THE PERIODIC TABLE.

PERIODS.		GROUP 0.	GROUP I	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period		2 He 4·002	1 H 1 0078 3 Li 6·940	4 Be 9·02	5 B 10 82	6 C 12·00	7 N 14·008	8 O 16·000	9 F 19·00	
Second short period		10 Ne 20 183	11 Na 22 997	12 Mg 24 32	13 Al 26·97	14 Si 28·06	15 P 31·02	16 S 32·06	17 Cl 35·457	
First long period	Even series	18 A 39·944	19 K 39·10	20 Ca 40·07	21 Sc 45·10	22 Ti 47·90	23 V 50·95	24 Cr 52·01	25 Mn 54·93	26 Fe 55·84 27 Co 58·94 28 Ni 58·69
	Odd ,,		29 Cu 63·57	30 Zn 65·38	31 Ga 69 72	32 Ge 72 60	33 As 74·93	34 Se 79 2	35 Br 79·916	
Second long period	Even series	36 Kr 82 9	37 Rb 85·44	38 Sr 87·63	39 Y 88·92	40 Zr 91·22	41 Nb 93·3	42 Mo 96·0	43 Ma .	44 Ru 101·7 45 Rh 102·91 46 Pd 106·7
	Odd ,,		47 Ag 107·880	48 Cd 112·4	49 In 114·8	50 Sn 118·70	51 Sb 121·76	52 Te 127·5	53 I 126·932	
Third long period		54 Xe 130·2	55 Cs 132·81	56 Ba 137 36	57 La 138·90	58 Ce 140 13 59 Pr 140·92	60 Nd 144·27 61 .	62 Sm 150·43 63 Eu 152·0	64 Gd 157·3 65 Tb 159 2	
Fourth long period			66 Dy 162·46 67 Ho 163·5	68 Er 167·64 69 Tm 169·4	70 Yb 173 5 71 Lu 175·0	72 Hf 178·6	73 Ta 181·4	74 W 184·0	75 Re 186·31	76 Os 191 8 77 Ir 193·1 78 Pt 195·23
Fifth long period	Even series		79 Au 197·2	80 Hg 200 61	81 Tl 204 39	82 Pb 207·22	83 Bi 209·00	84 Po [210]	85 ...	
	Odd ,,	86 Rn 222	87 ...	88 Ra 225 97	89 Ac ...	90 Th 232·12	91 Pa .	92 U 238·14		

A TEXT-BOOK OF
PHYSICAL CHEMISTRY.

VOLUME I.

GENERAL PROPERTIES OF ELEMENTS AND COMPOUNDS.

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With Frontispiece, 3 Plates and 198 other Illustrations.

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PREFACE.

To write a text-book of Physical Chemistry for advanced students is to court criticism. The task is much more formidable than would appear at first sight. Let him who doubts this try it for himself! To begin with, the whole subject has developed with such astonishing rapidity during the last few years that not the least problem confronting the author was that of selecting the most suitable themes for treatment. It is exceedingly difficult, in a rapidly moving field, to see things in their true perspective, and there is always a danger of over-emphasis in those sections which either interest the author most or are, for some reason or other, specially familiar to him. This is essentially a personal matter upon which, in all probability, no two authors would entirely agree. It can only be said that in selecting the material for this book the author has been guided by what he has found to be most helpful to his senior students at the Birmingham Technical College during the last ten years.

Again, it appears to be impossible to arrange the selected matter in perfectly logical sequence. An attempt has therefore been made to meet this disadvantage by providing a good index and frequent cross-references in the text.

Yet again, the author was confronted with the problem of deciding how much the reader might be expected to know when commencing to study this book. It has been assumed that he has already acquired a nodding acquaintance with the elements of physical chemistry, such as that required, say, for the London Intermediate Science Examination; but it has further been assumed that much of it has been forgotten and the fundamentals in particular have never been driven home. For this reason particular attention has been given to the contents of the first two chapters. If any reader finds that he is so familiar with the data therein that his memory needs no refreshment, so much the better for him. He can at once proceed to higher things.

Now shall the study of physical chemistry be purely abstract, or shall it be written as a really human story, with its bearing on modern problems of various kinds clearly indicated? The latter course has been chosen, and abstract theory has been sprinkled with concrete illustrations.

What about references? To have included full references to all the original papers consulted would have made the volume considerably more bulky and expensive. The author has therefore contented himself by giving, whenever desirable, the name of the investigator and the year of publication of the research. The student desiring to consult the original paper can easily hunt up the full reference in British Chemical Abstracts, and turn up the paper in a suitable library.

The author desires to express his great indebtedness to Messrs Adam Hilger, Ltd. for permission to reproduce figures 128, 129, and the photographs on Plate III; to Mr F. Twyman, F.R.S., Dr F. Simeon and Dr A. Harvey, of the Staff of Messrs Adam Hilger, Ltd., who have kindly read through Chapter XV and offered most helpful suggestions; to Dr S. R. Carter of Birmingham University, and Dr J. C. Duff and Mr R. H. Vallance, M.Sc., of this College, who have read through both the manuscript and the proof sheets and given invaluable help in one way and another. Finally, the author's best thanks are due to the Publishers, who have assisted him in every possible way.

The author begs to conclude with a brief quotation from the Preface to the *Principia* written by his great name-sake, Sir Isaac Newton, some years ago:

"I heartily beg that what I have here done may be read with candour and that the defects I have been guilty of upon this difficult subject may be not so much reprehended as kindly supplied and investigated by new endeavours of my readers."

J. NEWTON FRIEND.

THE TECHNICAL COLLEGE,
BIRMINGHAM,
September, 1932.

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PHYSICAL CHEMISTRY.

VOLUME I.

GENERAL PROPERTIES OF ELEMENTS AND COMPOUNDS.

CHAPTER I.

UNITS AND FUNDAMENTALS.

What is Physical Chemistry?—An ancient native name for Egypt is *Khem*, which signifies *black land*, and probably had reference to the black mud left by the Nile after its periodic overflows. The Greeks and Romans were greatly impressed by the skill manifested by the Egyptians in the working of metals, and referred to it as the "Art of Khem." This expression "Khem" has come down to us through the Arabic as *Alchemy* and, later, *Chemistry*. The modern science of metallurgy thus approaches very closely to the original conception of chemistry.

It is generally admitted that we are surrounded by something concrete, which we have agreed to call **matter**. As a working definition matter may be defined briefly as *that which can occupy space*. This does not commit us as to the composition or structure of matter, about which we shall learn more later. Many forms of matter exist, and all are capable of undergoing various changes, which may, for convenience, be divided into two types or classes, namely, **Physical Changes** and **Chemical Changes**. It is in the province of Physics to study the former, whilst the latter are dealt with by the science of Chemistry. There is no hard and fast line of demarcation between these two sciences, and it is not always easy to distinguish between physical and chemical changes; indeed, the two often occur at the same time. Generally speaking, however, the former are reversible and do not result in the production of new forms of matter, whilst the latter are usually more profound in character, inasmuch as the particular kinds of matter initially concerned in them may disappear and their place be taken by fresh bodies possessing entirely new properties.

An example will make this clear. Mercury or quicksilver is a mobile, silvery liquid, of high density and low melting-point. When dipped into liquid air it stiffens into a solid mass, like silver, crystalline, malleable and ductile. This is a physical change and, on warming to the ordinary temperature, the metal returns to its original liquid condition. If, however, it is heated in air for a considerable time at a temperature slightly below its boiling-point, a chemical change takes place, and a new red body appears on the surface of the mercury. The surrounding air has taken part in this change, for if the experiment is carried out in a closed vessel, the red body eventually ceases to be formed, and the gas which remains (mainly nitrogen) is found to differ from ordinary air, since it extinguishes a lighted match. When the new red body (mercuric oxide) is heated in a tube it darkens considerably in colour, and ultimately becomes almost black. This is only a physical change, and, on cooling, the body resumes its former appearance. A chemical change occurs, however, when the body is more intensely heated; mercury is observed on the cool parts of the tube, and a colourless gas (oxygen) is produced that is easily shown to differ from ordinary air since a splint of wood that is just glowing in air bursts into flame when plunged into the gas, and if the heating is prolonged sufficiently, the red body completely disappears. This experiment is of very special historical interest, as both Scheele and Priestley, during the years 1771 to 1774, were led independently to the discovery of oxygen by heating red mercuric oxide, or "mercurius calcinatus per se," by concentrating the sun's rays upon it with a lens.

A chemical change also takes place when a little mercury and sulphur are rubbed together vigorously in a mortar. Much of the mercury and sulphur disappear, and a new black body (mercuric sulphide) makes its appearance.

Chemical changes are a matter of common observation in daily life; the burning of coal, oil and gas, and the decaying of dead vegetable and animal matter are familiar processes which are readily seen to come under this heading.

Physics and chemistry are closely interwoven in that branch of science known as **Physical Chemistry**, which deals essentially with the nature of the mechanism of chemical changes. For this reason the science is frequently defined as *the application of physical methods to the elucidation of chemical problems.*

Laws and Hypotheses.—A scientific *law* is a generalisation, the truth of which can be demonstrated by experiment. On the other hand there are many generalisations which we have every reason to believe are true, but which cannot be confirmed by direct experiment; these are termed **hypotheses**. Sometimes an attempt is made to distinguish between hypothesis and theory. The line of demarcation is not very definite, but in general it may be stated that a **theory** embodies the application of certain hypotheses. For example, Dalton's Atomic Theory is an attempt to explain certain chemical facts by means of the hypothesis that matter consists of atoms possessing well-defined properties.

Mixtures and Homogeneous Substances.*—Simple inspection reveals the fact that many substances do not possess identical properties throughout their mass. Thus, for example, granite is seen to consist of three different materials, known to the mineralogist as quartz, mica and felspar. Upon crushing the granite into small fragments the three materials become mechanically separated. Such substances as granite, therefore, are termed **mixtures**, and are said to be **heterogeneous**.

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* It is a fundamental law that when a number of *bodies* are found to agree exactly in a few of their properties, further examination shows them to agree exactly in all their properties; such bodies are said to be specimens of one and the same *substance*. The "substance" is therefore a conception derived by abstracting the properties common to all its specimens. By *properties* or specific properties is here understood those, such as colour, hardness, specific gravity, etc., which are the same in all parts of the bodies, excluding the *attributes* of mass, shape, etc., which differentiate the different specimens, and the *conditions* of pressure, temperature, etc., which may be altered at will.

On the other hand, a substance, such as Iceland spar, which ordinary observation does not show to consist of different parts, is said to be **homogeneous** ; the minutest portion that can be detached mechanically possesses the same specific physical properties as does the substance in bulk. A homogeneous mass is also referred to as a **phase**.

Solutions.—If a small quantity of common salt be added to water, it disappears, and, either as the result of long standing or of stirring, a homogeneous liquid mass is obtained, termed a **solution** of salt in water. If further additions of small amounts of salt be made, they too disappear, until eventually a limit is reached, after which further quantities of salt cease to disappear or **dissolve**, and remain in the solid state. The solution is then said to be **saturated** with the salt. The salt is termed the **solute** and the water the **solvent**. Common salt and water may thus be brought together in any proportions between certain limits, with the production of a homogeneous liquid. Moreover, continuous variations in the relative amounts of salt and water are associated with continuous changes in the physical properties of the resulting liquid. In this instance, the inferior limit to the amount of salt is zero ; the superior limit is found to vary both with temperature and pressure.

Although the constituents of the solution, salt and water, cannot be detached mechanically, as in the case of a heterogeneous mass, the separation can nevertheless be effected by physical means, namely, by causing one of the bodies to undergo a change of state. For instance, by supplying heat to the solution the water may be converted into vapour and thereby separated from the salt, which remains in the solid state. Or, by cooling the solution, water may be continuously removed as ice, until, in this instance, after the remaining solution has reached a certain concentration, further cooling results in the production of a heterogeneous solid mass of ice and salt.

A **solution**, then, may be defined as *a homogeneous mass, the composition of which may undergo continuous variation (between the limits of its existence), and which may be separated into two (or more) homogeneous substances by processes involving change of state.* This definition does not restrict solutions to any particular state of matter. Accordingly there may be gaseous, liquid and solid solutions, and a substance is classed as a solution when, by processes involving change of state, it can be separated into a number of other substances A, B, C, . . ., and forms one member of a series of substances the compositions of which range over all the possible proportions of A, B, C, . . . comprised between certain limits.

Solutions are usually classed as mixtures, being referred to as "homogeneous mixtures" in order to distinguish them from the class of mixtures previously mentioned.

Elements and Compounds.—The word *element* is stated to be derived from the three letters L, M, N, these being used in much the same manner as the letters A, B, C, to denote rudiments of things. The so-called "Aristotelean elements," Fire, Air, Earth and Water, had been postulated by Empedocles at least half a century before Aristotle was born. These were termed the "roots" of all things, and were regarded as homogeneous, indestructible and unchangeable ; from their admixture arose the different substances with which we are familiar. But whilst Empedocles regarded the four "elements" as tangible and concrete bodies, Aristotle (384 to 322 B.C.) appears to have viewed them as *qualities* or *essences*, which could permeate matter and thus yield different substances. They were not therefore quite identical with the material fire, air, earth and water, as we know them.

A nearer approach to the modern conception of an element was that of Anaxagoras (500 to 427 B.C.), who assumed as many elements as there were simple substances. As, however, simple physical changes such as mechanical division and solution, and such changes as could be effected by varying the temperature, were practically the only means of separating substances, the number of simple substances was, of necessity, inordinately large.

The word "element" was first used in its modern significance by Boyle (1627 to 1691), and was clearly defined by Lavoisier, in 1789, as implying *a substance that cannot be split up by any known means into anything simpler.*

The same idea may be expressed in another way, namely, *an element is a distinct species of matter that has not yet been proved to be composite.*

Many substances that were regarded as elementary in Lavoisier's time have since been found to be composite, but these do not affect the definition. Approximately ninety elements are known to-day, and a list of their names, symbols and atomic weights will be found on pp. 35, 36. Of these, hydrogen and ten non-metallic elements are gaseous at the ordinary temperature, bromine and mercury are liquids, the remaining elements being solids under ordinary circumstances. Only a few occur in nature in the free state. Some elements are much more abundant than others; the following table gives, according to F. W. Clarke, the average composition of terrestrial material (including the earth's crust, the ocean and the atmosphere):

Element.	Per cent.	Element.	Per cent.	Element.	Per cent.
Oxygen	49·8	Potassium	2·28	Barium	0·09
Silicon	26·1	Hydrogen	0·95	Manganese	0·07
Aluminium	7·34	Titanium	0·37	Strontium	0·03
Iron	4·11	Chlorine	0·21	Nitrogen	0·02
Calcium	3·19	Carbon	0·19	Fluorine	0·02
Sodium	2·33	Phosphorus	0·11	Remaining elements	0·44
Magnesium	2·24	Sulphur	0·11		

A *compound* consists of two or more elements chemically united, and differs from a mixture in that its properties are entirely different from those of its constituents.

