparted to the flame is very characteristic.

Various methods for the separation and estimation of indium have been proposed ; one depends on the formation of the insoluble basic sulphite. Upon ignition the basic sulphite gives the oxide, in which form indium can be weighed. The separation from gallium has already been discussed.

The precipitation of indium as hydroxide is not wholly satisfactory, since indium hydroxide is appreciably soluble in excess of ammonia. Indium is, however, thrown down completely as hydroxide if dimethylamine is used as precipitant.[2]

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[1] A. Thiel and H. Koelsch, *Zeitsch. Anorg. Chem.* **66** (1910), 301.

[2] Compare C. Renz, *Ber.* **34** (1901), 2763.

THALLIUM

Atomic weight . . . 204·0

The Metal

Thallium, the remaining metal of Group IIIB, is a soft, heavy metal (specific gravity 11·8) resembling lead in general appearance; like that metal, thallium leaves a mark when drawn over paper. It melts at 302° C., a temperature considerably higher than the melting-point of indium, and a little below that of lead. Although the boiling-point is high, the vapour density has been determined and corresponds to the diatomic molecule, Tl_2.

The normal electrode potential of thallium[1] in a thallous salt solution is about — 0·62 volt on the calomel scale, which is equal to — 0·34 volt on the hydrogen scale. This value indicates that thallium stands close to cadmium in the potential series. As would be expected, thallium can evolve hydrogen when placed in dilute sulphuric acid, dissolving to form the soluble sulphate. Dissolution in hydrochloric acid, however, is hindered by the insolubility of the chloride formed, which no doubt forms a semi-protective film over the surface of the thallium. Thallium dissolves readily in nitric acid. Owing to the solubility of the hydroxide, thallium is slowly attacked by pure water in the presence of air, and at 100° C. it even decomposes air-free water with the evolution of hydrogen. When thallium is made the anode in an electrolytic cell containing either dilute sulphuric acid or an alkali, the metal passes into solution as monovalent (thallous) ions quite readily, so long as the current density does not exceed a certain limiting value, which depends on the rate of stirring, as well as on the character of the electrolyte.[2] If the E.M.F. applied to the cell is increased beyond this point, partial passivity sets in, although the thallium continues to pass into solution to some extent, apparently in a higher state of oxidation. Under strong anodic polarization, oxygen is evolved, and often ozone. The passivity observed is due to the formation of sparingly soluble sulphate or hydroxide, which can often be seen on the anode. The phenomenon of " pulsation " (alternate activity

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[1] G. N. Lewis and C. L. von Ende, *J. Amer. Chem. Soc.* **32** (1910), 732. Compare F. J. Brislee, *Trans. Faraday Soc.* **4** (1908), 162, who gives a rather similar value (— 0·319 volt, on hydrogen scale). T. W. Richards and C. P. Smyth, *J. Amer. Chem. Soc.* **44** (1922), 530, give — 0·6192 volt on the calomel scale.

[2] W. J. Müller, *Zeitsch. Phys. Chem.* **69** (1909), 460; E. P. Schoch and C. P. Randolph, *J. Phys. Chem.* **14** (1910), 723, criticize Müller's views.

and passivity) is often met with upon a polarized thallium anode.

Thallium is generally stated to be fairly resistant towards atmospheric corrosion; the bright lustre of the freshly-cut metal is rapidly lost, owing to the formation of the grey or greenish-black oxide layer, but it is generally stated that this action is confined to the surface. Recent work,[1] however, appears to show that the dendritic form of thallium can be converted entirely to oxide by the combined action of air and moisture; the oxidation therefore is not confined entirely to the surface.

Laboratory Preparation. Starting from the sulphate, which is the salt of thallium that is most easily obtained in a state of purity, metallic thallium can be thrown down as a tree by the action of zinc. It should be washed quickly without undue exposure to the air, otherwise it will be largely washed away as the soluble hydroxide. Alternatively, the metal may be obtained by the electrolysis of a solution of thallium sulphate containing free acid.

Compounds

In the case of gallium and indium, the majority of the compounds were those in which the metal was trivalent; lower chlorides certainly existed, but there were no other stable salts corresponding to them. Thallium, however, has a complete series of lower or "thallous" salts, which are more stable than the higher "thallic" compounds. The relationship of gallium, indium and thallium is thus a repetition of that existing between members of the previous group, where monovalent salts, absent in zinc, and unstable in cadmium, were seen to be well developed in the case of the last member, mercury.

The thallic compounds, in which the metal is trivalent, are analogous, and on the whole similar, to the salts of indium, gallium, and alluminium; they have certain points of resemblance to the salts of lead and mercury, metals which fall on either side of thallium in the periodic table. On the other hand, the thallous compounds may be compared to the corresponding compounds of various monovalent metals; they are in some respects akin to the mercurous compounds, but are more allied to the compounds of silver, and have much in common even with the derivatives of the alkali metals.

A. Compounds of Monovalent Thallium (Thallous Compounds).

The thallous compounds may be regarded as being derived from **thallous oxide** (Tl_2O), a grey body which is formed superficially

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[1] A. Kölliker, *Chem. Zeit.* **43** (1919), 231.

upon thallium metal by exposure to the air. The **oxide** is, however, more easily produced by heating the hydroxide.

Thallous hydroxide, TlOH, unlike the hydroxides of nearly all the other heavy metals, is a readily soluble body, and the solution has a distinctly alkaline reaction to turmeric paper. For this reason it cannot conveniently be prepared by precipitation of a thallous salt solution with alkaline hydroxides; but by acting on thallous sulphate with barium hydroxide, a precipitate of insoluble barium sulphate is produced, and thallous hydroxide is obtained on evaporating the filtrate. It crystallizes in yellow needles, having the composition $TlOH.H_2O$. It is also produced when water acts on the metal in the presence of air. The solubility of the hydroxide constitutes a link between thallium and the alkali metals.

The soluble salts of thallium are white crystalline solids obtained by dissolving the metal or its hydroxide in the corresponding acid. The **sulphate,** Tl_2SO_4, is, like the sulphates of silver and monovalent mercury, only moderately soluble in water. The **chloride, bromide** and **iodide** are all, like the corresponding silver and mercurous bodies, curdy precipitates, obtained by the action of the sodium salts on thallous sulphate. The chloride is white, darkening in the light,[1] the bromide pale yellow, and the iodide a deeper yellow, so the analogy between thallium and silver is very close. Thallous chloride volatilizes at a high temperature, the vapour density corresponding to the formula TlCl.

The **carbonate,** Tl_2CO_3, unlike that of other heavy metals, is soluble, and gives an alkaline reaction; in this respect, again, thallium resembles the alkali metals. On the other hand the normal **phosphate,** Tl_3PO_4, is insoluble, and is produced as a white precipitate on mixing a thallous solution with potassium phosphate; the acid phosphates, however, are soluble.

The **sulphide,** like silver sulphide, is a black precipitate, but it can only be thrown down in neutral and alkaline solutions, as it is decomposed by dilute acids; it is prepared by the addition of ammonium sulphide to a solution of a thallous salt.

B. Compounds of Trivalent Thallium (Thallic Compounds).

The thallic compounds may be regarded as derived from the black **oxide,** Tl_2O_3, which can be formed by the action of oxygen on molten thallium. The oxide is also produced as a dark deposit when a thallium rod is made the anode to a solution of dilute

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[1] The conditions of darkening have been studied by C. Renz, *Helv. Chim. Acta*, **2** (1919), 704; **4** (1921), 950.

sulphuric acid. In this respect the anodic behaviour of thallium resembles that of lead.

The " **hydroxide** " is obtained, as usual, by the action of sodium hydroxide on the chloride. It can be prepared conveniently from thallous sulphate by the oxidizing action of potassium ferricyanide in an alkaline solution; when dried *in vacuo* it loses its water, and the anhydrous Tl_2O_3 is obtained.[1] It is noteworthy that the oxygen content of the product obtained by means of potassium ferricyanide is always slightly below the theoretical value.

The **chloride**, $TlCl_3$, referred to above in the preparation of the hydroxide, is best prepared by the action of chlorine on thallous chloride in the presence of water. It forms colourless deliquescent crystals. The **sulphate**, $Tl_2(SO_4)_3$, is formed in solution by the dissolution of the hydroxide in sulphuric acid; but it is difficult to isolate in the solid state since the solution readily hydrolyses, precipitating basic salts.[2] It can be prepared in solution from thallous sulphate (which is conveniently obtained in a state of purity) by electrolytic oxidation in a divided cell, a platinum anode being employed. The thallous sulphate solution should contain free sulphuric acid, since otherwise thallic hydroxide separates at the anode.[3]

C. Intermediate Compounds.

Many **chlorides,** intermediate in composition between the thallous and thallic bodies, have been described. One of these, which is formed by the direct action of chlorine on the metal, has a composition expressed most simply by the formula Tl_2Cl_3. It is usually represented $TlCl_3.3TlCl$, but may conceivably be a complex salt such as $Tl_3[TlCl_6]$, containing thallium in both cation and anion. Other intermediate chlorides have been described, but these are probably solid solutions.[4] There appears in fact to be a continuous series of mixed crystals, varying between $TlCl_3.xTlCl$ (where $x < 3$) and $TlCl_3.3TlCl$; the salt referred to above is thus the end-member of the series. These mixed crystals, which can be expressed by the general formula $TlCl_3.nTlCl$, have a yellow colour.

An **oxide,**[5] TlO, has been described; it is an intermediate product in the oxidation of thallous oxide to thallic oxide by hydrogen peroxide. The oxide is unstable and can only be isolated under special conditions. When a concentrated thallous sulphate

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[1] A. J. Berry, private communication.

[2] For details see R. J. Meyer and E. Goldschmidt, *Ber.* **36** (1903), 239.

[3] G. Grube and A. Hermann, *Zeitsch. Elektrochem.* **26** (1920), 292.

[4] R. J. Meyer, *Zeitsch. Anorg. Chem.* **24** (1900), 330, 350. Compare V. Thomas, *Comptes Rend.* **132** (1901), 1487.

[5] O. Rabe, *Zeitsch. Anorg. Chem.* **58** (1908), 23.

solution, made strongly alkaline with a great excess of 20 per cent. potash, is filtered and treated with 3 per cent. hydrogen peroxide at a low temperature (— 15° C.) a red silky precipitate is formed, which changes at once to a blue-black shimmering body ; this can be filtered off, washed with cooled alcohol and ether, and dried *in vacuo*. On treatment with water, it gives brown thallic oxide, together with thallous hydroxide, which passes into solution.

Analytical

Thallium compounds impart a green colour to a Bunsen flame ; like indium, thallium has a simple flame spectrum, consisting of a single green line.

Various methods have been proposed for separating thallium from other metals. On the addition of potassium iodide to a solution containing the metal previously reduced to the thallous condition, the whole of the thallium is precipitated as the insoluble iodide, while most other metals are left in solution. Lead, silver and mercury, however, which would also give insoluble iodides under these conditions, must, if present, be separated beforehand by saturating the acidified solution with hydrogen sulphide. Thallous iodide should be washed first with dilute potassium iodide solution and then with alcohol ; it may conveniently be collected on weighed filter paper, dried *in vacuo* over sulphuric acid, and weighed on the filter.[1]

Another method of estimating thallium is to precipitate it electrolytically as thallic oxide on the **anode**[2] from a sulphuric acid solution containing acetone. A roughened platinum dish is used as anode, and the electrolysis is conducted at about 55° C. Deposition requires 7–10 hours, after which the deposit is washed with water, alcohol, and finally with ether ; it is dried at 160° C., and weighed as Tl_2O_3. The acetone used in the bath has a favourable effect on the character of the anodic deposit, rendering it adherent. By this method thallium could probably be separated from all metals except lead, manganese, and possibly silver, but details on this point appear to be lacking.

TERRESTRIAL OCCURRENCE OF GALLIUM, INDIUM, THALLIUM AND GERMANIUM

The geo-chemistry of gallium, indium and thallium is so much interwoven that it can be discussed in a single section. The geochemistry of germanium—the rarest element of Group IVB—which is often found along with gallium will also be considered at the same time.

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[1] A. J. Berry, *Trans. Chem. Soc.* **121** (1922), 394.

[2] M. E. Heiberg, *Zeitsch. Anorg. Chem.* **35** (1903), 347.

The quantity of these four elements in the original molten magma must have been extraordinarily small. In very few places have the natural processes of differentiation, such as have led to the formation of the ores of commoner metals, brought the concentration high enough to allow the formation of minerals in which these rare metals are major constituents. Such minerals as

Argyrodite . . . . . $4Ag_2S.GeS_2$
Crookesite . . . . . $(Cu,Tl,Ag)_2Se$
and Lorandite . . . . . $TlAsS_2$

are so rare that their existence need scarcely be considered. On the other hand, all four metals occur commonly as minor constituents in certain sulphide ores, notably zinc blende. Evidently those conditions which are favourable to the natural concentration of zinc, are also favourable to the concentration of gallium, indium, thallium, and germanium. Many zinc ores contain gallium and indium, notably those of Freiburg (Saxony) and Oklahoma. Germanium occurs in both districts, the mineral argyrodite, already mentioned, being found in one of the Freiburg mines. Some zinc-ores also contain thallium.[1] Another mineral containing these rare metals in traces is iron pyrites, some samples of which constitute a convenient source of thallium. As is quite to be expected, many iron-ores of a secondary character, which presumably owe their iron to primary ores rich in the metals under consideration, contain an appreciable quantity of the same metals; some of the Cleveland iron-ores, for instance, contain an appreciable amount of gallium.[2] Traces of the same elements are found in many other minerals, such as bauxite, and certain manganese ores.[3] Thallium is found in some mineral springs; germanium occurs in the waters of Vichy.[4] Finally appreciable quantities of germanium are often present in the mineral euxenite,[5] and other minerals containing niobium, tantalum, and the rare earths.

EXTRACTION OF GALLIUM, INDIUM, THALLIUM, AND GERMANIUM

Few uses have been found for the four metals, and there cannot be said to be any organized metallurgical industry. Small quantities—such as are demanded from time to time for special purposes, or for research work—can be made from any industrial material which happens to be rich in the metal to be prepared. Many industrial products—made from ores containing the metals under consideration—contain noteworthy quantities of the elements.

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[1] W. N. Hartley and H. Ramage, *Trans. Chem. Soc.* 71 (1897), 540.
[2] W. N. Hartley and H. Ramage, *Proc. Roy. Soc.* 60 (1897), 35, 393.
[3] W. N. Hartley and H. Ramage, *Trans. Chem. Soc.* 71 (1897), 533, 547.
[4] J. Bardet, *Comptes Rend.* 158 (1914), 1278.
[5] G. Krüss, *Ber.* 21 (1888), 131.

For instance, many samples of Middlesborough pig-iron contain appreciable quantities of gallium; Freiburg zinc may contain indium in quantities up to 0·1 per cent. When pyrites containing thallium is burnt to give sulphur dioxide at the sulphuric acid works, the thallium, which is appreciably volatile at the temperature of the pyrites burners, is found in the flue dust.

The gallium used in recent research work in America has been obtained from the residues left in the retort when certain American zinc-ores—apparently obtained from the Joplin district—are distilled for zinc. Naturally, the non-volatile metals—of which lead is the chief—remain behind in the retort, and, since the ores used contain a noteworthy quantity of gallium and germanium, these "leady residues" form a convenient source of these metals.[1] Sometimes globules, consisting of an alloy of gallium and indium, are actually found in the residues, and can be picked out and worked up to give pure gallium. It is stated that prolonged heating of this alloy *in vacuo* at about 1,800° C. is sufficient to drive off practically all the indium, whilst leaving the less volatile gallium in a state of moderate purity.[2] A silica bulb heated in an oxygen illuminating gas flame can be used for the separation of the metals by volatilization.

A more general method[3] of obtaining gallium and germanium from retort-residues is to roast the residues, and then to dissolve the crude zinc oxide obtained in hydrochloric acid; potassium chlorate is added and the liquid is distilled. Germanium, which has a volatile chloride, comes over with the portion of the distillate boiling between 121° and 140° C., and can be obtained from this portion of the distillate by precipitation with hydrogen sulphide. From the white precipitate of germanium sulphide, other germanium compounds—or the metal—can be prepared (*see* "Germanium").

The liquid left in the flask contains zinc, lead, iron, aluminium, copper, tin, cadmium, and gallium. Mere dilution with cold water serves to precipitate much of the lead, as the sparingly soluble chloride. The liquid is rendered nearly neutral with ammonia (which is added until a precipitate begins to arrive). Then metallic zinc is added, and the liquid is boiled for several hours, and filtered; the precipitate consists both of metals and basic salts, and contains most of the gallium. This is redissolved in acid, treated with hydrogen sulphide to remove copper, lead, tin, and cadmium, rendered nearly neutral with ammonia and again boiled with zinc; the precipitate obtained on dilution consists of various hydroxides,

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[1] W. F. Hillebrand and J. A. Scherrer, *J. Ind. Eng. Chem.* **8** (1916), 225.

[2] P. E. Browning and H. S. Uhler, *Amer. J. Sci.* **41** (1916), 351.

[3] H. C. Fogg and C. James, *J. Amer. Chem. Soc.* **41** (1919), 947.

including gallium hydroxide. This is again dissolved in acid, and a further quantity of cadmium is removed by hydrogen sulphide. After this the gallium is precipitated as hydroxide, by adding ammonium chloride and ammonia, and boiling until the solution becomes faintly acid; the hydroxide is again dissolved in acid, and gallium is once more precipitated from a weakly acid solution by sodium formate; then follows further purification by means of hydrogen sulphide to remove final traces of copper and cadmium, and gallium and aluminium are again thrown down as hydroxides. The mixed hydroxides are dissolved in soda, and the solution is electrolysed to give globules of gallium.

Owing to the very small amount of gallium in the original residues, it is necessary to start with large amounts of material, and the completeness of separation should be checked at each stage by means of the spectroscope. Details of the process, which is naturally laborious, should be sought in the original paper.

Indium can also be prepared from the residues obtained in the zinc retorts. The separation from gallium can be effected in various ways. The methods founded on the precipitation of indium as hydroxide are rather unsatisfactory owing to the incomplete character of the separation. The fact that indium can be deposited electrolytically from solutions too acid for the deposition of gallium might be used. The fractional crystallization of the two alums appears to give satisfactory results.[1]

Thallium is usually extracted from a thallium-rich flue-dust, obtained from a sulphuric acid works using a variety of pyrites containing thallium. It can largely be extracted by boiling water, and precipitated as chloride by adding sodium chloride to the extract. The precipitate is washed, and reconverted to thallium sulphate by heating with sulphuric acid. The solution of impure thallium sulphate is freed from various metallic impurities by treatment first with hydrogen sulphide, and then with ammonia. Afterwards, by electrolysis of the purified solution containing free acid thallium may be obtained in the metallic condition on the cathode; the free acid serves to prevent the formation of an oxide deposit on the anode.[2]

Thallium has been used in optical glass, to which it imparts an exceptionally high refractive index.[3] The flue-dust from the pyrites burners at sulphuric acid works, and similar waste material, provide a source for the comparatively small quantities of thallium compounds required.

[1] P. E. Browning and L. E. Porter, *J. Amer. Chem. Soc.* **43** (1921), 126.

[2] F. Foerster, *Zeitsch. Anorg. Chem.* **15** (1897), 71.

[3] E. Cahen, *Discovery*, **1** (1920), 143.

GROUP IVB

	Atomic Weight.	Normal Electrode Potential.
Carbon	12·005	
Silicon	28·3	
Germanium	72·5	
Tin	118·7	−0·146 volt
Lead	207·20	−0·132 ,,

The first two elements of Group IVB, carbon and silicon, are usually regarded as non-metals; germanium also possesses certain non-metallic properties. The two higher members of the group, tin and lead, are soft, readily fusible, metals, somewhat recalling the metals of Group IIIB.

Carbon and silicon have an almost invariable tetravalent character. Germanium, although normally tetravalent, has also compounds in which the metal is divalent. In tin, the salts of the divalent element are as stable as those in which the full valency of four is exerted, whilst in lead, the lower salts are by far the most stable. The compounds of tetravalent germanium, tin and lead, recall in many ways the tetravalent elements of Group IVA; we find once more volatile tetrachlorides, whilst the oxide corresponding to the same state of oxidation has acidic—rather than basic—properties; the germinates, stannates and plumbates may be regarded as analogous in some respects to the titanates and zirconates.

The Appearance of Non-metallic Properties. The most interesting feature of Group IVB is the appearance of non-metallic properties. All the elements so far considered tend—according to modern ideas—to *lose electrons*, when they enter into combination. The charged sodium atom, which exists in a crystal of sodium chloride and (in a more mobile form, the sodium "ion") in an aqueous solution of the same salt, is supposed to be a sodium atom deprived of one electron. As already explained in the introduction (Vol. I), the sodium atom has one more electron than the inert gas neon, and the loss of this one "valency electron" must be supposed to leave the outer shell of the sodium atom similar to that of a neon atom ; thus, the remarkable stability of the charged sodium atom is accounted for.[1] The electron lost by the sodium is gained by a chlorine atom. Chlorine lies on the extreme right of the periodic table, and has one electron less than the inert gas " argon." By the absorption of this one extra electron, the chlorine atom comes to assume a stable character comparable to that of an inert gas.

According to this notion, *non-metallic properties* (i.e. the power to *absorb electrons*) will be confined to those elements which precede the inert gases, that is to elements on the right-hand side of the Periodic Table, as arranged in this book. This is actually the case. Group IVB is the first group in which marked non-metallic properties occur. Carbon and silicon, the two lowest elements, are invariably regarded as non-metals, although one form of carbon has the lustre and the type of electrical conductivity associated with metals. The remaining three elements may indeed be looked upon as metals, but they form a few compounds in which they undoubtedly play the part of a non-metal. Thus germanium forms a gaseous hydride, GeH_4, analogous to those formed by carbon (CH_4) and silicon (SiH_4). There is evidence that similar gaseous hydrides can exist in the case of tin and lead.

These gaseous hydrides must be distinguished from any hydrides which we have yet considered, with the possible exception of boron hydride.[2] The hydrides of the different elements can be assigned to three classes :—

(1) **Solid hydrides** formed by elements on the *left*-hand side of the Periodic Table. Here the hydrogen functions as a non-metal,[3] and the element exerts its characteristic positive valency. Examples are lithium hydride (LiH), potassium hydride (KH), and calcium hydride (CaH_2).

(2) **Solid hydrogen-alloys,** possessing the physical characters of a metal, formed by metals of the *centre* of the Periodic Table, like palladium, iron, nickel, and platinum. These may be regarded as true alloys, both hydrogen and the element in question acting as metals.

(3) **Gaseous hydrides,** formed by elements on the *right*-hand side of the Periodic Table. Here hydrogen acts as the metal, and the element as a non-metal ; the element exerts its negative valency,

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[1] Compare I. Langmuir, *J. Amer. Chem. Soc.* **41** (1919), 868, 1543.

[2] Compare F. Paneth, *Ber.* **53** (1920), 1710.

[3] See also W. Nernst, *Zeitsch. Elektrochem.* **26** (1920), 323. An X-ray study of lithium hydride by J. M. Bijvoet and A. Karssen, *Proc. Amst. Acad.* **25** (1922), 26, appears to show a structure analogous to sodium chloride, the hydrogen taking the place of chlorine. D. C. Bardwell, *J. Amer. Chem. Soc.* **44** (1922), 2499, has shown that on the electrolysis of a solution of calcium hydride in a fused mixture of lithium and potassium chlorides, hydrogen is liberated at the *anode*, not the cathode.

which is determined by the distance of the element from the inert-gas group. Examples are given in tabular form below. It should be noticed that the stability of these hydrides increases, as we approach the inert gas group, but that—in a given group—it decreases as the atomic weight rises; the hydrides placed in brackets are extremely unstable.

Group IVB	VB	VIB	VIIB
CH_4	NH_3	OH_2	FH
SiH_4	PH_3	SH_2	ClH
GeH_4	AsH_3	SeH_2	BrH
(SnH_4)	SbH_3	TeH_2	IH
(PbH_4)	(BiH_3)	(PoH_2)	—

Such a view of the gaseous hydrides, which is largely due to Paneth, would confine the formation of these hydrides to elements which immediately precede the inert gases in the order of atomic numbers. From time to time, different experimenters have asserted that certain members of Group IVA, namely titanium,[1] thorium,[2] and possibly zirconium,[3] form hydrides similar to those of the members of Group IVB. If upheld, this contention would prove difficult to reconcile with Paneth's theory, but the most recent work[4] appears to indicate that the hydrides of titanium, zirconium, and thorium do not exist.

On account of their non-metallic character, carbon and silicon are not discussed in this work, and we shall proceed at once to the consideration of germanium.

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[1] A. Klauber, *Zeitsch. Anorg. Chem.* **117** (1921), 243; M. Billy, *Ann. Chim.* **16** (1921), 18.

[2] A. Klauber and J. M. von Mellenheim, *Zeitsch. Anorg. Chem.* **113** (1920), 306.

[3] C. Winkler, *Ber.* **23** (1890), 2665.

[4] R. Schwarz and E. Konrad, *Ber.* **54** (1921), 2122; F. Paneth, M. Matthies, and E. Schmidt-Hebbel, *Ber.* **55** (1922), 788, including foot-note.

GERMANIUM

Atomic weight . . . 72·5

The Metal

Germanium is a white element having a metallic lustre ; unlike the metals of previous groups, it is distinctly brittle ; the crystalline character of cast germanium is well displayed when it is broken. The arrangement of the atoms in crystalline germanium is found by the X-ray method to be the same as in the diamond, and in grey tin.[1] The melting-point of pure germanium is 958° C., but it is considerably depressed if the germanium contains dissolved oxide. Pure germanium is only slightly volatile even at 1,350° C. ; the "apparent volatility" observed by some investigators just above the melting-point is probably due to the expulsion of dissolved oxide.[2]

The electrode potential is uncertain, but since germanium is precipitated from its salts by metallic zinc, it must be distinctly more noble than that metal. It behaves in fact as a comparatively noble material towards acids. It is insoluble in hydrochloric acid, but dissolves in warm concentrated sulphuric acid, forming a white sulphate, and evolving sulphur dioxide. Germanium is readily converted to its dioxide by the oxidizing action of nitric acid ; the dioxide produced, owing to its feebly basic character, does not dissolve in the excess of acid to form a nitrate, but remains as a dense white precipitate. The same oxide is formed by heating the finely-divided metal in air, but compact germanium is only oxidized superficially when heated, and appears to be unaffected by exposure to the atmosphere at the ordinary temperature.

Laboratory Preparation. Germanium may be obtained from its oxide by reduction with carbon.[3] The oxide is preferably made into little pellets by means of starch (10–15 per cent.) ; these pellets are dried and heated in a porcelain crucible contained in a large closed crucible, the space between the two being filled with wood-charcoal. A bright red heat is applied for an hour. After cooling a grey powder is found, which may be remelted below borax to give a button of germanium.

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[1] N. H. Kolkmeijer, *Proc. Amst. Acad.* **25** (1922), 125.

[2] W. Biltz, *Zeitsch. Anorg. Chem.* **72** (1911), 315.

[3] C. Winkler, *J. Prakt. Chem.* **34** (1886), 177.

A more modern method of preparing the metal is to heat the oxide in a current of hydrogen in an electric furnace, the product being fused under a covering of sodium sulphate.[1]

Compounds

Like silicon, germanium forms stable compounds in which the element is tetravalent. A lower series of derivatives, containing divalent germanium, are also known.

A. Compounds of Tetravalent Germanium (Germanic Compounds).

Germanic oxide, GeO_2, is formed, as has been remarked above, when the element is oxidized either by heating in air, or by the action of warm nitric acid. It is also formed on the hydrolysis of germanic chloride in water. It is slightly soluble in water (1 per cent. at 100° C.) and the solution has a sour taste. Germanic oxide appears to have both acidic and basic properties, but both are very feebly developed. It is dissolved by sodium hydroxide, no doubt forming a " sodium germanate " ; no alkali-metal germanate appears to have been isolated in the pure state, although the insoluble magnesium germanate, Mg_2GeO_4, has been obtained by precipitation.[2] When the oxide is boiled with aqueous acids, it dissolves in part, and the solution no doubt contains germanium salts ; but any attempt to obtain these salts by evaporation of the solution results in hydrolysis, a hydrated form of germanic oxide being obtained.

Germanic chloride, $GeCl_4$, is, however, present in the vapours given off when the solution of germanium dioxide in hydrochloric acid is boiled. It is prepared more easily by passing chlorine over the metal. Like so many tetrachlorides, it is a volatile liquid; the boiling-point is 86° C., but vapour is given off freely at the ordinary temperature. This vapour reacts with the moisture present in ordinary air, hydrolysing to form the solid dioxide ; thus germanic chloride, in common with the other liquid chlorides, gives off dense white fumes when exposed to damp air. When germanic chloride is added to water, it reacts with much evolution of heat, forming hydrochloric acid and germanic oxide ; the reaction of germanic chloride with water is accompanied by a curious " crackling " sound.[3]

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[1] C. C. Bidwell, *Phys. Rev.* **19** (1922), 447.

[2] J. H. Müller, *J. Amer. Chem. Soc.* **44** (1922), 2493.

[3] L. M. Dennis and F. E. Hance, *J. Amer. Chem. Soc.* **44** (1922), 306.

On account of its volatility, germanium chloride can be obtained in a pure state by distillation, and is therefore a convenient starting material for the preparation of other germanium compounds.[1]

Germanium fluoride is obtained in solution by the dissolution of germanium dioxide in hydrofluoric acid; it forms well-defined complex salts with the fluorides of the alkali metals. For instance, by the addition of potassium fluoride to the solution, and evaporation, hexagonal crystals of potassium **germani-fluoride,** K_2GeF_6, are obtained; this body is comparable to the complex fluorides formed by silicon (K_2SiF_6), and also by the tetravalent elements of Group IVA, titanium (K_2TiF_6), and zirconium (K_2ZrF_6).

Germanic sulphide, GeS_2, is obtained on precipitating a solution of germanic oxide in excess of acid with hydrogen sulphide; it is a white insoluble substance, and, unlike most of the other sulphides which have been described hitherto, is soluble in ammonium sulphide. The solution obtained contains a germani-sulphide (or thio-germanate), probably $(NH_4)_2S.GeS_2$ or $(NH_4)_2[GeS_3]$, in which germanium exists in the anion. Several other metals of groups IVB and VB form analogous complex sulphides which are soluble.

Germanic hydride, GeH_4, is formed when hydrogen is being generated in a solution containing germanium. For instance, when zinc or magnesium is placed in an acidified solution containing germanium the gas produced always contains a little germanium hydride.[2] If the gas is burned, the germanium is liberated and may be deposited as a mirror on a cold porcelain dish held over the flame; the presence of germanium in the flame gives a bluish-red colour. Alternatively, if the hydrogen containing germanium hydride is passed through a heated glass tube, a shining mirror of germanium is deposited at the heated portion of the tube, due to the decomposition of the hydride. We shall discuss the properties of gaseous metallic hydrides further, when we come to consider arsenic hydride.

In forming a gaseous hydride and a liquid chloride, germanium shows a considerable resemblance to carbon, the non-metal which stands at the head of Group IVB. Various compounds of germanium are known, which are analogous in composition to the "organic" compounds of carbon. These peculiar substances are of more interest to the organic chemist than to the student of metals; they include the so-called "**germanium chloroform,**" $GeHCl_3$, a liquid obtained by the action of dry gaseous hydrogen chloride on germanium, and analogous to chloroform ($CHCl_3$). Another compound

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[1] See also J. H. Müller, *J. Amer. Chem. Soc.* **43** (1921), 1085.

[2] See also F. Paneth and E. Schmidt-Hebbel, *Ber.* **55** (1922), 2615; J. H. Müller and N. H. Smith, *J. Amer. Chem. Soc.* **44** (1922), 1909.

worthy of notice is "**germanium tetraethide**," $Ge(C_2H_5)_4$, a liquid prepared by mixing zinc ethide and germanium chloride; it may be considered as analogous to the hydrocarbon, **symmetrical nonane**, $C(C_2H_5)_4$.

B. Compounds of Divalent Germanium (Germanous Compounds).

The lower compounds of germanium are less numerous than the higher ones; **germanous oxide**, GeO, is obtained by heating the dioxide with magnesium, and is a grey substance. A brown hydroxide is prepared by precipitation of germanous chloride solution by caustic soda. It is soluble both in excess of alkalis and in hydrochloric acid.

The only other well-defined germanous compound is the **sulphide**, GeS, obtained when germanic sulphide is heated in a current of hydrogen; it is a dark grey body. The sulphide is converted by the action of hydrogen chloride to the **chloride**, $GeCl_2$, mentioned above as being the source of the hydroxide; this chloride does not appear to have been produced in a state of purity. Germanous sulphide is not soluble in pure colourless ammonium sulphides; but "yellow" ammonium sulphide, which contains free sulphur or polysulphides in solution, first converts it to germanic sulphide, which then passes into solution as a complex sulphide. The same state of affairs will be met with in the case of the lower sulphide of tin.

Analytical

Germanium is usually precipitated and estimated as sulphide, which can be thrown down in a distinctly acid solution by means of hydrogen sulphide. Several other metals are likewise precipitated, but only in a few cases—such as germanium, tin, arsenic and antimony—is the sulphide soluble in ammonium sulphide. Hence these four metals can be separated from the others. The complex "germani-sulphides" are more stable than the corresponding tin, arsenic and antimony bodies; upon the addition of just sufficient sulphuric acid to neutralize the liquid followed by dilution, tin, arsenic and antimony are thrown down, whilst germanium remains—for the most part—in the solution. If, after filtration, the filtrate is made strongly acid, and again saturated with hydrogen sulphide, germanium sulphide is thrown down. It should be washed with slightly acidified water saturated with hydrogen sulphide (being slightly soluble in pure water), then with alcohol saturated with hydrogen sulphide, and finally with ether, *A qualitative method*[1] *of separating germanium from arsenic*, and also from zinc and other metals with which it is commonly associated, consists in dissolving the material in hydrochloric acid, adding potassium permanganate, and distilling; the distillate carries over germanium as the volatile chloride, the germanium being afterwards precipitated from the distillate as sulphide. There appears to be no reason why this method should not be made quantitative.

The best method of estimating germanium in impure zinc oxide depends on distillation as the volatile chloride, the distillate being afterwards precipitated by hydrogen sulphide; the precipitate only comes down very slowly. The sulphide is converted to oxide by treatment with nitric acid, excess of which is afterwards driven off by heat, and the metal is weighed as GeO_2. Details of the process should be sought in the original paper.[2]

TERRESTRIAL OCCURRENCE

The terrestrial occurence of germanium as a minor constituent in various American and German zinc-ores, as well as in such rare minerals as

Argyrodite . . . $4Ag_2S,GeS_2$

has been discussed in connection with the occurrence of gallium, indium and thallium (see page 205). The richest source of germanium appears to be certain zinc blendes from Missouri and Wisconsin.[3] Germanium likewise occurs in various minerals containing rare earths, and also minerals of niobium and tantalum; its occurrence in euxenite has already been mentioned.

EXTRACTION

The recovery of germanium, as sulphide, from the "leady residues" left in the retorts when certain American zinc ores are distilled for zinc has been discussed in connection with gallium.[4] The crude zinc oxide obtained by roasting these residues is dissolved in hydrochloric acid, potassium chlorate is added and the liquid is distilled. The whole of the germanium present comes over as the volatile chloride, but since arsenic also has a volatile chloride,

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[1] P. E. Browning and S. E. Scott, *Amer. J. Sci.* **44** (1917), 313.

[2] L. M. Dennis and J. Papish, *J. Amer. Chem. Soc.* **43** (1921), 2140.

[3] C. H. Buchanan, *J. Ind. Eng. Chem.* **8** (1916), 585; **9** (1917), 661.

[4] L. M. Dennis and J. Papish. *J Amer. Chem. Soc.* **43** (1921), 2131; H. C. Fogg and C. James. *J. Amer. Chem. Soc.* **41** (1919), 947. See also G. Urbain, M. Blondel, and M. Obiedoff, *Comptes Rend.* **150** (1910), 1758, who give an alternative method.

the distillate may also contain arsenic. Treatment of the distillate with hydrogen sulphide throws down the sulphides of germanium and arsenic, and the mixture on roasting yields oxide of germanium, most of the oxide of arsenic being removed by volatilization. It is best to dissolve the roasted material in caustic alkali and to treat the solution with chlorine, which converts any remaining arsenic to the pentavalent condition. It is then possible to acidify the solution and to obtain the germanium by distillation as the volatile chloride.

TIN

Atomic weight . . . 118·7

The Metal

Tin, like germanium, is a silver-white lustrous metal, but it is rather heavier than germanium, the specific gravity being 7·3; moreover, it melts at a far lower temperature, 232° C., lower than any other common metal, except mercury. Ordinary white tin, such as is generally met with, crystallizes in the tetragonal system. The coarsely crystalline texture of ordinary tin is somewhat characteristic. Tin is distinctly less brittle than germanium, and is malleable enough to be rolled into foil. When a piece of tin is sharply bent, a curious sound known as the "cry of tin" is heard at the moment of deformation. Microsections of deformed tin show the existence of "twinning" on the side where the tin has been compressed, although it is usually absent on the side where the metal has been in tension. It is possible that the "cry" is caused by the atoms (on the compressional side) taking up their twin orientation.[1] Deformed tin undergoes recrystallization or grain-growth on annealing.[2]

The malleability and ductility of tin increases when the metal is heated to 100° C., but it is extremely brittle about 195° C.; the change is ascribed by most authorities to the appearance of a rhombic allotrope which is stable above 161° C.[3]

When ordinary white cast tin (produced by cooling fused tin to the ordinary temperature) is exposed to an extremely low temperature (−40° C.), it gradually commences to crumble, forming a greyish powder, which would seem to consist of another allotropic form of the metal; grey tin has actually a much lower specific gravity (5·8) than white tin (7·3). Grey tin belongs to the cubic

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[1] C. A. Edwards and H. C. H. Carpenter, *J. Iron Steel Inst.* **89** (1914), 138. P. Gaubert, *Comptes Rend.* **159** (1914), 680.