The elements present in a compound are said to be in a state of *chemical combination*, and the *chemical composition* of the compound is a statement, usually expressed in percentages, of the relative proportions in which the elements occur in that compound. It may be stated at once that, as would be expected, bodies which possess identical physical properties are also found to possess identical chemical composition; the converse, however, is not true.

We are naturally led to inquire as to what evidence exists that the substances we now term elements are really such, for the fact that they may so far have resisted chemical decomposition is not in itself conclusive. The evidence rests upon three main planks, namely:

(1) Leaving out of consideration the elements which are gaseous at ordinary temperatures, the atomic heats of the elements do not vary very greatly from the mean value of 6·4. This is **Dulong and Petit's Law** (1819) (see p. 216). On the other hand the molecular heat of a compound is the sum of the atomic heats of its constituent elements, and must therefore be a multiple of 6·4—**Kopp's Law** (1864) (see p. 224).

(2) When the elements are arranged in the order of increasing atomic weight, their general properties show a tendency to recur at regular intervals—the **Periodic Law** (Chap. XVI). These "periods" limit the number of possible elements, and afford no room for compounds or for radicals in what is known as the Periodic Table (see Frontispiece). For example, Berzelius in 1831 concluded that vanadium belonged to the same family as chromium and molybdenum. This conclusion was subsequently shown by Roscoe, in his classical researches on vanadium (1868 to 1870), to be an error, because Berzelius had been handling the oxide VO, when he thought he was dealing with the free metal. This misapprehension was due in part to the extreme difficulty of reducing vanadium compounds to the metal, and in part to the readiness with which the vanadyl radical enters into reactions like a simple metal. Roscoe established the intimate relation existing between vanadium and the members of the nitrogen family. This is confirmed by the Periodic Table (Frontispiece), reference to which shows that a very suitable place is afforded for an element like vanadium with an atomic weight of 51 at the head of Sub-group A in Group V, but there is no space for the radical VO, of "atomic" weight 67, which would locate it between zinc and gallium.

(3) The most convincing evidence, however, lies in the **atomic numbers** of the elements (see p. 337). These are determined from the X-ray spectra, and coincide with the serial numbers of the elements in the ideal periodic table (Frontispiece). For each element the X-ray spectrum is perfectly definite and independent of the state of chemical combination. Compounds do not yield distinct spectra, but those of their constituent elements. Thus, the vanadium monoxide referred to in the preceding paragraph yields the spectra of vanadium and oxygen, and is thus immediately seen to be composed of these two elements.

Metals and Non-metals.—The division of the elements into metals and non-metals is merely one of convenience. It is, moreover, imperfect, for no clearly defined line of demarcation between the two classes can be drawn. The non-metals include the gaseous elements and bromine, sulphur, selenium, tellurium, phosphorus, arsenic, carbon, silicon, boron and iodine ; the metals comprise the remaining elements. The names of the metals and non-metals discovered during the last hundred years usually end in **-ium** and **-on** respectively; the names " selenium " and " tellurium " do not conform to this rule, since these substances were originally classed among the metals. " Helium " also is exceptional, but this arises from the fact that the element received its name in 1868, long before its isolation, and when, indeed, the only evidence of its existence lay in the yellow D_3 line observed in the solar chromospheric spectrum. It would be more logical to re-christen the element *helion.*

The *metals* as a class are distinguished both by their physical and chemical properties. They are opaque in bulk, more or less malleable and ductile, and are good conductors of heat and electricity. Formerly all metals were considered to possess high densities, an idea that was abandoned when Davy isolated sodium and potassium and demonstrated their metallic character. The metallic nature of mercury was admitted in 1759, when it was first frozen.

In so far as their chemical properties are concerned it will suffice to add that with oxygen the metals yield basic oxides which react with acids to produce salts.

The *non-metals*, on the other hand, comprise, with perhaps the exception of hydrogen, all those elements that are gaseous at the ordinary temperature, one liquid, namely bromine, and a series of solids more or less brittle in character, varying in colour, and in general non-conductors of heat and electricity. Some of them, notably the halogens, possess powerful odours. They usually dissolve in carbon disulphide, they unite with oxygen to yield acidic oxides, and, in general, they form stable compounds with the metals, either alone or in conjunction with oxygen.

The difficulty of drawing a sharp dividing line between the metals and non-metals lies in the fact that in several cases the properties of the metals and non-metals overlap in an element. Thus zinc, bismuth and antimony are brittle, and hence were regarded throughout the Middle Ages as semi-metals. Again, iodine and tellurium are lustrous, whilst silicon, graphite and, at a red heat, boron, readily conduct electricity. Border-line elements such as these are frequently termed **metalloids,** a term introduced by Erman and Simon in 1802. Usually, the metalloids possess the form or appearance of metals, but are more closely allied to the non-metals in their chemical behaviour. Confusion in the nomenclature has been caused by the fact that in 1811 Berzelius employed the term " metalloid " as synonymous with " non-metal," and French chemists still use it in that sense.

Although to the chemist the elements are the ultimate forms of matter, from which other substances are built up, it does not follow that they do not possess a complex structure. In recent years elements have been discovered which *spontaneously disintegrate.* These changes, however, which proceed at definite rates in accordance with a simple law, would seem to be beyond the power of the chemist to control.

Physical Magnitudes.—In order to obtain a conception of the magnitude of a physical quantity a suitable **unit** must be chosen; further, each different kind of physical quantity requires its own particular unit. The magnitudes of these units may be, and often are, purely arbitrary. Experience has shown, however, that very definite relationships frequently exist between different kinds of physical magnitudes, so that it is possible, by carefully choosing certain units as fundamentals, to derive other units from them. A group of fundamental and derived units is known as an **absolute system of units**—a term introduced by Gauss in 1832.

In physics and chemistry the **fundamental units** generally employed are those of length, mass or quantity of matter, and time, which may be designated [L], [M] and [T] respectively. In the **c.g.s. system** the units employed are the centimetre, gramme and second. This system is used almost exclusively in the present volume, but where other units are in common use they may be referred to in order to familiarise the student with their relative magnitudes.

Derived Units.—In order to make a record of any length, mass or period of time, two items of information must be given, namely, (i) a term indicating the unit employed, and (ii) a numerical expression stating the number of times the unit is contained in the given quantity. Thus, the distance between two points may be written as l [L], where [L] represents the unit of length and l is the numerical item. In c.g.s. units this would normally be written as l cm. For the unit of area we might write [A]. But it is convenient to choose as our unit the area of a square the sides of which are each of unit length, so that [A] is a *derived unit*, and may be replaced by [L²]. Since the unit of area is independent of the units of mass and time, this fact may be stated as follows :

$$[A] = [L^2 . M^0 . T^0].$$

The right-hand portion of this expression gives what are termed the **dimensions** of the unit of area with respect to length, mass and time. Similarly the dimensions of the unit of volume [V] are $[L^3 . M^0 . T^0]$.

Another derived unit of great importance to the physical chemist is that of velocity, or speed, [S]. It is obvious that [S] is independent of the unit of mass, but it does depend upon the units of length and time. Since

$$\text{Speed} = \frac{\text{Length}}{\text{Time}},$$

it follows that the dimensional equation for speed with reference to length, mass and time is

$$[S] = [L^1 . M^0 . T^{-1}].$$

Other derived units are dealt with in succeeding sections as occasion requires.

Units of Length and Volume.—It has long been recognised that for purposes of trade certain standard measures are desirable. Thus, in Holy Writ we read that there were deposited in the Ark of the Covenant Aaron's Rod, a Golden Pot and Two Stones (Hebrews ix, 4). These were probably the Hebrew standards of length, volume and "weight" or mass, respectively. Under the Roman Empire standard weights and measures were kept in a temple ; they were lost after the fall of Rome.

Two standard units of length are recognised in Great Britain, namely the **Imperial Standard Yard** and the **Metre.**

Prior to 1834 the *standard yard* was in the custody of the Clerk to the House of Commons, but in the fire of 1834 at the House the standard was destroyed, and as no recognised standard copies had been prepared, the problem of replacing the standard yard was one of considerable difficulty. This was eventually surmounted, however, and in 1855 the yard was defined as follows :

> "The straight line or distance between the centres of the middle transverse lines in the two gold plugs in the bronze bar deposited in the Office of the Exchequer shall be the genuine standard yard at 62° F., and if lost it shall be replaced by means of its copies."

The composition of the alloy used in the construction of the bar was Cu : Sn : Zn as 16 : 2·5 : 1. The standard yard is now preserved at the Standards Department of the Board of Trade in accordance with the Weights and Measures Act of 1878. There were originally four official copies deposited elsewhere. One is at the Royal Mint, another in the care of the Royal Society, one at the Royal Observatory, Greenwich, and another buried in the wall of the New Palace at Westminster. A fifth was added in 1886 and deposited at the Board of Trade (Standards Department). Copper alloys are now known not to be suitable for standards of length, and a platinum-iridium copy of the standard was prepared in 1902.

The *metre* was recognised by Parliament in 1897, and owes its origin to the French Republic of 1795. It was decided that the metre should be a physical constant, namely exactly one ten-millionth (10^{-7}) of the Earth's quadrant, or, more precisely, of the distance between the North Pole and the Equator measured over the surface of the Earth along the meridian passing through Paris. It was thought that by this means if ever the standard were lost it could be replaced. The actual measurements were carried out by Delambre and Méchain between Barcelona and Dunkirk, and to Borda was entrusted the task of constructing the standard metre. It was soon realised, however, that, if the metre were defined as above, every time a more accurate determination was made all the copies in general use would require altering, which would be disconcerting to trade and almost fatal to scientific progress. The metre was, in consequence, converted into a purely arbitrary unit, like the British yard, and was defined as the distance between the ends of Borda's platinum rod at 0° C. (According to the latest measurements the *mean* meridian quadrant measures 10,002,100 metres.) The *International Prototype Metre* is a copy of the original Borda platinum standard—the *mètre des archives*. It is made of an alloy of 90 per cent. Pt and 10 per cent. Ir, used also for the International Kilogram (see p. 10), this alloy being hard and durable, very resistant to corrosion, and possessed of a low coefficient of expansion with rise of temperature. The metre is here the distance between the centres of two lines engraved upon the standard, when measured at 0° C. Platinum-iridium copies of this metre, called *National Prototype Metres*, were made at the same time and distributed about 1889 to the different Governments, and the British copy is housed at the Standards Department of the Board of Trade. The metre length does not differ greatly from the yard, but it is a more convenient unit because its multiples and sub-multiples are decimally connected, whereas the British measures are inconveniently complicated. The legal equivalents, those legalised by the Order in Council of May 19, 1898, are as follows :

$$1 \text{ metre} = 1{\cdot}0936143 \text{ yards},$$
$$1 \text{ yard} = 0{\cdot}914399 \text{ metre}.$$

For scientific purposes the *centimetre* is largely used as the unit of length, but in measuring very minute distances the following terms are employed :

1 micron, μ, $= 10^{-3}$ millimetre,
1 millimicron or micromillimetre, $\mu\mu$ or mμ, $= 10^{-6}$ „
1 Ångström unit, Å or simply A, $= 10^{-8}$ centimetre.

The first two units are largely used for measurements connected with substances in the colloid state (see Chap. XXII). The Ångström unit is employed in measuring the wavelength of light and the distances between atoms within a molecule.

The international prototype metre has been measured in terms of the wavelengths of three lines in the cadmium spectrum as determined in dry air at 15° C. and 760 mm. pressure. The three lines occur in the red, green and blue regions respectively; the metre is found equal to 1,553,164·1 wavelengths of the red ray. It would thus be possible to replace the standard with great accuracy, even if all its copies were destroyed with it.

It is sometimes useful to remember that the diameter of a halfpenny is one inch, or approximately 25·4 mm.

The unit of **volume** may be a derived unit, and once the unit of length has been chosen, the volume of a cube each of whose sides is of unit length becomes automatically the unit of volume. In other words the dimensions of volume are $[L^3]$. In the c.g.s. system the unit of volume is the **cubic centimetre,** variously written as c.c. and $cm.^3$ Another unit in common use for measuring the volumes of gases and liquids is the **litre.** Although very nearly equivalent to 1000 c.c., the litre is entirely independent of the metric units of length, being the volume occupied by a given, arbitrary mass of water, under certain standard conditions (see p. 11). For expressing molecular dimensions the **Ångström unit of volume,** namely 10^{-24} c.c., is sometimes a convenient quantity to use.

Units of Mass.—Two standards of mass, as of length, are recognised in Great Britain, namely the **Imperial Standard Pound (Avoirdupois)** and the **Kilogram.** The former is the unit of the British System and the latter of the Metric System. The pound avoirdupois has been in use in Great Britain continuously since the fourteenth century, although not as a standard, and its mass has varied slightly at different times.

Prior to the fire in the House of Commons in 1834, the pound troy was the legal standard, and was in the custody of the Clerk to the House. Its loss in the fire, however, led to the appointment of a Commission to consider the question of standard weights and measures, and as a result of the Commission's report in 1841, it was decided to take the *pound avoirdupois* as the standard and fix its mass definitely as 7000 grains. A standard " weight " was therefore prepared under the direction of a Committee in the form of a cylinder of platinum marked " P.S., 1844, 1 lb." The letters P.S. mean " Parliamentary Standard." This standard is kept at the Standards Department of the Board of Trade, and five copies are kept, one each at the five places where the five standard yards are deposited (see p. 8), in the custody of the Warden of the Standards. The Act of Parliament (1878) states that the weight *in vacuo* of the platinum cylinder shall be the legal standard measure of weight from which all other weights and measures having reference to weight shall be ascertained.

The *grain,* referred to above, is the smallest British unit of mass. It is supposed to represent the average mass of a grain of corn, whence its name from the Latin *granum,* seed. It is now defined as one seven-thousandth part of the standard pound. Old English weights were based upon the wheat grain, thirty-two of which were at one time equal in weight to one penny. Thus, during the reign of King Henry III (1267) an Act was passed which said :

> " An English peny called a sterling round and without clipping, shall weigh thirty-two wheat corns in the midst of the ear ; and 20d do make an ounce and 12 ounces one pound and eight pounds do make a gallon of wine, and eight gallons of wine do make a London Bushel which is the eighth part of a Quarter."

Gold, silver and precious stones are still weighed by the system of Troy weights. This system is named after the French town of Troyes, whence it was brought to England. The system starts from the barleycorn, 24 barleycorns being equal to one pennyweight.

At one time nearly every town in England was bound by law to keep a set of standard weights. Many of these weights are now lost, but the city of Lancaster has a set dating from the time of King Henry VII (1485 to 1509).

The *kilogram* is the mass of a lump of platinum prepared by Borda to represent the mass of a cubic decimetre, that is 1000 c.c., of pure water at the temperature of its maximum density, namely 4° C. It is called the " *Kilogram des Archives*." This kilogram was prepared at the close of the eighteenth century with the very greatest care, but during succeeding years methods of measurement became increasingly refined and by 1872 it was realised that the experimental error in the determination was greater than was permissible for accurate work. So instead of defining the kilogram as the mass of 1000 c.c. of water under the foregoing conditions, it was decided to make the mass of the platinum the arbitrary unit. The *International Prototype Kilogram* is the mass of a cylinder of platinum-iridium alloy (90 : 10) similar in composition to the alloy used in the preparation of the metre, and for similar reasons ; it is a copy of the original Borda standard. Copies of this standard have been prepared and distributed as *National Prototype Kilograms* to different Governments. The British copy, made of iridio-platinum, is cylindrical in shape, and is kept at the Standards Office.