[2] J. Czochralski, *Int. Zeitsch. Met.* **8** (1916), 1. Compare H. C. H. Carpenter and C. F. Elam, *J. Inst. Met.* **24** (1920), 83, who worked on tin containing 1½ per cent. of antimony in solid solution. See also G. Masing, *Zeitsch. Metallkunde*, **12** (1920), 457.

[3] Just as in the case of the alleged allotropic change in zinc at 170–180° C., so there is a little doubt about the existence of the allotropic change in tin at 161° C. S. Nishakawa and G. Asahara, *Phys. Rev.* **15** (1920), 38, have compared the X-ray patterns given by tin at 140°, 150°, 160°, 170°, and 200° C., and state that there is no evidence of any change of atomic arrangement. But so many other authorities have obtained by different methods evidence of the change that the balance of evidence appears to be in favour of its exist-

system,[1] the atoms being arranged in the same way as carbon atoms in the diamond. There would appear, therefore, to be three solid allotropes of tin,[2] namely:

Grey cubic tin, stable below 20° C.

White tetragonal tin (malleable), stable from 20° to 161° C. (?), and probably

Rhombic tin (brittle), stable from 161° (?) to 232° C.

Since the temperature in this country is commonly below 20° C., it will be evident that the soft grey form is really the stable condition at ordinary temperatures, and that the familiar white variety is metastable. Apparently, when molten tin is allowed to solidify, and the white tin is cooled to ordinary temperatures, we meet with a case of supercooling, such as is commonly noticed when metals are cooled only a few degrees below a transformation point. According to Cohen, the transformation of white tin into grey tin *can* take place at any temperature below 20° C., but at temperatures only just below 20° C. the velocity of transformation is so slow as to be negligible. The velocity increases as the tin is cooled down and reaches a maximum at — 48° C., below which point the velocity diminishes. Even at 0° C. the velocity of transformation is quite appreciable, if a little "grey tin" is placed in contact with the white, so as to provide a nucleus for the change. It would appear that the presence of stannous salts also accelerates the change at such temperatures. The reason is almost certainly to be ascribed to the formation of a short-circuited cell or couple:

Grey tin	Tin salt solution	White tin

Below the transition temperature (20° C.), the grey tin acts as cathode, and the unstable white tin as anode; thus white tin is dissolved away, and the same amount of fresh grey tin is deposited. Consequently the transformation of white to grey tin proceeds apace. The E.M.F. of the above-mentioned cell has been measured at various temperatures; it is found to become zero at the

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ence. See E. Cohen and E. Goldschmidt, *Zeitsch. Phys. Chem.* **50** (1905), 225; P. W. Degens, *Zeitsch. Anorg. Chem.* **63** (1909), 207; W. Werner, *Zeitsch. Anorg. Chem.* **83** (1913), 275. However, V. M. Goldschmidt, *Zeitsch. Metallkunde,* **13** (1921), 450, Note 1, says that the so-called rhombic tin is really stannous sulphide. A. Smits and J. Spuyman, *Proc. Amst. Acad.* **23** (1921), 687, as a result of researches on the thermo-electromotive force of tin-iron and tin-copper couples, state that the change from tetragonal to rhombic tin occurs at 200° C.

[1] A. J. Bijl and N. H. Kolkmeijer, *Chem. Weekblad,* **15** (1918), 1264.

[2] E. Cohen, *Zeitsch. Phys. Chem.* **33** (1900), 57; **35** (1900), 588; **36** (1901), 513; **48** (1904), 243; *Trans. Faraday Soc.* **7** (1911), 122.

transition-temperature, whilst above that point the cell would tend to send current in the opposite direction, grey tin being converted to white.

Under ordinary conditions, white tin can be stored for a number of years without appreciable change. Most of the actual cases where tin has become "grey" are due to exceptionally low temperatures. For instance, during the severe winter of 1867–8, several samples of tin stored at St. Petersburg were found to be affected by what was called the "tin plague"; some of the tin had actually crumbled to powder. It is noteworthy that tin which has been stored for several centuries, even in ordinary climates, has been found to have become changed (at any rate in places) to the grey condition.

Tin falls a little on the "reactive" side of hydrogen in the potential series, and will precipitate more noble metals from solutions of their salts; thus tin boiled with a solution of antimony chloride in hydrochloric acid will enter into solution, the antimony being precipitated as a black powder. On the other hand tin is itself reduced to the metallic state, when a solution of tin salt is treated with more reactive metals; if a piece of zinc is placed in a tin solution, a fine dendritic growth of metal known as the "tin tree" is produced.

Since tin is slightly more reactive than hydrogen, it is capable of dissolving in dilute sulphuric or hydrochloric acid with the evolution of that gas; but the change only takes place if the solution is warmed, the rise of temperature reducing the "overpotential" of hydrogen-evolution. In contact with platinum, a material of low overpotential, tin dissolves in hydrochloric acid more readily; the platinum, acting as the cathodic member of the corrosion couple, affords a surface upon which the gas can be evolved without difficulty.

Oxidizing acids attack tin readily. Nitric acid yields different products according to the temperature and dilution. If the acid is strong, stannic nitrate is the main product; being not very soluble in the acid, it is largely precipitated in the solid state. If water is present, hydrolysis of the stannic nitrate occurs, and we get in addition yellowish basic nitrates or stannic hydroxide; whilst if the solution is warmed these bodies quickly change to the so-called "metastannic acid" (see below). Finally, if the nitric acid is sufficiently dilute, the tin is not oxidized to the stannic condition at all, and the only product is stannous nitrate.[1]

Tin also dissolves in caustic alkalis, evolving hydrogen and forming stannites, or—in presence of air—stannates.

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[1] A. Kleinschmidt, *Monatsh.* **39** (1918), 149.

Metallic tin keeps its lustre well in ordinary air, and suffers no appreciable corrosion.

The **anodic behaviour** of tin [1] is of interest. When current is forced through an electrolytic cell furnished with a tin anode, and containing a *chloride* solution, the tin is corroded at a current efficiency in the neighbourhood of 100 per cent., calculated on the assumption that tin passes into the solution in the divalent condition. In a *sulphate* solution, the efficiency of anodic dissolution is much lower owing to the formation of a film of light brown oxide; this is sometimes closely adherent and obstructive, sometimes loose and incoherent; the current efficiency varies between 6 per cent. and 84 per cent. under these different conditions. In a *nitrate* solution the oxide-film produced is of a loose character, and does not appear usually to interfere with the attack. The efficiency of anodic attack is high; according to G. R. White a current efficiency of 170–190 per cent. is usually obtained, calculated on the assumption that tin is passing into the divalent condition. It is difficult to find a satisfactory explanation for these high values. If the electrolyte is *alkaline* [2] (e.g. a solution of sodium hydroxide), tin passes from the anode, under favourable conditions, exclusively into the divalent state; in other words, the sole primary product of the anodic attack is sodium stannite. But this salt is unstable and may become converted by secondary changes to stannate. Under ordinary conditions, access of air will convert the stannite to stannate; even if this is prevented, the stannite solution is able slowly to deposit a grey precipitate of metallic tin, stannate being left in solution:

$$2Sn^{II} = Sn + Sn^{IV}.$$

Apart from this slow change, as soon as any considerable amount of stannite has accumulated in the bath, it will begin to be oxidized anodically to stannate. If a film of clinging insoluble obstructive matter, e.g. stannic acid, comes to be formed on the anode surface, causing total or partial passivity, the passage of tin into the solution will be obstructed; the anodic potential will then become more positive, and the oxidation of stannite to stannate will become the most important electrodic change.

Laboratory Preparation. The metal may be prepared by the electrolysis of an aqueous solution of a tin salt. Deposition from a chloride solution at low current density produces a loose deposit of bright crystals. Deposition from certain complex salt solutions, such as ammonium tin oxalate, preferably in the presence of peptone, gives a smooth deposit.

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[1] G. R. White, *J. Phys. Chem.* **15** (1911), 757.

[2] F. Foerster, *Zeitsch. Elektrochem* **16** (1910), 599.

Tin can be obtained as a crystalline " tree " by placing zinc in an acidified solution of a tin salt. A dry method of obtaining tin from the compounds consists in heating the oxide with charcoal and potassium cyanide; the cyanide probably acts as the real reducing agent, becoming converted to cyanate, which is then reconverted to cyanide by the carbon. If tin oxide and carbon are heated alone, without the presence of cyanide, a much higher temperature is needed for the reduction.

For the preparation of pure tin from impure metal, it is possible to distil it in a current of chlorine. Tin passes over as the volatile tetrachloride, whilst most of the impurities remain behind. The tin is then precipitated from the distillate as sulphide, which is afterwards dissolved in a solution of sodium sulphide containing free alkali. By electrolysis of this solution, pure tin can be obtained.[1]

Compounds

Tin forms two classes of compounds, derived from the oxides SnO and SnO_2; these correspond to the two series of germanium compounds. Both the oxides mentioned are " amphoteric," that is, they dissolve in acids, forming stannous and stannic salts, and also in alkalis, forming " stannites " and " stannates " respectively. But all these solutions hydrolyse very readily and under certain conditions deposit hydrated oxides of tin spontaneously.

A. Compounds of Tetravalent Tin (Stannic Compounds).

Stannic oxide is formed in the anhydrous state when excess of air is passed for some time over molten tin; at first the lower (stannous) oxide is formed, but this is finally oxidized to the higher compound. But it is more conveniently produced by igniting any of the forms of hydrated oxide (stannic acids) discussed below. As usually produced, the oxide is a heavy white powder, but it is known in three different crystalline forms, respectively isomorphous with the three forms of titanic oxide. The most important form belongs to the tetragonal system and is found in nature under the name " cassiterite "; it will therefore be discussed in the section on geo-chemistry. This form can be obtained in the laboratory by the crystallization of stannic oxide from fused borax.

The hydrated oxide, usually known as **stannic acid**, is formed when a stannic salt (e.g. stannic chloride) is precipitated with an alkali (such as calcium carbonate), or when a stannate is decomposed with hydrochloric acid. When thrown down from a cold solution, it is usually a rather voluminous precipitate soluble either in acids, yielding stannic salts, or in alkalis yielding solutions of the

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[1] J. Bongartz and A. Classen, *Ber.* **21** (1888), 2900.

stannates. But, like so many hydrated oxides, it undergoes "ageing"—slowly at ordinary temperatures, but quickly on warming—giving rise to a product which reacts much less readily both with acids and alkalis. So different is the behaviour of the product obtained in the cold to that obtained on warming, that they have been assigned distinct names; the product obtained in the cold is called α-**stannic acid**, and the product obtained on warming β-**stannic acid** or **metastannic acid**. The latter is usually prepared by the action of nitric acid on metallic tin at 100° C.; at ordinary temperatures, nitric acid acting on tin gives a nitrate of tin (stannous nitrate or stannic nitrate according to the concentration of the acid).

The behaviour of α-stannic and β-stannic acids to acids and alkalis is very different. Weak alkalis, such as ammonia or sodium carbonate, peptize the α-acid but not the β-acid. Strong acids or alkalis dissolve α-stannic acid, yielding a solution from which crystalline stannic salts or stannates can be isolated. But the β-stannic acid is merely peptized, and under certain circumstances excess of the reagent causes the β-acid to be thrown down once more. For instance, β-stannic acid treated with concentrated hydrochloric acid is not dissolved, but if after some time the mixture is diluted with a large volume of water, a more or less clear colloidal solution is obtained; addition of excess of hydrochloric acid—or alternatively a very much smaller amount of sodium sulphate—renders the solution cloudy owing to the reprecipitation of β-stannic acid. However, continued boiling of the β-acid with a concentrated acid or alkali converts it to a true solution of a stannic salt or a stannate.

Some chemists regard α- and β-stannic acids as definitely distinct individuals. According to one view,[1] α-stannic acid is written H_2SnO_3, and β-stannic acid is regarded as its polymeride $(H_2SnO_3)_5$. It seems, however, more probable that α- and β-stannic acids are really the same substance. It will be recollected that in the case of hydroxides of (ferric) iron, a series of products can be obtained differing in colour, general appearance, and chemical properties, and yet this sensational variation in properties is now attributed mainly to the size of the primary particles. It seems very likely

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[1] A. Kleinschmidt, *Montash.* 39 (1918), 149. The view is based upon the analysis of the products obtained by the action of acids or alkalis on metastannic acid. These products are stated by earlier writers to have a rather variable composition, and are generally regarded merely as adsorption products. But Kleinschmidt assigns them definite names and formulæ, such as metastannyl chloride $Sn_5O_5(OH)_8Cl_2$, metastannyl nitrate $Sn_5O_5(OH)_8(NO_3)_2$, and sodium metastannate $Sn_5O_5(OH)_8(ONa)_2$, which would suggest that metastannic acid itself was $Sn_5O_5(OH)_8(OH)_2$ or $(H_2SnO_3)_5$.

that a similar series exists in the case of the stannic acids; the products in which the primary particles are small are those which we call α-stannic acid, whilst those in which the primary particles are largest are called β-stannic acid.[1] This view explains why the β-product is less reactive in its chemical behaviour. Probably the same explanation may be extended to the analogous case of the titanic acids (Vol. II, page 241).

Another view of the spontaneous change from α-stannic acid to β-stannic acid depends on the amphoteric character of stannic hydroxide; the change is regarded as being of the nature of salt-formation.[2] α-stannic acid can be regarded either as stannic hydroxide ($Sn(OH)_4$) or as stannic acid (H_4SnO_4); these may combine to form a salt, stannic stannate, water being eliminated. According to this view, the so-called β-acid is a salt of this kind. It is stated that when the two products are dried in air, the β-body contains less water than the α-body.

If α-stannic acid is liberated in very dilute solutions, it is not precipitated, but remains as a nearly clear **colloidal solution.** For instance, if a solution of highly diluted sodium stannate is acted upon with an acid, or a highly dilute solution of a stannic salt with an alkali, no precipitate is observed; often, when stannates or stannic salts suffer hydrolysis by dilution, no gelatinous hydroxide appears—at any rate for some time. It is possible to remove most of the electrolytes from the liquid by dialysis, and thus to obtain a colloidal solution of α-stannic acid. However, when the colloidal solution is treated with a trace of hydrochloric acid, a precipitate of gelatinous α-stannic acid is usually obtained.

The charge on the colloid particles of stannic acid appears to depend on the mode of formation. If the stannic acid is produced in alkaline solution, the charge is negative; if in acid solution the charge may be positive. For instance, by the addition of dilute stannic chloride to excess of very dilute ammonia, followed by dialysis, a negative sol is produced[3]; the charge on the particles is possibly due to adsorbed $(OH)'$ions. On the other hand, by the hydrolysis of stannic chloride, a gel can be obtained which is positively charged, no doubt owing to the adsorption of hydrogen ions from the hydrochloric acid, which is also a product of hydrolysis. If this acid is gradually removed by washing the gel, the colloid becomes first neutral and finally negatively charged.[4]

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[1] W. Mecklenburg, *Zeitsch. Anorg. Chem.* **64** (1909), 368; **74** (1912), 207; **84** (1913), 121.

[2] G. E. Collins and J. K. Wood, *Trans. Chem. Soc.* **121** (1922), 441, 1122.

[3] W. Biltz, *Ber.* **37** (1904), 1095.

[4] S. Glixelli, *Koll. Zeitsch.* **13** (1913), 194. Compare F. Powis, *Trans. Chem. Soc.* **107** (1915), 823.

When gelatinous stannic acid is treated with small quantities of sodium hydroxide, peptization occurs, and a colloidal solution is obtained. The gels consist, of course, of flocks of considerable size consisting of aggregates of the small primary particles in loose union. With small amounts of alkali, these flocks break up to a large extent, but the liquid still seems to contain fairly large "secondary aggregates." As the amount of alkali is increased, these are broken up completely into the very small primary particles, and the "sol" becomes more stable.[1] Finally, when the alkali is present in large excess, the primary colloid particles are attacked, and the particle-size becomes molecular, an ordinary solution of sodium stannate being formed; this has, of course, considerable stability. The gradual passage from suspensions containing flocks of visible size through colloidal solutions to true salt solutions is, no doubt, a phenomenon common to most systems of the kind; a rather similar transition is met with in the treatment of ferric or aluminium hydroxide with gradually increasing amounts of hydrochloric acid.

The Stannates. Sodium α-stannate[2] can be prepared in the solid state by treating precipitated α-stannic acid with hot sodium hydroxide; the stannic acid dissolves quickly, and sodium stannate soon comes down as a crystalline precipitate of composition $Na_2Sn(OH)_6$, or $Na_2SnO_3.3H_2O$. It can also be obtained by heating metallic tin with sodium hydroxide and sodium nitrate.

The soluble α-**stannic salts** are mostly white substances which are at once hydrolysed when treated with pure water, yielding gelatinous precipitates containing α-stannic acid or a basic salt. This can be prevented by the addition of free acid. The **nitrate** can be obtained by the action of cold concentrated nitric acid on tin, but the solution readily gelatinizes if allowed to become warm, yielding metastannic acid. The **sulphate**, $SnO_2.2H_2SO_4$, is formed when stannic oxide is dissolved in sulphuric acid. It can be obtained in rhombohedral crystals closely resembling cubes by cautious evaporation of the solution.[3]

Stannic chloride, $SnCl_4$, like germanium chloride, is a heavy liquid, obtained by the action of dry chlorine on molten tin. When brought into contact with water, it dissolves readily, heat being evolved; from the solution various crystalline hydrates, such as $SnCl_4.5H_2O$, can be obtained. The anhydrous chloride fumes in damp air, the white fumes apparently being due to a solid hydrate.

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[1] R. Zsigmondy, *Zeitsch. Anorg. Chem.* **89** (1914), 210. Compare W. Pauli, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 15.

[2] For further details see H. Zocher, *Zeitsch. Anorg. Chem.* **112** (1920), 5.

[3] A. Ditte, *Comptes Rend.* **104** (1887), 172.

The dilute solution hydrolyses on keeping, and more rapidly when boiled, a gelatinous precipitate being as usual produced.

Crystalline double salts with potassium chloride and with ammonium chloride exist; they are usually known as **potassium stannichloride**, $K_2[SnCl_6]$, and **ammonium stannichloride,** $(NH_4)_2[SnCl_6]$; the latter is sometimes called *pink salt.* The appearance of the common co-ordination number, six, will be noted. It is interesting to observe that the arrangement of the atoms in the crystals has been ascertained by the X-ray method. It is found that the six chlorine atoms are actually grouped around the tin atom at equal distances from it, being much closer to the tin atom than is the atom of potassium (or the radicle NH_4).[1]

The **insoluble** stannic salts are prepared by precipitation. When hydrogen sulphide is passed through an acidified solution of stannic chloride, the **sulphide,** SnS_2, is produced as a yellow precipitate. The same body is obtained when tin and sulphur, preferably in the presence of ammonium chloride, are heated together; under these circumstances tin sulphide sublimes, collecting as minute golden crystals. Like germanium sulphide, it is soluble in excess of ammonium or potassium sulphide forming such complex salts as $(NH_4)_2SnS_3$ and K_2SnS_3. These bodies, known as "**stannisulphides**" or "**thiostannates,**" have in several cases been isolated in the solid form, by crystallization of the solution.

Stannic phosphate is obtained by precipitation in the usual way; it may also be obtained by boiling tin with nitric acid in the presence of any phosphate. Unlike nearly all other phosphates of the heavy metals, it is insoluble in nitric acid, and on this fact depends the use of tin in the analytical estimation of phosphates.

B. Compounds of Divalent Tin (Stannous Compounds).

Stannous oxide, SnO, is obtained as a grey powder when stannous oxalate is heated. The ignition of an oxalate is a useful general method of obtaining the lower oxide of a metal; the decomposition of oxalates always involves the evolution of carbon monoxide, and in presence of this reducing gas, the lowest oxide of the metal is in many cases produced. The **hydroxide** $Sn(OH)_2$ may be obtained by the normal method of precipitating a stannous salt with caustic alkali; when dried over sulphuric acid, it is said to have the composition $Sn(OH)_2.H_2O$.

The precipitated hydroxide is dissolved by excess of caustic alkali, and the solution contains a "**stannite**" analogous to a zincate. Such solutions are, however, very unstable. They are

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[1] R. G. Dickinson, *J. Amer. Chem. Soc.* **44** (1922), 276. The X-ray study of stannic iodide (SnI_4) is of special interest, since it appears to show the existence of well-separated molecules in the crystalline state. See R. G. Dickinson, *J Amer. Chem. Soc.* **45** (1923), 958.

readily oxidized by air yielding stannates. Even if oxygen is excluded, a solution of sodium stannite gradually decomposes to sodium stannate and metallic tin, the last-named substance appearing as a grey precipitate. It is stated that potassium stannite is more stable than sodium stannite.[1]

The soluble stannous salts are colourless crystalline bodies, best obtained by the action of the acid upon the metal. For the production of the **nitrate** very dilute nitric acid must be used, since otherwise stannic nitrate will be formed along with it. The **sulphate** is formed when tin is dissolved in sulphuric acid. Both salts show a marked tendency to hydrolysis, and a clear solution can only be obtained from the crystals by the addition of free acid. Stannous sulphate is also formed by the action of sulphuric acid on stannous chloride below 90° C.; if the temperature is raised further (130°–200° C.), the sulphuric acid acts as an oxidizing agent, and stannic sulphate is the main product.[2]

Stannous chloride is the best-known salt of tin. It is obtained by dissolving the metal in hot hydrochloric acid and can be crystallized in colourless monoclinic crystals having the composition $SnCl_2,2H_2O$. The solution in pure water is always cloudy, owing to hydrolysis, but is clarified by the addition of hydrochloric acid. The solutions, like those of all stannous salts, are strong reducing agents; they can convert mercuric chloride to mercurous chloride, or even to metallic mercury; they also act upon gold chloride, forming the so-called "Purple of Cassius," a form of colloidal gold.

Stannous sulphide is a brown precipitate obtained when hydrogen sulphide is passed through an acidified solution of a stannous salt. It is not of itself soluble in pure colourless ammonium sulphide, but dissolves readily in the yellow mixture which often passes under that name. This mixture contains enough free sulphur or polysulphide to convert stannous to stannic sulphide, and the latter compound quickly dissolves in ammonium sulphide, forming ammonium stannisulphide.

C. Miscellaneous Compounds.

Tin Hydride.[3] Tin shows much less disposition to combine with hydrogen than germanium, just as germanium has less affinity for hydrogen than carbon and silicon. The existence of tin hydride has only recently been established. When an alloy of tin and magnesium is dissolved in hydrochloric acid, the hydrogen evolved contains tin hydride and—if passed through a heated tube—deposits

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[1] F. Foerster, *Zeitsch. Elektrochem.* **15** (1910), 601, including footnote.

[2] R. G. Durrant, *Trans. Chem. Soc.* **107** (1915), 625.

[3] F. Paneth and K. Fürth, *Ber.* **52** (1919), 2020; F. Paneth, M. Matthies and E. Schmidt-Hebbel, *Ber.* **55** (1922), 775.

a distinct mirror of tin. Tin hydride is very unstable and has only been prepared in any appreciable quantity when diluted with a very large proportion of hydrogen, but it has been possible to prove that its composition corresponds to the formula SnH_4.

As in the case of germanium, various organic derivatives of tin are known. As an example, the **tetra-ethide** $Sn(C_2H_5)_4$, analogous to germanium tetra-ethide $Ge(C_2H_5)_4$, may be mentioned.

Analytical

The easy reducibility and low melting-point of tin make it a simple matter to obtain a bead of the metal by heating a compound suspected to contain it with charcoal and sodium carbonate in the reducing flame of the blowpipe. The bead can be dissolved in hydrochloric acid, and the solution tested for stannous chloride by the addition of mercuric chloride. A borax bead, which has been rendered blue by the addition of a trace of copper, is turned to a ruby red colour when heated in the reducing flame with a trace of tin salt. (The ruby colour is, of course, the same as that obtained in the commercial variety of ruby glass which contains copper reduced with tin.)

Many of the so-called wet tests for tin salts depend upon the reducing action of stannous compounds; stannic salts will not respond to them. A stannous salt, for instance, will reduce auric chloride to finely divided gold (" Purple of Cassius ") ; but other reducing agents, such as ferrous sulphate, also reduce gold to the metallic condition, although they do not, as a rule, produce the gold in a form having the characteristic appearance of " Purple of Cassius." Again, mercuric chloride is reduced to the white insoluble calomel by the addition of stannous chloride solution, or even to the grey metallic state ; but the same reduction is brought about by certain other reducing agents.

More characteristic, therefore, of tin compounds as a whole is the action of sulphuretted hydrogen ; if this gas be bubbled through an acidified solution of a tin salt, the whole of the metal is thrown down as a sulphide, which is brown or yellow according as it is produced from a stannous or stannic solution. Both of these sulphides are soluble in "*yellow* ammonium sulphide," complex stannisulphides being in each case formed. Only a few metals, namely tin, molybdenum, germanium, and two members of the next group, arsenic and antimony, give sulphides which are soluble in excess of ammonium sulphide ; the separation of tin from all other metals presents, therefore, no difficulty.

Of the five elements mentioned above, molybdenum and germanium are but rarely met with in mixtures containing tin; methods of separating these metals have been described in the sections devoted respectively to molybdenum and germanium. The separation of tin from arsenic and antimony is more difficult. The best method of separating tin from arsenic depends on the fact that tin sulphide is not thrown down from a strongly acidified solution. All the metals are first converted to the highest state of oxidation by treatment with chlorine in alkaline solution. The solution is afterwards acidified with hydrochloric acid, boiled to decompose chlorates, and cooled in ice; hydrogen sulphide is then bubbled through the ice-cold solution, under which conditions only arsenic is precipitated; antimony and tin remain in solution. The separation of tin from antimony is similar in principle, but is carried out in a hot solution acidified with oxalic acid; under these conditions, antimony is precipitated, but tin still remains in solution.[1]

An electrolytic method of separating antimony from tin depends upon the electrolysis of a solution of the mixed sulphides in concentrated sodium sulphide; the solution should be made alkaline with sodium hydroxide and should also contain potassium cyanide, which serves to destroy polysulphides and to reduce any pentavalent antimony compounds to the corresponding trivalent compounds. If the E.M.F. applied to the cell be adjusted correctly, the whole of the antimony is deposited, whilst the less noble tin remains in solution.[2]

When tin has been freed from other metals, it is usually brought into the stannic condition and precipitated by means of ammonia in the presence of ammonium nitrate, which prevents the dissolution—or peptization—of the precipitate by an excess of ammonia; the precipitate is washed with a hot dilute solution of ammonium nitrate. The precipitate is afterwards ignited, and the tin weighed as stannic oxide (SnO_2). An accurate method of estimating tin is to deposit it electrolytically from a solution containing excess of ammonium oxalate; a good deposit of tin can be obtained upon a platinum cathode. The solution must be kept slightly acid during the process, sulphuric acid being added after electrolysis has been in progress for about six hours.[3] The process is rather slow; in an unstirred bath, the electrolysis lasts about twenty-four hours.

Another peculiarity of tin which serves to distinguish it from other metals, except antimony, is the action of fairly concentrated

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[1] Details given in F. P. Treadwell's "Analytical Chemistry." Translation by W. T. Hall (Chapman & Hall).

[2] A. Fischer, *Zeitsch. Anorg. Chem.* 42 (1904), 363.

[3] F. Henz, *Zeitsch. Anorg. Chem.* 37 (1903), 40.

hot nitric acid upon the metal. When this acid acts upon tin, it converts it into "metastannic acid," which is insoluble in nitric acid; antimony is under the same conditions changed to an oxide insoluble in nitric acid, but the metals of more pronounced basic characters give soluble nitrates.

On the peculiar action of nitric acid upon tin and antimony rests a rapid but rather inaccurate method for the separation and estimation of these metals in alloys, especially in type-metal, which contains lead, antimony, tin, and often copper. When such an alloy is heated with 90 per cent. nitric acid, the tin and antimony pass into insoluble hydrated oxides, which may be washed and filtered off, while the other metals are converted to soluble nitrates, and may be estimated in the filtrate. The mixed oxides are dried, ignited, and weighed. When the combined weight is known, that of the antimony alone is arrived at by treating the mixture with hydrochloric acid, adding crystals of pure metallic tin, and boiling. The metallic tin reduces the "noble" antimony to the metallic state, throwing down a heavy black precipitate of elemental antimony; this does not adhere to the massive tin, but can easily be washed off on to a filter paper, dried at 100° C., and weighed.[1] The weight of the antimony being known, that of the tin in the mixed oxides is obtained by difference. The inaccuracy of the method is caused by the danger of the formation of soluble tin nitrates in place of the insoluble metastannic acid. Another cause of error is the partial retention of other metals in the precipitate of tin and antimony.

Many volumetric methods exist for the determination of tin. Of these, the titration of a solution containing tin in the stannous condition with iodine appears to be the most convenient.[2] A little starch is added near the end-point to serve as indicator.

TERRESTRIAL OCCURRENCE

The geo-chemistry of tin is of exceptional interest.[3] The metal, which existed—like other valuable metals—in only small amounts in the original magma, has become concentrated during the consolidation of igneous masses in the highly siliceous portions which have remained liquid to the last. Practically all the tin ores are connected with highly siliceous igneous rocks (granites), and the

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[1] M. Mangin, *Chem. News*, **70** (1894), 93.

[2] The different methods are compared by J. G. F. Druce, *Chem. News*, **121** (1920), 173.

[3] See H. G. Ferguson and A. M. Bateman, *Econ. Geol.* **7** (1912), 209; W. Lindgren, *Trans. Amer. Inst. Min. Eng.* **30** (1900), 613; J. H. L. Vogt, *Trans. Amer. Inst. Min. Eng.* **31** (1901), 125.

tin generally occurs in—or close to—the quartz-veins which are found cutting the granite-mass. The quartz-veins represent the most siliceous part of the granitic magma, which remained liquid after the rest was solid, and which apparently in the very last stage of the solidification was squeezed out through any cracks which had formed in the already solid part of the granite and hardened in them. This siliceous portion was naturally comparatively rich in tin, and, if the tin merely occurred *within* the quartz-veins, its presence there would cause no surprise. But, curiously enough, the tin is found not only in the quartz-veins, but within the granite walls on either side of the quartz-veins. The granite has undergone marked changes where the stanniferous quartz-veins have passed through it ; the felspar has become changed to mica—often a lithium-bearing variety—and various minerals not present in ordinary granite are found in the changed granite, or "greisen," as the rock is called. The minerals found in greisen include compounds containing boron, such as :—

Tourmaline . . . $(Na_6,Li_6,Mg_3,Ca_3,Fe_3,Al_2,B_2)SiO_5$;

compounds containing fluorine, like :—

Topaz . . . . $(AlF)_2SiO_4$
Fluorite . . . . CaF_2
and Fluo-Apatite . . . . . . $(CaF)Ca_4(PO_4)_3$;

compounds containing lithium, such as :—

Triphyllite . . . $LiFePO_4$
and Lepidolite (lithia-mica) . $KLi[Al(OH,F)_2]Al(SiO_3)_3$;

and—most important for our purpose—the oxide of tin,

Cassiterite . . . . . . SnO_2.

The character of the change in the granite suggests the view—now generally held—that it has been brought about by hot vapours given off from the rock in the last stage of the consolidation process ; it is noteworthy that the elements fluorine, boron, and lithium have all volatile compounds, and their presence in an ore-deposit is generally regarded as evidence of pneumatolytic origin. The almost invariable association of tin with fluorine suggests that the tin has actually been given off as the vaporous fluoride, SnF_4. This has probably acted upon the silicates of the granite, yielding cassiterite (SnO_2) and minerals containing fluorine, whilst the lithium and boron also present in the vapours yield minerals like lepidolite and tourmaline. The latter mineral appears to be formed mainly from the felspar of the granite. There is little object in attempting to express these changes by definite equations, since evidently each mineral can equally well be regarded as being formed in a number of different ways. The simplest possible mode of formation of cassiterite from tin fluoride would be through hydrolysis by the aqueous vapour present

$$SnF_4 + 2H_2O = SnO_2 + 4HF,$$

and if this is regarded as the primary reaction, we must suppose that the hydrofluoric acid formed next acts on the silicates producing fluorides.

A good deal of controversy has arisen at different times among geologists as to whether various ores have been deposited by the action of vapours (*pneumatolytic agency*) or of thermal waters (*hydrothermal agency*); but the matter is possibly less important than is usually supposed. Many of the substances evolved from the rock magma must—at the moment of evolution—be above their "critical temperatures," the point at which all distinction between the liquid state and the gaseous state vanishes. For convenience we may refer to the water given off from the magma as being in a "gaseous" state at the moment of its liberation, and as becoming "liquid" during its passage upwards through the fissures in the earth's crust; thus the tin ores which are formed low down can be regarded as "pneumatolytic" in origin, whilst the ores of copper, lead, and zinc, which appear at a higher point, are spoken of as being formed in a "hydrothermal" manner. But it is not certain that there is any *sharp* distinction between the two classes of ores.

The mineral, cassiterite, referred to above, crystallizes in the tetragonal system, and where the crystals have been allowed freedom of growth well-developed tetragonal pyramids or prisms are often obtained; in other cases, botryoidal growths of tinstone, showing a radiating fibrous structure when broken open, are met with. The lustre is adamantive; the colour may be white if pure, but is more often dirty yellow or brown, giving the mineral a "wooden" appearance; sometimes, if very impure, cassiterite may be black. It is a heavy mineral, the specific gravity being about 7·0.

The ordinary ores of tin, produced by pneumatolytic agency, generally occur much deeper in the earth than the ores of copper, lead, and zinc, the origin of which is commonly ascribed to ascending waters. In fact, as already mentioned, the veins of tin usually occur within, or very close to, the intrusive igneous mass from which the tin was derived. Thus the tin-ores are to a large extent free from such heavy metals as copper, lead, and zinc, although commonly mixed with tungsten minerals. In Cornwall, for instance, the copper-ores and tin-ores are connected with the same series of intrusions, but the copper-veins are comparatively near the surface, whilst the tin-veins exist at a much lower depth.[1]

The main tin-fields of the world are found in the regions affected by folding of the Hercynian (post-carboniferous) system. It is quite likely that tin-ores have been produced by the later earth-movements which occurred in tertiary times, but they lie too deep to be accessible. In the case of the earlier ores, time has been allowed for denudation and subsequent earth-movements to render these ores accessible from the surface.[2]

The fact that tin-veins are often only a few inches in thickness and that the tin occurs largely in the wall-rock, makes it impossible to mine the tinstone without bringing up a large amount of worthless material.

It is probable that the majority of tin-ores have the pneumatolytic origin suggested above, but there are certain cases where they have been formed in other ways. Certain ores in Perak,[3] which occur in limestone, appear to have been deposited from thermal waters given off from an intrusive mass, like the typical ores of such metals as zinc, lead, and copper. On the other hand, in certain American ores, notably those of Carolina,[4] the tin occurs within dykes of pegmatite, whilst it is practically absent from the walls of the rocks through which the pegmatite passes; evidently here the cassiterite was deposited from the fused state.

Where rocks threaded by tin-bearing veins are subjected to weathering, the cassiterite crystals withstand the action of the agents of change fairly well; they are not chemically attacked but are carried off by the running waters, and, along with other detrital matter, find a way into streams. But as is invariably the case with heavy minerals suspended in water, the cassiterite-grains are dropped as soon as the velocity of the water becomes reduced, along with other heavy minerals, like wolfram, and also the coarser sand-particles. Thus important placer-deposits and gravels containing grains of cassiterite ("stream-tin") are formed in the beds of the rivers which rise in hills containing primary tin-ores.

The principal tin-ores of the world are found around the Pacific Ocean. The important deposits of Bolivia[5] are perhaps a little

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[1] Compare H. Louis, *J. Soc. Chem. Ind.* **39** (1920), 194R.

[2] J. W. Gregory, *Trans. Chem. Soc.* **121** (1922), 770.

[3] W. R. Rumbold, *Trans. Amer. Inst. Min. Eng.* **37** (1906), 879. Compare R. A. F. Penrose, *J. Geol.* **11** (1903), 135.

[4] L. C. Graton, *U.S. Geol. Surv. Bull.* **293** (1906), 31–57. See especially page 43.

[5] A. F. Wendt, *Trans. Amer. Inst. Min. Eng.* **19** (1890), 90; W. R. Rumbold, *Econ. Geol.* **4** (1909), 321; H. Bancroft, *Trans. Amer. Inst. Min. Eng.* **47** (1913), 173.

exceptional. The tin compounds are generally found in veins containing sulphides of silver, iron, copper, zinc, and lead, which are thought by some geologists to have been deposited by ascending thermal waters, although other authorities hold that even here the tin is mainly pneumatolytic. The tin is mainly present as cassiterite, but some of the ores are said to contain complex sulphides such as

Stannite (tin pyrites). . . . $Cu_2S.FeS.SnS_2$.

Tin appears again in Mexico, but ores of a more normal character are found in Alaska[1]; these occur in greisen, and are associated as usual with compounds of fluorine and boron. Placer-deposits derived from the original lodes are also present.

On the other side of the Pacific, some tin-ore is found in China, Burma, and Siam, but far more important deposits occur in the Malay States (especially Perak and Selangor), Siam, and in the islands of Banka and Billiton (Dutch Indies). Here the tin-ores are associated with lodes, some of which cut granite, but others are found in limestone[2]; some geologists regard the tin-ore in the limestone as having been deposited from ascending thermal waters, rather than as due to pneumatolytic action. Derived from the tin lodes, a rich series of stanniferous alluvial deposits occur in the various river valleys; until recently these alluvial deposits constituted the only important source of the tin-ore, although the lodes are now also worked. Tungsten occurs in considerable quantities in some of these ores. Tin-ores are also found in Queensland, New South Wales, and Tasmania.

Outside the Pacific Circle, the most characteristic ores of tin are the tin-veins connected with the granite intrusions of Cornwall, England, which have already been referred to. Here also we find the conversion of granite into greisen and tourmaline-granite. Tungsten is present in many of the ores.

Tin-ores also exist in Nigeria and in South Africa.

METALLURGY AND USES

In view of what has been stated in the preceding section, it is not surprising that the average tin-ore—as mined—contains only a comparatively small amount of cassiterite (perhaps 1–5 per cent.) dispersed throughout a large amount of material, most of which is worthless, although minerals containing certain other valuable metals—such as tungsten—also occur in the same ores. It is

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[1] A. J. Collier, *Eng. Min. J.* **76** (1903), 999.

[2] W. R. Rumbold, *Trans. Amer. Inst. Min. Eng.* **37** (1906), 879; W. B. Middleton, *Trans. Inst. Min. Met.* **24** (1914–15), 300.

necessary to subject the crude ore to a concentration process, firstly in order to eliminate the main part of the worthless matter, and secondly to separate tin and tungsten from one another. Afterwards the tin concentrate is subjected to the true metallurgical process ; since tin is an easily reducible metal, the metallurgy proper is actually a simpler problem than the preliminary dressing of the ores. Finally the crude metallic tin is refined.

There is an obvious advantage in conducting the concentration at the place where the ore occurs, so as to avoid the transport of the vast mass of worthless matter. And since the reduction process is sufficiently simple to be capable of being carried on even in a comparatively undeveloped region, the metallurgy also is often conducted on the spot. For instance, the ore found in the Straits Settlements and Malay Peninsula is largely smelted in those regions, an important smelting centre being Pulo Brani, an island near Singapore.[1] On the other hand, there is a considerable tin-smelting industry in several of the more highly-developed countries, depending on ores or concentrates obtained from overseas. The British tin industry, which originally grew up owing to the existence of the Cornish tin-ores, now depends largely on concentrates from Bolivia[2]; a number of mines in Cornwall were still producing in 1920,[3] but the mining industry has since come almost to a standstill.[4]

Concentration of Tin Ores. The first stage of the concentration usually depends on the fact that cassiterite is much heavier than the quartz and other siliceous material with which it occurs. Where lode ore—as opposed to " stream-tin "—is being used, it must first be reduced to small size, by means of stamps or rolls. The crushed ore is carried by a stream of water to the Wilfley tables, where the heavy particles of cassiterite are caught behind riffles whilst the lighter gangue particles are washed over them. These tables, however, fail to retain the smaller particles of cassiterite, and usually the more finely-crushed portions of the ore are treated separately on a " vanner."

Where—as is usually the case in the Malay Peninsula—the main ore is of the nature of a placer-deposit, stamping is unnecessary, and the gravel is " washed " like gold-gravel ; the suspension of " dirt " and water is passed through a series of sluice-boxes. The heavy cassiterite gets caught behind the riffles of the sluice-boxes and is thus recovered.

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[1] J. McKillop and T. F. Ellis, *Proc. Inst. Civ. Eng.* **125** (1896), 145.

[2] R. Pezet, *Min. Eng. World*, **42** (1915), 643.

[3] *J. Soc. Chem. Ind.* **39** (1920), 207R.

[4] See B. Scott, *Min. Ind.* **30** (1921), 676.

But, although gravity separation succeeds in removing the light silicate-minerals, it leaves the tinstone mixed with other heavy minerals present in the ore; these include wolfram, which is of value as a source of tungsten, iron pyrites and often arsenides, such as mispickel (FeAsS). Sometimes copper minerals, like copper pyrites ($CuFeS_2$), may be present in small quantities. The separation of these materials from the tin concentrates depends on the fact that they are slightly magnetic, or at least become magnetic on roasting, whereas the tinstone is practically non-magnetic. The concentrates are first roasted; multiple-hearth muffle roasters are used at one American works,[1] oil being used as fuel, whilst in works under British management roasting in revolving cylinders is generally preferred. During the roasting process, most of the sulphur and arsenic are eliminated as oxide, and the latter can be recovered in a suitable condensing plant; most of the iron is converted to the magnetic oxide (Fe_3O_4). The roasted ore is then treated in a magnetic separator; one of the patterns designed by Wetherill (such as have been referred to in connection with the ores of tungsten and thorium) is commonly used for tin-ores (see Fig. 23). The ore is fed at H on to a travelling belt A; the belt carries it first below a comparatively weak magnet M_1, which, however, is able to lift the highly magnetic iron oxide from the travelling belt, and to keep it pressed against the under-side of the belt B which is running at right-angles; thus the iron is removed. A second magnet, M_2, considerably stronger, is able to lift the

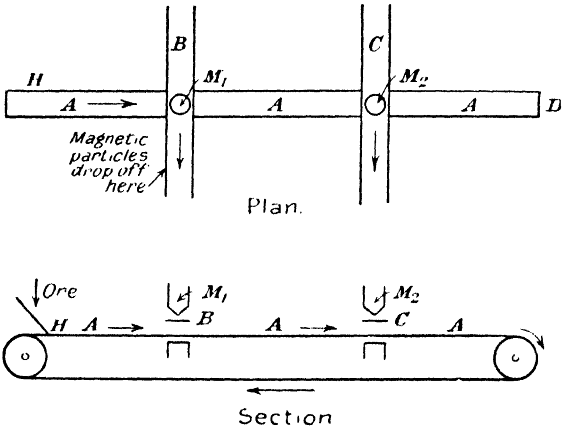

FIG. 23.—Wetherill Magnetic Separator.

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[1] R. H. Vail, *Eng. Min. J.* **101** (1916), 927.

slightly magnetic wolfram, which is removed by the belt C, collected separately as a "tungsten concentrate," and sent to the tungsten works; the non-magnetic cassiterite remains on the original belt, and falls off at D. The tin-concentrate obtained by this—or similar—ore-dressing process is known as "black tin." It may contain 65–90 per cent. of pure tin oxide (SnO_2), that is, about 50–70 per cent. of metallic tin.

Smelting. The crude tin oxide ("black tin") obtained by concentration is next smelted to the metallic state, by heating with carbon—usually in a reverberatory furnace. Since there is always a little siliceous matter left in the concentrates, it is generally necessary to add fluxing materials such as lime and fluorspar, and a little slag will accordingly be formed. The amount of slag produced should, however, be kept as low as possible; for whether the slag be siliceous or basic in character, it will certainly act as a solvent for tin oxide, which is an amphoteric substance, being dissolved by siliceous slags as tin silicate and by calcareous slags as calcium stannate. However carefully the composition of the slag is adjusted, the slag almost invariably contains tin, and is generally treated in a subsequent operation for the recovery of this metal.

The type of reverberatory furnace used in tin-smelting is shown in Fig. 24. The fire burns on the grate G, and the flames, passing over the fire-bridge B, are deflected on to the charge placed upon the hearth H. In a typical furnace the dimensions of the hearth may be 16–20 ft. in length, and 8–12 ft. in width.[1] But some modern American furnaces are considerably longer (38 ft.)—a feature which is, of course, characteristic of American metallurgical design.[2]

The charge consists of cassiterite concentrate ("black tin"), coal (sometimes charcoal), and often miscellaneous tin dross or similar tin-bearing material which accumulates in the subsequent refining of tin, and in other industrial processes; fluxing materials, such as lime and fluorspar, are added—as already explained—in small quantities. The charge is shovelled on to the hearth, through a door, C, in the side, and is spread out, the fire being damped down during the charging. Then the damper is opened, and the temperature raised until the charge melts and the tin oxide becomes reduced to the metallic state by the coal. The charge is rabbled from time to time. After some hours, the tin and slag have separated into two layers; they may be run out separately, or, alternatively, they are run out together into a settler where they are allowed to separate. The tin is sent to the refinery; the slag,

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[1] Compare W. H. Jacobson, *Met. Ind.* (*New York*) **20** (1922), 103.

[2] R. H. Vail, *Eng. Min. J.* **101** (1916), 927.

which often contains 5 per cent. of tin, is afterwards smelted with iron or anthracite in a reverberatory furnace—usually at a rather higher temperature—for the recovery of the metal ; limestone is sometimes added as a flux.

Although the reverberatory furnace is most commonly employed for tin-smelting in Europe, blast-furnaces are in use at Banca, and in primitive works under Chinese management throughout the Malay Peninsula. Water-jacketed blast-furnaces are used in America. The blast-furnace gives a higher temperature than the reverberatory furnace and is likely to cause the reduction of iron and other impurities to the metallic state, thus tending to produce a very impure tin ; however, where, as at Banca, the ores are very pure, or where—as in America—the metal is intended for subsequent electrolytic refining, this objection is not fatal. The employment of the blast-furnace involves a certain loss of tin by volatilization.

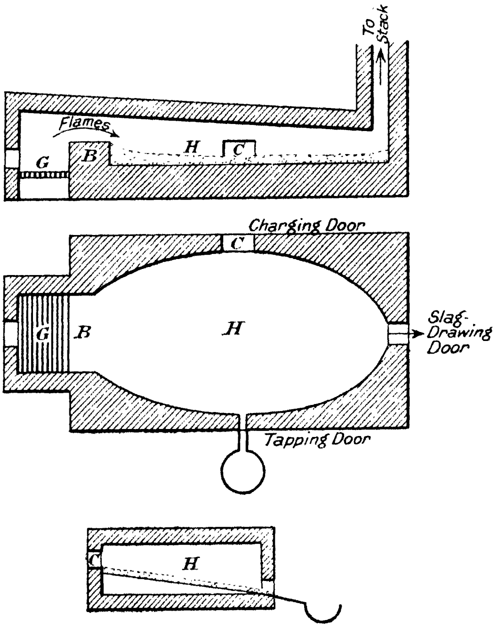

FIG. 24.—Reverberatory Furnace for Tin-smelting.

Electrothermal smelting-processes for tin have found their advocates,[1] although the use of so expensive a method of heating would

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[1] See *Met. et Alliages*, 7 (1914), No. 10, p. 1.

seem difficult to justify for the reduction of such a readily reducible metal. The experiments made on this subject are, however, of interest as showing that, in spite of the high temperature usually associated with the electric furnace, loss of tin by volatilization and by passage into the slags can be made small.

Refining. Even tin produced in the reverberatory furnace will, of course, be contaminated with other metals present in the concentrates; the main impurity is iron, but arsenic, sulphur, and tungsten are often present. Much of the iron and tungsten can be removed by "**liquation.**" This can be carried out in several ways, but the principle is always the same. The crude tin may be introduced into a gently-heated reverberatory furnace, provided with a sloping hearth; the tin melts, and runs away, but a more infusible material is left behind. This is essentially an alloy of iron and tin often containing sulphur, arsenic, and tungsten. It can be melted by further raising the temperature, and separates on cooling into two layers, the upper layer being impure tin, and the lower being a material called "**hardhead**" consisting of iron, tin, and arsenic.[1]

The liquated tin is still not pure, and is further treated by **poling,** that is, by plunging poles of wood below the surface of the molten metal contained in a pot. It should be noticed that the poling of tin is an *oxidizing* process, not a reducing process like the poling of copper; the evolution of gases simply serves to agitate the metal, shooting up globules into the air, and thus bringing the tin into contact with oxygen; iron, tungsten, and bismuth are oxidized and collected as a "scoria" on the surface, which can be removed. Other and more rational means of agitating the liquid in order to oxidize the impurities have been used. In America, an agitation by compressed air has been employed, whilst at Pulo Brani a certain amount of purification is said to be obtained by ladling the molten tin from one kettle to another, each ladle-full being poured from a considerable height (4 ft.), so that the molten metal falls in a thin stream into the kettle, and is thus brought into contact with the air.

After these refining processes, the tin is generally pure enough for most purposes; it is allowed to stand for some time, so as to allow the heavier surviving impurities to settle, and is ladled out into moulds. The tin obtained from the upper portions is the purest.

Some ores, especially those of Bolivia, yield a tin which is very

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[1] For experiments on the elimination of iron and arsenic from hardhead by bessemerization, see D. M. Levy and D. Ewen, *Trans. Inst. Min. Met.* **18** (1909), 466.

difficult to purify by thermal methods, and the **electrolytic refining** of tin has been started on an industrial scale in New Jersey. The problem is rendered difficult owing to the fact that the deposit of tin obtained on the cathode by the electrolysis of an ordinary tin salt solution is usually of an incoherent dendritic crystalline character. However, baths containing the tin as fluo-borate, fluo-silicate, or sulphate—rendered distinctly acid and treated with a colloid such as gelatine or peptone—appear to give fair results. In the New Jersey plant, a fluo-silicate bath containing glue as an addition agent was used at first, but sulphuric acid was added to precipitate the lead which was always present in the crude anode material. Later it was found possible to replace the fluo-silicate bath by a bath of tin sulphate ; the addition agents are understood to be glue and phenol-sulphonic acid.[1]

Uses of Tin. The main applications of tin depend upon the resistance of the metal towards corrosion. In moderately pure air, tin retains its brightness indefinitely. The air of towns, which usually contains sulphur dioxide and sometimes hydrogen chloride, may cause—it is true—a discoloration of a tin surface; but there is no real corrosion.

Tinfoil has been used largely for the packing of perishable materials, although aluminium foil is tending to displace it for this purpose. A much larger proportion of tin is used for coating less resistant metals, such as iron, lead, and copper. Copper vessels are often tinned internally, copper wire for electrical purposes is often protected with a layer of tin, whilst lead piping is sometimes covered with tin. But far more important is the employment of tin for coating mild steel in the production of tin-plate.

Tin-plate

The production of tin-plate is one of the most important industries in South Wales and Monmouthshire, whilst large amounts are made in the United States, Germany, and other countries. Tin-plate consists of thin sheets of low-carbon steel covered with a very thin film of tin. It is almost always manufactured by dipping the steel sheets into molten tin. If the tin layer extends completely over the iron surface, the rusting and pitting of the latter metal is completely prevented ; but, if, owing to the presence of dust-particles on the iron surface at the time when it is dipped into the molten tin, pinholes are left in the tin layer, the tendency to rust at these points is actually increased by the presence of the

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[1] E. F. Kern, *Trans. Amer. Electrochem. Soc.* **33** (1918), 155 ; **38** (1920), 143, 164.

more noble metal. In this respect, as has been explained more than once, " tinning " is actually inferior to " zincing," as a means of preventing the corrosion of the iron. But, for this very reason, tinned iron is permissible for the canning of fruit and meat because, if any solution of metal by the acid in the fruit does occur, it will be the non-poisonous iron, and not the poisonous tin, which will pass into solution ; while the use of zinc-covered iron would have fatal results. Other important uses of tin-plate vessels include the storage of petrol, biscuits, confectionery, and tobacco.

The sheets to be tinned are usually made by the hot-rolling of bars of steel containing about 0·1 per cent. of carbon. By progressive rolling, the thickness is gradually reduced until it is only about $\frac{1}{100}$ in. The sheets are then pickled in dilute sulphuric acid to remove the oxide-scale, " size " or dextrin being sometimes added to the acid, to restrain its attack on the metal below the scale.[1] They are then annealed, rolled cold to give smoothness and polish, and annealed a second time. Afterwards they are pickled a second time to render the surface free from iron oxide, and, after washing, are ready for tinning.

The baths of liquid tin, contained in open tanks, are kept molten by a small fire below ; very little fuel is needed to keep the metal liquid owing to the low melting-point. Where the plates pass into the bath the surface of the molten metal is covered with a layer of fused zinc chloride, to prevent the formation of a scum of tin oxide ; each plate, upon entering the bath, is caught mechanically upon a revolving drum which turns it over, and guides it through the tin and finally passes it out of the bath. Where the sheets emerge from the bath, they pass through a layer of palm oil, or hydrogenized cotton-seed oil,[2] and a pair of rolls removes excess of tin. Each sheet passes mechanically through about four of these baths, and is then taken out, and dusted by being passed between felt rollers.[3]

One of the problems of the maker of tin-plate is the satisfactory working up of the " dross " or " tin scruff " which collects on the surface of the molten tin. This contains chlorides of tin and zinc, besides palm oil and its decomposition products, and much metallic tin. It is skimmed off, and is periodically treated for the recovery of tin. Much of the tin, which is already in the metallic state, can be obtained by " liquation " in a furnace, but a large amount passes away as the volatile chloride. If the gases from the furnace are passed through depositing towers, a great deal of tin is deposited as oxide in them. The gases should pass through wash-towers,

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[1] H. J. Bailey, *Chemistry and Industry*, **42** (1923), 364.
[2] W. D. Collins and W. F. Clarke, *J. Ind. Eng. Chem.* **12** (1920), 149.
[3] T. L. Bailey, *J. Soc. Chem. Ind.* **37** (1918), 113T.

in which the free hydrochloric acid is absorbed by water, before they are discharged into the atmosphere.

The character of the protective layer existing on tin-plate is a little uncertain. Many authorities consider that alloying of the tin and iron occurs, and ascribe to this fact the remarkably good adhesion of the tin layer to the underlying metal. Some microsections have, however, been published, which would seem to show that the passage from the protective layer of tin to the steel is usually an abrupt one, although it is found that an intermediate layer appears if the immersion of the iron in the tin has been prolonged.[1]

Wet Tinning Processes. The immersion of metal in molten tin is, essentially, such a simple operation that for most purposes there is no formidable rival to that method of tin-plating. In the immersion of small manufactured articles of brass and iron, such as "hooks and eyes," obvious difficulties will arise, however. Objects of this kind are often plated with tin electrically.

The articles are made the cathodes of the plating cell; they are usually placed in tinned sieves immersed in a solution of a tin salt, and large anodes of pure tin are hung above them. An E.M.F. is applied, and tin is dissolved at the anode and deposited on the articles, which are turned over occasionally. As in the analogous case of silver-plating, the concentration of tin should be maintained by the dissolution of the anode. If, however, the current density at the anode once becomes too high there is a danger that the tin will become passive, and the current commences to cause, instead of the dissolution of the metal, an evolution of oxygen. On this account the electrolytic deposition of tin needs constant care.

Much work has been devoted to the investigation of different solutions with a view to obtaining a bath which will give a really good deposit. None of the baths appear to be ideal; the solutions generally contain either ammonium oxalate, sodium phosphate, or sodium tartrate in addition to stannous chloride. No doubt complex anions containing tin are produced, a state of affairs which is favourable to the production of a smooth deposit of the metal, just as, in silver-plating, the best deposits are obtained from a complex cyanide bath. One additional advantage of the presence of tartrates is that they prevent the precipitation of stannic acid through hydrolysis. But, if a tin deposit of any thickness is required, difficulty is likely to be met with owing to the tendency of tin to form a dendritic crystalline deposit—a tendency common to all soft metals. It is stated that by the addition of certain colloids—notably peptone—to a plating bath containing ammonium

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[1] L. Mayer, *Stahl u. Eisen*, **38** **(1918)**, **960.**

tin oxalate, good smooth deposits can be obtained.[1] Another bath which is said to give good results contains phenol-sulphonic acid.[2]

Tin-recovery from Tin-plate Scrap. In the manufacture of biscuit-tins, meat-cans, and similar articles, a great quantity of cuttings and shavings of tin-plate are produced, which may represent an amount of tin worth recovering. It might also be expected that, in view of the high price of tin, the disused tins which are obtainable in quantities at the refuse-destructors of all big cities would also prove to be an important source of the metal. This, however, is not usually the case; the layer of tin on the iron surface is very thin, and the volume occupied by the average cannister is very large in proportion to the surface; hence it will often come about that a truckload of old tins will not contain enough of the valuable metal to pay for the haulage to the works where the tin would be recovered.

Tin-plate cuttings are, however, compact, and are produced on the spot, and it may often prove profitable to treat them for the recovery of the metal. What is needed is some chemical reagent which will dissolve the tin and leave the iron unattacked; most reagents, e.g. acids, attack the iron preferentially, owing to its more reactive character. On the other hand, certain alkaline liquors, such as a boiling solution of sodium hydroxide and sodium nitrate, attack tin with great avidity, but leave the iron in the passive condition. The solution produced deposits crystals of sodium stannate on cooling. The stannate is redissolved and the solution is precipitated with sodium bicarbonate, giving stannic oxide—which is used in the enamel industry. This process is used on a large scale in America.[3]

It is found that if tin-plate is exposed to dry chlorine, the tin on the surface is attacked before the iron layer below. The **Goldschmidt process,**[4] based upon the extraction of tin by dry chlorine gas, is worked on a large scale at Essen, and elsewhere. The scrap is cleaned, carefully dried, and packed in baskets, placed in closed vessels, and treated with chlorine gas until the pressure becomes constant, which is a sign that all the tin has been attacked. The gas is then drawn out by aspiration, and comes out charged with the vapour of stannic chloride; the stannic chloride is condensed and is generally sent to the silk mills for use in the weighting

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[1] F. C. Mathers and B. W. Cockrum, *Trans. Amer. Electrochem. Soc.* **29** (1916), 405, 411. Compare F. C. Mathers and W. H. Bell, *Trans. Amer. Electrochem. Soc.* **38** (1920), 135.

[2] W. Lange, *Zeitsch. Metallkunde*, **13** (1921), 272.

[3] See *Met. Chem. Eng.* **17** (1917), 187; L. Hackspill, *Chim. et Ind.* **2** (1919), 1161.

[4] K. Goldschmidt, *Stahl u. Eisen*, **28** (1908), 1919.

of silk, whilst the iron left behind is washed and is then sufficiently free from tin to be used at the steel-works for steel-making.

Various attempts have been made at different times to recover the tin electrolytically. In most of these processes, the tin-scrap, packed in baskets, is made the anode of an electrolytic cell, the intention being to dissolve the tin at the anode and to deposit it on the cathode. Those electrolytic processes in which an acid bath was used were fore-doomed to failure, since in the presence of acid the iron is attacked in preference to the tin. Processes using an alkaline solution have given better results. The method was used for a time in Germany, but was abandoned as being more costly of operation than the chlorine method described above; moreover it was found that the tin upon the anode was liable to become passive. Since that time, electrolytic detinning has been employed at Birmingham (England), and at several works in Italy. In Italy it is said to have given better satisfaction than the chlorine process.[1]

Technically Important Compounds. Certain tin salts such as stannous chloride, stannic chloride, and sodium stannate, have proved useful in dyeing as " mordants "; at one time ammonium stannic chloride (" pink salt ") was largely employed. Tin salts are also used considerably in the " weighting " of silk. The silk is treated first in a solution of stannic chloride or of pink salt, and then in a bath containing sodium phosphate; tin phosphate is precipitated within the fabric.

Stannic oxide has a high refractive index and is largely used in the ceramic industry as an opacifier in the preparation of non-transparent glazes, and also in the preparation of enamel for coating iron-ware.

Alloys of Tin

A very considerable proportion of the tin manufactured is devoted to the making of alloys; the copper-tin alloys (**bronzes**) have already been discussed, but the alloys of tin with lead, and the alloys of tin with small amounts of antimony and copper, remain to be considered.

Tin-lead Alloys. Fig. 25 shows the probable equilibrium diagram of tin-lead alloys.[2] Most of the alloys have a lower

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[1] *Met. Chem. Eng.* **10** (1912), 202.

[2] This is founded on the diagram of W. Rosenhain and P. A. Tucker, *Phil. Trans.* **209** [A] (1908), 89, but simplified by the later work of D. Mazzotto, *Int. Zeitsch. Met.* **1** (1911), 289, and of N. Parravano and A. Scortecci, *Gazetta*, **50** (1920), i, 83. These later workers regard the thermal change found by Rosenhain and Tucker at 149° C. to be due simply to supersaturation of the

melting-point than either metal, and an alloy with about 37 per cent. of lead and 63 per cent. of tin has the lowest melting-point of all, consisting entirely of a eutectic; alloys with more lead contain—in a state of equilibrium—crystals of stanniferous lead embedded in the eutectic, whilst those with less lead have crystals of nearly pure tin embedded in the eutectic.

In some cases, the employment of these alloys depends on their ready fusibility. The common **solder** used by plumbers and others for making junctions between metals contains 66 per cent. of lead, although some varieties of solder have less. Other easily fusible alloys of tin and lead are used in electrical fuses. **Pewter** may contain 15 per cent. of lead; in spite of its low melting-point, it is sufficiently hard to be wonderfully durable, and can take a good polish; most of the pewter used for pewter table utensils contains, however, some third element, e.g. antimony, as a "hardener." Pewter articles used for food should not contain more than 18 per cent. of lead, owing to the danger of lead-poisoning.

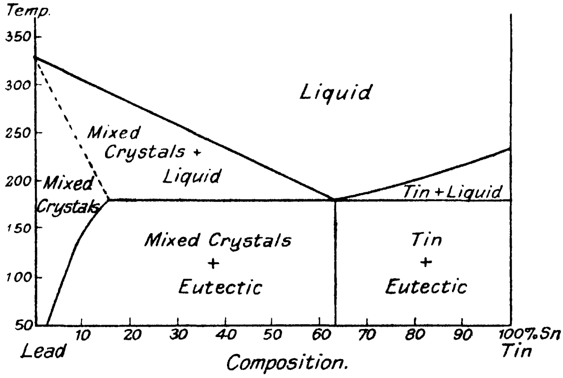

FIG. 25.—The System Tin-lead.

Alloys of Tin with small Amounts of Antimony and Copper. The alloy known as **Britannia Metal**[1] consists of tin with about 5–9 per cent. of antimony and 1–3 per cent. of copper; both copper and antimony render the metal harder, and if the alloy is intended for casting, they may be present in rather larger amount than if the alloy is to be rolled or spun. The casting alloy may contain

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crystals of stanniferous lead with tin. The solubility of tin in solid lead decreases with the temperature, and when the alloys are cooled below 149° C., the supersaturation becomes so great that the excess of tin suddenly separates, causing a marked evolution of heat.

[1] F. C. Thompson and F. Orme, *J. Inst. Met.* **22** (1919), 203.

small amounts of lead in order to make the metal more fluid. The alloy has many valuable properties, being hard enough to withstand wear and yet malleable enough to be rolled, cold or hot, without difficulty. Britannia metal is largely used for domestic utensils, such as tea-pots, mugs, and the like, although to some extent it has been displaced by German silver.

The structure of Britannia metal shows a white constituent embedded in a dark ground-mass. The nature of each constituent is uncertain ; Thompson and Orme have made a suggestion, which may provisionally be accepted, that the white constituent is a solid solution of tin and antimony, and the dark ground-mass is a copper-tin eutectic.

If the copper and antimony be increased somewhat, the structure of the alloy changes considerably. Fig. F of the frontispiece shows an alloy containing 4 per cent. of copper and 9 per cent. of antimony. The remarkable white crystals of cubic form[1] consist of an inter-metallic compound (probably SbSn), whilst the long white needles contain tin and copper (being possibly Cu_3Sn). These are both hard materials, but they are set in a soft matrix, consisting mainly of tin, which is yellowish in freshly-polished alloys, but darkens on etching with alcoholic nitric or hydrochloric acid. The cubic outline of the inter-metallic compound SbSn is often remarkably perfect, but if the alloy is hammered the cubes sometimes show cracks.[2] The cubes are considerably lighter than the matrix in which they are embedded, and, unless care is taken with the casting of an alloy containing tin and antimony, nearly all the cubes will be found at the top of the solidified metal. This is less likely to happen, however, if the alloy contains copper, because the heavy needle-shaped crystals of the compound Cu_3Sn entangle the cuboids of SbSn, and prevent them from rising to the surface.[3] Such alloys (**Babbitt metals**) are mainly used as bearing materials.[4] A typical bearing metal contains 9 per cent. of antimony and 4 per cent. of copper, but the content of copper varies considerably in different " white metals " used for this purpose. The British Admiralty specify for the bearings of marine engines an alloy with 2 to 7 per cent. of copper and 8 to 9 per cent. of antimony.[5] Alloys of this character are found by experience to

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[1] For further information regarding these white cuboids see *Metallographist*, **1** (1898), 197; W. Reinders, *Zeitsch. Anorg. Chem.* **25** (1900), 113; R. S. Williams, *Zeitsch. Anorg. Chem.* **55** (1907), 12.

[2] H. E. Fry and W. Rosenhain, *J. Inst. Met.* **22** (1919), 217.

[3] Compare W. Ramsay, *J. Inst. Met.* **22** (1919), 234.

[4] B. H. Jarvis, *Mech. World*, **68** (1920), 63; P. W. Priestley, *Met. Ind.* (New York) **19** (1921), 66.

[5] Sir G. Goodwin, *J. Inst. Met.* **22** (1919), 224.

reduce friction at the bearings to a minimum. Most varieties of bearing metal contain a little lead (up to 3 per cent.), and in the cheaper varieties the tin is largely replaced by the less expensive metal. Some authorities state that these "*lead-base alloys*," which were of necessity used largely during the war owing to the shortage of tin, have actually proved more satisfactory than the tin-rich materials.[1]

It is a matter of some interest to inquire why these particular white metals should be more successful as "anti-friction materials" than other alloys. It is found that materials which are suitable for use as bearing metals contain both hard and soft constituents. In Babbitt metal, we have the hard cuboids of SbSn and the hard ray-like crystals of Cu_3Sn, set in a soft plastic matrix (the tin-rich ground-mass). The hard grains are supposed to give the necessary resistance to wear, but the fact that they are set in a yielding matrix allows a certain amount of accommodation at any point where the opposing surfaces come too close together and press upon one another. It is noteworthy that another class of alloys which have proved valuable as bearing metals, the plastic bronzes, also consist of a hard and a soft constituent (see page 72); but here the soft constituent (lead) appears to be dispersed through the hard constituent, whilst, in the white bearing metals, the hard constituent is distributed through the soft matrix.

Another suggestion has recently been made regarding the special value of alloys containing hard and soft materials. It is absolutely essential that a continuous film of oil should be maintained all round the bearing; if the oil-film is interrupted at any point, seizing is likely to occur. It is considered that, on the surface of a material like Babbitt metal, "the hard constituents stand up in slight relief, the softer matrix thus forming numerous evenly distributed channels, which maintain the oil by capillarity."[2] It seems possible that the value of the interfacial tension between an alloy and lubricating oil may be of significance in determining the merit of a given alloy as a bearing material.[3]

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[1] E. T. Keenan, *Mech. World*, **71** (1922), 189.

[2] A. H. Mundey, C. C. Bissett, and J. Cartland, *J. Inst. Met.* **28** (1922) 142.

[3] Compare the views of W. B. Hardy and J. K. Hardy, *Phil. Mag.* **38** (1919), 32; W. B. Hardy, *Phil. Mag.* **40** (1920), 201; *J. Soc. Chem. Ind.* **38** (1919), 7T.

LEAD

Atomic weight . . . 207·20

The Metal

Lead, *the remaining metal* of Group IVB, is considerably heavier than tin, the specific gravity being 11·3. It is also softer than tin, but melts at a higher temperature, namely, 327° C.; the fused metal has a slightly greater density than the solid metal, so that lead expands when it solidifies. At ordinary temperatures, pure lead is so pliable that it can be moulded into shape by gentle pressure between the fingers, but traces of certain impurities render it much harder. Lead is malleable enough to be rolled in foil; lead wire can be produced, but is lacking in strength.

A freshly-cut section of lead shows a brilliant silvery lustre, which soon dulls to a dark grey when exposed to ordinary air. The "lead tree" obtained by precipitation of a lead acetate solution with metallic zinc is a wonderful growth of long leaf-like crystals of shining lead. The same tendency to form dendritic crystal-growths is displayed when a layer of molten lead is allowed to solidify in a shallow dish.[1] Under favourable circumstances, however, it is possible to obtain octahedra by the crystallization of fused lead.[2] This fact—together with the study of the etching figures produced on a section of lead by certain corrosive agents—serves to indicate that lead crystallizes in the cubic system. X-ray analysis has proved that the atoms are arranged on a face-centred cubic space-lattice.[3]

Lead stands on the reactive side of hydrogen in the Potential Series, but the difference between the normal electrode potentials of the two elements is very small (0·13 volts) and lead does not readily displace hydrogen from dilute acid solutions. Concentrated hydrochoric acid causes an evolution of hydrogen, which increases when the acid is heated, owing to the reduction of "overpotential." Dilute hydrochloric and sulphuric acids are almost without action, but when lead is brought into contact with platinum black in 1·3N hydrochloric acid, tiny hydrogen bubbles rise from the point of contact.

One factor which is unfavourable to the dissolution of lead in

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[1] J. C. W. Humfrey, *Phil. Trans.* **200** [A] (1903), 225.
[2] F. Stolba, *J. Prakt. Chem.* **96** (1865), 180.
[3] L. Vegard, *Phil. Mag.* **32** (1916), 65.

dilute hydrochloric and sulphuric acids is the comparative insolubility of the chloride and sulphate of the metal, which may lead to the formation of protective films on the surface of the lead.

Lead is readily attacked by nitric acid, the soluble lead nitrate being formed; the gases evolved include nitrous oxide, as well as the higher oxides of nitrogen.[1] The solvent action of hot concentrated sulphuric acid is appreciable, although very small; this question, which is of practical importance, is considered in the technical section.

Acetic acid only very slowly attacks lead at ordinary temperatures, but the rate of attack is immensely increased if hydrogen peroxide is present, as that reagent acts as an oxidizing depolarizer.[2]

Lead is practically unattacked by dry air; in an ordinary damp atmosphere, as already stated, the bright surface of the freshly-cut metal soon becomes tarnished owing to the formation of a dark-coloured oxidized layer, which, however, protects the metal from further oxidation. Lambert and Cullis[3] have shown that the darkening is much less rapid in the case of lead which is perfectly pure and uniform. Lead which has been purified by distillation *in vacuo*, and which has been allowed to become physically homogeneous by preservation *in vacuo* for a year, can be exposed to air for some days before losing its metallic lustre.

The specially pure, homogeneous lead prepared by Lambert is only very slowly oxidized by water containing oxygen. But *ordinary* " pure " lead, although practically unattacked by air-free water, is more quickly acted upon by water containing oxygen, a dark brown oxide and a whitish hydroxide being produced. In the presence of dissolved carbon dioxide in the water, a film of insoluble carbonate is formed. Under certain circumstances, this substance prevents further oxidation of the metal; but clearly if there is also a reagent present in the water which can cause a partial solvent action upon the protective film, or even a peptizing action, the attack of the metal will continue, and gradually an appreciable quantity of lead will pass into solution. This is a matter of very great practical importance, and will be considered further in the technical section.

Laboratory Preparation. The metal may be prepared from a solution of a lead salt by the action of zinc, or it may be deposited upon a cathode by electrolysis. The tree obtained can be melted

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[1] G. O. Higley, *Amer. Chem. J.* **17** (1895), 23.

[2] O. P. Watts and N. D. Whipple, *Trans. Amer. Electrochem. Soc.* **32** (1917), 267.

[3] B. Lambert and H. E. Cullis, *Trans. Chem. Soc.* **107** (1915), 210.

down under a suitable flux (e.g. potassium cyanide) to yield the compact metal.

To obtain pure lead from the impure metal, it should be dissolved in acetic acid, and reprecipitated as sulphate. The sulphate can be converted to carbonate by the action of ammonium carbonate, and the lead carbonate can be reduced to metallic lead by fusion with potassium cyanide.[1]

If lead of extraordinary purity is needed, Lambert's method of distillation *in vacuo* is available, quartz apparatus being used; the original paper, which has already been referred to above, should be consulted for details.

Alleged Allotropy of Lead. Ordinary pure lead when kept in contact with a lead salt solution undergoes certain changes which have been interpreted as being allotropic transformations. Not only do small changes in density occur,[2] such as are met with in other soft metals (tin, thallium, cadmium and zinc), but in certain cases the whole appearance of the lead alters. For instance, pure lead immersed in a concentrated solution of lead acetate containing nitric acid loses its malleability, and becomes converted to a grey variety which can readily be rubbed to powder between the fingers [3]; in fact it sometimes crumbles spontaneously. Some samples of compact lead immersed in acidified lead nitrate actually yield a lead "tree" similar to that obtained by the immersion of zinc in the same solution; the compact lead behaves as though it were a metal different from the crystalline lead forming the tree, being apparently more reactive than the latter. This would seem—at first sight—to afford considerable support for the theory of allotropy.

Closer investigations suggest, however, that the production of the tree is due to another cause.[4] It only occurs under conditions where, as a result of corrosion, a layer of basic salts appears over parts of the lead surface; in such a state of affairs diffusion will be slow between the liquid within the channels threading the layer and the main body of the solution outside. Below the layer—in contact with the metallic lead—the solution will come to contain lead *nitrite*; the external solution, on the other hand, contains lead *nitrate*. Since the concentration of lead ions ($Pb^{\cdot\cdot}$) is much greater in a nitrate solution than in a nitrite solution, a concentration cell will be set up, and lead will pass into solution con-

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[1] An elaborate method of obtaining lead quite free from other metals is described by J. S. Stas, *Bull. Acad. Belg.* **10** (1860), 295.

[2] E. Cohen and W. D. Helderman, *Proc. Amst. Acad.* **17** (1914), 822.

[3] H. Heller, *Zeitsch. Phys. Chem.* **89** (1915), 761.