In the c.g.s. system the unit of mass is the **gramme**, which is one-thousandth part of the kilogram.

The connection between these units and the British unit is complicated. Thus the legal equivalents (1898) (see p. 9) are :

1 pound = 0·45359243 kilogram,
1 kilogram = 2·2046223 pounds.

From the foregoing it is evident that the kilogram is now an entirely arbitrary unit, in no way connected by definition with the unit of length. Hence any connection must be determined experimentally. Now for purposes of trade and science alike, volumetric measurements of both gases and liquids are extensively used. But whilst it is difficult, and often extremely so, to determine accurately the capacity of a hollow containing vessel by direct measurement of its internal dimensions, it is relatively easy to determine with accuracy the mass of a given liquid required to fill the vessel. Hence it is not surprising that volumetric units have come into use which are not defined with reference to length, but to the volumes occupied by specified masses of a given liquid—usually water. Thus, for example, the **gallon** is the volume occupied by a mass of 10 lb. or 70,000 grains of distilled water, weighed in air against brass weights, at 62° F. The gallon is not used for high precision measurements. A **litre** is defined as the volume occupied by a mass of one kilogram of pure water at its temperature of maximum density and under normal atmospheric pressure. Since the kilogram is not exactly equivalent to 1000 c.c. of water, the litre, as defined above, is independent of the metric units of length. The most probable value for the litre in terms of the cubic centimetre is

$$1 \text{ litre} = 1000{\cdot}027 \text{ c.c.};$$

the estimated error does not exceed one unit in the third decimal place.

Whilst for most purposes the cubic centimetre may be regarded as one-thousandth part of a litre, the Joint Committee for the Standardisation of Scientific Glassware in 1924 unanimously recommended that, to avoid confusion, the thousandth part of a litre should be referred to as the **millilitre** or **mil** (ml.), and that standard volumetric glassware should be graduated in terms of litre and millilitre rather than of litre and cubic centimetre—a very sensible and logical procedure.

The use of metric weights and measures was legalised in Great Britain in 1897, and the connection between the metric and British systems is as follows:

$$\begin{aligned} 1 \text{ litre} &= 1{\cdot}76077 \text{ pints,} \\ &= 0{\cdot}220097 \text{ gallon;} \\ 1 \text{ gallon} &= 70{,}000 \text{ grains of water,} \\ &= 277{\cdot}274 \text{ cubic inches,} \\ &= 4{\cdot}5434 \text{ litres.} \end{aligned}$$

By **density** is understood the *mass of unit volume.* In the c.g.s. system it is the mass in grammes of 1 c.c. of a substance. In the case of gases, however, the unit of volume chosen is frequently the litre, as the mass of 1 c.c. is so small (see p. 116). The term **specific gravity** expresses a *ratio,* which is frequently termed the *relative density.* It represents the number of times heavier a substance is than an equal volume of water at the same or at another specified temperature. Thus, whilst D_{15} indicates the mass in grammes of unit volume of a substance at 15° C., the symbols S_{15}, S^{15}_{15} or ${}_{15}S_{15}$, and S^{15}_{4} or ${}_{15}S_{4}$, indicate that, bulk for bulk, the substance is S times as heavy at 15° C. as water at 15° C. or 4° C. respectively. The actual numerical difference between these two sets of figures is small at or near the ordinary temperature. For example, if the density at 15° C. of a substance is given as 5·0000 grammes per c.c., the specific gravity at 15° C. relative to water at the same temperature will be $5{\cdot}0 \div 0{\cdot}999126$ or 5·0044, since the density of water at 15° C. is 0·999126, whilst the specific gravity at 15° C. with reference to water at 4° C., *i.e.* S^{15}_{4}, is 5·0000, or numerically equal to the density at 15° C., since the mass of 1 c.c. of water at 4° C. is almost exactly one gramme.

Sometimes it is convenient to express gaseous densities relatively to the air. Under normal conditions of 760 mm. pressure and 0° C., the weight of a litre of air varies, as a rule, between 1·2927 and 1·2933 grammes, the variation being attributable to the fact that the air has not a perfectly constant composition. For this reason it is useless to determine with great accuracy the density of a gas relatively to air unless the composition of the latter is simultaneously ascertained.

For most purposes a mean value of 1·2930 at 0° C. and 760 mm. will be a sufficiently accurate figure to adopt.

The inverse of density is termed **specific volume**, which is thus the *volume of unit mass.*

For vapours and gases the litre is frequently chosen as the unit of volume, and the densities are defined as the masses of a litre of the substances under well-defined conditions (p. 116).

By **specific surface** is understood the *surface area of unit volume.* For example, the surface of a sphere is given by $4\pi r^2$, and its volume by $\frac{4}{3}\pi r^3$, whence

$$\text{Specific surface of sphere} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} = \frac{6}{d}.$$

In other words, a sphere of radius 3 cm. or diameter 6 cm. has unit specific surface. Similarly it may be shown that the specific surface of a cube is $6/l$, so that a cube with an edge 6 cm. long also has unit specific surface. To obtain a large specific surface it is essential to reduce at least one dimension. When this is done very thoroughly a film is produced. Reduction of two dimensions leads to a thread, whilst reduction of all three dimensions leads to the formation of fine particles. The following table shows the enormous increase in specific surface undergone by a cube of unit volume when decimally divided into smaller cubes :

Length of Cube Edge, l.	Number of Cubes, n.	Specific Surface, $6l^2n$ or $\frac{6}{l}$.
1 cm.	1	6 sq. cm.
1 mm.	10^3	60 ,,
1 μ	10^{12}	6 sq. metres.
1 $\mu\mu$	10^{21}	6000 ,,
0·001 $\mu\mu$	10^{30}	6 sq. kilometres.

It is clear that the specific surface is a factor of very great importance in many chemical and physical changes. For example, the purification of sugar with charcoal is largely a surface phenomenon. A manufacturer might purchase one cubic metre of charcoal consisting of, say, small cubes of 1 mm. edge. The total area would thus be some 6000 square metres, assuming no porosity. If, however, his granules had an edge of 1 μ, the total area would be some 6 million square metres, and the charcoal would thus be about 1000 times more active. The dependence of chemical activity upon the areas of the reacting bodies may be stated in terms of **Wenzel's Law**, namely that

the amount of chemical change in unit time is proportional to the absolute surface.

Units of Time.—The usual scientific unit of time both in the British and Metric systems is the **mean solar second.** It is usually defined as one 86,400th part of the mean solar day. The ordinary solar day is the somewhat variable interval of time between two successive transits of the sun across the meridian, and the mean solar day is the average interval between the successive transits of the sun across the meridian of any one place during a whole year. The sidereal day is the interval between two successive transits of the first point of Aries—one of the fixed stars—across any selected meridian, and is thus practically represented by the period of complete axial rotation of the earth with respect to the fixed stars ; it is very slightly shorter than the mean solar day, comprising 23 hours, 56 minutes, 4·09 seconds. It is used as a unit of time in astronomical work. The mean solar second is one 86,164·09th part of a sidereal day. Units of time based on the rate of rotation of the earth, however, are open to the objection that the rotation may not be perfectly constant. There is reason to believe that it is gradually, though at present inappreciably, slowing down, so that the day is gradually growing longer.

By **velocity** is understood the *rate at which a point changes its position*, and in order to measure its magnitude two facts must be known, namely the distance travelled and the time taken. Uniform velocity, u, in any given direction is measured by the distance, l, travelled over in a given time, θ. Whence

$$u = l/\theta.$$

By inserting the symbols for these units, the expression becomes :

$$u[\mathrm{U}] = l[\mathrm{L}] \div \theta[\mathrm{T}].$$

If l and θ are each unity, u must also be unity and we obtain the dimensional equation

$$[\mathrm{U}] = [\mathrm{L} \,.\, \mathrm{T}^{-1}].$$

The unit of velocity is thus a derived unit, of dimensions $[\mathrm{L} \,.\, \mathrm{T}^{-1}]$. The c.g.s. unit is 1 cm. per second.

Acceleration is *change in velocity.* When positive, the velocity increases ; when negative, the velocity decreases. Negative acceleration is thus a retardation or slowing up. Uniform acceleration is measured by the change in velocity of a particle in unit time. Thus, if a particle is moving with a velocity u_1 at any given instant, but changes its velocity to u_2 during the time θ, the acceleration, a, is given by the equation

$$a = \frac{u_2 - u_1}{\theta} = \frac{u_3}{\theta}$$

where u_3 is the change in velocity.

From this it is easy to derive the dimensional equation

$$[\mathrm{A}] = [\mathrm{U}][\mathrm{T}^{-1}].$$

Substituting for the derived unit of velocity in the dimensions found above, it follows that the dimensions of acceleration are

$$[\mathrm{A}] = [\mathrm{L} \,.\, \mathrm{T}^{-2}].$$

Acceleration is thus expressed in terms of distance travelled per second per second or per sec.^{2}

In the foregoing it has been tacitly assumed that the particle under consideration has moved in a straight line, that is, without change of direction. A moment's consideration will show that if, for example, the movement of a point on the end of the hand of a clock be described, the description must vary according to the way in which we view the motion. The point certainly moves over equal spaces in successive equal times, otherwise as an indicator of the passage of time it would be of little value; its velocity is therefore uniform. On the other hand, the direction of its velocity is continuously changing, so that from this point of view the velocity is variable. The speed with which the point moves round the circular face of the clock, divided by the radius, r, gives its **angular velocity,** ω, that is,

$$\omega = \frac{u}{r}.$$

The unit of angular velocity is one *radian* per second. A radian is the angle subtended at the centre of a circle by an arc of length equal to the radius; it equals 57·296°. The unit of **angular acceleration** is in consequence one radian per sec.^{2}

Acceleration due to Gravity.—Every substance possesses what is termed "weight"; this is only another way of saying that every substance is attracted to the earth. Now if a body a small distance above the surface of the earth is allowed to fall freely, experiment shows that it moves with a constant acceleration, designated as g. Since the earth is not a perfect sphere, but is flattened somewhat at the poles, the value for g rises as we travel north from the equator; but the particular value at sea level and latitude 45° N has been chosen as the standard—a purely arbitrary one. A line joining Turin (Italy), Bordeaux (France) and Ottawa (Canada) would lie on this latitude almost exactly, and at sea level the value for g is 980·617 cm./sec.^{2} or 32·172 feet/sec.^{2} The value for g likewise falls when a body is raised up above sea level, as the body is then further from the centre of the earth. The connection between g, latitude and height above sea level is given by **Helmert's formula** as follows:

$$g = 980{\cdot}617 - 2{\cdot}593 \cos 2\lambda - 0{\cdot}0003086h,$$

where λ is the latitude and h the height in metres above sea level. The value of g as calculated in this manner agrees fairly well with the observed values for many latitudes, although in the neighbourhood of large mountain ranges, such as the Himalayas, some discrepancy occurs. In the table opposite are given the values calculated for g at several places.

Newton's First Law of Motion states that

> *every body continues in its state of rest or of uniform motion in a straight line unless acted upon by some external* **force** *which compels it to change that state.*

As no formal proof, experimental or otherwise, can be given to the foregoing statement, it is clear, from the definitions of law and hypothesis already given (see p. 2), that strictly speaking this should be termed a hypothesis rather than a law. Common usage, however, compels us to refer to it as a "law." The reason we cannot demonstrate experimentally its truth lies in the impossibility of getting rid of all external forces during the motion of a body. An approximation to this state may be realised by projecting a smooth piece of hard dry

	Latitude, λ.	Height above Sea Level, h (metres).	g.
North Pole	90° 0′ 0″ N	0	983·210
Christiania Observatory .	59 54 42 N	25	981·90
Aberdeen University . .	57 8 58 N	21	981·68
Glasgow University . .	55 52 31 N	46	981·56
Copenhagen Observatory .	55 41 12 N	14	981·56
Manchester University . .	53 27 53 N	39	981·37
Birmingham Technical College	52 28 0 N	144	981·24
Leyden Observatory . .	52 9 20 N	6	981·26
Kew Observatory . . .	51 28 6 N	5	981·200
Paris Observatory . .	48 50 11 N	59	980·95
Montreal, McGill Observatory	45 30 24 N	57	980·64
Rome, College Observatory .	41 53 54 N	59	980·32
Washington Bureau of Standards	38 53 12 N	102	980·097
Cairo Observatory . .	30 4 38 N	33	979·32
Equator	0 0 0	0	978·024
Sydney Observatory . .	33 51 42 S	44	979·63
Cape Town	33 56 0 S	12	979·64

ice upon a level and smooth sheet of ice. The only forces acting on the piece of ice in the direction of its motion are the resistance of the air and the friction between the ice surfaces, and the less the magnitude of these factors the further the piece of ice will travel. Newton's hypothesis adapted to this special case is a kind of extrapolation ; it states that if the ice surfaces were perfectly smooth and if there were no resistance from the air and no other forces acting on the detached piece of ice, the ice would travel for ever in a straight line with uniform velocity. A very powerful argument in favour of the validity of the hypothesis lies in the fact that it is one of the pillars of the science of Dynamics, and hence of Astronomy. As the theoretical solutions we obtain to problems, applying this " law," agree with observation, we conclude that our fundamental assumption must be correct.

Newton's First Law provides us with a convenient conception of **Force,** explaining it as that which *tends to produce a change of motion in a body on which it acts.* We also gather from the law that a body has no innate tendency to change its state of rest or of uniform rectilinear motion. This is termed the **Principle of Inertia,** and we say that every body has inertia.

Newton's Second Law of Motion gives us a method of measuring force. It states that

the rate of change of momentum of a body is proportional to the impressed force and takes place in the direction of the straight line in which the force acts.

The product of mass and velocity gives us the " quantity of motion " or **momentum** of a body. The dimensions of this quantity are $[M . L . T^{-1}]$, and in the c.g.s. system momentum is expressed as gramme-centimetres per second. Any change in the momentum of a body must therefore be due to a change in velocity, since the mass remains constant, and hence the rate of change of momentum must be given by the product of the mass and acceleration. In other words, denoting the impressed force by f,

$$f=\frac{m(u_2-u_1)}{\theta}=ma,$$

from which the following dimensional equation may easily be derived :

$$[F]=[L . M . T^{-2}].$$

In the c.g.s. system the unit of force is the **dyne** (Greek *dynamis*, power), and is such as will produce an acceleration of one cm. per sec.^{2} in a mass of one gramme. As this unit is very small, the **gravitational unit** is frequently employed, namely the *weight of one gramme* at sea level and at a latitude of 45°. This is equal to 980·6 dynes, so that a dyne is very nearly equal to the " weight " of a milligram.