[4] A. Thiel, *Ber.* **53** (1920), 1052, 1066; **54** (1921), 2755.

tinuously beneath the layer of basic salts, whilst at the places where no basic salts exist, lead will be deposited in dendritic form.

The crumbling of lead foil in a solution containing nitrates and free acid is probably due to preferential attack upon the lead at the boundaries between the crystal grains. The corrosive liquid eats its way into the lead between the grains, which finally fall apart. The phenomenon is probably comparable to the " season-cracking " of brass. A specimen of lead consisting of a single large crystal does not show this crumbling effect. If the explanations of the tree-production and crumbling just suggested are correct, there is no reason to suppose that any allotropic change is involved.

Careful measurements of the potential difference of lead against a lead nitrate solution show—it is true—that the potential is distinctly altered by immersion in concentrated lead acetate containing nitric acid.[1] But the lead actually becomes more " active," whereas if it were converted to a more stable allotrope it would become more " noble." The slight activation caused by treatment with this highly acid solution is not without a parallel among the other metals, which generally become more active (or less passive) when treated with acids. In the opinion of the present writer, there is no evidence of the existence of allotropes of lead at low temperatures.

Compounds

There are two main series of lead compounds, corresponding to the stannous and stannic compounds of tin ; they may be regarded as derived respectively from the two oxides, PbO and PbO_2. As usual with elements of high atomic weight, it is the lower type of salt that is best developed, all the stable salts of lead belonging to the " plumbous " series. Even in the case of tin it was noticed that the stannic compounds were very easily hydrolysed, and, on passing to lead, we find that the plumbic salts are so quickly decomposed by water that their formation in aqueous solution is very difficult ; in fact, only a few of the derivatives of tetravalent lead have been prepared under any conditions. Both of the lead oxides are amphoteric, like those of tin, and form compounds (plumbites and plumbates) when acted upon by alkalis. It should be noticed that whereas basic properties are best developed in the lower oxide, the acidic properties are most marked in the higher oxide—a very common state of affairs met with in many metals (e.g. chromium). Thus the plumbates are better developed than the plumbites.

[1] F. H. Getman, *J, Amer. Chem. Soc.* **40** (1918), 611.

A few unstable compounds, in which lead appears to be monovalent, have also been shown to exist.

A. Compounds of Divalent Lead (Plumbous Compounds).

Plumbous oxide, PbO, is formed when molten lead is exposed to the air. The colour of the oxide varies considerably, red, brown, yellow, and yellow-green forms having been described; the variation of colour may be partly due to the size and porosity of the particles,[1] but the red and yellow varieties seem to be distinct crystalline forms.[2] If the temperature be only just high enough to fuse the metal, a yellowish powdery form (*massicot*) is produced; but if it be sufficiently high to melt the oxide also, a more compact mass, of a pink-yellow colour, known as *litharge,* is obtained. The hydrated oxide (probably not a definite hydroxide [3]) is prepared as a white precipitate when ammonia or a caustic alkali is added to a lead salt solution. The precipitate dissolves in excess of caustic alkali, a soluble "**plumbite**" being no doubt formed; but the solution readily hydrolyses, lead hydroxide being reprecipitated; the plumbites are scarcely known in the solid state.

The **plumbous salts** are prepared when lead oxide is dissolved in acids; they are also formed when oxidizing acids dissolve metallic lead, or when other acids act on the metal in the presence of air, or hydrogen peroxide. They are mostly heavy white bodies, and on the whole resemble the corresponding barium compounds in their solubility relations; but, in forming an insoluble coloured iodide, lead displays a similarity to thallium and mercury, which fall beside it in the periodic table. The plumbous salts also show a general analogy to the stannous salts, but hydrolyse much less easily; they can be isolated without difficulty in the solid state by crystallization.

Of the *soluble* plumbous salts, the nitrate and acetate are the most important. The **nitrate** $Pb(NO_3)_2$ is most easily produced by dissolving the metal in nitric acid; the **acetate** $Pb(C_2H_3O_2)_2.3H_2O$, is best prepared by the action of acetic acid on the hydrated oxide or carbonate. When solutions of the nitrate or acetate are boiled with lead oxide, the oxide is dissolved, forming basic salts, which are soluble in hot water, but which crystallize out when the solution is cooled.

The *insoluble* salts can be prepared by precipitation with the corresponding sodium salts. These include the **sulphate,** a heavy white precipitate formed when a soluble sulphate or sulphuric acid is added to a lead salt solution. The precipitation is not quite

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[1] S. Glasstone, *Trans. Chem. Soc.* **119** (1921), 1689, 1914.

[2] M. C. Applebey and R. D. Reid, *Trans. Chem. Soc* **121** (1922), 2129.

[3] Compare S. Glasstone, *Trans. Chem. Soc.* **121** (1922), 58.

complete under ordinary circumstances, since lead sulphate is appreciably soluble in water; if, however, alcohol is added to the liquid, the solubility is diminished, and practically the whole of the lead passes out of solution. Lead sulphate is quite soluble in a concentrated solution of ammonium acetate.

The lead halides are also comparatively insoluble bodies, and are obtained on adding the chloride, bromide or iodide of potassium, to a solution of lead nitrate or acetate. The **chloride** and **bromide** are white, the **iodide** yellow; as in the case of the silver salts, the chloride is the most and the iodide the least soluble. All are very much more soluble in hot than in cold water, and, on boiling any of the precipitates with excess of water, they give clear solutions, which, however, redeposit the salts in a minute crystalline form when cooled again. The iodide obtained by recrystallization in this way forms minute golden flakes, which have a characteristic silky appearance when stirred up with water and held in the sunlight; the silky appearance is due to the fact that the water, moving past the crystals, turns them so that the longer axes of all the crystals point in the same direction, namely, the direction of the water currents.

The **sulphide,** PbS, is a black precipitate insoluble to dilute acids; it is produced when hydrogen sulphide gas is bubbled through a lead salt solution. It differs from tin sulphide in being insoluble in yellow ammonium sulphide.

The addition of sodium phosphate to a lead solution causes a white precipitate with lead phosphate. The precipitate formed when sodium carbonate is added to a soluble lead salt consists mainly of a basic carbonate; but the normal carbonate is produced if carbon dioxide is the precipitant.

B. Compounds of Tetravalent Lead (Plumbic Compounds).

Plumbic oxide (*lead peroxide*), PbO_2, is obtained by the action of an oxidizing agent, such as hydrogen peroxide, on a solution of a lead salt in the presence of alkali; it can be prepared pure by adding hydrogen peroxide to a solution of lead nitrate in 20 per cent. sodium hydroxide.[1] It is also readily obtained by the anodic oxidation of the metal. When a sheet of lead is made the anode to a dilute sulphuric acid solution, it becomes covered first with a layer of white insoluble plumbous sulphate; upon continuation of the electrolysis, this compound of divalent lead is oxidized further and forms the brown peroxide, PbO_2, no doubt in the hydrated form. The layer of peroxide, when once produced, protects the lead from further anodic attack, and the current is afterwards expended

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[1] V. Zotier, *Bull. Soc. Chim.* **21** (1917), 244.

almost entirely upon the evolution of oxygen ; but if the peroxide is scraped off as it is formed, more metal will be oxidized, and finally, the greater part of the metal can be converted into the form of the higher oxide. Lead peroxide is a brown powder, which evolves oxygen when strongly heated, plumbous oxide being left behind. It even loses oxygen on exposure to the sunlight; in this case the intermediate red oxide (Pb_3O_4) is produced. It is a strong oxidizing agent, and is employed as such in organic chemistry.

Plumbic Salts. Lead peroxide is evidently nearly insoluble in *dilute* sulphuric acid, since otherwise it could not be prepared by the electrolytic method mentioned above. There is no doubt, however, that a certain small amount of solution does take place, and that the sulphuric acid used always comes to contain a little **plumbic sulphate**, $Pb(SO_4)_2$. By electrolysis of *concentrated* sulphuric acid, in a divided cell fitted with a lead anode, solid plumbic sulphate can actually be obtained from the anode compartment.[1] A cooling arrangement must be provided to keep the liquid in the anode compartment below 30° C., otherwise lead peroxide is produced by the hydrolytic decomposition of the plumbic sulphate. Plumbic sulphate is a white substance, usually with a tinge of greenish yellow. The solution in strong sulphuric acid is distinctly greenish yellow. If placed in pure water, it is at once hydrolysed to lead peroxide and sulphuric acid.

If lead peroxide is heated with sulphuric acid, oxygen is evolved, and plumbous sulphate produced; plumbic sulphate cannot, therefore, be made in that way. Again, when lead peroxide is treated with concentrated hydrochloric acid, it dissolves, forming a yellow or brown solution, which no doubt contains plumbic chloride ($PbCl_4$) ; but any attempt to obtain this chloride by evaporation fails, for the solution at once evolves chlorine on being heated, and plumbous chloride is left. If, however, ammonium chloride be added to the solution, the yellow double salt $2NH_4Cl.PbCl_4$ or $(NH_4)_2PbCl_6$, which is not very soluble, crystallizes out. When this salt is cautiously added to concentrated sulphuric acid kept at a low temperature, pure **plumbic chloride,** $PbCl_4$, is produced, as a heavy yellow, fuming liquid, resembling stannic chloride. With a small quantity of water it combines, forming a crystalline hydrate ; but, if treated with excess of water, it suffers hydrolysis, giving lead peroxide and hydrochloric acid.

One other plumbic compound that must be mentioned is the **acetate,** $Pb(C_2H_3O_2)_4$. This is too unstable to be produced in aqueous solutions. When, however, warm glacial acetic acid acts on the red oxide Pb_3O_4, a solution is obtained, which deposits

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[1] K. Elbs and F. Fischer, *Zeitsch. Elektrochem.* 7 (1900), 343.

plumbic acetate in colourless crystals on cooling. The crystals are decomposed by water into plumbic oxide, PbO_2, *and acetic acid.*[1]

Plumbates.[2] Lead peroxide is insoluble in dilute alkalis, but dissolves in boiling concentrated potassium hydroxide. The solution obtained can be concentrated further by allowing it to stand over strong sulphuric acid and will then deposit white crystals of potassium plumbate $K_2[Pb(OH)_6]$, isomorphous with $K_2[Sn(OH)_6]$ and $K_2[Pt(OH)_6]$. The solution cannot be evaporated by boiling, since it then deposits lead peroxide by hydrolysis. Sodium plumbate can be prepared most easily by the anodic oxidation of a solution of lead hydroxide in sodium hydroxide, using a platinum anode; the plumbate crystallizes out from the solution without evaporation.[3]

Attention may be called at this point to the recurrence of the co-ordination number six in the plumbates, and also in the complex chlorides, such as $(NH_4)_2[PbCl_6]$, which were mentioned above.

C. Intermediate Oxides of Lead.

Besides the two oxides, PbO and PbO_2, which correspond to definite series of compounds, intermediate oxides, Pb_3O_4 and Pb_2O_3, are known.

Red lead, Pb_3O_4, is obtained by roasting in air at a dull red heat the unfused powdery form of plumbous oxide (massicot), or lead carbonate; under the pressure of oxygen occurring in the atmosphere, an additional quantity of oxygen is absorbed, and the product finally comes to have a composition corresponding roughly—although often not exactly[4]—to the formula Pb_3O_4; it may be remembered that other intermediate oxides (e.g. those of molybdenum) have also a variable composition. Red lead can be produced in a wet way by heating lead nitrate with 50 per cent. sodium hydroxide at 150–160° C.[5] The colour varies with the method of preparation; when prepared from massicot, it is a bright red powder.

Chemically, red lead behaves as though it were a loose combination of plumbous and plumbic oxides; for instance, dilute acids decompose it, forming a plumbous salt which passes into the solution, and leaving brown lead peroxide undissolved. Possibly red lead is really a " plumbous plumbate," $2PbO.PbO_2$, a combination of the basic oxide PbO, and the acidic oxide PbO_2.

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[1] A. Colson, *Comptes Rend.* **136** (1903), 676; A. Hutchinson and W. Pollard, *Trans. Chem. Soc.* **69** (1896), 212.

[2] I. Bellucci and N. Parravano, *Zeitsch. Anorg. Chem.* **50** (1906), 101, 107.

[3] G. Grube, *Zeitsch. Electrochem.* **28** (1922), 273.

[4] For details of methods of obtaining pure Pb_3O_4 see J. Milbauer, *Chem. Zeit.* **38** (1914), 477, 559, 566, 587.

[5] V. Zotier, *Bull. Soc. Chim.* **21** (1917), 246.

Red lead dissolves in glacial acetic acid, giving a solution with strong oxidizing properties, from which ammonia reprecipitates another oxide, Pb_2O_3; this can be regarded as another plumbous plumbate $PbO.PbO_2$, less basic than red lead. The same oxide, which is yellow when wet, but brownish when dry, may be prepared when an alkaline solution of plumbous oxide (i.e. an alkaline plumbite) is oxidized in the cold with bromine.[1] If the proper conditions are observed the product corresponds closely to the formula Pb_2O_3, but some of the methods yield products of which the composition is distinctly variable.

D. Compounds of Monovalent Lead.

The possibility of the existence in aqueous solution of salts containing lead in the monovalent condition has been demonstrated in more than one way. If a hot solution of lead acetate is made to pass over metallic lead, it is found to dissolve traces of lead, but deposits most of the metal in spongy form when cooled, provided that a piece of lead is added as a nucleus.[2] This would appear to indicate that a small amount of lead sub-acetate is formed at the higher temperature, but decomposes on cooling owing to the shifting of the equilibrium point of balanced reaction,

$$Pb + Pb(C_2H_3O_2)_2 \rightleftharpoons 2Pb(C_2H_3O_2).$$

The case is, of course, perfectly analogous to the formation of cuprous sulphate by the dissolution of copper in cupric sulphate.

The existence of monovalent lead is also indicated by the anodic behaviour of lead in certain solutions. In many solutions (potassium hydrogen tartrate, hydrosilicifluoric acid, etc.) a lead anode is attacked electrolytically at a rate which indicates quantitative dissolution in the divalent state; but in a solution of sodium acetate or sodium thiosulphate, the anodic current efficiency calculated on that assumption appears to exceed 100 per cent., and such a state of affairs would seem to indicate that lead is passing into solution to some extent as monovalent ions.[3]

The **suboxide**, Pb_2O, can be prepared by heating lead oxalate in a vessel which is kept evacuated by means of a Sprengel pump.[4] The heating should be commenced at 270°–275° C., and the pressure kept below 5 cm. of mercury, since otherwise the carbon monoxide produced may reduce the suboxide to metallic lead; towards the

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[1] S. Glasstone, *Trans. Chem. Soc.* **121** (1922), 1456.

[2] H. G. Denham and A. J. Allmand, *Trans. Chem. Soc.* **93** (1908), 424. The type of continuous-circulation apparatus needed to show the dissolution and redeposition of lead conclusively is described in this paper.

[3] N. M. Bell, *Trans. Faraday Soc.* **11** (1915–16), 79.

[4] H. G. Denham, *Trans. Chem. Soc.* **111** (1917), 29.

end of the process, when the pressure has sunk nearly to zero, the temperature can be raised to 335° C. or even higher.

The suboxide is a dark powder. When treated with aqueous acids, it does not yield the corresponding salts, but a mixture of metallic lead and the ordinary plumbous salts. However, the salts of monovalent lead can be prepared by heating the suboxide with appropriate organic esters, the method being analogous to that used in preparing solid cuprous sulphate. Thus, by heating lead suboxide in the vapour of ethyl chloride (C_2H_5Cl) or of ethyl bromide (C_2H_5Br), the greyish **subchloride,** PbCl, and **subbromide,** PbBr, can be obtained.[1] Similarly the dark grey **sub-sulphate,** Pb_2SO_4, is obtained by the action of methyl sulphate on the suboxide, whilst the bluish-grey **sub-acetate,** $Pb(C_2H_3O_2)$, is prepared by heating the sub-oxide with acetic anhydride.[2] These salts are decomposed by acids into metallic lead, and the corresponding normal (plumbous) salt.

When fused lead is added in small quantities to fused plumbous chloride, a metallic " fog " consisting of particles of lead of colloidal size suspended in the molten salt can be obtained. A similar " fog " is obtained by adding potassium cyanide to the fused lead chloride. The solid crystals of lead chloride formed on cooling the fused mass are dark, but should not be regarded as being a sub-chloride, since particles of metallic lead can be detected in them by means of the ultra-microscope.[3] It is, in fact, somewhat exceptional to find a crystal of lead chloride—prepared by fusion—quite free from fog, unless the chloride is specially treated in the molten state with gaseous chlorine and hydrogen chloride.

E. Miscellaneous Compounds.

Lead Hydride. The very unstable hydride of lead is of special interest, since evidence for its existence was first obtained by Paneth and Nörring by a radioactive method.[4] These experimenters exposed magnesium powder to thorium emanation, until it was covered with a deposit of thorium B and C, and then kept it in a desiccator for half an hour, so as to ensure the disappearance of any adsorbed emanation ; after this interval, the magnesium was dissolved in hydrochloric acid and the hydrogen produced was passed through a cotton-wool filter into a heated glass tube and was found to give a radioactive deposit upon the glass. The study of the

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[1] H. G. Denham, *Trans. Chem. Soc.* **113** (1918), 249.

[2] H. G. Denham, *Trans. Chem. Soc.* **115** (1919), 109.

[3] R. Lorenz and W. Eitel, *Zeitsch. Anorg. Chem.* **91** (1915), 46.

[4] F. Paneth and O. Nörring, *Ber.* **53** (1920), 1693. See also F. Paneth, *Ber.* **51** (1918), 1710; F. Paneth, M. Matthies, and E. Schmidt-Hebbel, *Ber.* **55** (1922), 775.

radioactivity of this deposit, which was present in too small an amount for chemical tests, indicated that it contained both thorium *B and thorium C. Since these bodies are not volatile in the elementary state, it is fairly certain that they must have passed* over as volatile hydrides. But thorium B and thorium C are respectively isotopic with lead and bismuth ; and, if it be admitted that the two radioactive elements have volatile hydrides, it is fairly certain that ordinary lead and bismuth will also have volatile hydrides, although, in the case of the non-radioactive elements, the detection of those hydrides may be more difficult. When, however, the existence of the hydride of the radioactive isotope of lead was once rendered fairly certain, Paneth and Nörring were encouraged to make extended experiments to isolate the hydride of ordinary lead. They finally succeeded in showing its existence in the hydrogen given off when dilute sulphuric acid was electrolysed in a special apparatus provided with a thin lead rod as cathode ; this cathode was surrounded by a sleeve so that the lead was only in contact with the acid at the tip of the rod. A very high E.M.F. (220 volts) was applied and the apparatus was arranged so that sparking occurred at the cathode. The hydrogen evolved deposited a visible amount of lead when passed through a heated glass tube, showing that the gas must contain a lead hydride.

Organic Derivatives of Lead. Like other members of the group of elements containing carbon, the lead atom has a remarkable power of attaching itself to hydrocarbon groups. Thus many of the organic bodies, which were noticed in the case of germanium and tin, find their counterpart among the compounds of tetravalent lead. Of these **lead tetra-methyl,** $Pb(CH_3)_4$, a volatile liquid produced by the action of methyl iodide on a lead-sodium alloy, may be cited as an example ; its formation may be expressed thus :

$$Pb + 4CH_3I + 4Na = Pb(CH_3)_4 + 4NaI.$$

Analytical

Lead is a metal quite easy to reduce by heating with carbon in the reducing flame of the blowpipe, and the bead of the molten metal obtained is gradually converted by heating in the oxidizing flame to the yellowish oxide.

In aqueous solution, there are various features in the behaviour of lead salts which serve to distinguish them from those of other metals. The white precipitate of sulphate, obtained when sulphuric acid is added to a lead solution, is met with in the case of no other metals except barium and strontium. The precipitate obtained with hydrochloric acid dissolves in hot water, and so may be distinguished from most other insoluble chlorides (silver or mercurous chlorides); the yellow precipitate obtained by adding potassium iodide is also characteristic, although silver and thallous salts give a yellow iodide under the same conditions.

The quantitative separation from most other metals depends on its precipitation by sulphuric acid as lead sulphate. In order to render the precipitation complete an equal volume of alcohol is added, and the hot solution is allowed to stand for some time. The precipitate is then filtered off and washed with a mixture of alcohol and water. It should be dried at 100° C., and transferred as far as possible to a weighed crucible. The filter-paper, to which a little lead sulphate always adheres, may be burnt on the crucible lid; during this burning the lead is usually partly reduced to the metallic state, but may be reconverted to sulphate by the action of concentrated sulphuric acid. Before weighing, the sulphate should be completely dried by moderate heating of the crucible, but it must not be heated so strongly that it becomes converted to oxide.

Besides the estimation of lead as **sulphate**, the metal is sometimes precipitated and weighed as **sulphide**, or in exceptional cases as **iodide**. These methods could be employed in the presence of other metals, like barium, which have soluble sulphates.

Lead is also conveniently estimated as the **peroxide**, obtained electrolytically. When a hot lead salt solution containing plenty of free nitric acid is electrolysed at a high anodic current density, the whole of the lead is precipitated as peroxide on a platinum *anode*. The presence of most other metals, which are not deposited upon the anode, does not interfere with the estimation of the lead in this way. But manganese and thallium, if present, which might also be precipitated on the positive electrode, must be separated before the electrolysis. Unfortunately the lead peroxide is always produced in a hydrated condition, and the water is not completely driven off even when the electrode is heated to 200° C. However, the small amount of water retained under certain fixed experimental conditions has been determined empirically and a correction can therefore be applied.[1]

It may be mentioned here that compounds containing lead, tin, or zinc (three easily fusible metals) should not be heated in platinum vessels, since there would be a danger of the formation of platinum alloys of these metals, and consequent damage to the vessels.

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[1] H. J. S. Sand, *Trans. Faraday Soc.* **5** (1910), 207.

TERRESTRIAL OCCURRENCE

The terrestrial occurrence of lead has already been considered in connection with that of zinc, with which metal lead occurs in intimate association in nature (see page 138). It is only necessary here to recall the fact that the principal ore of lead is the sulphide

	Galena	PbS

which occurs in heavy shining cubes, and often contains silver. In the oxidized portions of the zinc-lead ores the minerals

	Cerussite	$PbCO_3$
and	Anglesite	$PbSO_4$

are found, but these are of much less practical importance. Other minerals containing lead such as

	Crocoite	$PbCrO_4$
	Wulfenite	$PbMoO_4$
and	Vanadinite	$3Pb_3(VO_4)_2.PbCl_2$.

are much rarer and owe their importance mainly to the second metal which they contain, and not to the lead.

METALLURGY AND USES [1]

The preliminary treatment of the zinc-lead ores to give

(*a*) a concentrate containing *zinc*,
and (*b*) a concentrate containing *lead* and *silver*,

has already been discussed in the section devoted to zinc. Where lead-ore occurs free from zinc, the concentration can be simplified; a rough gravity-separation on jigs and tables generally serves to remove the greater part of the gangue from the heavy galena.

It is now necessary to describe the smelting of the lead-silver concentrate to yield an argentiferous lead, and then to indicate the principal methods of "desilverizing" the lead, so as to recover as much as possible of the precious metal, and leave the lead in a state of moderate purity.

It should be mentioned that even where the lead-ore—as found in nature—contains little or no silver, advantage is sometimes taken of the efficiency of lead as a "collector" of silver, and a silver-ore—of a variety which does not contain sufficient lead for

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[1] See H. O. Hofman, "Metallurgy of Lead" (1918), (McGraw-Hill); C. Schnabel and H. Louis, "Handbook of Metallurgy" (Macmillan), 1921 edition; W. R. Ingalls, "Lead Smelting and Refining" (*Engineering and Mining Journal*); H. F. Collins, "Metallurgy of Lead" (Griffin); J. A. Smythe, "Lead" (Pitman).

direct smelting—is purposely mixed with it; thus an argentiferous lead is obtained from which the precious silver is extracted by a subsequent desilverizing process.

The **smelting** of lead can be carried out in

(1) shallow hearths,
(2) reverberatory furnaces, or more commonly in
(3) blast-furnaces.

Since lead occurs generally in the ore or concentrate as sulphide, the simplest possible method of smelting will consist essentially in the burning off of the sulphur. It can be carried out in one stage by blowing a hot blast of air over an ore-charge, placed on a **shallow hearth.** The reaction as a whole can be written in a very simple form,

$$PbS + O_2 = Pb + SO_2.$$

Alternatively the smelting can be carried out in a **reverberatory** furnace, in which case it is customary to conduct the process in two separate stages. During the first or "roasting" stage, the temperature is kept below the fusion point of the ore-charge, and air is admitted to convert part of the lead sulphide to oxide or to sulphate,

$$\begin{aligned} PbS + 3O &= PbO + SO_2 \\ PbS + 4O &= PbSO_4. \end{aligned}$$

During the second, or "reaction" stage, a higher temperature is used, so as to melt the charge, and the oxide or sulphate is reduced by the excess of lead sulphide to metallic lead.[1]

$$\begin{aligned} 2PbO + PbS &= 3Pb + SO_2 \\ PbSO_4 + PbS &= 2Pb + 2SO_2. \end{aligned}$$

It is extremely likely that, even when the process is carried out on a shallow hearth in one operation, the smelting really takes place in these two separate stages.

At the present time most of the world's supply of lead is obtained in the **blast-furnace.** Before the introduction of the ore into the blast-furnace, roasting is necessary, and this is carried out under such conditions that the fine ore or concentrate is agglomerated to a hard compact lump, suitable for the blast-furnace charge; fine powder is, of course, useless for blast-furnace smelting. The roasted mass, containing most of the lead as oxide, is then mixed with fuel and smelted in a blast-furnace, where the oxide is reduced,

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[1] These are both balanced reactions. For equilibrium conditions, see W. Stahl, *Chem. Zeit.* **39** (1915), 885; R. Schenck and A. Albers, *Zeitsch. Anorg. Chem.* **105** (1918), 145.

mainly by carbon and carbon monoxide—although, to some extent, by the surviving lead sulphide—to metallic lead.

A distinct method of obtaining lead from sulphide ores is by heating with scrap-iron, usually in a reverberatory furnace. This process is rarely used as the main method of smelting an ore, but is sometimes used for working up slaggy residues containing galena.

Smelting in Shallow Hearths. The method of hearth-smelting was developed mainly in Scotland. It was afterwards adopted in America, but became largely superseded by blast-furnace smelting; lately there has been a tendency to revive it in an improved form (the "mechanical" Scotch hearth) in places where rich lead *concentrates* are available for smelting in quantity insufficient for economical blast-furnace treatment.[1]

Fig. 26 shows the essential scheme of an ore-hearth. The sump A is filled with molten lead, which is able to overflow down the sloping plate B into the lead-pot C. Upon the lead in A floats a pile of ore and fuel (coal, charcoal, or even wood) and usually a little lime. Upon this charge plays a blast of air from the tuyere D. The blast oxidizes the lead sulphide to oxide (or sulphate), which is then reduced to metallic state by the undecomposed sulphide, or by the fuel, and thus the volume of lead in the sump is increased, and lead overflows into the lead-pot. Every five or ten minutes, the workman draws out the lower portion of the charge, which has become sintered to form a hard mass, on to the sloping plate, and separates the half-decomposed ore, or "browse," from the slag, which is removed. The half-decomposed ore is then put back on to the hearth, and fresh charge is added to make up for what has disappeared.

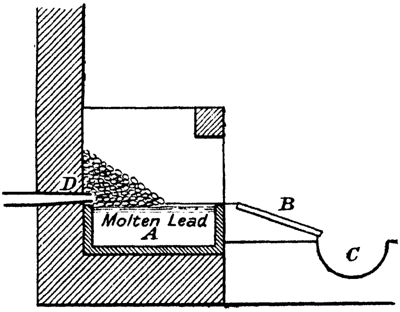

FIG. 26.—Ore Hearth.

The early Scotch and English hearths used to become so hot that every ten hours the working had to be interrupted, so as to allow the hearth to cool. Modern hearths are usually water-cooled, and can be used continuously. The main disadvantage of the hearth method of lead-smelting is the amount of lead carried off by the blast. Formerly this was a source of serious danger to the workmen

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[1] W. E. Newnam, *Eng. Min. J.* **106** (1918), 101. Compare A. S. Dwight, *Eng. Min. J.* **102** (1916), 671.

employed, but the methods of carrying off the fumes are now very much improved by the installation of suction fans. The production of fume involves a serious loss of lead, although the development of water-cooled hearths in America has greatly reduced this loss. It may be mentioned that in some American works the production of fume is actually aimed at, the dust being recovered by filtering the gases leaving the hearth in a bag-house. This dust is used in the manufacture of lead-pigments—a subject which will be considered later.

It is not advisable to use the ore-hearth for lead-ores rich in silver, as considerable loss of the precious metal would occur.

Smelting in Reverberatory Furnaces. Reverberatory smelting was largely developed in this country, notably in Flintshire, Shropshire, and Derbyshire, whilst different forms of the process have been evolved—more or less independently—in Silesia and Carinthia. The shape and size of the furnace, as well as the temperature of working, differ considerably in the various districts, but the essential features of a lead reverberatory furnace are shown in Fig. 27. The principal point to which attention should be called is that the hearth-bottom is made to slope towards an opening in the side through which the molten lead can be tapped, a pot P being placed outside the furnace to receive it.

The ore is usually charged in through a hopper H. It is roasted for two to six hours by means of hot gases coming from the grate G, plenty of air being admitted by the open doors D, D, D in the side. During the roasting the ore is frequently turned over. When sufficient oxide and sulphate have been produced, the doors are shut, and the charge is more strongly heated. During this stage the sulphide reduces the oxide and sulphate, producing metallic lead, which begins to settle into the sump of the hearth. The difference between the gravities of lead and the unreduced sulphide is not sufficient to produce a very complete separation into two layers. Therefore the separation is often aided by " stiffening " the sulphide phase with lime. A charge of lime is stirred into the mass above the sump; this mixes with the unchanged galena and slag, and raising the melting-point of the slag makes it pasty, but leaves the lead in the fluid condition. It then becomes comparatively easy for a skilled workman to draw up, with a rabble, the whole of the non-metallic mass on to the upper part of the hearth. Upon further cautious heating, any metallic lead which has been drawn up with it drains back into the sump, from which the metal may be tapped in a molten state.

In England it is customary to heat the charge rather rapidly in reverberatory furnaces; this makes a high rate of output in proportion to the size of the furnace, and minimizes the fuel consumption; on the other hand, it involves a considerable loss of lead in the fume.

It is usual in England to commence the second ("reaction") stage whilst lead sulphide is still in considerable excess of the amount required for reaction with the sulphate and oxide present; consequently after the reaction stage has yielded all the lead possible, the residue is again roasted, and then heated again strongly to yield a second quantity of metallic lead. Even after this repeated treatment the slag left contains unaltered lead sulphide, and is sometimes further worked up for the recovery of the residual metal.

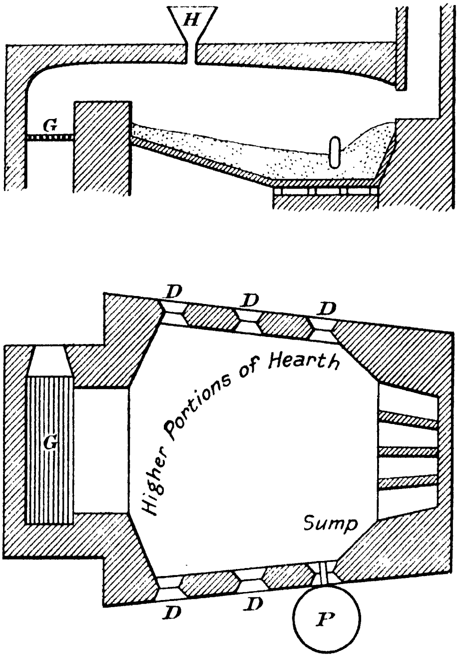

FIG. 27.—Reverberatory Furnace for Lead-smelting.

In Silesia, a lower temperature is employed, and the loss of lead by volatilization is much less. The process commences with a long roast, followed by alternate short roasting and reaction periods. The lead tapped during each reaction period is collected separately; most of the silver is concentrated in the earlier tappings. A similar method is used in Belgium and in Carinthia; the process commonly described as the "Carinthian process," carried out in very small furnaces, is almost obsolete.

Blast-furnace Smelting.[1] Although the smelting of lead-ores in hearths or reverberatory furnaces is suited for comparatively small lead-producing districts such as exist in Europe, in those regions where large supplies of lead-concentrates have to be handled the blast-furnace method is generally preferred. The greater part of the lead produced in the United States is obtained in the blast-furnace.

The ore or concentrate is first *roasted* so as to convert sulphide to oxide ; the first part of the roasting may be conducted in the ordinary multiple-hearth roaster, or in a reverberatory furnace ; but the roasting must be finished in some form of plant which gives a sufficiently high temperature to sinter the mass and thus to produce a hard, coarse product which is suitable for a blast-furnace charge. This sintering is often carried out in a **Dwight-Lloyd** plant, which has already been described in connection with the agglomeration of the finer ores of iron and other metals (see Vol. III, page 62) ; in that plant, the fine partly-roasted concentrates are mixed with fuel and sintered in a "downward" draught of air. Another older method, known as the **Huntingdon-Heberlein** process, employs an "updraft" of air to agglomerate the ores.

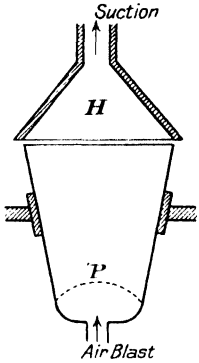

FIG. 28.—Huntingdon-Heberlein Pots.

This latter process is conducted in a circular iron pot (Fig. 28) of capacity varying from 1 to 15 tons (usually about 8 tons), fitted with a perforated plate P as a false bottom. Below the plate a pipe enters the pot, through which a blast of air can be forced, and when roasting is in operation the pot is surmounted by a hood, H, connected with a pipe through which the fumes produced can be sucked away to a bag-house or other dust-collecting plant. The pot is commonly mounted on trunnions like a converter, so that the contents can be tipped out at the completion of the process.

In charging the pot, a small amount of coal is placed on the perforated plate, and above it, a quantity of partially roasted ore, still hot from the furnace, as a "kindling charge." A gentle blast is then turned on, and the remainder of the pot is filled up with partially roasted ore—cold and previously moistened with water—

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[1] A. S. Dwight, *Eng. Min. J.* **102** (1916), 671. I. A. Palmer, *Min. Eng. World,* **41** (1914), 755.

mixed with lime. Then the blast is increased and the reaction commences. The sulphide is oxidized to oxide, and the temperature rises high enough to sinter the charge, and cause it to agglomerate. When the process is complete, the contents of the pot are turned out, often coming out almost as a solid block. It is broken up and is then in a suitable state for charging into the blast furnace.

The presence of lime in the charge is a distinctive feature of the Huntingdon-Heberlein process. Several different views have been put forward to account for the beneficial effect of the lime. The inventors[1] of the process considered that it acted as an oxygen-carrier, calcium dioxide (CaO_2) being alternately formed and decomposed, and that the roasting was thus accelerated. Another authority[2] thinks that calcium plumbate is formed as an intermediate product. Numerous other explanations have been put forward.[3] The true cause of the action of lime is probably to be ascribed to the fact that the change

$$PbS + 3O \rightleftharpoons PbO + SO_2$$

is a balanced reaction. Any substance like lime which absorbs sulphur dioxide will favour the change in the "left to right" direction. It should be noted that when the ore is roasted in the *absence* of lime, part of the galena is not converted to lead oxide but to sulphate, according to the change

$$PbS + 4O = PbSO_4.$$

Since no sulphur dioxide is produced in this alternative change, there is no reason to think that the presence of lime will be favourable to it. We should expect, therefore, that the charge roasted in the presence of lime would contain more oxide and less sulphate than a charge roasted, to an equal extent, in the absence of lime; analysis has shown that this is actually the case.

There is, however, but little doubt but that the beneficial action of the lime is in part that of a diluent, allowing the air access to the sulphide, and preventing the whole mass from agglomerating before the oxidation is complete. It has been shown that various inert substances such as quartz, slag, cinder, or iron-ore, which can scarcely play any chemical part in the oxidation, nevertheless act beneficially in the roasting of lead ores.[4] In one method of pot-roasting, known as the Carmichael-Bradford process, which has attained some importance in Australia, calcium sulphate (gypsum) is used in the place of lime.

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[1] T. Huntingdon and F. Heberlein, *Eng. Min. J.* **81** (1906), 1005.

[2] W. Borchers, *Metallurgie,* **2** (1905), 1.

[3] C. O. Bannister, *Trans. Inst. Min. Met.* **21** (1911–12), 346.

[4] C. Guillemain, *Eng. Min. J.* **81** (1906), 470.

At some American works, attempts have been made to carry out the preliminary roasting in the Dwight-Lloyd plant, followed by sintering in the Huntingdon-Heberlein plant, thus dispensing with the multiple-hearth roasting furnaces altogether.

The sintered mass—broken up if necessary into lumps of appropriate size—is mixed with coke and suitable fluxes, and is charged into the **blast-furnaces.** These are usually rectangular water-jacketed furnaces, rather similar to those used in the metallurgy of copper (see page 29), but the water-jacketing is not usually carried to the top. The average size is about 18 × 4 ft., with an ore-column about 16 ft. high. At one big Australian works, furnaces have been employed with a working height of 28 ft.[1] The reactions occurring in the hotter portions of the furnace are essentially a reduction of lead oxide by carbon or carbon monoxide; but where the charge still contains unconverted lead sulphide, this aids in the reduction of the lead to the metallic state. Of the products obtained at the bottom of the furnace the lead is drawn off through a "siphon tap"; a certain amount of matte and slag flow out into a settler, where they separate into two layers.