In the foot-pound-second system the unit of force corresponding to the dyne is the **poundal**. It is a much larger quantity than the dyne, and the relationship between the two can readily be calculated by making use of their dimensions. If [L], [M] and [T] refer to the dimensions of the dyne, and $[L_1]$, $[M_1]$ and $[T_1]$ refer to those of the poundal, then

$$\frac{\text{Poundal}}{\text{Dyne}}=\left[\frac{L_1}{L}\right]\left[\frac{M_1}{M}\right]\left[\frac{T^2}{T_1{}^2}\right].$$

$[L_1/L]$ is the ratio of the foot to the centimetre, namely 30·480 ; $[M_1/M]$ is the ratio of the pound to the gramme, namely 453·59 ; $[T^2/T_1{}^2]$ is unity, since the second is the unit of time in both cases. Hence the number of dynes equivalent to a poundal is the product of 30·480 and 453·59, or 13825·5 (approx.).

The gravitational unit of force in the British system is the *weight of one pound*, and is equal to 32·172 poundals, since g at sea level and 45° latitude is 32·172 feet/sec.^{2}

It will be noted that the dyne and the poundal are absolute units of force. They do not depend upon the value of g, which varies with the locality, whereas the gravitational units, namely the gramme weight and pound weight, do vary with this quantity.

Weight and Mass.—It is essential to distinguish carefully between weight and mass. Weight is a force and is expressed numerically by the product of the mass of a substance and the acceleration, g, due to gravity. We may write, therefore, $w=mg$. The weight of a substance is thus liable to vary with the locality, whereas the quantity of matter it contains, that is, its mass, remains unaltered. Thus, a mass of, say, platinum, weighing one kilogram in London, would have no weight at the centre of the earth, since the effect of gravity there is zero ; but if it happened to be in motion there, the same force would be required to stop it as would be necessary on the surface of the earth, for its mass would be unaltered.

From the definition just given it is evident that the weight of a substance at any one place other than the centre of the earth is proportional to the mass of that substance, and independent of the kind of matter composing the substance. We can therefore make a direct comparison of the masses of two substances by comparing their weights. For this purpose instruments known as **balances** are used.

Pressure is *force per unit area.* In the c.g.s. system the unit of pressure is termed the **bar** (Greek *baros*, weight), and represents the force of one dyne acting over an area of one sq. cm. This unit, however, is very small, and is sometimes replaced by the **megabar**, which represents 10^6 dynes per sq. cm. Frequently high pressures are measured in terms of the weight of a kilogram per sq. cm.; that is equivalent to 980,617 dynes per cm. or 0·9806 megabar at sea level and latitude 45°. Another convenient unit of pressure is that termed an **atmosphere.**

That the air possesses weight was first recognised apparently by Jean Rey, *c.* 1630, an observation that was confirmed by Torricelli in 1643 and by Pascal in 1648. Rey made his discovery by observing that tin, on calcination in air, increases in weight, and thus anticipated the results of Lavoisier by nearly a century and a half. Torricelli tackled the problem in an entirely different manner. He filled with mercury a glass tube, closed at one end and measuring some 3 feet in length. When the tube was inverted with its open end dipping under mercury in a trough, it no longer remained filled with the liquid. It held a column of mercury some 30 inches in height, but above this was empty. This space came to be known as the Torricellian vacuum, and its discoverer correctly attributed its formation to the fact that the open air acting on the surface of the mercury in the trough is able to support by its pressure a column of mercury of definite length, and no more. Pascal extended Torricelli's experiments by employing tubes filled with other liquids such as oil, alcohol and water. In every case he found that the height of the column of liquid supported by the air was inversely proportional to the density of the liquid; in other words, the weight supported was constant, and irrespective of the chemical composition of the liquid. Pascal also surmised that if air is a ponderable fluid, it will exert a greater pressure at sea level than on the top of a mountain, and that this difference should be capable of measurement by observing the relative heights of mercury columns in such situations. Experiment proved this to be the case. Boyle christened Torricelli's tube, containing mercury, a **barometer** (Greek *baros*, weight, and *metron*, measure), and it is customary to express the pressure of the air in terms of the height of the column of mercury which the air is capable of supporting at the particular moment.

The pressure of the air, as already mentioned, varies with altitude; indeed, at one and the same place it does not remain constant in consequence of variation in composition, the influence of wind, etc. A standard pressure, known as an *atmosphere*, has, however, been chosen. The British unit is the pressure of a column of mercury 29·905 inches in height, measured at 32° F. in London, and is 14·697 lb. per square inch. The metric unit is the pressure of a column of mercury 760 mm. (29·921 inches) in height, measured at 0° C. at sea level at latitude 45°. Since the density of mercury is 13·5955 at 0° C., the pressure of the normal atmosphere is equal to the weight of $13{\cdot}5955 \times 76$ or 1033·258 grammes. To convert this to dynes we multiply by 980·617, which gives 1,013,240 dynes.

From the foregoing it follows that

1 atmosphere (metric) = 1,013,240 dynes per sq. cm.
= 1·01324 megabars
= 1033·26 grammes ,,
and 1 megabar = 0·9870 atmosphere,
1 kilogram per sq. cm. = 0·9678 ,,

The British atmosphere is 0·99968 that of the metric unit.

Pressure exerted by the atmosphere as a result of the earth's attraction is static. Another kind of pressure must now be considered, namely that which occurs as the result of *collision* or *impact* between moving bodies. This is dynamic in character, but it can be expressed in the same units as static pressure. Suppose, for example, a ball of mass m moving with a velocity u strikes a wall perpendicularly. Its velocity is reduced to zero, so that it has suffered a negative acceleration u. If both ball and wall are perfectly elastic, the ball rebounds, following its original track with a velocity u, but in the opposite direction. Its acceleration is again u. The total acceleration is thus $2u$, so that the force exerted upon the target was $m \times 2u$ or $2mu$, that is, twice the original momentum of the ball. These considerations are of special importance in connection with the kinetic theory of gases (see Chapter III).

The Balance.—Some kind of balance must have been in use from very remote ages for purposes of trade, and the desire of the Eastern trader for a true balance is indicated by several passages in Holy Writ; thus—" A false balance is abomination to the Lord; but a just weight is His delight" (Prov. xi, 1). During the Middle Ages scientists appear to have been able to weigh substances with very considerable accuracy, for three Arabian glass coin weights of A.D. 780 have recently been re-weighed and found equivalent to 2·1165, 2·1167 and 2·1168 grammes respectively, the maximum error thus being only 3 in 20,000. Further, the Arabian Al Khazini, in 1121, wrote a book entitled *The Book of the Balance of Wisdom* in which he discussed the balance and gave the density of lead as 11·33, a value we accept to-day [Cohen and Heldermann (1915) give 11·3299 at 25° C.].

It is to Lavoisier, however, that the credit is usually given of installing the balance in its proper place in the technique of chemistry. Without its aid modern physical chemistry could not exist.

Requisites of a Good Balance.—The common balance as used by the chemist consists of a rigid beam made of some incorrodible, non-magnetic metal, to which are attached two scale pans, at equal distances from the fulcrum at the centre of the beam. The balance is thus a lever of the first class, and to be of value it must fulfil the following conditions:

(i) The balance must be ***true***; that is, when equal masses are placed in the scale pans the beam must remain horizontal. Variation in the value of g for different localities makes no difference, as each pan is affected to the same extent.

(ii) The balance must be ***sensitive,*** so that a small difference in the masses in the two scale pans shall cause an appreciable inclination of the beam to the horizon. If M_1 and M_2 are the two masses in the scale pans, and θ the angle of inclination of the beam, the sensitiveness of the balance is easily seen to be measured by $\tan \theta/(M_1 - M_2)$. In general tan θ, and thus the sensitiveness of the balance, is increased by having a long but light beam, and by reducing as far as practicable the distance of the centre of gravity below the central knife-edge or fulcrum.

(iii) The balance must be *stable*, so that, after disturbance, the beam returns to its horizontal position.

There is a further point, of practical importance, namely that the balance must not take an undue time in returning to rest. To a certain extent this conflicts with great sensitiveness in that rapidity of movement is facilitated by the use of a short beam and a greater distance between the centre of gravity and the fulcrum. In practice a compromise is effected.

Work.—A force is said to do work on a body when its point of application moves in the direction of the force. The amount of work done, W, is measured by the product of the impressed force, f, and the distance, l, through which its point of application moves. Thus

$$W = fl,$$

from which it follows that the dimensions of work are $[L^2 . M . T^{-2}]$.

In the c.g.s. system the unit of work is termed the **erg** (Greek *ergon*, work). It is the work done when a body acted upon by a force of one dyne moves through a distance of one centimetre in the direction of the force. Since the dyne is nearly equal to the force with which the earth attracts one milligramme (p. 16), on raising a milligramme through 1 cm. approximately 1 erg of work is done. The erg is thus a very small unit, and for many purposes it is convenient to use 10^7 ergs as the unit, and this is termed a **joule.** In the British system the unit of work is the **foot-poundal,** equivalent to $4{\cdot}214 \times 10^5$ ergs.

The rate at which work is done, that is, the amount of work done in unit time, is termed **power**; in the c.g.s. system the practical unit of power is the **watt** or joule-second, equal to 10^7 ergs per second. The British unit is the **horse power,** of 550 foot-pounds per second, equivalent to 746 watts.

Energy is the capacity for doing work, and is of two kinds, namely **kinetic** and **potential** (Greek *kineō*, I move; and Latin *potens*, powerful). A body in motion possesses kinetic energy, which is measured by the amount of work the body can do before its velocity is destroyed. Suppose, for example, that before a body of mass m, moving with velocity u, is brought to rest, a force f has acted on it through a distance l; it follows that the work done by the body is fl. The negative acceleration of the body, which has lost a speed u in the distance l, is $u^2/2l$; the force is therefore $\frac{mu^2}{2l}$, and the kinetic energy, which is measured by the work the body can do, is

$$f \times l = \frac{mu^2}{2l} \times l = \tfrac{1}{2}mu^2.$$

It is necessary to distinguish carefully between the kinetic energy of a moving body and its momentum. Thus, a ball of mass 10 grammes moving with a velocity of 1000 cm. per second possesses $\frac{1}{2} \times 10 \times 1000^2$ or 5,000,000 ergs of kinetic energy. Its momentum, however, is only 10×1000 or 10,000 gramme-cm. per second (see p. 16).

The potential energy of a body is measured by the work it can do in virtue of its position in passing from its present state to one of zero condition. For example, a mass m, raised to a height h above sea level, possesses potential energy equivalent to mgh.

Temperature.—The melting point of pure ice under a pressure of one atmosphere is defined as 0 on the Centigrade scale (Latin *centum*, hundred; *gradus*, step). The "freezing point" of water is not chosen, as water may easily be supercooled; but ice is not liable to overheating. The boiling point of water under the normal atmospheric pressure (see p. 17) is chosen as 100 on the same scale, the temperature interval being divided by use of the constant volume hydrogen thermometer into 100 parts, termed degrees Centigrade. Temperature is thus defined independently of length, mass and time, so that dimensions are not required.

The unit of heat is the **gramme-calorie**, that is, the amount of heat required to raise one gramme of water through one degree Centigrade. As this amount varies very slightly it is usual, in accurate work, to specify the temperature of the water. Thus the *15° calorie* is the quantity of heat required to raise one gramme of water at 14·5° C. to 15·5° C. see p. 211). This is equivalent to $4{\cdot}184 \times 10^7$ ergs or 4·184 joules (see Vol. II), an expression known as the **mechanical equivalent of heat.** Conversely, 1 joule = 0·2389 gramme-calorie at 15° C. or 0·2392 at 20° C.

The Litre-atmosphere.—It is frequently convenient to know the amount of work that must be done in order to displace the atmosphere to the extent of a litre. In a chemical reaction, for example, in which a gas is liberated, how much work must each litre of gas do against the atmosphere to make room for itself? Clearly the work is equal to that done when an area of one square centimetre is raised against atmospheric pressure to a height of 1000 cm.,

$$\begin{aligned} &= 1000 \times 76 \times 13{\cdot}596 \times 980{\cdot}6 \text{ ergs,} \\ &= 10{\cdot}133 \times 10^8 \text{ ergs,} \\ &= 10{\cdot}133 \times 10^8 \div 4{\cdot}18 \times 10^7 \text{ gramme-calories,} \\ &= 24{\cdot}24 \text{ gramme-calories.} \end{aligned}$$

The Conservation of Mass.—The quantitative study of chemical changes has led to the formulation of a fundamental law, which applies to all changes, both physical and chemical. This is the **Law of the Conservation of Mass**; it may be stated in the form

the mass of a system is unaltered by any change that occurs within it,

or

in a chemical change the total mass of the substances that disappear is equal to the total mass of the substances produced.

For example, referring to one of the changes already mentioned, the mass of the mercuric sulphide formed is precisely equal to the sum of the masses of the mercury and sulphur that disappear. In the chemical change that takes place when carbon burns in air, the law does not appear, at first sight, to hold. This, however, is due to the fact that two of the three forms of matter concerned in the change, namely the air and the oxide of carbon produced by the combustion, are colourless gases. When the diminution in the mass of the surrounding air is determined, and also the mass of the gaseous substance produced, it is found that the latter exceeds the former by exactly the mass of the carbon that disappears.

The discovery that, in the formation and decomposition of mercuric oxide, the combined masses of the mercury and oxygen taking part in the changes are equal to the mass of the mercuric oxide, is due to Lavoisier, who was the first chemist to enunciate the law. It is not difficult to realise that such a law should have escaped the attention of the early chemists, unacquainted as they were with the existence of different gases, and unaccustomed to placing any reliance on measurements of mass (or weight) in interpreting the nature of chemical changes.

Since, as we have already seen, the weight of a substance is proportional to the mass, the foregoing law may also be stated in the form that

the total weight of a system is unaltered by any change that occurs within it.

This law is tacitly assumed to be true every time we attempt to balance a chemical equation, and it has never yet failed us. Nevertheless, it should be clearly understood that the law rests upon a purely experimental basis and can therefore never be proved to be valid except within the limits of unavoidable experimental error. The indirect evidence of the validity of the law is supplemented by the results of direct experiments, especially undertaken with the object of putting the law to the test. Four different reactions were studied by Landolt in 1893 with the greatest care, the method employed briefly being as follows: The materials used in a reaction were contained in the limbs of a sealed, inverted U-tube, which, after being weighed against a similar counterpoise, containing the same ingredients in similar amounts, was righted in order to mix the materials and cause the reaction to take place. The weight was then observed again. The contents of the counterpoise were then mixed, and a third weighing made. The conclusion finally reached by Landolt (1831 to 1910), the "patriarch of physical chemistry," was that in these reactions there was no difference between the masses of the systems before and after chemical change greater than could be attributed to error in weighing. The latter was usually less than 0·02 mgrm., the masses of the reacting systems ranging from about 100 grms. to 300 grms. The four reactions studied were as follows:

(i) Silver sulphate and ferrous sulphate:

$$Ag_2SO_4 + 2FeSO_4 = 2Ag + Fe_2(SO_4)_3.$$

(ii) Hydriodic and iodic acids:

$$5HI + HIO_3 = 3H_2O + 3I_2.$$

(iii) Iodine and sodium sulphite:

$$I_2 + 2Na_2SO_3 = 2NaI + Na_2S_2O_6,$$

or

$$I_2 + Na_2SO_3 + H_2O = 2HI + Na_2SO_4.$$

(iv) Potash and chloral hydrate:

$$KOH + CCl_3.CHO.H_2O = CHCl_3 + H.COOK + H_2O.$$

The reactions thus were fairly simple and not accompanied by great heat evolution. In these experiments the law was found to be accurate to at least one part per million.