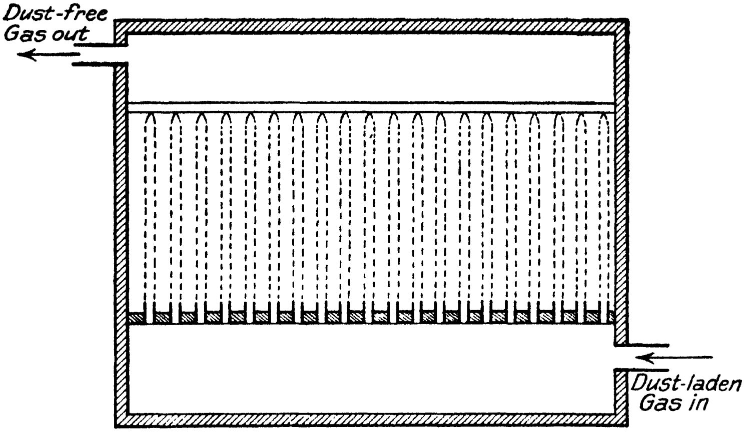

FIG. 29.—Principle of Bag-House.

The gases emerging from the blast-furnaces, roasters and Huntingdon-Heberlein plant (if installed) are in all modern works led through a bag-house so as to catch the dust. The bag-house consists of a large number of long cylindrical bags of wool or cotton hung side by side (Fig. 29). The length of the bags may be 25 ft., whilst the diameter is usually about 20 in. The dusty gases are

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[1] H. O. Hofman, *Min. Ind.* **28** (1919), 424.

passed into the interior of the bags, and are drawn by a fan through the fabric, thus being filtered free from suspended solids. In the early bag-houses the area of the bags needed to filter the gases was extremely large, because many of the pores in the fabric soon became choked with solid particles. Modern bag-houses are fitted with devices whereby the bags are periodically freed from the solid matter which has accumulated. Such devices provide not merely for a mechanical shaking of the bags, but also a periodical reversal of the pressure, so that the distended bags suddenly collapse, dropping the solid matter contained within them into hoppers beneath, whence it is discharged. By improvements of this kind, it is possible to reduce the bag area needed for filtration very considerably.[1] For the finer fume, which would not easily be removed by filtration, electrostatic precipitation has proved invaluable.

In many American works where arsenical ores are treated, the dust from the blast-furnaces consists largely of arsenious oxide, and is used as a source of arsenic.

Lead Refining and Desilverization

The lead produced in any of the processes mentioned above contains small amounts of other metals, such as silver, copper, arsenic, antimony, iron, zinc, bismuth, and tin ; it usually also contains some sulphur. The most valuable impurity is silver—which is always present—except in the lead made from non-argentiferous ores, such as those of Missouri or Carinthia. In many cases, especially where the lead has been used as a " collector " of silver from a silver-ore, the silver represents a large fraction of the value of the metal. It is therefore necessary to employ some method which allows the recovery of the whole of the silver, without sacrificing more of the lead than is necessary, and which at the same time leaves the lead as far as possible free from other impurities which are for different reasons objectionable. The three main processes of desilverization used are dependent on—

(1) Extraction of silver by molten zinc (Parke's process).
(2) Electrolytic parting (Betts's process).
(3) Fractional crystallization (Pattinson's process, and later processes on the same principle).

Parke's process[2] is more largely used than the others, but as the method only serves to remove silver and gold, and would

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[1] Compare H. O. Hofman, *Eng. Min. J.* **105** (1918), 93; W. E. Gibbs, *J. Soc. Chem. Ind.* **41** (1922), 192T.

[2] E. Schlippenbach, *Met. u. Erz.* **15** (1918), 323.

leave the objectionable impurities in the lead, the latter is first subjected to preliminary refining (" softening ") in a reverberatory furnace. The lead is slowly melted, and some of the impurities—which are only partially miscible with molten lead at temperatures a little above the melting-point—rise to the surface as a " dross " and are skimmed off ; the dross usually consists of copper, sulphur and arsenic, together with a certain amount of lead. When the dross has been removed, the temperature is raised to a good red heat, and air is admitted to the furnace. Under these oxidizing conditions, the easily oxidized impurities such as tin, arsenic and antimony are eliminated, partly as a fume consisting of volatile oxides of arsenic and antimony, but largely as scums consisting mainly of lead stannate in the early stages and lead arsenate and antimoniate in the later stages. These scums are removed and the furnace is tapped.

The extraction of silver from lead by molten zinc is analogous to the extraction of fatty bodies from aqueous solutions by means of ether or benzene. Silver is soluble in molten lead, but it is far more soluble in molten zinc. If molten lead be stirred up with molten zinc, the metals do not mix completely, but form separate phases, just as do ether and water. At a temperature of 350° C., the lead will only dissolve 0·6 per cent. of zinc, the rest of the zinc remaining as a separate phase. If the lead originally contained dissolved silver, this silver will distribute itself between the two phases in such a way that the silver-concentration in the zinc is far greater than in the lead. Consequently, even if only a *small* quantity of zinc be stirred into molten argentiferous lead, it will take up practically the whole of the silver, together with any gold and platinum present.[1] The zinc is lighter than the lead, and therefore forms a layer above it, after the stirring. If the metal be now allowed to cool and the light crust of zinc which solidifies first and floats on the surface be ladled out, it will be found to contain nearly all the silver ; the liquid lead below is comparatively free from the precious metal, but now contains some zinc.

In order, however, to extract the silver completely, two (sometimes three) successive additions of the solvent zinc are usually made. The total amount of zinc added is about 1—2 per cent. of the lead. Most of the silver is contained in the zinc crusts skimmed off after the first addition of zinc.

The various zinc crusts contain zinc and silver and a great deal of lead, most of which has been brought out mechanically adhering to the crystals. Owing to the comparatively small amount of zinc containing the silver, it would not be entirely fatal to the economy

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[1] D. A. Landsberg, *Met. u. Erz.* **15** (1918), 37.

of the process if the former metal were largely sacrificed in the extraction of the precious element. In practice, however, 50–80 per cent. of the zinc can be recovered. The usual method of separation of zinc from silver is based upon the volatility of the first-named metal, the zinc being driven off by distilling the alloy from retorts set in a hot furnace. The zinc distils over and is condensed in adapters, as in the ordinary smelting of zinc, whilst the silver and lead remain behind.

After the zinc has been removed by volatilization, a silver-lead alloy remains. This is always treated by "**cupellation**"; that is to say, it is exposed, in the molten state, to a strong blast of air, which oxidizes the lead to litharge, but leaves the more noble silver in the metallic state. The litharge which flows away molten from the hearth has a very appreciable value.

The furnace usually employed for the oxidation of the lead is a special form of small reverberatory furnace. In order to facilitate the relining, the hearth is generally made movable, although in the so-called "German" furnace the hearth itself is fixed and only the hood which covers it is removable; even in Germany, however, furnaces with the hearth completely removable are now common. Fig. 30 shows the furnace preferred in England and America, along with the carriage used in removing and replacing the hearth. The hearth is lined with marl, magnesite, or cement, which is beaten down so that the top has the form of a shallow saucer; when fixed in position it is charged with the lead-silver alloy to be treated. The charge is heated strongly by hot gases coming from the grate G, and the molten metal is exposed to the air-blast forced in under pressure from the tuyere T placed just above the surface. The oxidation of the lead commences slowly, but as soon as the formation of litharge has begun, the latter substance acts as an oxygen-carrier, and the formation of further litharge proceeds apace. The litharge formed on the surface is blown along by the air-blast from the tuyere, and flowing over the surface of the lead, runs out continuously through a channel in the opposite side of the hearth. Finally, when the whole of the lead has been oxidized to litharge, and the last portion of the oxide scum clears off from the silver, the bright surface of the precious metal suddenly becomes visible, and the extraction of the silver from the lead is complete. The silver—

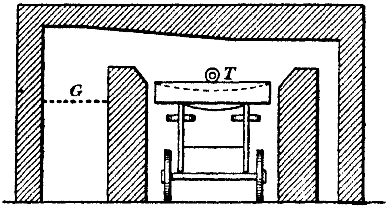

Fig. 30.—Cupellation Furnace.

which generally contains a trace of gold—is sent to the silver-refinery for "parting."

In some German establishments, it is customary to collect the first portions of the litharge, which usually contain the easily oxidizable element antimony, separately from the purer material obtained later. This antimonious litharge has a lower value for the manufacture of lead pigments than the purer oxide, but may profitably be smelted to obtain the lead-antimony alloy known as "hard-lead."

The desilverized lead obtained from the Parkes process contains enough zinc to render it hard and rather brittle. It is therefore "softened" again, usually by passing steam through the metal, which oxidizes and removes the zinc. The Parkes process—although the cheapest method of desilverizing lead—leaves the lead more impure than the other two processes. Any bismuth, for instance, which may exist in the lead before the desilverization, remains in the lead at the end. It is mainly for the treatment of lead containing bismuth that the other two processes of desilverization are used.

Betts's Electrolytic Process.[1] The Betts method for separating lead and silver depends upon the differences between the anodic behaviour of the two metals. The principle is the same as that employed in the electrolytic parting of silver and gold, but difficulties were experienced in working out an electrolytic method of lead-refining owing to the fact that from most solutions lead is deposited—not as a smooth adherent coating upon the cathode—but as a loose mass of dendritic crystals. Betts solved the problem by the employment of a bath of lead silicifluoride ($PbSiF_6$) containing free silicifluoric acid, together with glue as a colloid addition. Anodes of the argentiferous lead to be refined are hung in this bath. Thin cathodes of pure lead are hung opposite to them. When a moderate current is passed between the electrodes, lead is deposited as a compact deposit on the cathode, whilst a similar quantity of the same metal is dissolved at the anode; the current efficiency of the process is said to be about 90 per cent. The silver present in the anode-material is not dissolved, but is found as a dark sludge adhering to the anode. This anode sludge is periodically scraped off; it will usually contain other impurities of a "noble" character, such as arsenic, antimony, bismuth, copper, gold and selenium. The treatment of the anode sludge varies in different places and according to its composition. It is sometimes treated in a reverberatory furnace under oxidizing conditions to remove the oxidizable arsenic, antimony, and the remaining lead; the

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[1] A. G. Betts, *Metallurgie*, **6** (1909), 233.

gold-silver bullion left behind can be parted electrolytically to give pure silver.

The Betts process is worked on a large scale at Trail, British Columbia, and also at Newcastle-on-Tyne. The process is particularly successful where the crude lead contains bismuth, as the bismuth is completely removed from lead by the refining method, and is found in the anode slimes ; the bismuth forms an additional valuable by-product. It is stated that it is mainly due to the separation of bismuth that the process can compete with the Parkes process. Where the anode slimes contain much bismuth, they are sometimes cast once more into the form of anodes, and subjected to further electrolytic refining in a cell containing bismuth chloride solution. Bismuth is dissolved at the anodes and deposited on the cathodes, whilst the anode residues on this occasion consist mainly of silver and gold.[1]

Pattinson's Process. The method which was at one time most extensively used for the desilverization of lead was due to Pattinson. It depends upon that fact that when an argentiferous lead is melted in a pot, and allowed partially to solidify, the crystallized portion of lead contains less silver than that remaining liquid. Since the crystallized portions can be fished out with a perforated ladle, and separated fairly well from the still molten portions, a means is provided of dividing the lead into two fractions respectively rich and poor in silver. Each of these fractions can be treated again in the same way, and it is obvious that finally, by continued fractional crystallization upon a methodical system, a lead practically free from silver can be obtained on the one hand, and an alloy comparatively rich in the precious metal can be arrived at on the other. It is not, however, possible to carry the silver-content above 2·5 per cent., since this is the composition of the lead-silver " eutectic," and on allowing a mixture of eutectic composition partially to solidify, the solid will necessarily have just the same composition as the liquid. But an alloy containing 2·5 per cent. of silver is rich enough for profitable " cupellation " ; it is roasted in a blast of air, and the more oxidizable lead is converted to molten litharge whilst the silver remains in the metallic state. The litharge produced has a considerable value, and any small loss of lead involved is of little account compared to the value of the silver.

The crude process as suggested above involves a great deal of labour, but mechanical processes upon the same principle are still used to some extent. In one of these, the mixing of the molten lead is carried out by means of a steam-jet, and the separation of

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[1] A. T. Ward, *Min. Ind.* 28 (1919), 56.

the liquid from the crystalline lead is effected by drawing off the former by a tap at the bottom of the vessel. In general, however, there has been a tendency for the Pattinson process to be replaced by the processes of Parkes and Betts.

Uses of Lead

The general usefulness of lead is due to a variety of causes. Owing to the plentiful supply of ore, and the ease with which the reduction is effected, it is a comparatively inexpensive material; in fact, it is—in the normal state of the metal market—the cheapest of all metals, except iron. Furthermore, as has been pointed out, it is practically unaffected by exposure to air and water; superficial oxidation certainly does take place at first, but the products of oxidation protect the metal from further attack. It is therefore much employed in the flat portions of house-tops; the rate of corrosion is generally slow, but varies, not only with the state of the atmosphere, but also with the character of the material on which the lead is laid [1]; it should not be placed in contact with cement. Lead pipes are commonly used for the conveyance of water except in case of plumbo-solvent waters (*see below*). The softness and malleability of lead adds to the value, for lead may be cut and bent without difficulty at the ordinary temperature; and again pieces of lead can be joined together by solder, or by autogenous welding, owing to the low melting-point of the metal, whereas iron must generally be fastened by bolts or rivets. Where a slightly harder and stiffer material may be required, lead can be hardened by alloying with a little arsenic, antimony, or tin.

Lead is likewise used largely in the protective sheathing of telegraph and telephone cables which are to be buried. The metal, however, is not altogether immune from attack, and cases of corrosion of the sheathing are becoming increasingly common, many of them being due to stray electric currents caused by leakage from tramway systems.[2] Sometimes curious intergranular cracks develop in the lead sheathing, comparable to those met with in the season-cracking of brass. They develop especially where the grains of lead have smooth and straight boundaries, since under these conditions small stresses are able to pull the individual grains apart, either through the gradual flowing of the plastic intergranular cement, or through its preferential removal by corrosion.[3]

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[1] Compare J. S. S. Brame, *J. Soc. Chem. Ind.* **37** (1918), 397.

[2] Girousse, *Comptes Rend.* **157** (1913), 705.

[3] L. Archbutt, *Trans. Faraday Soc.* **17** (1921), 22.

This parting of the grains from one another naturally takes place most readily where the lead is in tension.[1]

Special uses of lead depend upon its stability in the presence of certain chemically active substances; the chambers and pars used in the manufacture of sulphuric acid are lined with lead, the only cheap metal which withstands the acid at the temperatures involved. Much discussion [2] has taken place regarding the relative merits of pure lead and impure lead in resisting the action of the acid. Some authorities condemn the lead produced by the Parkes process, and ascribe the bad resisting power of that material to the presence of antimony and bismuth; it is, however, believed that the bad effect of antimony can largely be counteracted if a little copper is also added to the lead.

Lead-lined wood tanks are frequently used for chemical operations on a large scale, in cases where the only alternatives would be comparatively costly vessels of stoneware. Moreover, in electrolysis, lead is the only cheap metal thoroughly suitable for use as an insoluble anode in a sulphate solution; the comparatively insoluble lead sulphate is first formed upon the anode surface, and is then oxidized further to lead peroxide. When the lead is completely covered with the brown peroxide layer, it becomes almost immune to further attack, and the only effect of continued electrolysis at the anode is to cause an evolution of oxygen. It is true that the peroxide sometimes flakes and drops off, being replaced by further slow attack of the lead. But this can be prevented by binding the anode round with fabric, and a cloth-surrounded lead anode may be regarded almost as a permanent electrode in a sulphate solution.

Lead Plating. During the war the plating of steel with lead was used for certain purposes, notably for the lining of certain gas shells. The same silicifluoride bath which has been mentioned in the electrolytic desilverization process was sometimes employed, whilst another bath containing lead as fluo-borate gave good results.[3] Baths containing perchlorates [4] have also found advocates.

Iron is also occasionally given a protective coat by dipping

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[1] H. S. Rawdon, A. I. Krynitsky, and J. F. T. Berliner, *Met. Chem. Eng.* **26** (1922), 109.

[2] Compare the views of D. W. Jones, *J. Soc. Chem. Ind.* **39** (1920), 221T, with those of C. E. Barrs, *J. Soc. Chem. Ind.* **38** (1919), 407T, and those of W. G. McKellar, *J. Soc. Chem. Ind.* **40** (1921), 137T.

[3] W. Blum, F. J. Liscomb, Z. Jencks, and W. E. Bailey, *Trans. Amer. Electrochem. Soc.* **36** (1919), 243. Compare W. Lange, *Zeitsch. Metallkunde*, **13** (1921), 267.

[4] F. C. Mathers, *Trans. Amer. Electrochem. Soc.* **26** (1914), 99; W. E. Hughes, *J. Phys. Chem.* **26** (1922), 316.

into molten lead, or into an alloy of lead with tin or antimony.

Plumbo-solvency. When lead is used, for instance, as a roofing material, any minute amount of dissolution that occurs may be neglected until, in the lapse of time, it calls for a replacement of the metal. But, in the case of a lead pipe used for the conveyance of drinking-water, it is necessary to consider the effect of corrosion, not only upon the pipe, but also upon the water. Owing to the poisonous character of the metal, the presence of even a small trace of lead in water is a very serious matter.

The main fact determining whether lead will pass into solution or not in the presence of dissolved oxygen is the possibility of the formation of a protective film on the lead. Hard waters containing much bicarbonate and sulphate of calcium are likely to produce a protective film of the corresponding insoluble lead compounds on the metal. Furthermore, the reaction of the water upon the lead necessarily involves a drop of the hydrion concentration; and, where the calcium originally exists in the water as bicarbonate, this diminution in the hydrion concentration may cause a deposition of calcium as carbonate, just at the place where the lead is being attacked. Thus we obtain upon the interior of the pipe a protective layer of chalky scale, which is very efficient in preventing the entry of lead into the solution, although, in extreme cases, the scale may ultimately block up the pipe, and may thus cause trouble of another kind.

On the other hand, soft waters such as are derived from moorland districts, cause little or no scale on the metal, and lead may pass into solution. This is particularly the case if the water contains anions which would tend to form a soluble complex salt of lead. Thus waters containing nitrites have a distinctly "plumbo-solvent" action. Excess of free carbon dioxide—as opposed to calcium bicarbonate—is favourable to the solvent action. Such waters—which are very common where the collecting-area is a moorland region—require to be treated before they can safely be supplied to a town where lead pipes are used. It is stated that the formation of calcium bicarbonate is the most effective method; as little as 2 parts per 100,000 is said to be sufficient to cause a "plumbo-protective coating" upon lead.[1] Many slightly acid waters—such as are drawn from reservoirs in the North of England and Wales—are treated with lime, whiting or chalk, so as to reduce the acidity and ensure the presence of calcium bicarbonate in the water.

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[1] J. F. Liverseege and A. W. Knapp, *J. Soc. Chem. Ind.* 39 (1920), 27T. Compare *Engineering*, 97 (1914), 55.

Alloys of Lead

Pure lead is too soft for many purposes, but can be hardened by the addition of comparatively small quantities of other metals. The "hardener" appears to exist in the alloy—at least in some cases—as a eutectic surrounding the grains and stiffening the whole structure; thus the hardening of lead by means of a second metal is essentially different to the hardening of copper and gold, where the hardener usually enters into solid solution.

The number of possible hardeners are very numerous, recent researches[1] having added to the list. Tin, antimony, arsenic, copper and calcium have all been used in practice. Of these metals the alloys of tin with lead have already been mentioned. Alloys of lead and antimony are of considerable importance. They consist for the most part of a lead-antimony eutectic in which primary crystals of lead (or of antimony) are buried. The alloy containing 13 per cent. of antimony consists entirely of eutectic. The addition of small amounts of phosphor-copper to these alloys increases the hardness, and renders the grain finer. Alloys of lead containing 0·5 to 15 per cent. of antimony are known under the general term of "**hard lead.**" They combine durability with a high degree of resistance to chemical action; consequently hard-lead is employed in the pumps which are used at chemical works for the circulation of acid liquors, and also for the grids of accumulators and many other purposes. **Type metal**, which often contains 25–30 per cent. of antimony, and usually some tin (10 per cent., or sometimes, for high-class work, even 25 per cent.) is much used by printers. The presence of tin increases the hardness through the formation of the hard inter-metallic compound SbSn, which was referred to in the discussion of bearing-metals. For linotype work an alloy with less tin (2·5–3 per cent.) and antimony (10 per cent.) is used; this alloy melts at about 238° C.[2] Type metal combines easy fusibility with considerable hardness, but its special value lies in the fact that—in contrast with many alloys—it expands at the moment of solidification, and thus a sharp impression of the type is obtained. Similar white alloys containing lead, antimony, usually tin, and sometimes copper, are included under the general term "**white metal.**"

Lead containing a small amount of arsenic (0·5 per cent. or sometimes more) is used in the manufacture of **shot**. The arsenic fulfils two functions; it serves to render the lead more fluid in the liquid state—an important factor in the formation of the shot

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[1] C. O. Thieme, *J. Ind. Eng. Chem.* **12** (1920), 446.

[2] A. H. Mundey, C. C. Bissett, and J. Cartland, *J. Inst. Met.* **28** (1922), 152.

in the shot tower ; when the shot has solidified it acts as [illegible] An alloy of lead and calcium, known as "Ulco," originally introduced as a substitute for lead-antimony alloys, is said to be quite efficient as a bearing-metal. "Frary metal," another alloy which has been recommended as a bearing material, consists of lead, calcium and barium. It is made by the electrolysis of a fused mixture of calcium and barium chlorides using a molten lead cathode.[1] It should be noticed that alloys containing reactive metals like calcium are liable to lose their hardness on repeated re-melting, owing to the removal of the hardener by oxidation.

The Lead Accumulator

The simplest form of the lead accumulator can be made by immersing two lead plates in dilute sulphuric acid. If a current be now sent through this cell, the anode-plate becomes covered, first with white plumbous sulphate, and then with brown lead peroxide ; finally enough peroxide is formed to protect the lead below from further attack, and oxygen begins to come off at this pole. The accumulator is then known to be charged, and can be used when required to furnish a current ; when the cell is discharging, i.e. generating a current, the lead peroxide becomes reduced again to lead sulphate at the positive pole, whilst the lead metal becomes oxidized to the sulphate at the negative pole. After the battery has been discharged, it can be re-charged a second time by passing an external current through it, when the lead sulphate is reduced to spongy metal at the one pole and oxidized to peroxide at the other. The amount of active material (i.e spongy lead and peroxide) increases during the first few operations of charging and discharging.

The simple form of accumulator suggested above is unsatisfactory for various reasons ; only a small amount of the lead is attacked, a thin coating of peroxide being sufficient to protect the lead below from further oxidation. Thus the capacity of the cell is small compared to the weight and volume. Moreover, the peroxide is liable to drop off from the flat surface of the positive plate on to the bottom of the cell. It may even come in contact with the negative lead plate, with which it will react, without producing any current in the external circuit. This disintegration of the electrode material is rendered all the more probable owing to the change in volume which occurs when the sulphate is converted to metal or to peroxide, and also when the metal and peroxide is turned to sulphate. All of these disadvantages are, how-

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[1] *J. Soc. Chem. Ind.* **41** (1922), 8R.

ever, to some extent overcome by using—in the place of flat lead plates—grooved or striated plates; the increased surface area brings about an increased capacity, whilst the spongy lead and peroxide adheres better to the grooved surface than to a plane surface.

The type of plate in which the active material (spongy lead or lead peroxide) is produced from compact lead *in situ* by electrochemical means is known as the "**Planté type**" of plate. The positive (peroxidized) plate of some modern accumulators is still made in that way. The anodic conversion of the surface of a lead plate into lead peroxide is more readily carried out in a solution which contains—besides sulphuric acid—some substance like perchloric, nitric, or acetic acid, which yields a soluble lead salt. Part of the lead enters the solution as a soluble salt, and is reprecipitated on the anode as peroxide by a secondary change. Thus the film of lead sulphate produced on the anode is less continuous and consequently less protective than if only sulphuric acid is present, and the conversion of lead into peroxide proceeds more quickly, and extends to a more considerable depth.

But in modern accumulators the negative plates, and usually the positive plates also, belong to the so-called "**Faure type**" consisting of a grid of cast lead, the pockets of which are filled with the finely-divided "active material." The grid is usually made of lead hardened with a little antimony. Into the pockets of the grid, a paste consisting of lead oxide and sulphuric acid is introduced. After this has hardened to a porous mass, the plates are introduced into their position in the accumulator. On charging, the lead monoxide is reduced to spongy lead at the negative pole, and is oxidized to the peroxide at the positive. Faure plates have a much higher capacity compared to their weight than Planté plates, and are almost universally used for automobile storage batteries.[1]

In order that the capacity may be as large as possible—and also in order that a high rate of charging and discharging may be allowable without fear of buckling—the areas of both positive and negative plates are made as large as possible. In practice it is convenient to join a number of positive plates and a number of negative plates "in parallel," instead of having a single positive and a single negative plate of very large area. The capacity of the cell, i.e. the number of ampère-hours of electricity which it can safely give out on its discharge, depends primarily on the amount of active lead or lead oxide in the plates. It is never advisable to convert more than a small fraction of the spongy lead or lead peroxide into sulphate, since this would involve volume changes

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[1] W. G. Brooks, *Trans. Amer. Electrochem. Soc.* **31** (1917), 311.

which would tend to loosen the material. If an accumulator is allowed to stand in an undischarged condition, the finely-divided sulphate present tends to "agglomerate" into a less reactive form, and the accumulator is said to be "sulphated." An accumulator, when sulphated, has a greatly reduced capacity, and requires special treatment before it regains its normal efficiency.[1] To avoid danger of sulphating, an accumulator should never discharge itself completely, and consequently the practical capacity of an accumulator is always far less than would be calculated, with the help of Faraday's law, from the amount of active material present, on the assumption that the whole of the metal and peroxide may pass to sulphate during the discharge.

The final reaction which occurs when an accumulator is charged and discharged is usually written

$$2PbSO_4 + 2H_2O \rightleftharpoons Pb + PbO_2 + 2H_2SO_4.$$

The equation read from left to right represents the charge; when read from right to left, it represents the discharge. It is known that the lead peroxide at the positive plate is appreciably soluble in the sulphuric acid as plumbic sulphate, and actually the plumbic ions $Pb^{\cdot\cdot\cdot\cdot}$ present in the liquid within the channels of the porous mass should probably be regarded as the real agents in the electrodic reaction. If so, we can write the essential ionic reactions at the two plates separately in the very simple form :—

At the negative plate, $Pb^{\cdot\cdot} + 2e \rightleftharpoons Pb$
At the positive plate, $Pb^{\cdot\cdot} \rightleftharpoons Pb^{\cdot\cdot\cdot\cdot} + 2e$.

It is noteworthy, however, that the amount of sulphuric acid removed from solution during the discharge is only about half that which we should expect from the equation

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O.$$

Various suggestions have been made to account for this. According to one view,[2] the positive plate contains, in the charged state, higher oxides than PbO_2, for instance, Pb_2O_5, and that they become reduced to PbO_2 during the discharge; if this were true, then no sulphuric acid would be removed from solution at the positive pole at all. Other work,[3] however, has suggested the view that the oxide formed on the positive pole in the charged state is mainly

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[1] See G. A. Perley and C. W. Davis, *J. Phys. Chem.* **20** (1916), 164.

[2] C. Féry, *J. Phys.* **6** (1916), 21; *Bull. Soc. Chim.* **25** (1919), 223. Recent work by S. Glasstone, *Trans. Chem. Soc.* **121** (1922), 1469, 2091, supports the view that a higher oxide may be present in anodically formed lead peroxide, but only in very small quantities.

[3] D. A. MacInnes, L. Adler and D. B. Joubert, *Trans. Amer. Electrochem. Soc.* **37** (1920), 641.

PbO_2; it seems likely that, on the discharge, it is not immediately reduced to plumbous sulphate ($PbSO_4$), but to Pb_3O_4, or perhaps to basic sulphates, xPbO.$PbSO_4$, which would involve the fixing of very little sulphuric acid. Such a view accounts for the fact that comparatively little sulphuric acid is removed from the liquid, and also accords with the fact that as soon as the formation of white plumbous sulphate on the plates becomes obvious to the eye, the accumulator is known to be over-discharged.

An accumulator never gives out the whole of the energy put into it; in usual practice, at least 20 per cent. is lost. The energy loss may be attributed to three main causes:—

Firstly: the **E.M.F.** needed to charge the cell at a reasonable rate slightly exceeds the equilibrium E.M.F. (about 2 volts), whilst the E.M.F. of the cell when furnishing current is always slightly less than the equilibrium value. As a matter of fact, the polarization of the lead accumulator is remarkably low compared to that of many cells, and is chiefly due to slight differences in the concentration of the acid arising from the limited rate of diffusion through the channels of the porous mass.[1] The potential difference falling over the liquid within the cell during the charging or the discharging is very small—owing to the high conductivity of the acid—and the loss of efficiency due to this cause is only slight.

Secondly: the **current** used to charge the battery may not be devoted entirely to the production of lead and lead peroxide. Some oxygen, for instance, is produced at the positive pole towards the end of the operation, and likewise hydrogen at the negative pole. This "gassing" is clearly accompanied by the loss of current efficiency, and according to some authorities [2] causes disintegration of the negative plate. Many makers mix a little mercury with the active material, and this probably serves to restrain "gassing" at the negative pole,[3] since the hydrogen "overpotential" on amalgamated lead is higher than on ordinary spongy lead.

Thirdly, when an accumulator stands in a charged condition, the reactive materials tend gradually to disappear. The lead peroxide being in contact with the lead of the grids, forms short-circuited cells of the type

$$PbO_2 \mid H_2SO_4 \mid Pb$$

and becomes slowly converted to lead sulphate in a manner which produces no current in the external circuit. Further, if a trace

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[1] F. Dolezalek, "Theory of Lead Accumulator"; translation by C. L. von Ende (Chapman & Hall).

[2] A. Langer, *Chem. Zeit.* **44** (1920), 749.

[3] According to A. J. Allmand, "Applied Electrochemistry" (Arnold).

of a metal like copper or silver is present in the active lead of the negative pole, corrosion couples of the type

$$\mathrm{Pb} \mid \mathrm{H_2SO_4} \mid \mathrm{Cu}$$

are set up, which will rapidly convert the active lead into its sulphate; for this reason, manufacturers of accumulators take the very greatest precaution to avoid the presence of metallic impurities in the lead. If iron salts are present in the acid, they cause a loss of charge at both poles. They are oxidized to the ferric condition by the lead peroxide on the positive pole, and then, diffusing to the negative pole, are reduced to the ferrous state by the spongy lead. Manganese is another objectionable impurity.

Assuming that an average E.M.F. of 2·3 volts is needed for the charge, and that 1·9 volts is obtained upon discharge, and assuming further that the number of ampère hours obtained on discharging is 95 per cent. of that consumed in charging, the energy efficiency of the accumulator will be

$$\frac{1{\cdot}9}{2{\cdot}3} \times 95\% = 78\%$$

The form of the lead accumulator varies considerably according to the purpose for which it is intended. At central stations, where the size and weight of the cells is of less importance than length of life, and where rough usage can be avoided, the negative and positive plates are often suspended in acid at safe distances from one another in tanks of glass or lead-lined wood. There may be, perhaps, six negative and five positive plates in each cell, arranged alternately, the negative ones being on the outside. If a positive plate were placed at the outside it would tend to buckle seriously owing to the unequal volume changes on the two sides. The acid used is of specific gravity 1·15 to 1·20, and the changes of specific gravity (observed by means of a hydrometer) are noted from time to time, as they serve to indicate the state of the cell. In these stationary cells, the positive plates are often of the Planté type, the negative plates of the Faure type.

In accumulators intended for transport purposes, the plates are almost always of the Faure type. They are smaller, and placed close together, being prevented from touching by means of separators made of wood or hard rubber; in this way, the size of the cell, and the weight of the liquid is reduced. The whole is contained in a jar of celluloid or hard rubber. Various devices have been adopted to render these transport accumulators more durable under hard service and also lighter; some forms are very little heavier than the nickel accumulator. The so-called "iron-clad" battery has the active material contained in a number of thin vertical cylinders or " pencils " of hard rubber, perforated to admit the electrolyte ; a row of pencils is supported in a frame of lead-antimony alloy. A core of lead-antimony alloy passes down the centre of each pencil and serves to make electrical connection between the active material and the terminal.[1]

Lead Pigments

A very large amount of metallic lead is employed in the manufacture of lead pigments, of which **white lead** (basic carbonate), **sublimed white lead** (basic sulphate), **red lead,** and **chrome yellow** (lead chromate) are the most important ; the last-named pigment has already been mentioned in the section devoted to chromium.

White lead is generally described as a basic carbonate of lead, and has a composition approximately represented by the formula $2PbCO_3.Pb(OH)_2$. It very possibly contains a definite chemical compound,[2] although some authorities [3] regard it as the product of the adsorption of lead hydroxide upon lead carbonate. It is perfectly easy to obtain a precipitate of the composition in question very simply by the interaction of a solution containing sodium hydroxide and sodium carbonate with a solution of lead acetate ; but experience has proved that the product obtained by rapid precipitation is practically valueless as a pigment. Almost all the white lead actually manufactured is obtained by the " corrosion " of metallic lead by carbon dioxide, usually in the presence of acetic acid.

Until recently nearly the whole of the white lead of commerce was produced by the old empirical **Dutch process,** and that process is still used extensively in this country. It is carried out in tall chambers, or " corrosion sheds," built of brickwork. Large numbers of earthenware pots are used in the method, each pot containing a small quantity of acetic acid. The floor of the corrosion-shed is first covered with tan bark upon which is placed a layer of these pots containing acid ; the layer of pots is covered with a layer of lead " buckles," or strips of thin lead studded with holes. Above the lead buckles are placed boards which are themselves covered with a second layer of tan bark. Upon that comes another layer of pots containing acid, then another layer of lead buckles, then boards covered with tan bark, and so on. In this way, the

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[1] For further details of types of lead accumulator, and practical instructions on use and handling, see *U.S. Bur. Stand. Circ.* **92** (1920).

[2] R. S. Owens, *Trans. Amer. Electrochem. Soc.* **25** (1914), 477.

[3] E. Euston, *J. Ind. Eng. Chem.* **6** (1914), 382.

shed is filled up with alternate layers of bark, pots, and lead. When the " stack " is complete, the doors are closed. The stack is now left for 75 to 100 days. During this time the fermentation of the tan bark proceeds apace, and carbon dioxide is evolved; much heat is generated by the fermentation process, and the temperature of the lead rises to about 60–75° C. At that temperature, the lead is slowly attacked by the vapour of the acetic acid in the presence of air, and the basic acetate formed is converted by the carbon dioxide into basic carbonate. Thus when, after about three or four months, the stacks are taken down, the lead buckles, although retaining their original form, consist no longer of " blue " (metallic) lead, but of white basic carbonate.

The corroded buckles are removed to the grinding rooms where they are broken up by rollers. Any remaining " blue " lead is removed by the passage of the mixture through a sieve, and the product is then freed from any soluble acetate by washing with water. The white lead is then ground between buhrstones, mixed with water, and subjected to a process of gravity separation—in order to separate the unduly coarse " sandy lead " from the fine pigment, and, at the same time, to remove any tan bark which may be mixed with the pigment. A suspension of the white lead in water is run through a series of vats, the motion of the water being sufficient to keep the fine matter in suspension, but to allow the coarse material to settle. The finer portions settle in a further series of vats; they are thoroughly washed to remove soluble lead acetate, and are finally drained as free as possible from excess water.

The white lead is often crushed again whilst moist, dried and packed for transport. Alternatively it can be mixed with oil whilst still wet. When the oil is stirred into the pasty mixture of white lead and water, the pigment particles gradually leave the watery phase and pass into the oil; finally the water, free from suspended lead, appears as a limpid fluid upon the sticky mixture of oil and pigment. The passage of the white lead from the water into the oil is determined by the relative value of the interfacial tension existing between the three materials.[1] The mixture of white lead and oil requires to be mixed with a thinner such as turpentine before use as a paint.

The details of the Dutch process vary in different places. In some works, instead of a large number of layers of small pots, a comparatively small number of layers of rather large pots are employed, and rolls of lead are actually placed within the pots. In the original form of the process as used in Holland, horse-

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[1] W. Reinders, *Chem. Weekblad*, **10** (1913), 708.

manure was used to generate the carbon dioxide and heat; this is found, however, to give off hydrogen sulphide, and thus sometimes leads to a dark product containing lead sulphide. In England it was long ago replaced by tan bark.

But the fermentation of tan bark would scarcely seem to be the most rational way of producing heat and carbon dioxide. The temperature and the supply of carbon dioxide will both vary with the character of the tanning material, in a manner which it is difficult for the manufacturer to control. The temperature is particularly variable, and depends to some extent upon the retention of heat by the walls of the chamber; thus the best quality of white lead is only obtained when the corrosion-sheds have been in use for some little time and when the brickwork has consequently become heated. A more modern method known as the **Chamber process** is used largely both in this country and on the Continent; in this process the carbon dioxide is obtained chemically, e.g. by the "burning" of limestone or of coke, and the heat is generated by fuel in the usual way. Lead sheets are hung over horizontal poles placed in large chambers into which the vapour of acetic acid and carbon dioxide are introduced. Since the temperature and the supply of carbon dioxide are easily regulated by the men in charge of the process, the product is certainly more uniform than that of the Dutch process. The white lead obtained by the Chamber process is stated by unprejudiced authorities—who are interested in both processes—to be of equal or greater practical value than that of the Dutch method; but many buyers insist on having the product of the older process.