Further evidence of the great accuracy of the law is afforded by the results of recent atomic weight determinations, which show remarkable agreement amongst themselves (see pp. 29, 30).

Although, as will be explained later (Vol. II), there is reason to believe that the law is not *absolutely* exact as it stands, we do know that any changes in mass that occur during the course of chemical reactions are far too minute to be of any practical importance to the chemist. The Law of the Conservation of Mass may therefore be classed among the exact laws.

The Conservation of Energy.—Corresponding to the principle of the conservation of mass there is another fundamental physical principle concerning *energy*. The general statement of the principle of the **Conservation of Energy** is as follows :

The total energy of any material system is a quantity which can neither be increased nor diminished by any action between the parts of the system, though it may be transformed into any of the forms of which energy is susceptible.

The energy content of the products of a chemical change is, in general, however, different from that of the starting materials, and this is manifested as a rule by the evolution or absorption of heat during the reaction. This phenomenon will be discussed in some detail in a later chapter.

The total quantity of energy in the universe is usually regarded as constant, but it is not all *available* to man for doing work. During every transformation some energy is converted into heat, which becomes uniformly diffused and is therefore generally regarded as being unavailable, inasmuch as further change is deemed impossible. *If this be granted,* it is clear that the total available energy is steadily diminishing, while the unavailable energy is as steadily increasing, and a time must come when all the available energy of the universe will become unavailable, the universe itself becoming a uniformly hot, inert mass. This doctrine is known as the **Dissipation of Energy.** The fact, however, that we are not at present acquainted with any method of rendering uniformly diffused heat available does not necessarily imply that it is actually incapable of being rendered so ; and it may well be that, by processes not yet understood, the so-called unavailable energy is being continuously transformed into available energy, so that the universe may never reach the state of equilibrium and inertness referred to above.

It is, of course, impossible to prove the absolute accuracy of this law, but experience shows that it must be almost absolutely true in so far as terrestrial reactions are concerned.

Relationship of Mass to Energy.—According to modern views, which are more thoroughly discussed later on (Vol. II), matter is composed only of positive and negative electricity. It has been calculated that when matter loses energy it loses also a certain amount of mass, and, conversely, that when matter absorbs energy it gains proportionately in mass. In other words, a body possesses greater mass when it is in motion than when at rest, or when it is hot than when it is cold. The relation between the two is given by the expression

$$dm = 1{\cdot}111 \times 10^{-21} dE,$$

where dm and dE represent the changes in mass and energy respectively. Hence a body emitting radiant energy loses mass to the extent of $1{\cdot}111 \times 10^{-21}$ gramme for every erg radiated.

An example will make this clear. When gaseous hydrogen and oxygen unite to form liquid water, a certain amount of energy is evolved as heat in accordance with the equation

$$(H_2) + (O) = H_2O + 68{,}400 \text{ calories.}$$

Since 1 grm.-calorie is equivalent to $4{\cdot}2 \times 10^7$ ergs, the total loss in mass during the formation of a gramme-molecule of water is

$$68{,}400 \times 4{\cdot}2 \times 10^7 \times 1{\cdot}111 \times 10^{-21} \text{ gramme,}$$
$$= 3{\cdot}19 \times 10^{\ 9} \text{ gramme.}$$

This quantity is far too small to be capable of experimental verification. Nevertheless, it is a definite amount, and to this extent the laws of the conservation of mass and energy, *as enunciated separately*, are not absolutely correct. By coupling the two laws together, however, we obtain the statement that *the sum total of the mass and energy of a system is unaltered by any change that occurs within the system*, and this, so far as we know, is absolutely true.

Le Chatelier's Theorem (1884) may be mentioned here on account of its great importance and wide applicability to all systems, whether chemical or physical. The theorem is usually stated as follows :

> *If a system in equilibrium is subjected to constraint by which the equilibrium is shifted, a reaction takes place which tends to annul the constraint.*

For example, when common salt dissolves in water there is a small but definite contraction in volume. By increasing the pressure, therefore, the solubility of the salt is increased, so that a greater contraction in volume takes place (see p. 369). Many other examples are dealt with in succeeding pages.

CHAPTER II.

THE ATOMIC THEORY.

As early as 1200 B.C. the Hindoos had concluded that matter was discontinuous, being composed of minute particles separated from each other by empty space. Cohesion was explained on the assumption that the particles attracted one another.

The Greeks either borrowed this view or independently arrived at similar conclusions, adding the suggestions that the particles were indestructible and always in motion. The particles were called **atoms** (Greek *a* not, *temno* I cut) or "indivisibles." Democritus (460 to 360 B.C.) appears to have been the first Grecian philosopher to develop these views. At the time they were very unpopular, but in later years they were revived by the Epicureans.

Lucretius, at the end of the first century of the Christian era, expressed views which sound very similar to those current to-day. A solid he regarded as atoms squeezed closely together; a liquid as similar atoms less closely packed; and a gas consisted of but few atoms with much freedom of movement. The atoms were imperishable, and always in motion; and on the manner in which they combined depended the properties of the substance formed.

Coming down to later times, an atomic theory of matter was very much in vogue in the seventeenth century, and for various phenomena explanations based on the theory were largely sought by Bacon, Boyle, Hooke and others. Newton, in 1675, went so far as to show, on the assumption of the atomic composition of matter, that Boyle's law for gases must necessarily follow.

The development of quantitative ideas concerning the combination of atoms did not really begin, however, until the close of the eighteenth century, when two Irish chemists, Bryan Higgins (1737 to 1820), and particularly his pupil and nephew William Higgins (1769 to 1825), endeavoured to arrive at a knowledge of the number of atoms or ultimate particles which united chemically to form single ultimate particles of new compounds. Influenced by the principle which Newton had laid down that the particles of any one gas are mutually repellent, these workers arrived at the view that chemical combination would most readily occur between a single ultimate particle of one substance and a single ultimate particle of a second different substance. Thus a single particle of an acid united in all cases with one alkaline particle, and was unable to take up a second, because the first alkaline particle repelled the second and prevented combination. William Higgins, however, recognised combination in multiple proportions, though he held that the union of a single particle of each component substance resulted in the formation of the compound of greatest stability.

These views are similar to those at which John Dalton arrived some years later. The exact origin of Dalton's Atomic Theory was contested throughout the nineteenth century, but a survey of the evidence renders it almost certain that Dalton formulated an atomic theory from the experiments made by him, prior to 1803, on the purely physical properties of gases. This conclusion was reached by Roscoe and Harden in 1896 as the result of studying Dalton's laboratory note books preserved by the Literary and Philosophical Society of Manchester. It is contrary to the earlier view, held generally by Dalton's contemporaries, that the theory was devised to account for the observed facts of combination in multiple proportions (see p. 28).

Dalton's Atomic Theory may be summed up briefly as follows :

1. The atoms of any one element are all alike, and possessed of a definite and characteristic mass. They differ from the atoms of any other element both in their physical and their chemical properties.
2. Chemical compounds are formed when the atoms of two or more elements unite in simple numerical proportions.

From this it is evident that an atom is the smallest part of an element that can take part in a chemical reaction. The smallest part of a compound that can exist must contain at least two atoms, and is termed a **molecule** (dim. of Latin *moles*, mass), in accordance with the suggestion of Cannizzaro. As explained later, the relative weights of the atoms of the elements are expressed in terms of one of them chosen as standard and are known as the **atomic weights**. **Molecular weights** are the sums of the weights of the atoms comprising molecules.

Symbols and Formulæ.—Symbolic chemical notations have been in use from very early times, but these were purely qualitative in character. A few of the symbols used by the alchemists are shown in fig. 1. Thus gold was represented by a circle denoting the sun, gold being regarded as the "king" of metals. The crescent moon denoted silver, and the idea survives in the term *lunar caustic*, denoting silver nitrate (Latin *luna*, the moon). Lead was designated by the scythe of Saturn, the part circle possibly suggesting a connection with silver. Iron was appropriately represented by the shield and spear of Mars, and copper by Venus's looking glass.

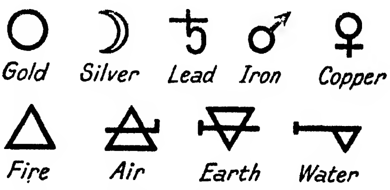


FIG. 1.—Symbols of the Alchemists.

Dalton was the first to introduce a quantitative chemical notation. Conceiving the atoms as hard, impenetrable masses, he suggested **symbols** of the kind shown below :

⊙ Hydrogen.
○ Oxygen.
⦶ Nitrogen.
● Carbon.
⊕ Sulphur.

⊙○ Water.
⦶⊙ Ammonia.
⦶○⦶ Nitrous oxide.
○●○ Carbonic acid.

Each symbol represents one atom, and one atom only ; it therefore denotes a definite quantity of the particular element. By grouping the necessary atoms together the composition of a compound may be indicated. Whilst these symbols were not difficult to use when relatively simple substances were dealt with, such as water and ammonia, which were regarded as binary compounds, they became unwieldy when more complex molecules required representation.

In 1811 Berzelius introduced a notation practically identical with that employed to-day. It consists in denoting an element by a symbol which is the initial letter of its name, generally in Latinised form, with sometimes a second letter added when several elements have the same initial letter. Thus carbon, copper (Latin *cuprum*), chlorine and cæsium are denoted by C, Cu, Cl and Cs respectively. A full list of symbols is given on pp. 35, 36. In order to attach a quantitative significance to these symbols, it might at first appear the simplest plan to regard the symbol for an element as standing for *one combining weight* of the element. The **formula** of a compound could then be represented by writing down the symbols of its constituent elements side by side, and its quantitative chemical composition indicated by attaching numerical suffixes to the symbols, in order to denote the relative numbers of combining weights of each element present. A difficulty arises, however, in the compilation of a table of combining weights, since many elements possess more than one combining weight. Accordingly, instead of letting the symbol for an element denote a combining weight, it is chosen to represent *one atom* or *one atomic weight* of the element. Thus the symbols previously given stand for one atom or 12 parts by weight of carbon, one atom or 63·57 parts of copper, one atom or 35·46 parts of chlorine, and one atom or 132·8 parts of cæsium, respectively ; whilst the formula C_1Cl_4, for example, denotes a compound of carbon and chlorine (carbon tetrachloride), in which for every atom of carbon there are four atoms of chlorine. The affix unity is always omitted, so that the formula is written CCl_4. It is clear that the formula C_nCl_{4n} would do equally well to denote the composition of the substance, n being any integer. However, it is usual, whenever possible, to write the formula of a compound so that it represents a molecule, so that on adding up the weights of all the atoms represented in the formula, the molecular weight of the compound is obtained. Such **molecular formulæ** can only be written for substances of known molecular weight. The molecular weight of carbon tetrachloride having been found to be 153·8, it is clear that the simple formula CCl_4 is also the molecular formula, and denotes that one molecule of the substance contains one atom of carbon and four atoms of chlorine. When the molecular formula of a compound is unknown, it is usual to employ the simplest formula that expresses the composition, this being termed the **empirical formula.** The empirical formula of cupric chloride is $CuCl_2$, but its molecular weight has not been determined.

When the atomic and molecular weights of an element are both known, a molecular formula can be given. Thus the molecular formulæ of mercury, oxygen and phosphorus in the gaseous state are Hg, O_2 and P_4, as the molecules are monatomic, di-atomic and tetra-atomic respectively.

By means of formulæ, it is possible to express in a very concise manner the results of a chemical change. The formulæ of the reacting substances are written down on the left, and connected together with plus signs to indicate that they have reacted together; on the right, the formulæ of the substances produced are written down, and connected with plus signs to indicate that they are all produced together. A sign of equality between the two groups of formulæ denotes that the substances on the left have been transformed into those on the right, and the necessary numerical coefficients are placed before the various formulæ to make the number of atoms of each element the same on both sides. Such a symbolic representation is termed a **chemical equation,** and was first employed by Lavoisier as a means of expressing chemical reaction. When we write, for example,

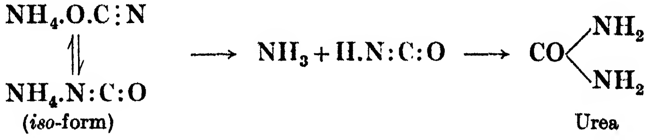
$$2Hg + O_2 = 2HgO,$$

we definitely indicate that two atoms of mercury have united with one molecule of oxygen to yield exactly two molecules of mercuric oxide. Since, by Dalton's Atomic Theory, the atoms of each element possess distinctive weight, it is clear that the above equation is strictly quantitative in character, and indicates that 400 parts of mercury (using round figures) have united with 32 parts of oxygen to yield 432 parts of oxide, and neither more nor less.

The **Law of Definite Proportions** is tacitly assumed in the foregoing equation. This law is generally expressed in the form :

A definite compound always contains the same elements in the same proportions.

It has already been mentioned (p. 2) that, whilst two substances possessing identical properties must have the same composition, the converse is not necessarily true. For example, the diamond and graphite are both forms of the same element, carbon ; their chemical composition is thus the same, but their properties are different, because their atoms are arranged differently, or in other words their structures are different. They are therefore called allotropic forms or simply **allotropes** (Greek *allos* other, *tropos* manner) of carbon. In a similar manner two or more compounds of identical chemical composition may possess widely different properties because their structures are different. These are known as **isomers** or **isomerides** (Greek *isos* equal, *meros* part). A classical example is that discovered by Wöhler in 1828, who observed that merely on evaporating an aqueous solution of ammonium cyanate an organic substance, namely urea, is produced. Thus



$$\begin{array}{c} NH_4.O.C{:}N \\ \upharpoonleft\downharpoonright \\ NH_4.N{:}C{:}O \\ (\textit{iso}\text{-form}) \end{array} \longrightarrow NH_3 + H.N{:}C{:}O \longrightarrow \begin{array}{c} CO\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix} \\ \text{Urea} \end{array}$$

This was an important observation, because chemists had hitherto believed that organic substances could only be produced by the action of a **vital force,** and could not be prepared from inanimate or inorganic matter in a laboratory. Thousands of experiments since 1828 have shown that organic chemistry obeys similar laws to inorganic chemistry, and that "vital force" is not essential for the synthesis of organic compounds.

From the results of experiments on the interaction of elements and compounds, Richter, *c.* 1792 to 1794, deduced a law which is generally termed the **Law of Equivalent Ratios.** This law may be expressed in the following manner:

The ratios of the masses of two elements that combine with one and the same mass of a third element bear a simple numerical relationship to the ratios of the masses of the two elements that combine either with one and the same mass of any other element or with one another.

It is interesting to note that this law was enunciated several years before the advent of Dalton's Atomic Theory, which later afforded it a very thorough and satisfactory explanation. Richter showed, and correctly explained the fact, that when two neutral salts interact, the resulting salts are still neutral; and, from the fact (previously observed by Bergmann) that when one metal is precipitated from a solution of a neutral salt by another metal the resulting solution is likewise neutral, he also deduced that the masses of two metals which neutralise the same mass of an acid also combine with equal masses of oxygen. He further showed that the quantities of various bases (basic oxides) which neutralise a fixed quantity of one acid are in the same ratios as the quantities of the bases which neutralise a fixed quantity of another acid.

Richter's experimental results were only rough approximations to the truth, and the first experiments having any pretensions to accuracy which served to demonstrate the truth of the Law of Equivalent Ratios were not made until several years after Dalton's theory had been published. Modern work, however, confirms the great exactness with which Richter's law is obeyed. For example, analysis shows that for nitrogen tetroxide, N_2O_4, the ratio of the weights of nitrogen and oxygen is (Guye and Drouginine, 1910):

$$\text{Nitrogen} : \text{Oxygen} = 1 : 2{\cdot}28404,$$

whilst for nitrogen sulphide, N_4S_4 (Burt and Usher, 1911):

$$\text{Nitrogen} : \text{Sulphur} = 1 : 2{\cdot}28901.$$

Now $$2{\cdot}28404 : 2{\cdot}28901 :: 1 : 1{\cdot}0022,$$

and according to the law, there should be a simple numerical relationship between this ratio and the ratios in which oxygen and sulphur combine together. Analysis of sulphur dioxide shows that the ratio of oxygen to sulphur is 1 to 1·0020, which is practically equal to the preceding ratio.

The Law of Multiple Proportions may be stated in the following manner:

When two elements unite in more proportions than one there is a simple ratio between the different amounts of the first element combining with a fixed amount of the second element.

The name of Dalton is usually associated with this law. Its history is of special interest, for it is almost certain that Dalton first of all deduced the law as a necessary consequence of his Atomic Theory, and afterwards found in the compositions of olefiant gas and marsh gas on the one hand, and carbon monoxide and dioxide on the other, experimental confirmation of his views.

The early analyses, the results of which constituted the experimental basis of the Law of Multiple Proportions, were naturally somewhat crude and inaccurate; the perfection of analytical methods, effected since the law was enunciated, has enabled chemists, however, to submit the law to a more rigorous examination, and thereby to demonstrate its exactness. For example, gravimetric analysis of nitrous oxide (Guye and Bogdan, 1904) gave the following ratio:

Nitrogen : Oxygen = 1·75100 : 1;

nitric oxide (Gray, 1905) gave:

Nitrogen : Oxygen = 0·87563 : 1;

and finally nitrogen tetroxide (Guye and Drouginine, 1910) gave:

Nitrogen : Oxygen = 0·43782 : 1.

Now 1·75100 : 0·87563 : 0·43782

as 3·9994 : 2 : 1

or 4 : 2 : 1

within the limits of experimental error.

The Law of Equivalent or Combining Weights.—The laws of equivalent ratios and of multiple proportions just enunciated are really only part of a more comprehensive law which deals with the compositions of all substances. Al Jildaki, who died *c.* 1360, pointed out that substances do not react except by definite weights. This was a remarkable observation for the time, but no particular use appears to have been made of it; the time was not ripe.

Experiment shows that hydrogen combines with oxygen in the proportion of approximately one part by weight of hydrogen to 8 parts by weight of oxygen. Eight parts of oxygen are therefore said to be equivalent to (approximately) one part of hydrogen. For reasons which will be made clear later, oxygen has been chosen as our standard of combining weight, and the **chemical equivalent** or the **combining weight** of an element or group of elements is defined as *the number of parts by weight of that element or group of elements that can combine with or replace 8 parts by weight of oxygen.*

In view of the existence of the Law of Multiple Proportions, it is clear that an element may have a number of combining weights, which will be in the ratios of simple integers. The Law of Equivalent Ratios may now be stated in the following manner, and called the **Law of Equivalent or Combining Weights:**

Elements combine with one another in the ratios of their combining weights or in simple multiples of these.

Experiment shows that this more general law holds with as great an accuracy as the two previous laws.

The determination of combining weights is a matter of fundamental importance. According to the preceding law, the combining weight of an element may be determined either directly with reference to oxygen, or indirectly with reference to another element of known combining weight. The latter method is employed more often than the former, and thus it happens that the combining weights of certain elements are extremely important, since they are so often utilised in calculating the combining weights of the others. These **fundamental combining weights** include those of chlorine, bromine, iodine, hydrogen, nitrogen, carbon, sulphur, sodium and potassium. The following data will serve to illustrate the law :

The gravimetric composition of water gives us the ratio (Morley, 1895) :

$$\text{Oxygen} : \text{Hydrogen} = 8 : 1{\cdot}0076,$$

whence, by the definition on p. 29, the equivalent weight of **hydrogen** is **1·0076.**

Analysis of hydrogen chloride gives the ratio (Edgar, 1909) :

$$\begin{aligned}\text{Hydrogen} : \text{Chlorine} &= 1 : 35{\cdot}1935\\ &= 1{\cdot}0076 : 35{\cdot}461,\end{aligned}$$

and hence the equivalent weight of **chlorine** is **35·461.**

For silver chloride Richards and Wells (1905) found :

$$\begin{aligned}\text{Chlorine} : \text{Silver} &= 0{\cdot}328668 : 1\\ &= 35{\cdot}461 : 107{\cdot}893,\end{aligned}$$

whence the equivalent weight of **silver** is **107·893.**

Analysis of silver oxide by Riley and Baker (1926) gave the following mean value :

$$\begin{aligned}\text{Silver} : \text{Oxygen} &= 1 : 0{\cdot}074167\\ &= 107{\cdot}893 : \mathbf{8{\cdot}00210.}\end{aligned}$$

Now we began with the assumption that the equivalent weight of oxygen was exactly 8, and as the results of four entirely distinct researches carried out at different times in different countries we come back to the value 8·00210. This is a remarkable tribute not only to the rigidity with which the law of equivalent weights is obeyed, but to the high degree of experimental skill attained by modern investigators.

Gay-Lussac's Law of Volumes.—The laws previously discussed deal with the regularities that are noticed among the masses of substances concerned in chemical changes. The law which expresses the volume relationships observed in chemical reactions involving gases was discovered by Gay-Lussac. In 1805 Gay-Lussac and Humboldt noticed that when hydrogen and oxygen unite to form water, the respective volumes of these gases that enter into combination are in the ratio of two to one when measured at the same temperature and pressure. The simplicity of this relationship led Gay-Lussac to the study of other gaseous reactions, and in 1808 he enunciated the **Law of Combining Volumes,** which may be stated in the following manner :

Whenever gases unite, they do so in simple proportions by volume measured at the same temperature and pressure ; and this relationship also extends to the volumes of any gaseous substances produced.

Unlike the preceding laws, this law is not exact, but only approximately correct under ordinary conditions. For example, careful experiment has shown that, at normal temperature and pressure, the ratio of the combining volumes of hydrogen and oxygen is 2·00269 : 1 (Morley, 1896). Further, one volume of nitrous oxide yields 1·00717 volumes of nitrogen. These results are readily understood when the approximate character of the gas laws is taken into consideration.

It is probable, however, that under exceedingly small pressures the Law of Combining Volumes is an exact expression of the nature of gaseous reactions.

Dalton's Atomic Weight System.—In the connected account which Dalton gave in 1808 of his atomic theory, he pointed out how important it was to be able to arrive at a knowledge of the relative weights of atoms, since a list of such relative weights acts as a guide in investigating the composition of new substances. This application of his theory had, in fact, already enabled him to draw up a table of relative atomic weights as early as 1803.

Since the atoms are so extraordinarily minute that nearly 100 million hydrogen atoms, for example, placed side by side in a straight line would be required to form a line 1 cm. in length, it is clear that a determination of their **absolute weights** may be a matter of considerable difficulty. Dalton, therefore, decided to determine **relative atomic weights**, and chose hydrogen, on account of its lightness, as his standard. The atomic weight of any other element was therefore the ratio of the weight of its atom to the weight of an atom of hydrogen. Its value was arrived at by the analysis of a compound containing the element and either hydrogen itself or some element whose atomic weight had already been fixed by comparison with hydrogen. But here arose a serious difficulty. It was known that two elements might combine in more proportions than one. This fact, indeed, was the basis of the Law of Multiple Proportions. How, then, was it possible to determine how many atoms were involved? Dalton assumed that binary compounds would be the most stable; hence if only one compound of two elements was known, it was presumed to be binary. If, however, two compounds were known, one was deemed binary and the other ternary. This being granted, chemical analysis would furnish the desired atomic weights. For example, water at that time being the only compound of hydrogen and oxygen known, was assumed to be binary, and was represented by the formula HO. As hydrogen and oxygen combine in the ratio of 1 to 8 approximately,* the atomic weight of oxygen, taking hydrogen as the standard, was clearly 8. Similarly ammonia, the only known compound of hydrogen and nitrogen, was written as NH, and the atomic weight of nitrogen was thus taken as approximately 5.

Dalton's guiding principle, however, was faulty, and for many years chemists were groping in the dark. Atomic weight systems were successively introduced by Berzelius in 1818 and 1826, by Gmelin in 1843, and by Gerhardt and Laurent about the same time; but prior to 1860 no system was generally acceptable to chemists.

Curious to relate, a magnificent guiding principle had been discovered by Avogadro as early as 1811, but its value had not been recognised by chemists.

Avogadro's Hypothesis.—In 1811 Avogadro accepted the accuracy of Gay-Lussac's Law of Volumes (p. 30) and pointed out that it was a most natural assumption to conclude that

> *the numbers of molecules in equal volumes of all gases are the same under the same conditions of temperature and pressure.*

---

* Dalton found the value 7; but to avoid confusion we will keep to the approximate modern values.

If this is accepted it follows that

the relative masses of the molecules of the gases are proportional to the densities of the gases.

Avogadro's hypothesis cannot either be proved or disproved by direct experiment. Not only are gas molecules far too minute to be visible even with the aid of powerful microscopes, but they are present in such enormous numbers that, even if they could be seen, any method of counting them with accuracy would break down. We have, however, exceedingly strong reasons for believing the hypothesis to be very nearly true. It can hardly be perfectly true, otherwise we should expect gases to conform more closely to Gay-Lussac's Law than is the case.

Taking the atomic weight of oxygen as 16, and assuming, for reasons which will appear later, that its molecule contains two atoms, it follows that its molecular weight is 32. Experiment shows that 1 litre of oxygen at N.T.P. and at sea level at lat. 45° (see p. 14) weighs 1·4290 grammes. From this it follows that, under the same conditions, 32 grammes of oxygen, that is, a **gramme-molecule** of oxygen, will occupy 22·4 litres. This is termed the **gramme-molecular volume,** and by Avogadro's hypothesis this value is the same for all gases. The number of absolute molecules of gas contained in this volume is usually denoted by N, and is known as **Avogadro's Number,** the modern value for which is $6{\cdot}064 \times 10^{23}$ (see p. 52). It is, of course, impossible to realise the significance of such a vast crowd.

The Modern System of Atomic Weights.—This is based upon the suggestion of Cannizzaro in 1858 that Avogadro's hypothesis should be taken as the guiding principle. The molecular weights of substances in the gaseous condition were first to be found, and after that the atomic weights of the constituent elements.

The molecular weights of gases or volatile substances could clearly be obtained from the densities of the gases, as indicated in the following table :

Gas.	Mass in Grammes of 1 Litre at N.T.P.	Gramme-Molecular Weight, *i.e.* Mass of 22·4 Litres.
Hydrogen	0·0899	2·01
Oxygen	1·4290	32·01
Nitrogen	1·2504	28·01
Chlorine	3·2209	72·15
Hydrogen chloride	1·6392	36·72
Ammonia	0·7708	17·27
Nitrous oxide	1·9777	44·30
Nitric oxide	1·3402	30·02
Hydrogen sulphide	1·539	34·47

In order to obtain the atomic weights of the elements it is necessary to examine as many of their gaseous or volatile compounds as possible, and to determine by analysis the least amounts of those elements present in the gramme-molecules of any of their compounds. Thus, for example, analysis shows that in hydrogen chloride the proportions by weight of the constituent gases are:

$$\mathrm{H} : \mathrm{Cl} = 1 : 35{\cdot}5.$$

Since a gramme-molecule of the gas weighs 36·72 grammes (approx.), it follows that it contains 1 gramme of hydrogen and 35·5 grammes of chlorine (approximately). Analyses of other gaseous compounds of these elements show that smaller amounts than these are never present in a single molecule. Hence the maximum possible atomic weights of hydrogen and chlorine are 1 and 35·5, respectively. The formula for hydrogen chloride is thus HCl, since its molecule contains one atom of hydrogen and one of chlorine, and no more. Similarly the molecule of ammonia is represented by NH_3, giving an atomic weight for nitrogen of 14·008, instead of 5 on the assumption that ammonia was a binary substance, NH.

Avogadro's hypothesis has given us a method, therefore, of determining the maximum possible atomic weights of certain elements. Two questions naturally arise, namely (i) is there any evidence that these maximum values are also the minimum ones and not in reality multiples of the true value? and (ii) is there any means of deducing the atomic weight of an element that does not yield any volatile compound? A few rules were available to Cannizzaro, such as Mitscherlich's Law of Isomorphism and Dulong and Petit's Law of Specific Heats, and these often proved useful, though occasionally they broke down just when they were most required. In later years chemists found many more guides, chief amongst which have been Mendeléeff's Periodic Table (p. 332); the ratio of the specific heats of gases (p. 230); and, in very recent years, methods involving the use of X-rays (see p. 309; also Vol. II).

The Oxygen Standard.—The atom of hydrogen, being the lightest known, was chosen by Dalton as his standard in fixing the relative atomic weights of the other elements. The suitability of this choice was supported very materially by **Prout's Hypothesis,** in 1815, according to which the elements were composed of varying numbers of hydrogen atoms. Thus oxygen consisted of 16 hydrogen atoms, and its atomic weight was therefore exactly 16, and so on. William Prout, it may be added, was a lecturer in London and a pioneer in physiological chemistry (1785 to 1850).

Whilst, as will be seen later, Prout's hypothesis contained much that was essentially true, the atomic weights of the elements as we know them are never exact multiples of the atomic weight of hydrogen. The atomic weight of oxygen, for example, is not exactly 16 times that of hydrogen, but 15·876 times.