The Chamber process just described is considerably quicker than the Dutch process; the conversion of the lead sheets into basic carbonate occupies only about eight weeks. It could no doubt be accelerated further by increasing the supply of acetic acid, but the quality of the product would be likely to suffer.

A better way of increasing the speed of corrosion without altering the quality of the product is to increase the surface area of metal exposed to the gases. Thus in the various rapid methods of white-lead production—largely developed in America—finely-divided lead is used as the raw material. In the **Carter process,** molten lead is treated with an air-blast so as to produce a powder consisting of lead globules; this powder is then treated in a revolving cylinder with acetic acid, carbon dioxide and air, and converted quickly into basic carbonate. A good quality of white lead is obtained.

In the so-called "**mild process,**"[1] which is also American in origin, finely-divided ("atomized") lead is treated with air and

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[1] C. D. Holley, *J. Soc. Chem. Ind.* 28 (1909), 403.

water, being thus transformed to a hydroxide, which is afterwards converted to white lead by the action of carbon dioxide; in this process no acetic acid is employed.

One of the objections to processes in which a lead oxide (or hydroxide) is treated with carbon dioxide is that the white lead produced is liable to be discoloured owing to the presence of the higher oxides, which are practically unaffected by carbon dioxide. In the **Bischof process**,[1] which was developed in this country, the trouble is avoided in the following way. Litharge (PbO) is used as raw material. It is finely ground, and reduced at 220–260° C. in water-gas to the suboxide (Pb_2O). This is then "slaked" by water in the presence of air, giving a plumbous hydroxide quite free from higher oxides; the hydroxide when mixed with dilute acetic acid, and carbonated with carbon dioxide gas, gives white lead.

Many attempts have been made to obtain white lead from lead sheet by **electrolytic processes**.[2] If a sheet of lead is made the anode in a bath containing both sodium carbonate and sodium chlorate and a current is forced through the cell, a good deal of basic lead carbonate is formed. But if the sodium carbonate be in great excess, a protective film of lead carbonate is likely to appear on the anode, and this will interfere with further corrosion. On the other hand, if the chlorate is present in excess, the lead will dissolve freely as soluble chlorate, and this will yield white lead by interaction with the sodium carbonate (and hydroxide) in the body of the solution; but, as already stated, white lead obtained by precipitation in this way is almost always unsuitable for use as a pigment. Possibly a satisfactory material might be produced by regulating the quantity of chlorate and carbonate, so that most of the white lead is obtained by the direct corrosion of the anode, but just sufficient chlorate is formed to prevent the crust of carbonate being of the closely-adherent, protective character; this is a question upon which opinion is divided.

Owing to the highly poisonous character of lead compounds, the grinding and packing of the powdery white lead is a dangerous industry to those employed. The alternative method, in which the pigment is mixed with oil whilst still moist, involves far less danger. Elaborate filtration systems for freeing the air from any suspended matter have been installed at some English lead-works; where such systems exist, assuming that the various precautionary measures are rigidly enforced, the danger of lead poisoning, or

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[1] W. Ramsay, *6th Int. Cong. App. Chem.* (1907), Sect. II, p. 372; A. Salmony, *Chem. Zeit.* **31** (1907), 955, 971.

[2] C. Luckow, *Zeitsch. Elektrochem.* **9** (1903), 797; C. F. Burgess and C. Hambuechen, *Trans. Amer. Electrochem. Soc.* **3** (1903), 299.

"plumbism," can be rendered very small. In some countries the use of white lead has been restricted by legislation, and an international convention on the subject was adopted at Geneva in 1921.[1]

In mentioning the real danger of plumbism to those employed in white-lead factories, allusion may be made to certain false ideas which are prevalent as to the possibility of plumbism being caused by living in a freshly-painted room in which a lead-paint coat is drying. It is believed by many that a lead paint whilst "wet" emits a volatile lead compound which is capable of poisoning those who inhale it. This is, however, not the case.[2] No volatile compound containing lead is given off by a drying paint-film. It is true that all paints in which turpentine is used give out turpentine vapour, which does produce toxic effects on some persons. In addition they evolve certain aldehydic oxidation-products of the oil, and these vapours also may conceivably have a temporary disturbing effect upon some ultra-sensitive constitutions. This objection applies also to paints free from lead, but inasmuch as lead paints generally dry more quickly than others, they will cause a rather more rapid evolution of the substances in question.

Apart from the poisonous character of lead pigments, the main objection to their use is the liability to discoloration in the presence of hydrogen sulphide, black lead sulphide being produced. Leadless pigments do not suffer discoloration through exposure to this gas, but lithopone darkens when exposed to the light, whilst even zinc oxide paints occasionally suffer discoloration owing to a change occurring in the linseed oil.[3] It is perhaps right to add that probably many cases of discoloration which have been attributed to chemical and physical causes—such as those mentioned above—are really due to the paint-film becoming "dirty."

Basic Lead Sulphate ("sublimed white lead"). It has been mentioned that during the production of lead by means of the oxidizing action of an air-blast upon galena in the "hearth-smelting process," much lead is carried away by the blast, and is deposited in the dust-chamber. As to how much of this lost lead is carried over mechanically as solid particles, and much how "sublimes" as a vapour, is a question that still remains undecided. When, however, the walls of the furnace become hot, much sublimation must clearly take place. The product found in the dust-chamber contains apparently a basic sulphate mixed with normal sulphate. It has already been mentioned that the sublimate from many ores is a valuable pigment, and it is some-

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[1] *J. Soc. Chem. Ind.* **40** (1921), 453R.

[2] H. E. Armstrong and C. A. Klein, *J. Soc. Chem. Ind.* **32** (1913), 320.

[3] D. F. Twiss, *J. Soc. Chem. Ind.* **37** (1918), 179T.

times intentionally prepared for that purpose—especially in America.

Galena is volatilized from a hot furnace, in a strong blast of air, and the gases produced are cooled and drawn off through a bag-house by means of a fan. The product collected consists of " sublimed white lead." It is an apparently amorphous powder, and appears to be in a fine state of division, finer than the basic carbonate. It has good covering power and durability, and is stated to be less quickly blackened by hydrogen sulphide than ordinary white lead. Sublimed white lead may contain a definite basic sulphate; the existence of such compounds as $PbO.PbSO_4$ and $2PbO.PbSO_4$; is shown by maxima on the melting-point curve of lead oxide-lead sulphate mixtures.[1]

As already stated in the section on the metallurgy of zinc, many of the complex zinc-lead ores of the United States are sublimed to give a white pigment containing both metals. It is called " leaded zinc " when zinc oxide is the main constituent, and " zincy lead " when the basic lead sulphate is in excess.

Red lead (Pb_3O_4) is another lead compound much valued as a paint; it also serves, when mixed with a **small** proportion of linseed oil, as a plugging or luting material for filling up crevices, or for making secure the joints of metal pipes and similar purposes. The mixture of the red lead and linseed oil dries rapidly owing to the high oxygen-content of the former, and sets to a firm plaster. As a paint, the value of red lead depends partly upon the brilliance of its colour; the colour is much affected by small amounts of impurities, and by the exact conditions under which the pigment is produced. It is considered one of the best paints for the protection of iron from corrosion; no doubt the oxidizing character is favourable to passivity. It is also used in glass-making.

Litharge (PbO) is used as a drier in varnishes containing linseed or other drying oils, to bring about the absorption of atmospheric oxygen and the production of such solid bodies as " linoxyn." It is also used in the manufacture of accumulator plates.

The manufacture of litharge and red lead is closely connected. If lead be fused on the hearth of a reverberatory furnace in a good current of air it becomes oxidized. The lower oxide (PbO) is always formed first; if the temperature be high enough to fuse this oxide when formed, the compact variety known as **litharge** is obtained. If the temperature be only just high enough to melt the lead, the unfused yellow form, **massicot,** is produced as a dross which can be skimmed off. If this dross be now slowly roasted in an oven at

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[1] Compare R. Schenck and A. Albers, *Zeitsch. Anorg. Chem.* **105** (1918), 145.

a low temperature for 48 hours, it takes up some more oxygen and passes into **red lead.** The roasting must be conducted with great care, the powder being frequently raked up to ensure uniform oxidation ; it needs considerable experience to obtain with certainty red lead of the finest colour. It is much more difficult to convert the compact molten litharge into red lead by roasting ; the feathery massicot should be used.

By the calcining of white lead, a pigment is produced having a composition similar to that of red lead, but possessing an orange colour. This is known as "**orange oxide.**" The difference in its colour from that of red lead is no doubt due to the different state of aggregation. For the production of orange oxide, the less useful parts of the white lead, separated by the levigation of the crude material, are generally employed.

Theory of Pigments (see also Vol. I, pages 94–95). A paint film is essentially a suspension of "pigment" particles in a "vehicle," generally consisting of dried linseed oil. The film serves two separate purposes ; firstly, it serves to protect the wood or metal below the film from alteration due to exposure to the atmosphere—a matter which has already been referred to in connection with the corrosion of metals ; and, secondly, it should "conceal" the texture of the material below from view.

The comparative power of different pigments to "conceal" or "cover" the basal material can be measured by means of an instrument called the "cryptometer." [1] The principle of the instrument is very simple, although for the details the original paper should be consulted. A black enamel background is concealed behind a "wedge-shaped" layer of the paint to be tested. At the end where the layer is thin, the background is visible ; where it is thick, it cannot be seen. The thickness of the paint-film at the point where the background becomes *just* visible is an indication of the hiding power of the paint.

The fact that a layer of white paint can "hide" the basal material on which it is painted depends on the reflection of the light where it passes from vehicle to pigment, and from pigment to vehicle. For perfect "hiding" practically the whole of the light must be reflected before it reaches the material below the paint-film. The amount of light reflected at each interface depends primarily on the amount by which the refractive index of the pigment exceeds that of the vehicle. Thus—other things being equal—the pigments with the best covering power are those substances which have highest refractive indices.[2] This may be

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[1] A. H. Pfund, *J. Franklin Inst.* **188** (1919), 675.

[2] H. A. Gardner, *J. Ind. Eng. Chem.* **8** (1916), 794.

seen from comparison of the values of the refractive index given below :—

Silica (quartz)	1·55
Barium sulphate	1·6
Zinc oxide	1·9 +
White lead (basic carbonate)	2·0
Sublimed white lead (basic sulphate)	2·0
Zinc sulphide	2·2 to 2·37

A paint-film consisting of silica in linseed oil will be practically transparent since the refractive index of silica is almost equal to that of the medium. On the other hand, a film of white lead in linseed oil will be opaque, and will have good covering power, owing to the high refractive index of the lead compound.

But clearly the size of the pigment particles is also of importance. With small particles, the number of pigment-vehicle interfaces which the light must cross in penetrating a film of a given thickness will clearly be greater than with coarse particles. Thus, the covering power of a given pigment will be greater, the smaller the size of the pigment-grains ; this relation should hold good until the size of the pigment particles becomes so small as to be comparable to the wave-length of light.[1]

The relation between particle-size and covering power probably affords a reason for the inferiority of coarsely-ground natural barytes to finely-ground barytes, and the inferiority of finely-ground barytes to precipitated barium sulphate. But it can only afford a partial explanation of the fact that rapidly precipitated white lead is inferior as a pigment to that made by a slow process.[2] It is true that (according to the very meagre information at our disposal) the pigments made by processes similar to the Dutch process appear to consist of particles which are, on the average, smaller (·00014 mm.) than materials made by the more rapid methods (over ·0022 mm. diameter).[3] Nevertheless the size of the particles obtained by precipitation may—under certain conditions—be much smaller than that of the best " Dutch process " white lead, and yet the precipitated material has little practical value as a pigment. A microscopic study of the process of precipitation of white lead by the mixing of a carbonate solution with a solution of a soluble lead salt shows that the white lead produced first

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[1] W. Ostwald, *Koll. Zeitsch.* **16** (1915), 4, says that a " maximum of covering power " is reached when the grain-size is in the neighbourhood of the wave-length of light, and that further diminution of the grain-size would cause a diminution of covering power.

[2] U. R. Evans, *Trans. Faraday Soc.* **18** (1922), 75. Compare H. Green, *Met. Chem. Eng.* **28** (1923), 53.

[3] R. S. Owens, *Trans. Amer. Electrochem. Soc.* **25** (1914), 485.

appears as minute crystals or star-like growths, but finally these seem to collect into nodules of visible size which resemble small white seeds.[1] Probably these "seeds" are not the ultimate grains, but are merely secondary aggregates of the first formed crystals; such a view may help to explain why precipitated white lead has a lower density than the product of the corrosion processes, and why the former takes up more oil in making a paint of the required consistency—which is well known to be the case. A further study of the internal structure of the "seeds" may perhaps provide an explanation of the fact that the painter finds that the precipitated white lead does not "work so well under the brush" as the other forms of white lead.

In considering the grain-size of **coloured pigments,** such as **lead chromate** (chrome yellow), additional considerations arise. If an intense coloration is aimed at, it is essential to have the size of the individual particles sufficiently large; for, in order that selective absorption of the light may take place to any considerable extent, it must be allowed to penetrate through an appreciable thickness before being reflected. Lead chromate obtained from a hot solution has a deeper colour than that precipitated from a cold solution. The difference is here probably due mainly to the larger size of the particles which crystallize from the hot bath.[2] On the other hand, the red colour produced by the action of sodium hydroxide on lead chromate is probably due to the formation of a basic chromate.

Coloured pigments are commonly diluted with a cheap colourless material, such as barytes, silex, or asbestine. In the interests of economy, it is advisable to use the largest possible proportion of inert material that is possible without diminishing the colour unduly, and to reduce the proportions of the more costly coloured pigment. It is found best for this purpose to add the inert material in a comparatively coarse state of division,[3] as would indeed be expected from the theoretical view of pigments suggested above. Consequently, natural barytes, although possessing little covering power as a white pigment, is extremely efficient as a diluent in coloured paints, more efficient, in fact, than white lead, zinc oxide, or precipitated barium sulphate; these latter substances would cause the reflection of the light before it had passed through a sufficient thickness of the coloured pigment to cause appreciable selective absorption.

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[1] J. Scott, *Chem. Trade J.* **65** (1919), 327.

[2] See E. E. Free, *J. Phys. Chem.* **13** (1909), 130. Other factors besides grain-size may influence the colour.

[3] T. R. Briggs, *J. Phys. Chem.* **22** (1918), 216.

GROUP Vʙ

	Atomic Weight.
Nitrogen	14·008
Phosphorus	31·04
Arsenic	74·96
Antimony	120·2
Bismuth	208·0

In the elements of Group Vʙ, non-metallic properties are developed more strongly than in Group IVʙ, but they diminish as the atomic weight rises. Thus nitrogen and phosphorus are classified by all chemists as non-metals; arsenic and antimony are included by some authorities within the same term; but bismuth has most of the properties of a metal. All the elements are capable of exerting a negative valency of 3, forming the gaseous hydrides NH_3, PH_3, AsH_3, SbH_3, BiH_3. But whereas the hydride of nitrogen (ammonia) is a stable substance, the hydrides become increasingly unstable as we pass through phosphorus and arsenic to antimony, whilst bismuth hydride is so unstable that its very existence has only recently been established.

Nitrides, phosphides and arsenides of many characteristic metals are known, in which the elements of Group Vʙ clearly function as a non-metal and exert a uniform negative valency of 3. Examples are :—

Ag_3N,
Na_3P,
Na_3As, and
Cu_3As_2.

Similar compounds such as

Zn_3As_2,
Cu_3Sb, and
Mg_3Bi_2

are known as components of alloys. These bodies are clearly to be regarded as arsenides, antimonides, and bismuthides. They must be distinguished from the ordinary inter-metallic compounds formed by combination of true metals, since in the latter the formulæ have no apparent connection with the laws of valency.

A gradual transition from non-metallic to metallic properties is also seen in the physical characters of the elements themselves. Nitrogen is at ordinary temperatures a colourless gas. Phosphorus exists in more than one allotropic form ; of these the " yellow " form is translucent and lacks entirely the properties of a metal, but the so-called " red " phosphorus—when obtained in a crystalline condition—has something of a metallic lustre. Arsenic also exists in more than one form, the more stable variety being distinctly metallic in appearance, although a yellow non-metallic variety also exists. Antimony and bismuth are both lustrous, opaque substances of metallic aspect, although considerably more brittle than the majority of metals.

A similar transition is observed when the oxides and their derivatives are studied. In the two main classes of compounds, the elements exert a valency of 3 and 5 respectively. In the lighter elements, nitrogen and phosphorus, the compounds in which the full valency characteristic of the group (5) is exerted are the most stable ; but as we pass through arsenic to antimony, the lower series becomes more stable, whilst in bismuth nearly all the well-known compounds correspond to the lower state of oxidation. Again, in the lighter elements, nitrogen and phosphorus, both oxides have a distinctly acidic character, and well-defined salts, such as the nitrates, nitrites, phosphates, etc., exist. But as we pass through arsenic to antimony, weak basic properties begin to appear in the lower oxide, whilst bismuth possesses a well-defined series of normal salts, such as $Bi(NO_3)_3.5H_2O$, in which the metal is trivalent ; but even in bismuth, the salts readily become hydrolysed, if dissolved in water in the absence of free acid, insoluble basic salts being obtained.

Since this book is confined to the study of metals, nitrogen and phosphorus will not be discussed. Arsenic will be regarded as a metallic element, and will consequently be considered first.

ARSENIC

Atomic weight . . . 74·96

The Element

Arsenic is an element which exists in more than one form, resembling, in this respect, phosphorus, which stands above it in the periodic table. In its stable form, it is a steel-grey brittle substance of metallic appearance, and has a density 5·7. Crystals of this *metallic* form belong to the *rhombohedral* system, and appear to be isomorphous with antimony and bismuth, and possibly also with red phosphorus, although this point has been disputed.[1] If ordinary arsenic is sublimed, there is obtained, in addition to rhombohedral arsenic, a black or grey " *vitreous* " form, apparently amorphous, and much less dense, the specific gravity being about 4·6. If heated at about 360° C., the amorphous form crystallizes, yielding the ordinary metallic variety.[2] The " vitreous " variety is sometimes described as an allotrope ; but, if it be truly vitreous, it is best not to employ the word " allotropy."

Another distinct variety of arsenic is, however, known ; this is *yellow* arsenic. It is often formed when a tube containing arsenic vapour is cooled suddenly below 0° C., and can also be produced in other ways. Several experimenters have, however, failed to obtain it under the conditions laid down by the earlier workers, and have even questioned its existence. Such cases of apparent discrepancy are often met with in the preparation of metastable products (e.g. the metastable hydrates of salts), and seem to show that the production of metastable bodies depends upon some factor not fully appreciated. The existence of yellow arsenic is perfectly well established,[3] and it can actually be obtained in crystals, by crystallization from a solution in carbon disulphide at the low temperature of — 70° C. ; it crystallizes in the *cubic* system. Even at — 60° C. yellow arsenic begins to turn brown owing to transformation to the stable

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[1] W. Hittorf, *Ann. Phys.* **126** (1865), 193, says that it is probably isomorphous with red phosphorus. But G. Linck, *Ber.* **32** (1899), 888, denies that ordinary crystalline arsenic is isomorphous with red phosphorus, although suggesting that " mirror-arsenic " may be.

[2] For further details of this irreversible change, see P. N. Laschtschenko, *Trans. Chem. Soc.* **121** (1922), 972.

[3] G. Linck, *Ber.* **32** (1899), 892 ; H. Erdmann and M. von Unruh, *Zeitsch. Anorg. Chem.* **32** (1902), 437.

modification; the change takes place at still lower temperatures (— 180° C.) if the yellow arsenic is exposed to light. Yellow arsenic is probably isomorphous with yellow phosphorus, and also resembles yellow phosphorus in being soluble in carbon disulphide—a property which illustrates the non-metallic character of this variety of arsenic; true metals do not dissolve, without transformation, in such solvents.

It is interesting to notice that the yellow unstable form of arsenic appears under certain conditions to be formed momentarily, even at ordinary temperatures. For instance, when a solution of arsenious chloride containing free hydrochloric acid is reduced with stannous chloride, a brown precipitate of ordinary arsenic is produced. There is, however, distinct evidence that the precipitate, which is yellowish at the moment of formation, consists at first of the yellow form, but that it passes almost immediately into the stable brown variety.[1]

Ordinary metallic arsenic conducts electricity fairly well and in this respect resembles the typical metals. When heated it volatilizes at about 450° C. under atmospheric pressure, passing into a vapour without the intermediate passage through the fluid; under increased pressure, however, it may be melted to a liquid. The melting-point of arsenic is 830° C., but the liquid once melted can be cooled 40° to 50° below this temperature without solidifying.[2] The density of arsenic vapour varies with the temperature. At 900° C., it seems to indicate the presence of As_4 molecules; at 1,700° C., these would appear to be practically entirely split up into simpler As_2 molecules. The vapour has a yellowish colour, and an odour similar to that of garlic; it is very poisonous.

Arsenic is undissolved by dilute acids; it is, however, readily dissolved by the oxidizing substances, nitric acid or concentrated sulphuric acid. It remains unchanged when exposed to the air at ordinary temperatures, but if heated it oxidizes readily, white clouds of arsenious oxide being produced. A great deal of heat is developed and a bright flame is generally produced. Arsenic has considerable affinity for chlorine and takes fire spontaneously when introduced into the gas.

Laboratory Preparation. The element is best obtained by heating the oxide with carbon; metallic arsenic volatilizes, and the vapour may be condensed in a cool tube. If a wet method be preferred it is possible to reduce a solution of arsenious chloride by means of stannous chloride, arsenic then being obtained as a brown precipitate.

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[1] R. G. Durrant, *Trans. Chem. Soc.* **115** (1919), 134.

[2] W. Heike, *Int. Zeitsch. Met.* **6** (1914), 168.

If only a small quantity of pure metallic arsenic be required to demonstrate its chemical reactions, it is convenient to use the shining mirror of arsenic obtained by passing through a heated tube a current of hydrogen containing arsenic hydride (prepared by the action of sulphuric acid containing an arsenic salt upon zinc).

Compounds

The chief compounds of arsenic correspond to the oxides As_2O_3 and As_2O_5, in which arsenic has a valency of 3 and 5 respectively. As would be expected in an element of such weak metallic properties as arsenic, the basic character is very feeble, and is confined to the lower oxide. On the other hand, both oxides dissolve in alkalis, forming salts known as the arsenites and arsenates, which are analogous to the phosphites and phosphates ; the acidic properties are, of course, best developed in the higher oxide.

A. Compounds of Trivalent Arsenic (Arsenious Compounds).

Arsenious oxide (*white arsenic*), As_2O_3, is formed when elemental arsenic or the sulphide is heated in air. It is a white solid, which volatilizes easily when heated. The density of the vapour corresponds at very high temperatures (1,800° C.) to the simple formula As_2O_3, but at lower ranges the complexity of the gaseous molecule increases, and the vapour density seems to show the existence of As_4O_6. Arsenious oxide is known in more than one form ; when it is sublimed in a tube of which the temperature exceeds 400° C. in the lower portions, but is only 200° C. at the top, a cubic crystalline form is deposited in the highest and coolest portions, a rhombic form in the middle, whilst at the bottom an amorphous, vitreous variety of white arsenic is obtained. This vitreous variety is transparent, but if exposed to air for any length of time it becomes opaque, owing to crystallization. One important distinction between the amorphous and the crystalline varieties is that the former, if heated at atmospheric pressure, passes into the fused state, whilst the latter volatilizes without fusion. The vapour obtained from both forms is, of course, the same.

Arsenious oxide is slightly soluble in water, yielding an acid solution ; it is more readily soluble in hydrochloric acid, and also in caustic alkali. A solution of arsenious oxide has reducing properties, and reacts with iodine or chromic acid, the arsenic passing into the pentavalent condition.

Arsenious Salts. The basic properties of arsenious oxide are, as has been remarked, exceedingly feeble, and no salts can exist in water in the absence of free acid, since they would at once suffer hydrolysis. The fact that arsenious oxide is so much more soluble in hydrochloric acid than in water points to the existence of arsenious chloride ($AsCl_3$) in the solution; but any attempt to obtain the chloride by evaporation merely leads to the expulsion of hydrochloric acid vapour, arsenious oxide being left behind. The chloride may, however, be obtained by heating arsenious oxide with sulphuric acid and sodium chloride. The last two reagents produce hydrogen chloride which reacts with the arsenious oxide to form arsenious chloride; the chloride distils away, the water formed simultaneously being retained by the concentrated sulphuric acid, which thus serves to prevent hydrolysis. The same chloride is formed, together with the pentachloride ($AsCl_5$) by the direct action of dry chlorine on metallic arsenic. It is a colourless volatile oily liquid, boiling at 130° C. When added to water, it suffers hydrolysis; if only a small quantity of water is present, a basic chloride is formed, but excess of water causes complete dissociation into arsenious oxide and hydrochloric acid. The dense white fumes emitted when arsenious chloride is exposed to damp air consist, apparently, of a basic chloride.

Arsenious oxide is insoluble in dilute sulphuric acid, but, when it is acted upon by concentrated sulphuric acid containing excess of sulphur trioxide, crystalline compounds of the general formula $As_2O_3.nSO_3$ are formed. These may be looked upon as acid sulphates of arsenic; but they are very unstable, being at once decomposed to arsenious oxide and sulphuric acid on the addition of water. Probably the only soluble oxy-salt of arsenic which can be isolated in a solid state by crystallization from an aqueous solution is the double **sodium arsenious tartrate** $Na(AsO)\,H_4C_4O_6$, obtained when arsenious oxide is acted on by boiling sodium hydrogen tartrate; this is probably a complex salt containing arsenic in the anion. It is analogous to the well-known antimony salt, "tartar emetic," $K(SbO)H_4C_4O_6,nH_2O$.

Of the insoluble compounds of trivalent arsenic, the **sulphide** deserves mention; this is formed as a bright yellow precipitate when hydrogen sulphide is bubbled through a solution of arsenious oxide containing hydrochloric acid. In the absence of acid, a colloidal solution of arsenious sulphide is produced, which deposits the precipitate when a suitable electrolyte is added. It is a typical negative colloid, the particles owing their charge to adsorbed *anions*, probably $(HS)'$, derived from the hydrogen sulphide. In considering the flocculation of the sol by the addition of an electrolyte, it is the nature of the *cation* which is of importance. Salts of divalent metals like barium are more effective than salts of monovalent metals like potassium, whilst the salts of trivalent metals such as aluminium are more effective still. The following table[1] shows the respective concentrations of the chlorides of the three metals needed to cause flocculation of an arsenious sulphide sol under the same conditions :—

Potassium chloride . .	49·5 millimols per litre
Barium chloride . . .	0·691 ,, ,,
Aluminium chloride . .	0·093 ,, ,.

The sulphide can be obtained in an orange crystalline form by sublimation of the precipitated variety. Arsenious sulphide (like stannic sulphide) is soluble in ammonium sulphide, a complex ammonium arsenious sulphide (usually known as ammonium thioarsenite) being formed. Similarly it dissolves in caustic soda or potash, forming a mixture of arsenite and thioarsenite.

Arsenites. Arsenious oxide is freely dissolved by boiling caustic alkalis and ammonia, and from the solution soluble arsenites may be obtained by crystallization. For instance, **ammonium arsenite,** NH_4AsO_2, is obtained by dissolving arsenious oxide in concentrated ammonia. It is a colourless crystalline substance, very soluble in water. The arsenites of the heavy metals are mostly insoluble, and may be obtained by the precipitation of a solution containing a salt of the metal in question with ammonium or sodium arsenite. Copper arsenite is green, the ferric salt reddish-brown, and the calcium salt white ; silver arsenite again is a yellow precipitate. In many cases there exist several distinct arsenites containing varying amounts of the component oxides.

B. Compounds of Pentavalent Arsenic.

Arsenic pentoxide, As_2O_5. The compounds of pentavalent arsenic are less well developed than those of phosphorus. Arsenic when burnt in air gives rise to the lower oxide only, although the combustion of phosphorus leads to the formation of the pentoxide. Arsenic pentoxide can be produced by the oxidizing action of nitric acid on arsenious oxide ; the solution obtained yields on evaporation ortho-arsenic acid (*see below*), and this is converted to the anhydrous oxide by cautious heating. The pentoxide is a white deliquescent solid. It dissolves in water, giving a syrupy liquid, which deposits a hydrate on cooling. This hydrate has an empirical composition $As_2O_5.4H_2O$, but gradually loses water upon gentle heating, passing to **ortho-arsenic acid,** $As_2O_5.3H_2O$ or H_3AsO_4. On further gentle heating the remaining water is driven off ; it is stated to be driven off in definite steps, so that **pyro-**

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[1] H. Freundlich, *Zeitsch. Phys. Chem.* 73 (1910), 386.

arsenic acid $As_2O_5.2H_2O$ or $H_4As_2O_7$ is first produced, then **meta-arsenic acid** $As_2O_5.H_2O$ or $HAsO_3$, and finally the anhydrous oxide As_2O_5. These three acids correspond to the ortho-, pyro- and meta-phosphoric acids.

Arsenates. The soluble arsenates are formed when arsenic pentoxide or the syrupy solution (arsenic acid) is treated with alkali. The insoluble arsenates are formed by precipitation; the silver salt, Ag_3AsO_4, is red-brown, and the lead salt, Pb_3AsO_4, white. Most of the arsenates correspond in composition with the orthophosphates, and are isomorphous with them. But there are also pyro-arsenates and meta-arsenates, which correspond to the two acids mentioned above. When a soluble arsenate is precipitated with a magnesium salt in an ammoniacal solution, a double magnesium ammonium ortho-arsenate is precipitated, which gives magnesium pyro-arsenate upon ignition

$$2Mg(NH_4)AsO_4 = Mg_2As_2O_7 + 2NH_3 + H_2O$$

An exactly analogous change is observed in the case of the phosphorous compounds. The similarity between phosphates and arsenates is further shown by the fact that when ammonium molybdate and nitric acid are added to a solution containing an arsenate, a yellow precipitate is obtained.

Arsenic Salts. Basic properties are almost absent from arsenic pentoxide, which does not form salts with any oxy-acid. A **pentachloride** of arsenic, $AsCl_5$, probably exists in the product obtained on saturating liquid arsenious chloride with chlorine, but it has not been obtained in the pure state. Arsenic **pentasulphide**, As_2S_5, is formed as an insoluble yellow precipitate when hydrogen sulphide is passed into a solution of arsenic acid containing hydrochloric acid; like arsenious sulphide, it is soluble in ammonium sulphide. The compound formed is known as **ammonium thioarsenate.**

C. Lower Compounds of Arsenic.

Besides arsenious sulphide (As_2S_3) and arsenic sulphide (As_2S_5), a lower sulphide exists. This body, which has a composition expressed by the simple formula AsS, is obtained by heating sulphur and arsenic in the right proportions, or by heating arsenious sulphide (As_2S_3) with arsenic. Orange crystals of AsS sublime. This sulphide is very stable, as is shown by the fact that it occurs in nature (*realgar*).

A still lower sulphide, As_3S, has been described,[1] but it seems a little doubtful whether it is a definite chemical individual.

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[1] A. Scott, *Trans. Chem. Soc.* 77 (1900), 651.

D. Miscellaneous Compounds.

Arsenic Hydride. When an arsenic compound is added to dilute sulphuric acid and a piece of zinc is immersed in the liquid, the hydrogen produced is found to contain a gaseous hydride of arsenic, sometimes known as **arsine,** AsH_3. The arsine confers upon the gas a peculiar smell resembling that of garlic. When the gas is passed through a heated tube, the arsine is decomposed, and a bright mirror of metallic arsenic is formed. When, on the other hand, the gas is ignited, it burns with a pale bluish flame; the arsenic as well as the hydrogen becomes oxidized, water vapour and fumes of arsenious oxide being produced. But if a cold porcelain surface be held in the flame, a local lowering of temperature is caused, and the complete oxidation of the arsenic does not occur; a black deposit of the element is, therefore, formed on the porcelain.

When passed into a dilute solution of silver nitrate, arsine is oxidized to arsenious oxide and black metallic silver is formed. But, if passed into a stronger solution of the silver salt, a yellow precipitate, said to have the composition $Ag_3As.3AgNO_3$, is produced; this is a double arsenide and nitrate of silver.

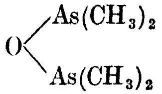
Arsenic hydride is much more stable than the gaseous hydrides hitherto considered, as is to be expected in view of the more pronounced non-metallic character of the arsenic. The hydride may, in fact, be prepared pure and undiluted with hydrogen, by the action of a dilute acid on zinc arsenide; but the preparation is extremely dangerous—owing to the poisonous character of the gas—and has cost the life of at least one chemist.

Arsenides. Arsenic hydride may be regarded as a weak acid, corresponding to the metallic **arsenides,** just as sulphuretted hydrogen corresponds to the sulphides. The arsenides cannot in every case be prepared by the action of arsine on the aqueous solutions of the metallic salts, since many of them would be hydrolysed by water. It has, however, been stated above that a double nitrate-arsenide of silver is formed when arsine is passed into concentrated silver nitrate solution. The **arsenides** of **potassium** (K_3As) and **sodium** (Na_3As) are produced when arsine is passed over the respective metals. **Arsenide** of **zinc,** Zn_3As_2, is prepared by alloying together zinc and arsenic, considerable heat being evolved when they combine. A grey deposit of **copper arsenide,** Cu_3As_2, is produced when a solution of an arsenious compound is reduced with metallic copper; the same arsenide is formed when arsine is passed into a copper salt solution.

The arsenides of zinc, sodium and potassium are decomposed by dilute acids with the production of arsine; this is, in fact, the best way to produce pure arsine. If sodium arsenide is decomposed with water a second hydride, AsH, is said to be produced, being left behind as a solid brown mass when the gaseous AsH_3 has passed away.[1]

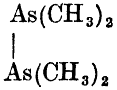
Organic Derivatives of Arsenic. Many organic compounds containing arsenic are also known. One of the most important is **cacodyl oxide,** which is formed when arsenious oxide is heated with anhydrous potassium acetate. The evil-smelling and poisonous liquid contains

Cacodyl oxide . . . .



and

Cacodyl . . . .



$$\begin{matrix} As(CH_3)_2 \\ | \\ As(CH_3)_2 \end{matrix}$$

The former is a basic substance, and forms salts with acids. Many compounds of a similar nature are known.

Analytical

The detection of small quantities of arsenic is a matter of considerable practical importance in the examination of foods or organic matter which are suspected to contain traces of the poisonous substance. One sensitive method known as the **Marsh test** depends upon the formation of the gaseous hydride. Zinc is acted upon by sulphuric acid in a flask and the hydrogen formed is made to pass, first through a drying tube filled with calcium chloride, and then along a glass tube, which is gently heated at one point with a flame. If the solution in the flask contains arsenic, a metallic mirror of arsenic will be produced at the heated point of the tube, owing to the decomposition of the arsine mixed with the hydrogen. Should a mirror be produced before the addition of the body to be tested, it will be known that either the zinc or the acid clearly contains arsenic and the materials are unsuitable for the test. If, however, the zinc and acid are found to be arsenic-free, the substance under examination (or more often a decoction of the latter in dilute hydrochloric acid) is run into the flask through a tap-funnel; and if subsequently a mirror is produced, the arsenic must have been introduced with the substance under examination. If the decoction is added slowly, the whole of the arsenic is reduced to metal at the heated portion of the tube, and, by comparing the mirror produced

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[1] J. V. Janowsky, *Ber.* 6 (1873), 220.

with standard mirrors produced from known quantities of the poison, a rough estimation of the amount present is possible. It is best to examine the mirror chemically to ensure that it consists of arsenic, and not of antimony—another element which forms a volatile hydride ; one method depends on the fact that sodium hypochlorite speedily dissolves the arsenic mirror, but only slowly dissolves antimony. Another distinguishing property is the greater volatility of arsenic.

In the Gutzeit test,[1] the acidified solution to be tested is treated with zinc, preferably in the presence of stannous chloride and ferrous salts (ferric salts should be absent). The mixture of hydrogen and arsine evolved is not sent through a heated tube—as in the Marsh test—but is first passed through lead acetate solution (to remove hydrogen sulphide) and is then passed up a tube containing a strip of paper soaked in mercuric chloride solution which becomes darkened by the action of arsine ; the darkening is due to the oxidation of the arsine by the mercuric salt, and consequent precipitation of metallic arsenic. The distance up the strip to which darkening extends gives a measure of the arsenic-content. The function of the tin salt appears to be that it sets up a zinc-tin couple which ensures the complete reduction of the arsenic to the state of arsine ; it also serves to reduce any ferric salts to the ferrous condition.

An old test for arsenic introduced by **Reinsch** has also been adapted for the examination of foods.[2] It depends upon the reduction of arsenical compounds to copper arsenide by the action of metallic copper. The substance to be tested is acidified with a standard quantity of hydrochloric acid, and copper strips are allowed to stand in it for a specified time. Afterwards they are taken out and dried, and then heated in a hard-glass tube. If any copper arsenide has been formed, this is decomposed by the heat, and the arsenic, subliming, condenses—mainly as oxide—on the cooler parts of the tubes. For rough quantitative purposes, this deposit may be compared with standard deposits produced by known amounts of arsenic under similar conditions.

For the gravimetric separation and estimation of arsenic in larger quantities (for instance, in minerals or alloys containing arsenic) the following method is used. The solution, acidified with hydrochloric acid, is saturated with sulphuretted hydrogen, when the arsenic, together with various other metals, is precipitated as

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[1] A convenient form of this test is described by W. S. Allen and R. M. Palmer, *8th Int. Cong. App. Chem.* (1912), Sect. I, p. 9. In some of the older forms of the test, silver nitrate is used in the place of mercuric chloride.