At the present time oxygen is employed as our standard, its atomic weight being fixed arbitrarily at **16·0000,** and all other atomic weights are expressed relatively to it. Thus the figure for hydrogen ceases to be unity, the value 1·0078 being accepted in 1931 (see Table, p. 35) as the most probable value, and so on. The main reasons for choosing oxygen as the standard were as follows:

1. Hydrogen does not in general yield well-defined compounds with the metals, whose atomic weights must therefore be determined through the medium of some non-metal such as oxygen. Hence every time a

re-determination of the combining ratio of hydrogen and oxygen gives a more accurate figure, all the atomic weights depending on that ratio must be recalculated.

2. The atom of hydrogen is so very light compared with the atoms of the majority of the elements that the small experimental errors incidental to even the best gravimetric analyses become proportionately magnified.

Dalton's atomic theory is now known to be only partially correct. It is true that all the atoms of any one element possess identical chemical properties, but in many cases it has been found that they are not all alike physically. For example, three kinds of oxygen atoms are known, termed O(16), O(17) and O(18), since their relative masses are 16, 17 and 18, respectively. The two latter atoms are relatively few in number, so that the mean atomic weight chosen arbitrarily as 16 is only very slightly greater, namely 1·00022 times, than that of the main constituent O(16), the variation being of the order of 1·25 parts per 10,000. Since the relative amounts of these different kinds of atoms remain fairly constant, the fact that oxygen is really a mixture is not at present of great significance to the pure chemist when determining his atomic weights by purely chemical methods. When, however, atomic weights are determined by purely physical methods, as, for example, Aston's isotopic method, which is described later (see Vol. II), the standard is O_{16}, and the results must be multiplied by the **conversion factor** 1·00022 (1932 value) in order to render them comparable with the purely chemical data. The same kind of correction would still be necessary if hydrogen were taken as standard, since ordinary hydrogen has now been shown (Urey, 1932) to contain traces of an isotope H(2).

The different kinds of atoms of any one element are known as **isotopes** because they occupy the same place in the Periodic Table (Greek *isos* equal, *topos* place). Although their masses are different, their chemical properties are identical.

In the following table are given the atomic weights of the elements as adopted by the Committee on Atomic Weights of the International Union of Chemistry for 1931. A list of the known isotopes has also been added.

TABLE OF ATOMIC WEIGHTS OF THE ELEMENTS, 1931.

Atomic Number.	Element.	Symbol.	Atomic Weight.	Isotopes. Mass Numbers in Order of Intensities.
13	Aluminium	Al	26·97	27.
51	Antimony	Sb	121·76	121, 123.
18	Argon	A	39·944	40, 36.
33	Arsenic	As	74·93	75.
56	Barium	Ba	137·36	138, 137, 136, 135.
4	Beryllium	Be	9·02	9.
83	Bismuth	Bi	209·00	209.
5	Boron	B	10·82	11, 10.
35	Bromine	Br	79·916	79, 81.
48	Cadmium	Cd	112·41	114, 112, 110, 113, 111, 116.
55	Cæsium	Cs	132·81	133.
20	Calcium	Ca	40·07	40, 44.
6	Carbon	C	12·00	12 (13).
58	Cerium	Ce	140·13	140, 142.
17	Chlorine	Cl	35·457	35, 37, 39.
24	Chromium	Cr	52·01	52, 50, 53, 54.
27	Cobalt	Co	58·94	59.
	Columbium (see Niobium)			
29	Copper	Cu	63·57	63, 65.
66	Dysprosium	Dy	162·46	..
68	Erbium	Er	167·64	164, 176.
63	Europium	Eu	152·0	..
9	Fluorine	F	19·00	19.
64	Gadolinium	Gd	157·3	..
31	Gallium	Ga	69·72	69, 71.
32	Germanium	Ge	72·60	74, 72, 70, 73, 76, 75, 71, 77.
79	Gold	Au	197·2	..
72	Hafnium	Hf	178·6	..
2	Helium	He	4·002	4.
67	Holmium	Ho	163·5	..
1	Hydrogen	H	1·0078	1, (2).
49	Indium	In	114·8	115.
53	Iodine	I	126·932	127.
77	Iridium	Ir	193·1	..
26	Iron	Fe	55·84	56, 54.
36	Krypton	Kr	82·9	84, 86, 82, 83, 80, 78.
57	Lanthanum	La	138·90	139.
82	Lead	Pb	207·22	208, 206, 207, 209.
3	Lithium	Li	6·940	7, 6.
71	Lutecium	Lu	175·0	..
12	Magnesium	Mg	24·32	24, 25, 26.
25	Manganese	Mn	54·93	55.
80	Mercury	Hg	200·61	202, 200, 199, 201, 198, 204, 196.
42	Molybdenum	Mo	96·0	98, 96, 95, 92, 94, 100, 97.

TABLE OF ATOMIC WEIGHTS OF THE ELEMENTS, 1931—(*continued*).

Atomic Number.	Element.	Symbol.	Atomic Weight.	Isotopes. Mass Numbers in Order of Intensities.
60	Neodymium	Nd	144·27	142, 144, 146, 145.
10	Neon	Ne	20·183	20, 22, 21.
28	Nickel	Ni	58·69	58, 60.
41	Niobium	Nb	93·3	..
86	Niton or Radon (Rn)	Nt	222	..
7	Nitrogen	N	14·008	14, 15.
76	Osmium	Os	190·8	192, 190, 189, 188, 186, 187.
8	Oxygen	O	16·000	16, 18, 17.
46	Palladium	Pd	106·7	..
15	Phosphorus	P	31·02	31.
78	Platinum	Pt	195·23	..
19	Potassium	K	39·10	39, 41.
59	Praseodymium	Pr	140·92	141.
88	Radium	Ra	225·97	..
75	Rhenium	Re	186·31	187, 185.
45	Rhodium	Rh	102·91	..
37	Rubidium	Rb	85·44	85, 87.
44	Ruthenium	Ru	101·7	102, 101, 104, 100, 99, 96, 98.
62	Samarium	Sm	150·43	..
21	Scandium	Sc	45·10	45.
34	Selenium	Se	79·2	80, 78, 76, 82, 77, 74.
14	Silicon	Si	28·06	28, 29, 30.
47	Silver	Ag	107·880	107, 109.
11	Sodium	Na	22·997	23.
38	Strontium	Sr	87·63	88, 86, 87.
16	Sulphur	S	32·06	32, 33, 34.
73	Tantalum	Ta	181·4	..
52	Tellurium	Te	127·5	130, 128, 126, 125.
65	Terbium	Tb	159·2	..
81	Thallium	Tl	204·39	205, 203.
90	Thorium	Th	232·12	..
69	Thulium	Tm	169·4	..
50	Tin	Sn	118·70	120, 118, 116, 119, 117, 124, 122, 121, 112, 114, 115.
22	Titanium	Ti	47·90	48, 50.
74	Tungsten	W	184·0	184, 186, 182, 183.
92	Uranium	U	238·14	238.
23	Vanadium	V	50·95	51.
54	Xenon	Xe	130·2	128, 132, 131, 134, 136, 130, 129, 124, 126.
70	Ytterbium	Yb	173·5	..
39	Yttrium	Y	88·92	89.
30	Zinc	Zn	65·38	64, 66, 68, 67, 65, 70, 69.
40	Zirconium	Zr	91·22	90, 94, 92, 96.

Masurium (At. No. 43) and Illinium (At. No. 61) are not included in this table.

CHAPTER III.

THE GAS LAWS AND THE KINETIC THEORY.

GASES are characterised by their lack of definite shape and volume. When a given mass of gas is introduced into an evacuated vessel it assumes the shape and volume of the vessel, no matter what the size of the vessel may be, and exerts a uniform pressure on the walls. We owe the word " gas " to that erratic genius van Helmont (1577 to 1644), who is usually believed to have derived it from the Greek *khaos*, void. For many years after the introduction of this word, however, gases were known as " airs." Thus hydrogen was termed " inflammable air," and oxygen was variously known as " fire air " (Scheele), " dephlogisticated air " (Priestley) and " eminently pure air " (Lavoisier). The term " air " is now largely restricted to the predominant mixture of gases constituting our atmosphere.

By the **elasticity** of a substance is understood the ratio of the stress to the strain produced per unit volume. Since a gas resists compression, it possesses elasticity of volume. If a volume V of a gas is reduced to $V-\delta V$ when the pressure is raised from P to $P+\delta P$, the strain produced per unit volume is $\delta V/V$, and the elasticity, E, is given by

$$E=\delta P\div\frac{\delta V}{V}=V\frac{\delta P}{\delta V} \quad . \quad . \quad . \quad . \quad (1)$$

Boyle's Law.—The simplest law connecting the pressure and volume of a gas is that enunciated by Robert Boyle as the result of a series of experiments on gases, details of which were published in 1662. The law states that

Given a constant temperature, the volume of a gas varies inversely as the pressure.

Mathematically expressed, the law becomes

$$P\propto\frac{1}{V} \quad \text{or} \quad PV=\text{constant} \quad . \quad . \quad . \quad (2)$$

Boyle used a U-shaped glass tube for his experiments (fig. 2). The shorter limb was closed at A and calibrated, and the volumes occupied by the enclosed gas when subjected to different pressures obtained by varying the height of the mercury column CB were noted. The method was crude, and even if small deviations from the law had occurred within the range of pressures investigated, they must inevitably have escaped observation.

Mariotte independently discovered the same law some fourteen years later, and on the Continent the law frequently bears his name. But, if priority of discovery counts at all, the law should be known as Boyle's Law, although Mariotte appears to have had a better appreciation of it and its importance than had Boyle, and his book, entitled *Discours de la Nature de l'Air*, which appeared in 1676, exerted a more profound influence on Continental physics than did the publications of Boyle.

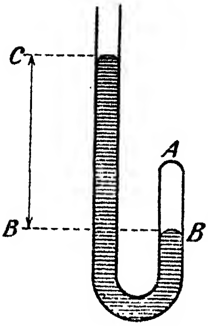


FIG. 2.—Boyle's Apparatus.

Boyle's Law assumes the temperature to remain constant, the changes in volume under pressure variation taking place isothermally. If the changes are effected adiabatically (Greek *a* not, *dia* through, *batos* passable), that is, if no heat is allowed to escape from or to enter the system, the equation connecting the change of volume with pressure is

$$PV^{\gamma} = \text{constant} \quad . \quad . \quad (3)$$

where γ is the ratio of the specific heats of the gas at constant pressure and constant volume respectively (p. 230). This is known as the **adiabatic gas equation.** The method of deriving it is given on pp. 238, 239.

The Law of Charles.—About the year 1787 the French engineer Charles observed that equal volumes of air and of several of the so-called "permanent" gases, namely oxygen, nitrogen and hydrogen, when heated under constant pressure from 0° to 80° C. expanded by equal volumes. The law lying at the root of this observation is frequently expressed as follows:

When a gas is heated through one degree centigrade its volume increases by 1/273 or 0·00366 of its volume at 0° C. provided the pressure remains constant.

Charles never published his results, and it was only by accident that Gay-Lussac became acquainted with them and published a brief summary in 1802. The latter also gave an account of extensive researches of his own along similar lines. Dalton had already in 1801 re-discovered the same law independently, and in consequence the names of both of these famous chemists are frequently attached to it. As a matter of historical interest it may be mentioned that Cavendish appears also to have made the same discovery simultaneously with, but unknown to, Charles, but like Charles refrained from publication.

The law may be expressed mathematically as follows:

$$V_t = V_0(1 + at) \quad . \quad . \quad . \quad . \quad (4)$$

where V_t is the volume of gas at t° C. which occupies a volume V_0 at 0° C., and a is the coefficient of expansion, namely 1/273.

Suppose, now, the temperature of a given volume of gas at 0° C. is raised through 1° C., the volume being kept constant. What will be the effect upon the pressure? The same effect precisely would be obtained by warming the gas at constant pressure, and then compressing it to its original volume. By Boyle's Law the pressure would then increase by the same amount as the volume had originally increased. The law connecting temperature and pressure at constant volume may therefore be stated as follows:

For each degree rise of temperature on the centigrade scale there results an increase in pressure amounting to 0·00366 of the pressure at 0° C.

The Gas Equation.—It follows from equation (4) that if the gas is cooled below 0° C. its volume will decrease by 1/273 of its volume at 0° C. for every degree its temperature falls. If, therefore, it is cooled from 0° through 273° on the centigrade scale, its volume should be reduced to zero. Actually, of course, this would not be the case, for the gas would liquefy and solidify before so low a temperature was reached, and once the gas had liquefied, further decrease in temperature would exert but a small effect upon the volume. As we shall see later, however, helium had to be cooled to extraordinarily low temperatures to effect its liquefaction, the boiling point of liquid helium being only four degrees above $-273°$ C. (p. 92). The theoretical conception of such a low temperature has proved most useful; and, as it is impossible to conceive of a substance as occupying a negative volume, it is convenient to regard $-273°$ C. as the lowest temperature attainable. It is therefore termed the **absolute zero.** Temperatures are frequently expressed with reference to this absolute zero, and are then usually designated as °*T*., °abs. (absolute) or °K. (Kelvin scale, Vol. II). Thus, for example, ice melts at 0° C., and this is 273° C. above the absolute zero; hence ice melts at 273° *T*. We therefore have:

$$T = t + 273,$$

where t represents the temperature on the centigrade scale.

Equation (4) may now, therefore, be written as:

$$V_t = V_0 \cdot \frac{273 + t}{273}$$

$$= V_0 T/273,$$

that is,

$$V_t/V_0 = T/273$$

or

$$V \propto T \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or, the volume of a gas is proportional to the absolute temperature, provided the pressure remains constant.

Combining equations (2) and (5):

$$V \propto T \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$V \propto 1/P \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we have

$$V \propto T/P$$

or

$$PV = \text{const.} \times T$$

$$= RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

R is known as the **Gas Constant,** and its value is conditioned by the units chosen. By a proper choice of units, however, it is possible to make R the same for every gas to which the equation applies. The chemist usually employs the molecular weight and molecular volume as his units, and in the most general form of the gas equation,

$$PV = RT,$$

P denotes the pressure and V represents the gramme-molecular volume, which, according to Avogadro's Hypothesis, is a constant quantity for all gases at the same temperature and pressure. Hence, provided the gramme-molecule of a gas is always dealt with, the value of R is independent of the *nature* of the gas, and its numerical value depends only upon the units in terms of which P, V and T are expressed.