[2] A. S. Delépine, *J. San. Inst.* 23 (1902), 244.

sulphide. Of the sulphides produced, however, only those of arsenic, antimony and tin (unless the rarer molybdenum and germanium are present) are soluble in ammonium sulphide. These three metals can be separated in the manner already indicated in the section on tin. The metals are converted to the highest state of oxidation by means of chlorine gas acting upon an alkaline solution; then the solution is made acid with hydrochloric acid, boiled to decompose chlorates, and cooled in ice. Hydrogen sulphide is now bubbled through the cold solution. Under these circumstances, only the arsenic is precipitated and may be filtered off.

When the arsenic has been separated from other metals it can be converted to the state of an arsenate, and then precipitated with a magnesium salt in the presence of ammonium chloride and ammonia; the precipitate of ammonium magnesium arsenate should be dried at 100°–120° C., and afterwards ignited carefully; it yields magnesium pyro-arsenate, $Mg_2As_2O_7$, in which form arsenic can be weighed. To guard against any possible reduction of arsenic, some authorities advocate adding ammonium nitrate to the precipitate before ignition; others say that there is no reduction, if the precipitate is ignited with proper precautions.[1] To guard against loss by volatilization, it is customary to place the crucible containing the precipitate in a larger crucible, and gradually to raise the latter to a red heat.

Alternatively arsenic can be reduced to the arsenious condition and titrated with iodine.

TERRESTRIAL OCCURRENCE

The arsenic present in rock-magma accumulates—like most other metals—in the last solidifying portions, and is expelled with the thermal waters in the final stages of consolidation. Most of it is deposited in the fissures through which the waters rise, but occasionally a mineral spring will be found still to contain the element when it issues out of the ground. For instance, the waters of a hot spring in the Yellowstone Park[2] deposit, where they emerge, the sulphides

	Realgar	AsS
and	Orpiment	As_2S_3

The same sulphides are commonly found in the mineral veins

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[1] See Sir W. Crookes, "Select Methods of Chemical Analysis" (Longmans); F. P. Treadwell, "Analytical Chemistry"; translation by W. T. Hall (Chapman & Hall).

[2] W. H. Weed and L. V. Pirsson, *Amer. J. Sci.* 42 (1891), 401.

which represent old fissures through which thermal waters have arisen in former geological eras ; they are respectively orange-red and lemon-yellow minerals, very soft, and easily fusible. Elementary arsenic is also found in some of the veins. Since the waters arising from an igneous mass invariably contain many other metals besides arsenic, we generally find arsenic intimately mixed with the ores of other metals ; the two minerals mentioned above are found especially in the ores of lead and silver. Small amounts of arsenic are, however, very commonly met with in the ores of almost all the heavier metals. Very often we find minerals containing both arsenic and another metal. The commonest arsenic compound is

Mispickel (Arsenopyrite) . . . . $FeAsS$

a mineral with steely metallic lustre, crystallizing in the rhombic system where free development has been allowed, but often columnar or compact. It is a very common accompaniment of the ores of lead and silver, and is also found in tin-ores ; it is frequently associated with pyrites, to which it is obviously allied.

Certain natural complex sulphides containing copper and silver have been mentioned in the sections devoted to those metals ; they include

Enargite . . . . . Cu_3AsS_4
and Proustite . . . . . Ag_3AsS_3

In some cases these minerals may be of secondary origin.

In addition, various arsenides of nickel and cobalt are found in the complex ores of nickel, cobalt and silver, such as exist in Ontario, and also in Europe (Saxony and Bohemia). These minerals, which have already been referred to in the sections dealing with cobalt and nickel, include :—

Smaltite	$CoAs_2$
Cobaltite	$CoAsS$
Niccolite	$NiAs$
Chloanthite	$NiAs_2$

In the upper oxidized portions of arseniferous ores, we find arsenious oxide, usually in whitish crusts or in an earthy form, but occasionally in octahedra (cubic system), in which form it is known as

Arsenolite . . . . As_2O_3

A second, monoclinic form, is known as

Claudetite . . . . As_2O_3.

Arsenates of iron, calcium, magnesium and manganese are also produced by oxidation of arsenical minerals containing these metals.

Seeing that arsenic is so widely distributed in mineral deposits, we may expect to find traces of it in the waters of rivers which arise in hills containing mineral veins. Arsenic is present in a minute quantity in many parts of the sea, the amount varying from 0·01 to 0·08 milligrams per litre; many deposits of rock salt contain traces of arsenic.[1]

TECHNOLOGY AND USES

Manufacture of White Arsenic. The result of the occurrence of arsenic in small amounts in most metallic ores is that most of the arsenic required for industrial purposes is obtained as a by-product of other metallurgical industries. Where the demand for arsenic exceeds the supply provided in this way, arsenical ores, such as mispickel, can be worked to provide a further quantity. The process employed is very simple; the ore is roasted in a rotary calciner, or a reverberatory furnace, and the gases leaving the furnace, which contain the volatile arsenious oxide, are conducted through dust-catchers where much of the "white arsenic" is deposited, and finally—in many cases—through an electrostatic precipitation plant. During the war—owing to the special demand for arsenic—a considerable arsenic industry sprang up.[2]

Under normal conditions, however, the by-product arsenic is sufficient for most of the world's needs. The fume obtained from the roasters and blast-furnaces used in the ordinary smelting of ores of copper, lead, zinc and tin is rich in arsenic. Wherever, in addition to—or in the place of—the ordinary dust-chambers or bag-houses, an electrostatic dust-precipitation plant has been installed, the yield of arsenic has increased, and the state of the atmosphere around the works has greatly improved. The white clouds that are sometimes seen hanging over districts where arsenical ores are smelted, consist largely of fine particles of white arsenic on which, no doubt, moisture has condensed.

One of the most important sources of white arsenic is provided by the fumes of the copper works in Montana and Utah[3]; at Anaconda, for instance, an electrostatic plant has been erected, and the dust collected in it contains much arsenic. The dust obtained from smelting an arsenical copper-ore may be treated in a reverberatory furnace, where it is again subjected to a distillation process. The arsenic, lead and zinc are volatilized, but, of these, the lead and zinc are deposited for the most part in the first set of dust-

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[1] A. Gautier, *Comptes Rend.* **137** (1903), 232, 374.
[2] C. A. Doremus, *Trans. Amer. Electrochem. Soc.* **35** (1919), 187.
[3] *Min. Ind.* **28** (1919), 34; A. E. Wells, *Min. Ind.* **30** (1921), 40.

catchers; then the gases are cooled and passed through the electrostatic plant—in order to catch the white arsenic.

In the recovery of white arsenic from arsenical dust by resublimation, careful regulation of the draught, and careful attention to the rate of cooling of the gases is necessary, since otherwise the arsenic, antimony and lead are liable to be deposited together.[1]

The complex ores of silver, cobalt, and nickel occurring in Ontario (Cobalt region) yield a considerable quantity of arsenic as a by-product, since the main cobalt and nickel minerals of these ores are actually arsenides. The treatment of these ores has already been discussed in the section on cobalt (Vol. III, page 166); but it may be recalled at this point that part of the arsenic is removed by sublimation as white arsenic during the smelting, whilst a further portion is removed at a later stage by fusing the "speiss" (or mixture of arsenides) with sodium carbonate and sodium nitrate, sodium arsenate being thus produced.

Manufacture of Metallic Arsenic. Metallic arsenic is easily obtained by the distillation of a mixture of white arsenic and carbon. The distillation is often carried out in a retort consisting of a large steel pipe set in a gas-fired furnace; the vapour of arsenic condenses to large crystals of metallic arsenic on the sides of a water-cooled condenser.[2] The temperature of distillation is about 650–700° C.; a little arsenious oxide is apt to pass over unchanged.

Uses of Arsenic and Compounds. Metallic arsenic is mainly employed for alloying with lead, in order to harden it. Arsenical lead is often used for making shot. Arsenic is added intentionally to copper and bronze as a toughener; the copper employed for locomotive fire-boxes, for instance, usually contains arsenic. The electro-deposition of arsenic—with or without nickel—is sometimes employed to give a dark "oxidized" finish to brass articles. A bath containing potassium cyanide, sodium phosphate and arsenious oxide is employed. If arsenic alone is present, a bluish-grey deposit is obtained, but in the presence of nickel a good black effect can be produced.[3]

The employment of arsenic compounds depends mainly on their poisonous character. Arsenious oxide (white arsenic) and sodium arsenite are used in rat-poisons, insecticides, weed-killers and sheep-dips. Various mixtures containing arsenites of copper are also used as insecticides. At one time, copper arsenite was used in colouring wall-paper, but this paper was found to be dangerous.

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[1] Compare E. C. Williams, *Eng. Min. J.* **110** (1920), 671.

[2] C. H. Jones, *Met. Chem. Eng.* **23** (1920), 957.

[3] *Met. Ind.* **21** (1922), 457.

Through the action of certain moulds,[1] the arsenic may be converted to a volatile compound, which has been identified as ethyl-cacodyl oxide $[As(C_2H_5)_2]O$, and may cause symptoms of arsenic-poisoning to those living in rooms decorated with such paper. Consequently arsenical wall-papers are no longer used in this country, although, in tropical countries, such wall-papers are sometimes used intentionally—owing to their insecticidal properties.

Arsenic in Medicine. Many of the complex organic compounds of arsenic[2] are of great value in medicine, and the number of useful arsenical drugs has increased greatly owing to continued research on the subject. The object of the investigations is usually to discover a compound which is, as far as possible, innocuous to the human system, but which is effective in destroying the protozoa, which are the immediate cause of certain diseases. Compounds of pentavalent arsenic were largely used at one time, and one of these, "atoxyl," $NH_2.C_6H_4.AsO(OH)ONa,xH_2O$, is still largely used in the treatment of sleeping sickness. For other purposes, the compounds of trivalent arsenic have proved more effective, and particularly the derivatives of the base

$$C_6H_3(OH)(NH_2)As : As.C_6H_3(OH)(NH_2).$$

The hydrochloride of this base is known as "salvarsan," whilst the methylene-sulphinate

$$C_6H_3(OH)(NH_2)As : As.C_6H_3(OH)NH.CH_2.O.SONa$$

is called "neo-salvarsan." Several other drugs containing trivalent arsenic have proved valuable; one of them ("luargol") contains silver as well as arsenic.[3]

Technological Significance of the widespread Distribution of Arsenic in Minerals. Far more important than the actual utility of arsenic is the effect upon industrial processes of the occurrence of arsenic in so many valuable minerals. Where arsenic occurs in ores intended for smelting it must—as already stated—be removed at some stage during the metallurgy, since otherwise the mechanical (or, in the case of copper, the electrical) properties of the metal produced are apt to suffer. Where arsenic occurs in minerals used for the production of chemicals, the chemicals obtained from such minerals are likely to contain arsenic. For instance, iron pyrites almost always contain arsenic, and the sulphuric acid made from an arsenical type of pyrites by the old

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[1] P. Klason, *Ber.* **47** (1914), 2634.

[2] For details and methods of preparation see G. T. Morgan, "Organic Compounds of Arsenic and Antimony" (Longmans, Green).

[3] A. Renault, L. Fournier, and L. Guénot, *Comptes Rend.* **161** (1915), 685. See also Dalimier and Lévy-Franckel, *Comptes Rend.* **162** (1916), 440.

"chamber process" generally contains arsenic compounds. In 1900, the use of arsenical acid in the manufacture of glucose destined for brewing, led to an alarming outbreak of arsenic-poisoning in the north of England.[1]

Where the sulphur dioxide obtained by burning pyrites is to be converted to sulphuric acid by the so-called "Contact process," trouble of a different kind is experienced, as the arsenic causes the "poisoning" of the platinum catalyst. Consequently the gas must be purified carefully before it is allowed to enter the catalytic plant—a matter which has already been discussed in the section on platinum. It follows that the sulphuric acid made by the contact process is generally free from arsenic, and is to be preferred for use in the manufacture of food-stuffs, and for other purposes where the presence of arsenic is undesirable.

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[1] A. S. Delépine, *J. San. Inst.* **23** (1902), 244.

ANTIMONY

Atomic weight . . . 120·2

Passing to the next member of the group, antimony, we find an element very similar to arsenic in most respects, but having a better-defined metallic character. Thus the lower oxide of antimony is somewhat more basic and less acidic than the corresponding arsenic compound, and the gaseous hydride is very unstable. In some respects the behaviour of antimony recalls that of tin, which falls beside it in the Periodic Table, but the element itself is far more brittle than tin.

The Metal

Antimony is a brittle crystalline metal, having a bluish-white colour and a bright metallic lustre. It is rather heavier than arsenic, the density being 6·7. It melts at 630° C. and, although much less volatile than arsenic, it gives off an appreciable amount of vapour at a red heat. The vapour density has a value at high temperatures which shows the presence of Sb_2 molecules, but they are mixed at lower temperatures with more complex molecules.

The ordinary *metallic* form of antimony crystallizes in the rhombohedral system, and is apparently isomorphous with the metallic form of arsenic. The metal expands when it solidifies. When a mass of fused pure antimony is allowed to solidify slowly in a crucible, the surface becomes covered with numerous fern-like markings, sometimes taking the form of a star. These markings are due to the fact that the liquid metal contracts as it cools, and thus the dendritic crystals produced during the first part of the solidification process are left in slight relief ; the aspect of the surface is greatly modified by the presence of impurities.

The form of the markings has served to indicate the crystalline system to which antimony belongs. The actual arrangement of the atoms in an antimony crystal has recently been ascertained by the X-ray method.[1] The atoms lie " on two interpenetrating face-centred rhombohedral space-lattices " displaced diagonally one from the other.

The white metallic form of antimony is much the most stable

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[1] R. W. James and N. Tunstall, *Phil. Mag.* 40 (1920), 233. Compare A. Ogg, *Phil. Mag.* 22 (1921), 163.

variety known; a *yellow non-metallic* modification, corresponding to the yellow form of arsenic, has been described[1]; but it is extremely difficult to preserve and passes back readily to the metallic variety. Like yellow arsenic, it can most easily be produced at very low temperatures; if air or oxygen be led into liquefied antimony hydride at —90° C., yellow antimony is formed. When brought to higher temperatures, it turns black. Like the yellow varieties of phosphorus and arsenic, yellow antimony is soluble in carbon disulphide.

A so-called "*amorphous*" form[2] is also sometimes produced when antimony vapour is volatilized in a current of nitrogen, and is rapidly condensed on the walls of a glass tube; it is a grey powder, which when examined under the microscope appears to be composed of clusters of little spheres. Since this form of antimony is not produced when the metal is sublimed in hydrogen, it would appear that the powder may consist of globules of ordinary antimony prevented from coalescing owing to a film of nitride or even of oxide; if this is the case, it is as misleading to call it an allotrope of antimony as to call "blue powder" an allotrope of zinc, or "flowers of mercury" an allotrope of mercury. The probability that this view is correct is increased by the fact that the "amorphous" antimony contains only about 98·7 per cent. of antimony.

The so-called *explosive antimony* (which was mentioned in Chap. XI, Vol. I) is also sometimes referred to as an "unstable allotrope." It is produced on the cathode, when a solution of antimonious chloride in hydrochloric acid is electrolysed at a high current density. Its power of violent disintegration is possibly only due to the state of internal tension such as is often met with in electro-deposited films,[3] but which gives rise to rather sensational results in the case of a highly brittle metal like antimony. When deposited from aqueous solution it is a grey lustrous coating, but if deposited from acetone solution it has a flaky appearance.[4] In both cases the deposit contains a considerable amount of antimony chloride, probably in solid solution.[5] When heated locally, or even when scratched, it flies to powder with explosive violence, the dissolved chloride being at the same time evolved as a vapour.

Antimony lies rather towards the "noble" end of the Potential Series and is precipitated from a solution of one of its compounds

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[1] A. Stock and O. Guttmann, *Ber.* **37** (1904), 898.

[2] F. Hérard, *Comptes Rend.* **107** (1888), 420.

[3] Compare G. G. Stoney, *Proc. Roy. Soc.* **82** [A] (1909), 172.

[4] R. C. Palmer and L. S. Palmer, *Trans. Amer. Electrochem. Soc.* **16** (1909), 79.

[5] A. Mazzucchelli, *Gazetta*, **44** (1914), ii, 418.

by a less noble metal, such as tin, iron, or zinc. Although the element remains bright and unaffected by air at ordinary temperatures, antimony burns when heated before the blowpipe, dense fumes of white oxide being produced. As in the case of arsenic, a good deal of heat is evolved in this reaction. Similarly, powdered antimony introduced into chlorine gas without previous heating combines with it with evolution of heat and light; the higher chloride is the chief product.

Being more noble than hydrogen, antimony cannot bring about the evolution of this gas, and is unaffected by boiling hydrochloric or dilute sulphuric acid. Nitric acid oxidizes it to a hydrated antimonic oxide $Sb_2O_5.xH_2O$ (usually with the lower oxides). Antimonic oxide is not sufficiently basic to dissolve in the excess of nitric acid, but remains as an insoluble white precipitate. Thus the behaviour of antimony with nitric acid recalls that of tin.

The anodic behaviour of antimony[1] is most interesting, since, unlike the metals of the four previous groups, it shows "valve-action" in numerous electrolytes. In contrast with aluminium, the presence of chlorides in the solution in no way hinders the maintenance of the non-conducting film on an antimony anode. Indeed in very dilute potassium chloride solution an antimony anode will withstand a pressure of no less than 700 volts without breaking down.

Laboratory Preparation. The metal may be obtained from the oxide by heating it with carbon, or from a solution by boiling with tin in the presence of hydrochloric acid; the latter method gives a dark precipitate of finely-divided antimony. A good deposit of antimony[2] can be obtained by electrolysis of an acidified sulphate solution, preferably warm, if the current density is not allowed to rise too high.

If it is desired to obtain antimony in the laboratory from the sulphide (which is the naturally occurring ore of antimony), it is possible to fuse the sulphide with a mixture of carbon and sodium carbonate; a variation of the process is to heat the sulphide with cream of tartar (a salt which yields a mixture of carbon and potassium carbonate on heating). In either case, a button of antimony is obtained when the fused mass is poured into a mould, but a good deal of antimony is lost by volatilization or in the "scoria," and the yield is very poor. A much better yield is obtained by fusing antimony sulphide with twice its weight of potassium ferrocyanide, under a layer of potassium cyanide, but the metal produced contains iron.

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[1] G. Schulze, *Ann. Phys.* **24** (1907), 43.

[2] F. Foerster, *Zeitsch. Elektrochem.* **18** (1912), 294.

The preparation of pure antimony from impure material can be carried out in a number of different ways.[1] It can be recrystallized as the complex tartrate, known as "tartar emetic" (*see below*); or alternately it may be brought into a solution as chloride or sulphate in the presence of acid, the solution being afterwards diluted with a large excess of water, so as to precipitate the basic chloride or sulphate; the basic sulphate can be freed from arsenic by heating with calcium fluoride, a treatment which eliminates arsenic as a volatile fluoride. Having at last obtained a pure antimony compound, it is converted to oxide and reduced to the metallic condition.

Compounds

Like arsenic, antimony forms two series of compounds in which it is apparently trivalent and pentavalent; they correspond to the oxides Sb_2O_3 and Sb_2O_5. The first-named oxide is weakly acidic and also weakly basic; the pentoxide has a more marked acidic character, but is only the feeblest of bases. Besides these oxides, an intermediate oxide, SbO_2, with some ill-defined compounds corresponding to it, exists. The majority of the compounds of antimony are colourless, but there are some exceptions.

A. Compounds of Trivalent Antimony (Antimonious Compounds).

Antimonious oxide, Sb_2O_3, is formed when the metal is heated with limited access of air, for instance in a loosely-covered crucible. If heated with full access of air, the product generally contains a higher oxide (SbO_2). Two forms exist, being respectively isomorphous with the two modifications of arsenious oxide. A light, flowery variety consisting of rhombic crystals is obtained when the heating is not too strong, but at higher temperatures this sublimes, yielding octahedra belonging to the cubic system. The oxide melts at a red-heat and volatilizes about 1,560° C.; the vapour density corresponds to the double formula Sb_4O_6. Like so many oxides, antimonious oxide, although practically colourless when cold, is distinctly yellow when hot.

Antimonious Salts. The oxide is almost insoluble in water, but dissolves in some acids and also in alkalis. The solutions in acids contain antimonious salts, the best solvents being hydrochloric and tartaric acids. The solution in the former contains **antimonious chloride,** $SbCl_3$, and, when distilled, yields first water, then the excess of hydrochloric acid; lastly, the anhydrous chloride distils over. The chloride is a crystalline substance,

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[1] See H. Moissan, "Traité de Chimie Minérale" (Masson), Vol. II.

sometimes known as "butter of antimony," which melts at 73° C. and boils about 223° C. Although readily hydrolysed by water, it is very soluble in hydrochloric acid, the concentrated solution being rather heavy. When the solid chloride is treated with unacidified water, or even when the solution in hydrochloric acid is diluted with much water, hydrolysis occurs and insoluble basic chlorides are formed. The basic chloride—or mixture of basic chlorides—prepared in this way is sometimes known by the old name of *Powder of Algaroth*. One of the basic chlorides which can be obtained crystalline, and is probably a definite compound, has the composition [SbO]Cl. It may be regarded as "**antimonyl chloride**" derived from the complex radicle [SbO].

Antimonious oxide will dissolve in cold fuming nitric acid and in hot concentrated sulphuric acid to give a **nitrate** and **sulphate**; the solution in hot sulphuric acid deposits long colourless needles of the sulphate on cooling. Both salts are very unstable, and the crystals are at once hydrolysed upon the addition of water. By partial hydrolysis of the normal sulphate, **antimonyl sulphate** $[SbO]_2SO_4$ can be obtained.

Among the most important oxy-salts of antimony are the double tartrates. One of these, known as **tartar emetic,** is produced when antimonious oxide is dissolved in "cream of tartar" (potassium hydrogen tartrate). It is a potassium antimonyl tartrate, $K[(SbO)C_4H_4O_6]nH_2O$, and is probably a complex salt containing antimony in the anion.

Antimonious sulphide, Sb_2S_3, is formed when a solution of antimonious chloride or tartar emetic containing hydrochloric acid is precipitated with sulphuretted hydrogen; it is an orange precipitate, which, when dried, is found to be soft and easily melted. If heated to about 212° C. the orange substance becomes black. The temperature at which the change from orange to black occurs is reduced by the presence of hydrogen chloride, ammonium chloride, and especially by antimony chloride; the latter substance depresses it to about 125° C. It is considered by a recent investigator that the blackening is not due to an allotropic change, since it does not occur at any definite transition temperature, and appears to be irreversible; it is probably caused by the formation of a trace of colloidal antimony through the partial decomposition of the sulphide.[1]

Precipitated antimonious sulphide dissolves readily in sodium or ammonium sulphide solutions, soluble thioantimonites ($xSb_2S_3.yNa_2S$) being formed; in this respect the sulphide of antimony resembles those of arsenic and tin. Such solutions

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[1] F. de Bacho, *Ann. Chim. Appl.* 12 (1919), 143.

readily absorb sulphur, passing to thioantimonates, which are also formed to some extent when antimonious sulphide is dissolved in a yellow sample of ammonium sulphide. Only the thioantimonites containing excess of sodium sulphide are soluble in water, those rich in antimony sulphide being brown or black insoluble compounds. All the thioantimonites are decomposed by acids, regenerating antimonious sulphide. Antimonious sulphide dissolves in caustic alkalis, giving a mixture of antimonites and thioantimonites.

Antimonites. It has been mentioned that antimonious oxide is appreciably soluble in caustic alkalis; from the solutions antimonites, corresponding to the arsenites, can be obtained. For instance, a solution of antimonious oxide in caustic soda yields sodium antimonite ($NaSbO_2.3H_2O$ or $Na_2O.Sb_2O_3.6H_2O$), whilst if the solution contains excess of antimonious oxide, an acid antimonite ($NaSbO_2.2HSbO_2$) is produced. The antimonites are white crystalline bodies, not very soluble in water.

B. Compounds of Pentavalent Antimony (Antimonic Compounds).

Antimonic oxide, Sb_2O_5, is formed in a hydrated condition when antimony is treated with nitric acid, and the anhydrous substance is formed as a yellow powder when the insoluble residue is cautiously heated below 275° C. As is so often the case, the colour is much darker when the oxide is warm. Antimonic oxide is practically insoluble in water.

Antimonic Salts. The basic properties of the higher oxide are very feeble. It is slowly dissolved by hydrochloric acid, but it is difficult to prepare the chloride from the solution. **Antimonic chloride,** $SbCl_5$, is, however, obtained by the direct action of chlorine on the metal, the combination being rather violent and causing the evolution of heat and light. Curiously enough it is a much better defined substance than arsenic pentachloride ($AsCl_5$), the very existence of which is still doubtful. Antimonic chloride is a volatile liquid, boiling about 140° C. It is not at once decomposed by ice-cold water, but hot water causes hydrolysis to hydrated antimonic oxide and hydrochloric acid. Various double chlorides are formed by adding alkaline chlorides to the solution.

A **pentasulphide,** Sb_2S_5, is described in chemical literature, but recent investigations have rendered it doubtful whether the substance exists[1]; the orange-red substance usually regarded as the pentasulphide probably consists mainly of a mixture of lower sul-

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[1] F. Kirchhof, *Zeitsch. Anorg. Chem.* **112** (1920), 67; A. Short and F. H. Sharpe, *J. Soc. Chem. Ind.* **41** (1922), 109T. Compare D. F. Twiss, *J. Soc. Chem. Ind.* **41** (1922), 171T.

phides (SbS_2 and Sb_2S_3) and some free sulphur. However, various ***thioantimonates*** are known, some having been isolated in the solid state. The solution of antimonious sulphide in yellow ammonium sulphide contains the ammonium salt ; it can be obtained in pale yellow prisms by crystallization. **Sodium thioantimonate** ($Na_3SbS_4.9H_2O$ or $3Na_2S.Sb_2S_5.18H_2O$) is formed—along with sodium antimonate—by dissolving antimonious sulphide and sulphur in caustic soda, and can be isolated from the solution in tetrahedra having a yellowish tinge. It is known as " Schlippe's salt." Several thioantimonates of the heavier metals, like the yellow zinc salt, $Zn_3(SbS_4)_2$, may be obtained by precipitation.

Antimonates. Antimonic oxide is only very slowly dissolved by caustic alkali solutions, but the various hydrated forms of the oxide obtained on the gradual hydrolysis of antimonic chloride dissolve more readily, presenting a greater surface area. Some of these water-containing varieties of " *antimonic acid,*" prepared by the earlier investigators, were assigned special names (pyro-antimonic acid, ortho-antimonic acid, etc.) to express a possible correlation between them and the various phosphoric and arsenic acids. But recent researches on the removal of water from " antimonic acid " by allowing it to stand over concentrated sulphuric acid are interpreted as showing that the compounds described were not definite hydrates.[1] Similarly, the attempts to classify the various antimonates as pyro-antimonates, meta-antimonates, have proved unsatisfactory. Some of the amorphous antimonates described in the literature appear to be adsorption compounds. However, when the hydrated forms of antimonic acid are allowed to stand in a solution of soda, various crystalline antimonates may be formed, the composition of which depend upon the amount of alkali present. The best developed sodium antimonate is obtained by the action of $\frac{N}{10}$ soda on hydrated antimonic acid and has the composition $Na_2H_2Sb_2O_7.6H_2O$. It crystallizes in cubes or cubo-octahedra, and is commonly known as **sodium acid pyro-antimonate,** although if the composition were written in the form $2NaSbO_3.7H_2O$, it could be regarded as a sodium meta-antimonate.[2]

The antimonates of the heavier metals, being mostly insoluble, may be obtained by precipitation from the sodium salts.

C. Intermediate Compounds.

Antimonious-antimonic oxide (SbO_2; usually written

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[1] G. Jander, *Koll. Zeitsch.* **23** (1918), 122.

[2] Compare G. von Knorre and P. Olschewsky, *Ber.* **18** (1885), 2353, especially pages 2356 and 2361.

Sb_2O_4) is formed when either the lower or higher oxide is heated in the air at a low red heat. It is conveniently prepared by oxidizing antimony with nitric acid, and heating the resultant mixture to dull redness until the weight is constant.[1] The oxide is a white solid. When heated strongly it yields antimonious oxide (Sb_2O_3).

The intermediate oxide may, of course, be regarded as a combination of the other two, in fact as antimonious antimonate, $Sb_2O_3.Sb_2O_5$ or $Sb(SbO_4)$. But since it seems to possess both a weak basic and weak acidic character, it is probably best regarded as a simple oxide derived from tetravalent antimony (SbO_2). When, for instance, the substance is fused with potash, a salt, $K_2Sb_2O_5$ (or $K_2O.2SbO_2$), is obtained, as a white body, soluble in hot water; and from this salt other less soluble "**hypo-antimonates**" are obtained by precipitation. Again, it seems likely that the corresponding **tetrachloride** ($SbCl_4$) is present in the dark brown solution obtained by the action of chlorine on antimonious chloride ($SbCl_3$). The chloride itself cannot be obtained from the solution, but the double chlorides, which are less soluble, can be prepared. Thus the rubidium compound, Rb_2SbCl_6, appears as a violet crystalline powder, when a solution containing antimonious and antimonic chlorides is treated with rubidium chloride.

The corresponding sulphide (SbS_2 or Sb_2S_4) is formed when zinc thioantimonate is decomposed by an acid. It is the main constituent of the so-called "**golden sulphide,**" obtained when a solution of sodium thioantimonate is acidified. This precipitate is usually described as being mainly antimony pentasulphide (SbS_5), but recent work[2] shows that it consists of the intermediate sulphide, Sb_2S_4, mixed with free sulphur, which can be extracted with carbon disulphide, and sometimes some Sb_2S_3. The sulphide Sb_2S_4 can be regarded as antimonious thioantimonate $Sb(SbS_4)$, or, alternately, as a simple sulphide of tetravalent antimony, SbS_2.

D. Miscellaneous Compounds.

Antimony hydride, SbH_3 (*stibine*), is a much less stable substance than the hydride of arsenic. "Stibine" is very difficult to prepare in a pure state, but is evolved, mixed with a large excess of hydrogen, when an antimony compound is added to dilute sulphuric acid in which zinc is placed. Like arsine, the stibine is decomposed when passed through a gently-heated tube, a mirror of antimony being formed. But it differs from arsine in its behaviour towards a dilute solution of silver nitrate. Hydrogen antimonide reacts with the silver nitrate in the normal way to give

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[1] J. von Szilàgyi, *Zeitsch. Anal. Chem.* **57** (1918), 23.

[2] F. Kirchhof, *Zeitsch. Anorg. Chem.* **112** (1920), 67.

black silver antimonide and nitric acid ; after filtration, therefore, the solution contains no antimony. On the other hand, hydrogen arsenide is oxidized by the silver nitrate to arsenious acid, which can afterwards be detected in solution, the black precipitate produced in this case being not silver arsenide, but metallic silver.

Various other antimonides are known as components of alloys, but it should be noticed that in addition to these salt-like antimonides, other true "inter-metallic compounds," having formulæ unrelated to the valency of antimony, are known. For instance, the melting-point curves of antimony-potassium alloys show maxima at two points corresponding to the compounds K_3Sb and KSb. The former compound (potassium antimonide) is greenish yellow, and ignites spontaneously when broken, whilst the latter has a metallic appearance resembling antimony, and is much less readily oxidized.[1] The compound K_3Sb is to be regarded as comparable to a metallic salt, whilst KSb is a true "inter-metallic compound."

Analytical

Antimony compounds, when heated on charcoal, give dense white fumes of oxide, and an incrustation of sublimed oxide on the charcoal. If this incrustation, when cold, be touched by a drop of ammonium sulphide, it is at once converted into orange antimony sulphide. In such a way, antimony is distinguished from other metals which give white incrustations on charcoal.

A clear solution of an antimonious compound in hydrochloric acid, when poured into excess of water, gives a cloud of basic salt or hydrated oxide owing to hydrolysis ; the solution is clarified on the addition of tartaric acid. But this phenomenon is not peculiar to antimony compounds.

The identification of antimony in solution, and its quantitative separation from other elements depend upon the fact that of the common metallic sulphides which can be precipitated in acid solution, only those of antimony, tin and arsenic are soluble in ammonium sulphide. The separation from tin and arsenic has already been discussed in the section dealing with the first-mentioned metal.

When antimony is to be determined by a gravimetric method it is usually precipitated from a hot acid solution by hydrogen sulphide, and the precipitate, filtered in a Gooch crucible, is heated at 230° C. in a current of carbon dioxide until the weight is constant.[2] The ignition at 230° C. is needed to volatilize any excess

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[1] N. Parravano, *Gazetta*, **45** (1915), i, 485.

[2] Th. Paul, *Zeitsch. Anal. Chem.* **31** (1892), 540.

of sulphur or to decompose any higher sulphide, leaving pure Sb_2S_3 in the crucible.

The approximate estimation of antimony in alloys has already been described in the section on tin. The alloy is treated with hot concentrated nitric acid, and all metals except tin and antimony are converted to soluble nitrates. By boiling the residue with compact tin and hydrochloric acid, all the antimony is reduced to the metallic state as a black powder, which may be dried and weighed.

In view of the difficulties attending the gravimetric estimation of antimony, volumetric methods have special interest. Various methods have been described, depending upon the titration of an antimonious solution with iodine,[1] potassium bromate[2] and potassium permanganate[3] respectively. Titration with permanganate has recently been shown to be possible even where (as is usually the case) the antimony solution contains hydrochloric acid; in general, it is difficult to titrate a solution containing hydrochloric acid with permanganate, since the acid itself decolorizes the permanganate, chlorine being liberated. In the new method, a small quantity of "Poirrier's orange" is added to the solution before titration; permanganate is now run in, and, as soon as it is in excess, chlorine appears in the solution and bleaches the colouring material. The disappearance of the orange tint therefore marks the end-point.

TERRESTRIAL OCCURRENCE

The geo-chemistry of antimony resembles that of arsenic, but for some reason which it is difficult at present to decide, antimony occurs somewhat less closely intermingled with other metals than does arsenic. Thus, the antimony is usually present in smaller amounts than arsenic in the ores of the heavy metals, such as copper and lead, whilst, on the other hand, extensive ores extremely rich in antimony exist in many places. The Chinese ores, for instance, contain 20 to 60 per cent. of the metal. Practically all the valuable ores contain antimony mainly as the sulphide

Stibnite (Antimony glance) . Sb_2S_3,

a rather soft mineral with grey metallic lustre, crystallizing in rhombic prisms. It has evidently been deposited in most cases from thermal waters arising from an igneous mass, and is generally accompanied by quartz. A reddish amorphous form of the same

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[1] F. H. Heath, *Amer. J. Sci.* **25** (1908), 513, describes a process for the iodometric determination of antimony in the presence of copper.

[2] J. B. Duncan, *Chem. News,* **95** (1907), 49.

[3] L. Bertiaux, *Ann. Chim. Anal.* **2** (1920), 273.

compound ("metastibnite") is found in the sinter of certain mineral springs which carry antimony.

In addition to stibnite, we also find native (elementary) antimony, whilst in the oxidized portions of the ores, numerous antimonates, as well as antimonious oxide, occur. Other antimony minerals, such as the silver-ore

Pyrargyrite . . . . Ag_3SbS_3,

are of interest chiefly as a source of the other metal which they contain.

Several of the important deposits of antimony are situated around the Pacific. The ore is met with in Bolivia and, to a a small extent, in California and Nevada, in British Columbia, in Alaska, and in Japan. By far the most important deposits occur, however, in China. As we pass southwards the ore reappears, on a much smaller scale, in Indo-China and on the borders of Burma, and again in Queensland, New South Wales, and Victoria; the Victorian ores are at present the most important of the Australian deposits.

Outside the Pacific ore-circle, antimony ore occurs around the Mediterranean Sea, namely, in Portugal, Spain, the South of France, Italy, Sardinia, Serbia, and Algeria. The French deposits are a stibnite associated with auriferous pyrites; the Algerian ores, which are quite extensive, are mainly of an oxidized character.[1] Antimony ores also occur in the Ural Mountains and in several localities in Siberia.

METALLURGY AND USES

Practically the whole of the world's supply of the metal is made from sulphide ore. In the exceptional cases where the ore mined contains, say, 90 per cent. of antimony sulphide, it can be smelted direct. Generally the sulphide is disseminated in small particles throughout a mass of worthless material (quartz, calcite, or barytes) and is sometimes mixed with pyrites, galena, and zinc blende. The two main processes for the separation of the antimony from the valueless matter are:—

(1) *Liquation* processes, depending on the easy *fusibility* of antimony sulphide, which melts at 540° C.; these are suitable for fairly rich ores containing, say, 40–70 per cent. of antimony.

(2) *Volatilization roasting*, depending on the fact that antimony ores yield a *volatile* oxide (Sb_2O_3) when roasted; this process is suited for poor ores with, say, 10–20 per cent. of antimony, and also for the residues from the liquation process.

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[1] K. C. Li, *Min. Ind.* **28** (1919), 28.

It should be noticed that these two methods of concentration give different products. Liquation yields the *sulphide* which is usually converted to metallic antimony by heating with scrap-iron, whilst volatilization roasting yields the *oxide*, which is generally reduced to the metallic state with carbonaceous fuel.

Liquation.[1] Crude and rather wasteful intermittent methods of liquation are still largely used in China—which is the most important antimony-producing country at the present time. The type of furnace employed is shown in Fig. 31. The ore is placed in perforated fire-clay pots (A) which are set in the furnace and heated, until the antimony sulphide melts and trickles out through holes in the bottom into other pots B set below ; most of the worthless material remains in the upper pots.

The product of the liquation process is known as "**crude antimony.**" It consists, it should be noticed, essentially of *antimonious sulphide* (Sb_2S_3) ; but as a little sulphur is usually burnt away during the liquation process, it generally contains some oxide, and also metallic antimony, formed no doubt by interaction between the oxide and sulphide.[2]

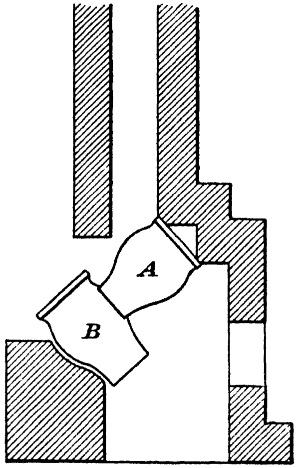

Fig. 31.—Chinese Liquation Furnace.

Preparation of Metallic Antimony from the Liquated Sulphide ("Crude Antimony"). The sulphide of antimony is not difficult to reduce, but the comparative volatility of the metal and its oxide is liable to make the process wasteful, if care is not taken. One method is to remove the sulphur by heating with iron. In an alternative process, sulphide is roasted to produce the oxide, which is mixed with coal and reduced to the metallic condition. The roasting of the sulphide to oxide is not, however, easy, as the sulphide tends to fuse and produce a fritted mass to which air does not readily get access ; much care is needed, if the whole of the sulphur is to be eliminated.[3]

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[1] K. C. Li, *Trans. Amer. Inst. Met.* **11** (1917-18), 92. Also A. S. Wheler, *Trans. Inst. Min. Met.* **25** (1916), 366.

[2] W. R. Schoeller, *J. Soc. Chem. Ind.* **33** (1914), 169 ; **34** (1915), 6.

[3] See also H. O. Hofman and J. Blatchford, *Met. Chem. Eng.* **14** (1916), 163.

Probably, therefore, the **iron-reduction process** is in general the more economical method of treating the liquated sulphide. This method, which dispenses with the need of a preliminary roasting to oxide, has long been used in certain British antimony works, and when carried out in pots is known as the "**English process**"; it is also used in China. The reaction may be represented

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb.$$

Since the iron sulphide is immiscible with the antimony, we may expect to get two liquid layers, the lower one consisting of fused antimony, and the upper one of liquid iron sulphide. The difference of specific gravity is not, however, great; and the separation of the two liquids is greatly facilitated if sodium sulphide is present in the iron sulphide phase, since the specific gravity is thereby reduced.

The operation is carried out either in graphite pots or—on a larger scale—in a reverberatory furnace; processes involving the principle of iron-precipitation have also been carried out in this country in water-jacketed blast-furnaces.[1] The antimony sulphide is mixed with excess of scrap iron, tinplate cuttings being preferred. Salt and scourings from a previous operation are generally added to assist the fluxing of any slag-forming material that may be present, and to reduce the losses by volatilization. Sodium sulphate is often added to the charge; it becomes reduced to sodium sulphide, and serves—as explained above—to reduce the specific gravity of the sulphide phase. When the molten product has separated into two layers, the metal is poured or ladled into moulds, the sulphide layer being separated either before or after the solidification.

The metal produced is, however, not pure antimony; for since excess of scrap is always used in the process, an alloy containing about 7 per cent. of iron is actually obtained. This iron is removed by fusing with excess of antimony sulphide. The ferrous sulphide produced separates as a matte, and the antimony obtained is free from iron, but now contains a small excess of sulphur, since antimony sulphide is slightly soluble in metallic antimony. The sulphur is extracted by fusing the product under a special flux, which consists of a molten mixture of potash and antimony sulphide. This flux no doubt contains potassium thioantimonite, and readily absorbs sulphur (forming the thioantimonate); in this way pure antimony is obtained. It is curious to note that antimony sulphide is used first to remove excess of iron, and then, in presence of alkali, to remove excess of sulphur.

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[1] W. R. Schoeller, *Trans. Inst. Min. Met.* **25** (1916), 380.

The purity of the metal is judged by the appearance of a " star " upon the crystalline surface of the metal when it is allowed to crystallize under the surface of a neutral slag. In the presence of impurities the star is absent, or is very poorly defined.

" **Volatilization roasting** " is the best method of dealing with ores too poor for liquation, as well as for the residues left in the pots after liquation ; these residues still contain some antimony. It is closely analogous to the process used for the volatile concentration of zinc ores. The **Herrenschmidt process**,[1] which was developed in France, and more recently has been applied on a large scale in China [2] and also in Canada,[3] has proved most successful. The ores as mined are mixed with gas coke or charcoal and are charged into a roasting furnace G (Fig. 32), where they rest upon horizontal fire-bars arranged step-wise. By means of the fan F sufficient air is drawn through the furnace to oxidize the antimony to the oxide Sb_2O_3, which, being quite volatile, sublimes away, and is condensed in the vertical air-cooled condensers C and may be removed from time to time through the doors D. The last trace of oxide is condensed in the coke tower T, down which water trickles.

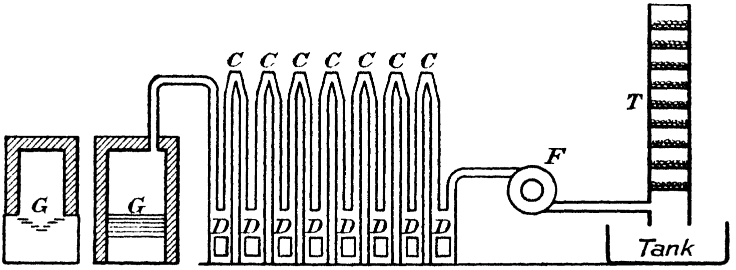

FIG 32.—Herrenschmidt Process (Diagrammatic).

Preparation of Metallic Antimony from the Volatilized Oxide. The oxide of antimony is used as the source, not only of the metal, but of most antimony compounds. Where it is desired to reduce it to the metallic condition, it is mixed with coal or charcoal, together with sodium carbonate which serves as a flux ; the mixture is heated by hot gases in a reverberatory furnace. Sometimes other sodium salts are added. The carbon reduces the antimony to the metallic state, and the sodium salts, forming a fused layer over the surface, prevent excessive loss of metal by

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[1] See C. Y. Wang, " Antimony " (Griffin).

[2] W. F. Collins, " Mineral Enterprise in China " (Heinemann) ; C. Y. Wang, *Trans. Amer. Inst. Min. Eng.* 60 (1919), 3.

[3] J. A. De Cew, *Met. Chem. Eng.* **16** (1917), 444.

volatilization. In spite of this precaution, however, a considerable fraction of the total antimony is usually carried off by the furnace-gases. The molten antimony produced by the reduction process is run off through a tapping-hole at the side. The covering mixture of slag and of sodium salts is only slightly affected by the process, and most of it, mixed with a little fresh material, can be used for the next charge.

The antimony thus produced is often impure, but a considerable proportion of the more reactive impurities can be removed by fusing under suitable fluxes containing alkali, antimony sulphide, and often sodium sulphide. In some cases an oxidizing flux, such as a mixture of nitre and carbonate of soda, is employed.

Blast-furnace Production of Antimony. The blast-furnace has also been used successfully in the metallurgy of antimony, and at certain English works has taken the place of the pot-furnace. It is suited for the direct treatment of certain ores with antimony-content of about 25–40 per cent.—that is, ores intermediate in character between those suited for liquation and those suited for volatilization-roasting. By treating a mixture of stibnite, coke, and fluxing materials in a water-jacketed blast-furnace a good yield of antimony can be obtained. Part of the sulphide is converted to oxide, which reacts with the remaining sulphide, yielding metallic antimony.[1] During the war, an American firm carried on the direct manufacture of lead-antimony alloys in a blast-furnace, by the treatment of ores containing galena and stibnite, mixed with certain oxidized ores from Mexico.[2]

Uses of Antimony. Antimony is too brittle to be employed in the unalloyed state, but various alloys containing antimony, along with lead, tin, or copper, are of great importance. They include **hard-lead, Britannia metal, type-metal,** and **Babbitt metal,** all of which have been discussed already.

Technically important Compounds.[3] Several antimony compounds are used as paints and colouring agents. "**Naples yellow**" is a basic antimoniate of lead, and is used in colouring glass. Antimonious oxide (Sb_2O_3) is used in colouring glass, and is now being manufactured in Australia as a pigment.[4] The intermediate oxide (Sb_2O_4) is used in ceramics as an opacifier. Antimony compounds are likewise used in the enamel industry.

Other antimony pigments include the "**golden sulphide,**" formed by heating the trisulphide with sulphur and sodium sul-

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[1] W. R. Schoeller, *Trans. Inst. Min. Met.* **27** (1918), 237.
[2] G. P. Hulst, *Met. Chem. Eng.* **21** (1919), 727.
[3] E. S. Bastin, *U.S. Geol. Surv. Min. Res.* (1916), I, 723.
[4] C. A. Klein, *J. Soc. Chem. Ind.* **41** (1922), 209R.

phide, so as to obtain Schlippe's salt ($Na_3SbS_4.9H_2O$), and then precipitating the filtered solution of that salt with acid. As already stated (page 315) this product is probably mainly a mixture of the sulphide SbS_2 and free sulphur. Various basic sulphides are also employed in yellow and red paints.

One of the chief uses of antimony sulphide is in the rubber industry, for the manufacture of the red " antimony rubber." It is partly added as a colouring material, but the free sulphur, and possibly some of the combined sulphur, play a part in the vulcanization process.[1]

The trisulphide of antimony, being a readily oxidizable substance, is employed in the manufacture of matches ; the heads of safety matches usually contain antimony sulphide and an oxidizing agent, such as potassium chlorate.

Antimony salts are also used as mordants in dyeing, usually in connection with tannin. If cotton is treated first with a solution of tannin, and then with a solution of tartar emetic, the " antimony tannate " precipitated within the fibre is capable of fixing certain classes of dye-stuffs.

Antimonial Medicines. In the Middle Ages antimony compounds were most prized by the so-called " iatro-chemists " (doctoring-chemists), who prescribed them as remedies for all sorts of disorders. The use of metallic substances in medicine subsequently declined, owing to the introduction of organic drugs ; but recently the employment of antimony compounds in medicine has again become of great importance. This is especially the case in connection with tropical diseases. Bilharziosis, a disease very prevalent among the Egyptian fellaheen and until recently regarded as incurable, is now treated with success by means of antimonial preparations—such as tartar emetic and colloidal antimony.[2] Even sleeping sickness, which has caused so much destruction in Equatorial Africa, can sometimes be treated successfully by a method in which both tartar emetic and " atoxyl " (an organic compound of arsenic) are used, provided the treatment is started whilst the disease is still in the preliminary stages. At present, comparatively simple compounds of antimony, like tartar emetic, are used. Attempts have lately been made to prepare complex organic compounds of antimony analogous to the organic arsenic compounds which have proved so valuable.[3] In many cases, however, the antimony compounds have proved less effective than the corresponding arsenic bodies.

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[1] B. D. W. Luff and B. D. Porritt, *J. Soc. Chem. Ind.* **40** (1921), 275T.

[2] H. B. Day, *Lancet*, **200** (1921), 525.

[3] R. G. Fargher, *J. Soc. Chem. Ind.* **39** (1920), 333R.

BISMUTH

Atomic weight . . . 208·0

The Metal

The last element of Group VB has a certain physical resemblance to antimony. Like the latter, bismuth is a hard, brittle, crystalline substance, having a whitish colour and bright metallic lustre. It differs from antimony, however, in possessing a slight pinkish tinge. It is also considerably heavier, having a density of 9·8, which is, however, rather lower than that of lead and the other metals of the same horizontal row of the Periodic Table. It is much more fusible than antimony, melting at 271° C., below the melting-point of lead, but above that of tin (232°); like antimony, bismuth expands when it solidifies. It is appreciably volatile at a red heat and boils at about 1,500° C.; the density of the vapour shows that it consists of a mixture of simple atoms (Bi) and more complex molecules (Bi_x) The vapour has a greenish-blue tinge.

Bismuth, like arsenic and antimony, crystallizes in the rhombohedral system; as is usually the case with metals of low melting-points, quite large crystals are obtained when the molten metal is allowed to solidify. If a crucible containing fused bismuth is cooled until a solid crust appears on the surface, and if the crust is then pierced and the liquid portion below is poured out, the solidified portions will be found, when broken up, to contain well-developed rhombohedra.

The arrangement of the atoms in crystalline bismuth has been determined by the X-ray method, and is found to be similar to that of the atoms in antimony.[1]

When bismuth is sublimed in nitrogen, a greyish powder, sometimes described as "amorphous bismuth," is often obtained where the vapour condenses. But this product appears always to contain a trace of oxygen, and probably consists of particles of ordinary bismuth, the coalescence of which is prevented by a film of oxide. No modification corresponding to the yellow non-metallic variety of arsenic and antimony has yet been reported; and, indeed, non-metallic characters are so feebly developed in bismuth that this is not surprising. Like most soft metals, bismuth undergoes

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[1] R. W. James, *Phil. Mag.* **42** (1921), 193; A. Ogg, *Phil. Mag.* **42** (1921), 165.

slight changes of properties (e.g. a slow alteration in volume) at comparatively low temperatures; these have been ascribed to "allotropic changes" by Cohen.[1] But it appears doubtful whether there is any allotropic change in the strict sense of the word.

Bismuth is slowly acted on by moist air, becoming covered with an iridescent film of oxide. If heated strongly in the air, it is attacked, forming a yellowish fume of oxide, but the oxidation proceeds less readily than in the case of antimony.

The metal stands near the "noble" end of the Potential Series. It cannot displace hydrogen gas from dilute hydrochloric acid, but dissolves slowly if the acid contains dissolved oxygen. By nitric acid (of specific gravity 1·4) bismuth is oxidized, the soluble nitrate being produced; in this respect, bismuth differs from the more feebly basic antimony, which yields an insoluble product with the same acid. More concentrated nitric acid (specific gravity 1·54) renders bismuth passive. Bismuth dissolves in hot concentrated sulphuric acid, sulphur dioxide being evolved.

The anodic behaviour of bismuth[2] recalls that of antimony, marked valve action being shown towards many electrolytes. In caustic potash, the film produced on a bismuth anode will withstand a potential of about 500 volts before it breaks down. But, in contrast with antimony, the film produced on a bismuth anode breaks down at a much lower potential if chlorides are present in the liquid. In a solution of sodium nitrate a bismuth anode is attacked with a current efficiency of approximately 100 per cent.[3]

Laboratory Preparation. Owing to the noble character of bismuth, the reduction to the metallic state presents no difficulty. In a wet way it is possible to obtain the metal from solutions of the salts by precipitation with iron or lead. The metal is also obtained by fusing the oxide in a crucible with potassium cyanide which acts as a reducing agent, or by heating a mixture of the oxide and carbon, or by heating the oxide in a current of hydrogen.

To obtain pure bismuth from impure material it is best to recrystallize the metal as normal nitrate from an acidified solution; the purified nitrate is converted to oxide by ignition and reduced by heating in hydrogen or with potassium cyanide.[4] It can be further purified by fractional crystallization of the metal fused under a layer of paraffin.

A considerable elimination of the more easily oxidizable impurities (lead, iron, arsenic, sulphur), from crude metallic bismuth can

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[1] E. Cohen, *Proc. Amst. Acad.* 17 (1915), 1236.
[2] G. Schulze, *Ann. Phys.* 24 (1907), 43.
[3] E. B. R. Prideaux and H. W. Hewis, *J. Soc. Chem. Ind.* 41 (1922), 167T.
[4] F. Mylius and E. Groschuff, *Zeitsch. Anorg. Chem.* 96 (1916), 237.

be effected by the simple expedient of melting the metal below an oxidizing flux (e.g. nitre, or a mixture of nitre and borax); for the elimination of copper, a flux containing sodium sulphide is best.

Compounds

The chief compounds of bismuth correspond to the oxide Bi_2O_3, and are analogous to the antimonious compounds. As so often occurs in the last metal of each group, the derivatives of the higher oxide are less well developed than in the preceding members. Accordingly, the compounds corresponding to Bi_2O_5 are unstable bodies, and the actual existence of the oxide itself, in an anhydrous state, seems rather doubtful. On the other hand, we find a certain number of lower compounds corresponding to the oxide BiO, which have no counterpart among the compounds of antimony.

A. Compounds of Trivalent Bismuth (Bismuthous Compounds).

Bismuthous oxide, Bi_2O_3, is formed by heating the metal in the air, or by igniting the carbonate or nitrate; the " hydroxide," prepared by precipitating a bismuth salt with a caustic alkali or ammonia, gives up its water on being heated and yields the anhydrous oxide. The anhydrous oxide is yellow, but the hydroxide obtained by precipitation is white. Cubic and rhombic forms of the oxide are known, which are respectively isomorphous to the two forms of antimonious oxide.

Bismuthous oxide has marked basic properties, dissolving in acids with the formation of salts; on the other hand, it has scarcely any acidic character, and is insoluble in alkalis. In these respects it presents a contrast with antimonious oxide, which is only feebly basic but shows the properties of an acid. The so-called " hydroxide " produced by precipitation of bismuth salts by alkali always contains basic salts. It is, curiously enough, redissolved by alkali if glycerol be present; the action of glycerol seems to depend upon the formation of complex organic salts containing the metal in the anion, somewhat analogous to the complex tartrates formed by antimony.

Bismuth salts are formed when the oxide is dissolved in acids, or when the metal is treated with oxidizing acids. Unlike the corresponding antimony compounds, the normal salts of oxy-acids are easy to prepare in the solid condition, and, although hydrolysed upon the addition of pure water, can easily be brought into a clear solution by the presence of a little acid. But the tendency to hydrolysis is still important, and, if the solution in acid be diluted with pure water, a cloud is formed, which indicates the formation of an insoluble basic salt ; in contrast to the corresponding " antimony clouds," the basic salts of bismuth are not dissolved by tartaric acid.

Bismuth nitrate, $Bi(NO_3)_3.5H_2O$, is a deliquescent, colourless crystalline body obtained when a solution of the metal in nitric acid is evaporated. When its solution in dilute nitric acid is poured into a large volume of water, a **basic nitrate** is produced as a white precipitate. The composition of the basic salt usually approximates to the formula $Bi(OH)_2NO_3$ or $[BiO]NO_3.H_2O$, but it varies according to the exact conditions of formation ; in fact, if sufficient water and sufficient time be allowed, hydrolysis continues until finally the hydrated oxide is left. The basic nitrate, as usually produced, contains, no doubt, a number of basic salts, and possibly some of the products described in chemical literature as " basic nitrates " really consist of hydroxide with adsorbed bismuth nitrate. The salt mentioned above can, however, be obtained in well-defined crystals and is probably a chemical individual. The basic nitrates are dissolved by acids, normal bismuth salts being produced.

The **chloride,** $BiCl_3$, is formed when the oxide is dissolved in hydrochloric acid. On evaporating the solution, the excess of water first evaporates off ; then the anhydrous chloride begins to distil, and may be condensed as a white solid in a cool tube. The same substance is formed on passing chlorine over gently-warmed bismuth in a tube. It melts at 227° C., and boils between 400° and 450° C. ; the vapour-density indicates the existence of normal molecules $BiCl_3$. The substance dissolves without change in a small quantity of water ; but, if the solution be diluted, hydrolysis occurs, and the insoluble **basic chloride** is formed. The latter body, usually known as " bismuth oxychloride," has the composition [BiO]Cl. It is probably a true chemical individual (" bismuthyl chloride "), not a mere adsorption product, since it can be obtained in well-developed crystals. These are best formed by diluting a boiling solution of bismuthous oxide in hydrochloric acid with boiling water ; the liquid is filtered and allowed to cool, when colourless tetragonal crystals separate.[1]

The **insoluble salts** of bismuth, such as the white **phosphate** and **arsenate,** are formed by double decomposition in the usual way ; when ammonium carbonate is added to a bismuth nitrate solution, the **basic carbonate** is produced as a white precipitate. The **sulphide** is obtained by passing sulphuretted hydrogen through a bismuth salt solution acidified with hydrochloric acid ; it is a

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[1] A. de Schulten, *Bull. Soc. Chim.* 23 (1900), 156.

dark brown precipitate, almost insoluble in alkalis and in ammonium sulphide, but appreciably soluble in a hot solution of potassium sulphide.

Bismuth iodide, BiI_3, is another rather sparingly soluble salt of bismuth and is obtained as a brown precipitate by adding potassium iodide to a bismuth salt solution, or as a grey crystalline sublimate by heating bismuth and iodine together.

B. Compounds of Tetravalent and Pentavalent Bismuth.

When chlorine is passed into a suspension of bismuthous "hydroxide" in a boiling solution of caustic potash, the white colour turns yellow, red, or brown, and a mixture of more highly oxidized compounds is obtained.[1] If the alkali is dilute (specific gravity 1·05 to 1·35) the main product is the oxide BiO_2, which may be separated from the unaltered lower oxide by treatment with nitric acid; the oxide is dark brown in the anhydrous condition, but the hydrate $BiO_2.H_2O$ is yellow. When the alkali employed is concentrated (specific gravity 1·4 to 1·6) the principal product is **potassium bismuthate** ($KBrO_3$), and by treating the mixture with nitric acid, it is possible to obtain bismuthic acid, $HBiO_3$, which may be regarded as a hydrated form of bismuth pentoxide (Bi_2O_5). Few of these bodies have been obtained pure. A method of obtaining **sodium bismuthate** in a state of moderate purity is to dissolve the impure bismuthic acid in 60 per cent. hydrofluoric acid, and then, after cooling the solution to 0° C., to add normal sodium hydroxide drop by drop.[2] The yellow precipitate thrown down is sodium bismuthate, and, after a small amount of washing, has a composition approximating to $Na_2O.Bi_2O_5.nH_2O$. A dry method of preparing sodium bismuthate consists in heating sodium hydroxide and bismuth nitrate together and adding sodium peroxide. The fused mass is allowed to solidify, and is ground up and washed with water. The product is by no means pure.[3] Sodium bismuthate obtained by this method is often used in the analytical estimation of manganese.

C. Compounds of Divalent Bismuth.

When bismuth basic oxalate is heated, a dark residue of composition BiO is obtained; this is generally considered to be a "**suboxide.**" An alternative method of obtaining the "sub-

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[1] C. Deichler, *Zeitsch. Anorg. Chem.* **20** (1898), 81. A useful table showing the effect of variation of the conditions upon the product obtained is given on page 102.

[2] O. Ruff, *Zeitsch. Anorg. Chem.* **57** (1908), 220.

[3] J. Reddrop and H. Ramage, *Trans. Chem. Soc.* **67** (1895), 268.

oxide " is by the partial reducing action of stannous chloride on a bismuth chloride solution containing caustic alkali. Some authorities[1] consider that the so-called suboxide is merely a mixture of bismuth and bismuthous oxide (Bi_2O_3). Others[2] argue that it must be a definite compound, since the density (7·9) is not equal to the calculated density of the mixture (8·9); the density of substances varies, however, so much with their mode of preparation, that this argument is not conclusive. It is, however, also stated[3] that when bismuthous oxide is reduced to the metallic state by means of carbon monoxide, and the progress of the reduction is plotted against the time, the curve shows a break at the point corresponding to the composition BiO. The existence of the suboxide, although very probable, must not be regarded as definitely proved.

By the action of methyl iodide vapour on the "suboxide" at about 260° C., it is possible to obtain red crystals of the **iodide,** BiI_2, which, being volatile, sublimes forward in the current of methyl iodide.[4] A non-volatile basic iodide, $2BiI_2.3BiO$, remains in the reaction vessel.

Analytical

All bismuth compounds heated with carbon before the blow-pipe give a brittle white bead of the metal, together with a yellow incrustation of the oxide. Bismuth salt solutions give clouds of basic salts when diluted with water, and these clouds are not dispelled by the addition of tartaric acid.

A good method[5] for the detection of bismuth in minerals depends upon the formation of the brown iodide. The substance to be tested is heated with cuprous iodide and sulphur upon a bright aluminium plate. If bismuth is present a brown sublimate will be seen upon the white aluminium ground; very small quantities of bismuth can be detected in this way. A sublimate of iodine (which might be mistaken for bismuth iodide) will not appear if the plate is heated before commencing the test.

The separation of bismuth from other metals is rather a long operation. The metal is one of those thrown down by sulphuretted hydrogen in the presence of hydrochloric acid. From the mixture

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[1] F. Treubert and L. Vanino, *Zeitsch. Anal. Chem.* **53** (1914), 564.

[2] S. Tanatar, *Zeitsch. Anorg. Chem.* **27** (1901), 437; W. Herz and A. Guttmann, *Zeitsch. Anorg. Chem.* **53** (1907), 64; W. Herz, *Zeitsch. Anal. Chem.* **54** (1915), 103.

[3] By F. J. Brislee, *Proc. Chem. Soc.* **23** (1907), 286.

[4] H. G. Denham, *J. Amer. Chem. Soc.* **43** (1921), 2367.

[5] W. M. Hutchings; described by Sir W. Crookes in "Select Methods of Chemical Analysis" (Longmans).

of sulphides obtained, the sulphides of tin, *antimony, and arsenic are dissolved out by the action of ammonium sulphide.* Of the remaining sulphides only those of bismuth, copper, cadmium, and lead are soluble in hot dilute nitric acid. The lead is first removed from the filtrate by precipitation with sulphuric acid (in the presence of alcohol). Subsequently the liquid is nearly neutralized with ammonia and treated with excess of ammonium carbonate, which precipitates the bismuth as a basic carbonate on warming, but leaves the copper and cadmium in solution; the separation is, however, incomplete, and it is necessary for accurate work to repeat the precipitation.

The precipitate may be gently ignited, and weighed as the oxide Bi_2O_3. Precipitates containing bismuth should never be heated strongly in porcelain crucibles, as they are likely to act as fluxes for the glaze.[1]

Alternatively the precipitate may be mixed with potassium cyanide, and heated; bismuth is reduced to metallic form, and solidifies on cooling to a button, which may be taken out and weighed.

Another method for the separation of bismuth from a solution containing copper and cadmium depends on the electrolytic deposition of the bismuth, with the proper control of the cathodic potential.[2] In order to separate bismuth from cadmium a solution containing nitric acid and tartaric acid should be used; in such a solution, if the potential at the cathode is kept within certain limits, it is possible to avoid the deposition of cadmium along with the bismuth. In the separation from copper, the solution should contain potassium cyanide, as well as sodium tartrate, sodium hydroxide, and formaldehyde; the cyanide serves to prevent the deposition of copper at a potential which is sufficiently depressed for the complete precipitation of bismuth.

TERRESTRIAL OCCURRENCE

The geo-chemistry of bismuth is generally similar to that of arsenic and antimony, but, owing to the more "noble" character of bismuth, it is quite commonly found in mineral veins in the elementary condition, as reticulated or arborescent growths of native bismuth. On the other hand, the sulphide known as

Bismuthinite (Bismuth glance) Bi_2S_3

often occurs in soft lead-grey masses, which may be yellowish or

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[1] W. W. Scott, "Standard Methods of Chemical Analysis" (Crosby Lockwood).

[2] H. J. S. Sand, *Trans. Chem. Soc.* **91** (1907), 373; A. Fischer, "Elektroanalytische Schnellmethoden" (Enke).

iridescent owing to tarnish. Bismuth minerals are very generally mixed with other metalliferous minerals, and indeed certain ores of tin, tungsten, lead, silver, copper and cobalt actually constitute the most important practical sources of bismuth. In the oxidized portions of bismuth ore deposits, the earthy, straw-coloured

Bismuth ochre . . . Bi_2O_3

occurs.

The principal ores of bismuth are found in the tin-mining districts of Bolivia, where the bismuth minerals are intimately mixed with compounds of tin and other metals. Certain copper ores in California contain notable amounts of bismuth. Some of the tungsten ores of Southern China are distinctly bismuthiferous, whilst considerable deposits of bismuth minerals—often associated with tungsten—occur in Queensland, New South Wales, and Tasmania.

Outside the Pacific circle, bismuth is to be found in many cobalt-mining districts. The complex ores of the Temiskaming district of Ontario, which contain cobalt, nickel, arsenic and silver, also contain bismuth, often, like the silver, in the native state. Bismuth is to be found in some of the mines of Saxony and Bohemia ; in the Saxon mines the bismuth is partly present in the elementary condition, and partly as sulphide. Considerable quantities of bismuthiferous ores also occur in Spain, Rhodesia, and India.

In some cases where small amounts of bismuth occur in the ore of another metal, it exists—at least in part—within the same crystals as the second metal. Thus bismuth appears to be capable of existing in galena crystals, apparently in a state of solid solution.

METALLURGY AND USES

The existence of bismuth in the ore of another metal—instead of adding to the value of the ore—usually detracts from it, since the presence of bismuth in the metal obtained by smelting such an ore is liable to cause mechanical weakness ; for instance, copper containing a mere trace of bismuth suffers from pronounced intergranular fragility.

Consequently the separation of bismuth from the principal metal in the ore must, perforce, be carried out at some state in the metallurgy. In the case of the ores of tin and tungsten, the bismuth—which occurs in distinct minerals—is separated from the cassiterite or wolfram in the preliminary ore-dressing operation. Consequently, a great deal of " bismuth concentrate " is produced in Bolivia as a by-product of the concentration of the tin ores mined in that country, whilst smaller quantities are produced in Australia and Tasmania, as well as in the tungsten-mining region of China. On the other hand, where bismuth occurs in the ores of copper, lead and silver, bismuth is usually allowed to remain in the metal until the last stage of smelting, and is finally eliminated when the metal is refined. The anode slimes produced in the electrorefining of copper, and those produced in the Betts electrolytic desilverizing process for lead, are often rich in bismuth, and form an important source of the metal.

Production of Metallic Bismuth from Concentrates. The bismuth concentrates from Bolivia, China and Australia are shipped partly to England and partly to the United States for smelting. The bismuth occurs largely as sulphide, although it is already partly in the elementary condition.

The conversion of the crude sulphide to the metal is carried out in a reverberatory furnace. The sulphide is subjected first to oxidizing conditions until partly converted to oxide, which is, in the second stage, reduced by carbon. Iron is often included in the charge—no doubt to remove residual sulphur; and fluxes, such as sodium carbonate, as well as lime and iron oxide, have usually to be added so as to produce a slag having a conveniently low melting-point.[1] An unduly high temperature causes losses by volatilization and should be avoided.

Where—as is the case in certain concentrates treated in Germany, derived from Saxon and other cobalt-ores—the bismuth exists mainly in the metallic condition, it can largely be separated by a simple liquation process ; but even there it is stated that the liquation process has, to a large extent, been abandoned, as it fails to remove the combined bismuth.

All bismuth obtained by thermal processes is very impure, and may contain lead, arsenic, antimony, and copper. A good deal of purification can be effected by the liquation of the crude product, and a further amount of arsenic can be removed as the volatile oxide by melting under oxidizing conditions ; under more drastic treatment (e.g. poling) antimony also can largely be removed. Where bismuth of fairly high purity is desired, however, it is preferable to use the product obtained from the electrolytic lead-refinery.

Production of Metallic Bismuth from Anode Slimes derived from the Electrolytic Refining of Lead and Copper. A large proportion of the bismuth manufactured in America is derived from the anode slimes obtained in the Betts process of desilverizing lead.[2] In fact it is largely due to this separation of

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[1] A. T. Ward, *Min. Ind.* 28 (1919), 56.

[2] J. M. Hill, *U.S. Geol. Surv. Min. Res.* (1918), I, 195; J. B. Umpleby, *U.S. Geol. Surv Min. Res.* (1917), I, 29.

bismuth from the lead that the Betts process is able to compete with the Parke process, which is cheaper to conduct, but which leaves much of the bismuth in the lead.

The anode slimes contain bismuth, antimony, arsenic, silver, and traces of gold, as well as residual lead. They are first treated in a suitable manner to remove the more oxidizable constituents, for instance, by fusion with a mixture of sodium hydroxide and sodium carbonate—a method which removes arsenic and lead; if much copper is present, sodium sulphide is added to the melt in order to remove that metal also. The residue, consisting mainly of bismuth (94 per cent.) with silver and gold, is cast into slabs, which are made the anodes in a second electrolytic refining process carried out in porcelain tanks. The electrolyte consists of bismuth chloride solution kept clear with an excess of hydrochloric acid, and the cathodes are of graphite, or—in some refineries—of pure bismuth obtained from a previous run. Bismuth is dissolved at the anode and deposited on the cathode, whilst the more noble metals gold and silver are left as anode slimes. If a suitable current density is used the cathodic deposit is very fairly pure, and consists of beautiful dendritic crystals of bismuth, which may be detached from the cathode from time to time and melted down; if, however, the solution becomes locally depleted of bismuth, or if it is not sufficiently acid, the deposit is black, spongy, and useless.[1]

The anode slimes are usually caught in porous boxes which surround the anodes; they are washed with hydrochloric acid to remove bismuth and antimony, and are then melted down to give a crude silver-gold bullion.

The recovery of bismuth from the anode slimes obtained in the copper refineries[2] is of much less importance, but nevertheless furnishes an appreciable part of the world's supply of bismuth.

Alloys of Bismuth.[3] Bismuth has no uses in the uncombined state, being altogether too brittle. The alloys of bismuth with other easily fusible metals—although not possessing specially good mechanical properties—are of value in possessing remarkably low melting-points. If we alloy bismuth (M.P. 270°) with lead (M.P. 327°) in suitable proportions we can get a eutectic mixture melting as low as 127° C., far below the melting-point of either pure metal. Similarly, if we alloy bismuth with tin (M.P. 232°) in the eutectic proportions, an alloy melting at 133° C. is obtained; the eutectic of tin and lead melts about 182° C. But by alloying bismuth

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[1] A. Mohn, *Electrochem. Ind.* **5** (1907), 314.

[2] L. Addicks, *Met. Chem. Eng.* **17** (1917), 169.

[3] See also A. T. Ward, *Min. Ind.* **28** (1919), 55.

(52 per cent.), tin (16 per cent.), and lead (32 per cent.), we can get a "ternary eutectic," melting at a still lower temperature, namely, 96° C.[1] Lower than this, we cannot go with only these three metals; but by adding a fourth metal, cadmium, still more fusible alloys can be arrived at. Numerous alloys are known melting well below 100° C. Of these, Wood's metal, containing 50 per cent. bismuth, 25 per cent. lead, 12·5 per cent. tin, and 12·5 per cent. cadmium, may be mentioned; it melts about 71° C.

Alloys of this kind—designed to melt at specified temperatures—are used for the fusible plugs which operate automatic fire sprinklers, alarms, electric cut-outs and the like. They are occasionally used for obtaining casts of objects which would be destroyed if brought into contact with an ordinary fused metal. Bismuth amalgam has been employed in dentistry.

Many bismuth alloys expand very considerably—as does the metal itself—when they solidify. These alloys are occasionally used by printers, in the place of ordinary type metal, where a specially clear impression is needed.

Uses of Bismuth Compounds. Certain salts of bismuth, notably the basic carbonate, are very largely used in medicine. Apart altogether from the specific medicinal value of the salt, large quantities are consumed in connection with the X-ray examination of the stomach and œsophagus. Owing to its high atomic weight, bismuth is nearly opaque to X-rays. If a patient is given a "meal" containing bismuth carbonate or basic nitrate, and is then examined by means of the X-rays, a "shadow" will be thrown by the bismuth salts in his stomach on to the screen or photographic plate, which will serve to indicate the shape of the stomach and may provide valuable information regarding the presence of ulcers. Similarly, in the examination of the œsophagus (gullet) it is possible for the doctor to watch the passage of food (containing bismuth) down the œsophagus, by means of the shadow cast upon the screen; thus any obstruction present can be detected and investigated.[2]

"Bismuth ointment" is a well-known household article, whilst "bismuth-and-iodoform paste" was much used in the war for the treatment of wounds.

Other bismuth compounds are used in the ceramic industry, as an ingredient in certain glazes, which they render easily fusible. Bismuth is likewise used in the painting of porcelain and the staining of glass. One method of gilding porcelain after it has been

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[1] G. Charpy, *Comptes Rend.* **126** (1898), 1569.

[2] Several papers regarding the use of bismuth in X-ray work appeared in the *Brit. Med. J.* (1908), ii, 711–716. See also *Brit. Med. J.* (1914), i, 246.

glazed consists in applying with a brush a paint containing finely-divided gold, bismuth basic nitrate and borax, suspended in a suitable oil-medium. On comparatively gentle burning the bismuth salt and borax fuse and thus " fix " the gold powder to the glaze proper. The gold, after burning, is only dull, but it may be brightened by burnishing with agate or even with fine sand.

AUTHOR INDEX

SUBJECT INDEX

ABRIDGED FORM OF PERIODIC TABLE.

O.	IA.	IIA.	IIIA.	IVA.	VA.	VIA.	VIIA.	Transition Elements.			IB.	IIB.	IIIB.	IVB.	VB.	VIB.	VIIB.	O.
2 He	3 Li	4 Be	5 B											6 C	7 N	8 O	9 F	10 Ne
10 Ne	11 Na	12 Mg	13 Al											14 Si	15 P	16 S	17 Cl	18 A
18 A	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
36 Kr	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 —	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
54 Xe	55 Cs	56 Ba	57 La	58 Ce														
			↓ 57–71 Rare Earth Metals	↙														
				72 Ha	73 Ta	74 W	75 —	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 —	86 Nt
86 Nt	87 —	88 Ra	89 Ac	90 Th	91 UX_2	92 U												

See VOLUME II VOLUME III VOLUME IV of this work