When a substance changes its volume under pressure, work is either done *by* the substance (if it expands) or *on* the substance (if contraction occurs), and so, in accordance with the method employed in measuring work, the product PV represents the work done when one gramme-molecular volume of gas is generated under a pressure P. The value of R, measured in work units, *i.e.* ergs, can be obtained as follows :

At 0° C. or 273° T., and 76 cm. pressure, V is 22,400 c.c. Since the density of mercury at 0° C. is 13·596 grammes, the pressure in dynes is :

$$P = 76 \times 13{\cdot}596 \times 981.$$

Hence
$$R = \frac{PV}{T} = \frac{76 \times 13{\cdot}596 \times 981 \times 22{,}400}{273}$$
$$= 8{\cdot}32 \times 10^7 \text{ ergs.}$$

The equation is sometimes expressed in another way. Since mechanical energy and heat energy are quantitatively transformable, $4{\cdot}184 \times 10^7$ ergs being equivalent to 1 gramme-caloric of heat (the mechanical equivalent of heat), R can also be expressed in heat units, obviously being approximately equivalent to 2 (more exactly 1·985) calories. Inserting this numerical value of R, we have

$$PV = 2T.$$

In this form the equation is of particular use in thermochemistry in cases where it is desired to determine heats of reaction between gases. If a reaction be accompanied by expansion or contraction, part of the heat effect observed is due to the work done during the alteration of volume, and this must be allowed for in deducing the actual heat of reaction. At t° C. the production of each gramme-molecular volume of gas corresponds to an absorption of $2(273+t)$ or $(546+2t)$ gramme-calories owing to the performance of external work (p. 20). Thus, for example, when a gramme-atom of zinc dissolves in dilute sulphuric acid, a gramme-molecule of hydrogen is liberated. At 18° C. the work done on the atmosphere in making room for this gas is given by

$$\begin{aligned} W = PV &= RT \\ &= 2 \times 291 \\ &= 582 \text{ gramme-calories.} \end{aligned}$$

If, on the other hand, we choose one atmosphere as our unit of pressure, and take the volume of a gramme-molecule of an ideal gas as our unit of volume, namely 22·40 litres at 0° C. or 273° abs., the value for R becomes :

$$R = \frac{PV}{T} = \frac{1 \times 22{\cdot}40}{273} = 0{\cdot}0821 \text{ litre-atmosphere.}$$

Finally, choosing the volume of 1 gramme of gas as our unit of volume, retaining the atmosphere as our unit of pressure, we have :

$$R=\frac{PV}{T}=\frac{1\times 22{\cdot}40}{273\times M}$$

where M is the molecular weight of the gas.

Graham's Law of Diffusion of Gases.—It is a common experience that heavy vapours, such as bromine, can travel upwards and make their presence known, if not by their colour, by their pungent or unpleasant odour. Early experimenters on gases found that a mixture of two gases of different densities does not separate out into layers, with the heavy one underneath, and Priestley found that when two gases are carefully brought together with the heavier one underneath, they slowly pass into a homogeneous mixture. Dalton, in 1803, also found that any two of the gases air, nitrogen, hydrogen, oxygen and carbon dioxide always mix when put into communication by means of tubes.

In 1823 Döbereiner observed that hydrogen collected in a flask with a very fine crack escaped into the air, and water rose into the flask, although no hydrogen escaped when the flask was surrounded by a cylinder of the same gas. The explanation of this phenomenon was furnished in 1832, when, on repeating Döbereiner's experiments, Graham found that as hydrogen escaped air entered the vessel. The actual law according to which this diffusion occurred was discovered by Graham in a series of experiments in which tubes, from 6 to 14 inches in length, were closed at one end by a thin porous plug of plaster of Paris, filled with gas over water, and diffusion then allowed to proceed. After a given time the residual gas was analysed in order to determine the amount of the original gas remaining and the amount of air which had entered by diffusion. Graham found that:

The rate of diffusion of a gas is inversely proportional to the square root of its density.

This is known as Graham's Law, and may be expressed mathematically as:

$$v\sqrt{d}=\text{const.} \qquad . \quad . \quad . \quad . \quad . \qquad (7)$$

where v is the velocity of diffusion. Graham based his deduction on the following results:

Gas.	Density. (Air = 1.)	$1/\sqrt{d}$.	Velocity of Diffusion. (Air = 1.)	$v\sqrt{d}$.
Hydrogen . .	0·06949	3·7935	3·83	1·01
Methane . . .	0·559	1·3375	1·344	1·00
Carbon monoxide .	0·9678	1·0165	1·1149	1·13
Nitrogen . . .	0·9713	1·0147	1·0143	1·00
Ethylene . .	0·978	1·0112	1·0191	1·01
Oxygen . . .	1·1056	0·9510	0·9487	1·00
Hydrogen sulphide .	1·1912	0·9162	0·95	1·03
Nitrous oxide . .	1·527	0·8092	0·82	1·01
Carbon dioxide .	1·529	0·8087	0·812	1·04
Sulphur dioxide .	2·247	0·6671	0·68	1·02

The plug of plaster of Paris may be replaced by other porous materials, such as stucco, but Graham eventually found (1863) the best material was a plate of artificial graphite, 0·5 mm. thick. To demonstrate the difference in the diffusive powers of different gases, use may also be made of thin-walled cells of unglazed porcelain.

Graham's Law was usefully applied some years ago in determining the molecular weight of ozone. Soret (1867) determined the relative rates of diffusion of mixtures of oxygen with ozone, carbon dioxide and chlorine respectively, and was able to show that the density of ozone and hence its molecular weight was a little higher than that of carbon dioxide (M. wt. 44), but distinctly lower than that of chlorine (M. wt. 71). The experiment was repeated with greater accuracy by Ladenburg (1898), who used a gas containing 84·4 per cent. of ozone obtained by evaporation of liquid ozone, and from the velocity of diffusion calculated the molecular weight as 47·0, thus confirming the formula O_3 for the gas.

If a thick porous plug is used, the rate of diffusion is no longer proportional to the square root of the gas density, for the friction of the gas with the sides of the pores reduces the velocity. The action is, indeed, similar to the passage of a gas through a narrow tube, a process which is called **transpiration**, and which is concerned with the passage of the gas bodily rather than on account of diffusion by molecular movement.

The facts concerning the rate of diffusion of a gas have received practical application in the process called **atmolysis**, whereby the constituents of a gaseous mixture can be partially separated. Thus, if electrolytic gas be passed slowly through a porous clay tube, so much of the hydrogen will escape by diffusion through the walls that the gas collected from the end of the tube will no longer explode. If, instead of electrolytic gas, steam be passed through the tube, heated to a white heat, it is possible to demonstrate that a partial dissociation occurs by the fact that the steam issuing is mixed with an excess of oxygen. Similarly, the products of the dissociation of ammonium chloride may be partially separated, or again, argon can be concentrated in its mixture with nitrogen.

It is a matter of historical interest that one of the methods used by Ramsay to confirm the presence of a heavy gas, now known as argon, in the atmosphere, consisted in passing a large quantity of air through a long train of stems of " churchwarden " tobacco-pipes, placed inside a glass tube in which a vacuum was maintained. The gases passing through the porous walls of the pipe-stems were pumped off and discharged, the air issuing through the pipes freed from oxygen and the density of the remaining " nitrogen " determined. The product was consistently denser than atmospheric " nitrogen," showing that the heavier gas, namely argon, was being concentrated in the nitrogen by this means.

The method has also been employed in an attempt to effect a partial separation of the isotopes of chlorine (Vol. II).

As a practical means of purifying gases the process of atmolysis is, however, of little use.

As will be shown later, Graham's Law can be deduced on the basis of the kinetic theory of gases (p. 56).

Investigations were also carried out by Graham in which a metal plate, pierced by a very fine hole, closed the tube containing the gas. In these experiments the gas was forced through the aperture by a slight excess of pressure in the tube, and its passage outwards under these conditions was termed **effusion.** For any one gas the rate of effusion was proportional to the difference of pressure on the two sides of the plate, and for different gases under the same pressure conditions the rates were, like the rates of diffusion, inversely proportional to the square roots of the densities. This was made, by Bunsen (1857), the basis of a convenient method for determining the approximate density of a gas when only a few cubic centimetres were available. The apparatus employed consisted of a glass tube open at the lower end, and closed by a tap at the upper end (fig. 3). Just beyond the tap, the tube, contracted to a small diameter, was closed by a sheet of platinum containing a hole so small as to be invisible to the unaided eye. The tube was filled with and inverted over mercury, and the gas introduced, the level of the mercury outside being sufficiently above that within the tube to drive the gas steadily upward. The tap was now opened and the time required for the mercury level to rise through a certain height in the tube (determined by the aid of a float) was noted. By a comparison under exactly the same conditions with a gas of known density, the density of the first gas could then be found.

More recently, Emich has modified the method for use at high temperatures (1400° to 2000° C.).

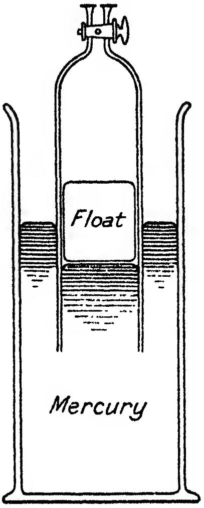


Fig. 3.—Bunsen's Effusiometer.

If d_1 and d_2 are the densities of two gases, v_1 and v_2 their rates of flow under the same difference of pressure through the small aperture, then, since their rates of flow are inversely proportional to the times θ_1 and θ_2 required for equal volumes to effuse, it follows that:

$$\frac{\theta_1^2}{\theta_2^2}=\frac{v_2^2}{v_1^2}=\frac{d_1}{d_2} \qquad . \quad . \quad . \quad . \qquad (8)$$

It is of interest to note that the method was used at the ordinary temperature by Perkins (1908) and by Debierne (1910) in the determination of the density of niton or radium emanation. The values obtained ranged from 110 to 117·5, the accepted value (1931) being 111. It may be mentioned also, in passing, that argon does not conform rigidly to Graham's Law, but effuses through a hole in a platinum plate some 3·5 per cent. more rapidly than would be expected when compared with oxygen.

Dalton's Law of Partial Pressures (1802) states that:

The pressure exerted by a gaseous mixture is equal to the sum of the pressures which the constituents would exert if each occupied separately the volume of the mixture.

This is really a particular case of dissolution, namely the dissolution of gases in gases, and as such is dealt with later (p. 342). As a matter of historical interest it may be mentioned that Cavendish had discovered this law twenty years earlier, as his laboratory notes bear witness, but he had omitted to publish his results.

Gay-Lussac's Law of Combining Volumes and **Avogadro's Hypothesis** have already been considered.

The Ideal or Perfect Gas.—So far we have omitted to consider the question as to the extent to which the gas laws are valid. As we shall see presently, no known gas is capable of conforming perfectly to their requirements. It is useful, however, to form a mental picture of an ideal or perfect gas in order that we may be able to study the extent to which known gases deviate from our theoretical laws. Thus:

(1) A perfect gas would respond to variation in pressure in strict accordance with Boyle's Law, whatever the temperature.
(2) A perfect gas would contract uniformly as the temperature fell, without liquefying or solidifying, and its volume would be zero at −273° C.
(3) A perfect gas would resemble every other perfect gas in possessing the same molecular volume under the same conditions of temperature and pressure. That is, perfect gases would conform to Avogadro's hypothesis.
(4) Gay-Lussac's Law of Combining Volumes would be accurately obeyed by interacting perfect gases.

As no gas is perfect, we shall now pass on to consider the ways in which gases deviate from the gas laws. In general it is found that the more readily liquefiable gases deviate to a greater extent than the so-called "permanent" gases, and the higher the temperature and the lower the pressure the more nearly do gases resemble the "perfect" gas.

The Validity of Charles' Law.—The coefficient of expansion with rise of temperature was at first supposed to be the same for all gases. That this is not so was first proved definitely by Regnault, whose results are given in the following table, a being the coefficient of expansion between 0° and 100° C., measured at a constant pressure of one atmosphere.

Gas.	a.	Boiling Point, °C.	Gas.	a.	Boiling Point, °C.
Hydrogen .	0·003661	−252·7	Carbon dioxide	0·003710	−78·2
Air . .	0·003671	c. −193·0	Nitrous oxide	0·003719	−88·7
Carbon monoxide .	0·003669	−190·0	Sulphur dioxide	0·003903	−10·0

Evidently the value of a departs more and more from that of the true gas (conveniently represented at atmospheric pressure by hydrogen) according to the ease with which the gas can be liquefied. The coefficients of increase of pressure with rise of temperature show the same tendency.

Deviations from Boyle's Law.—With regard to Boyle's Law, the discoverer's investigations were limited to a range of pressure extending between $\frac{1}{30}$ atmosphere and 4 atmospheres, and were only able to prove the substantial truth of the relationship. Early in the nineteenth century, Oersted, Despretz, Arago, Dulong and others turned their attention to the question whether or not Boyle's Law would be valid if pressures considerably greater than atmospheric were applied to a given volume of gas. No trustworthy data were obtainable, however, until the experimental results of Regnault were published in 1847.

Regnault designed his apparatus to give a wider range of pressure than his predecessors. He also employed a new device to reduce the error in reading the volume of the gas under pressure. Since the volume of the gas under, say, 10 atmospheres pressure would be only approximately one-tenth that at the ordinary pressure, the percentage error in reading the volume was obviously magnified about ten times. Regnault confined his gas in the tube G (fig. 4), kept at constant temperature, and applied pressure by means of a pump to the mercury in the reservoir. The height of the column of mercury, AB, enabled the pressure in G to be calculated. At the commencement of the experiment the mercury level in G was adjusted to D, and the height of the other mercury column noted. The pressure was then increased until the gas in G was compressed to the volume above C, and its amount again noted. The pressure was now kept constant and gas was pumped into G through F until the level of the mercury again fell to D. The pressure was now increased until the mercury again rose to C. By this means at each change of pressure the volume of the gas changed by the same amount and the small inevitable experimental error of reading at high pressures was not appreciably greater than that at low ones.

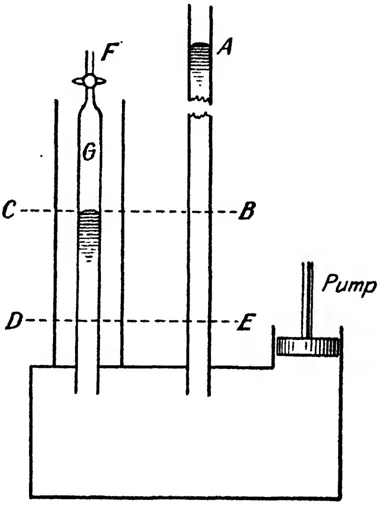


FIG. 4.—Regnault's Apparatus.

As the result of his experiments, Regnault found that not one of the four gases he employed, namely, hydrogen, nitrogen, air and carbon dioxide, obeyed Boyle's Law between pressures of 1 and 27 atmospheres, the range used; and further, he found that whereas hydrogen was less compressible than the law would lead us to expect, the three others were more compressible. Hydrogen is therefore said to be *ultra-*, *super-*, *hyper-* or *over-perfect*, whilst the other three gases are termed *sub-*, *hypo-* or *under-perfect* gases.

The small range of pressures adopted by Regnault led to inquiries by other investigators, the most important experiments being those of Amagat (1880 to 1893). Two series of determinations were carried out. In the first, the pressures employed reached 400 atmospheres and were measured directly, the manometer tube for the purpose being built in the shaft of a coal-mine. The tube was made of steel to withstand the pressure. To the top of the tube, which was made in sections and adjusted to the lengths of the mercury column, Amagat attached a wider tube of glass, so that readings could be taken by direct observation. In this way the behaviour of nitrogen, hydrogen, oxygen, carbon dioxide and air was tested, and, when known, enabled one of these gases, nitrogen, to be used in a manometer instead of a column of mercury.

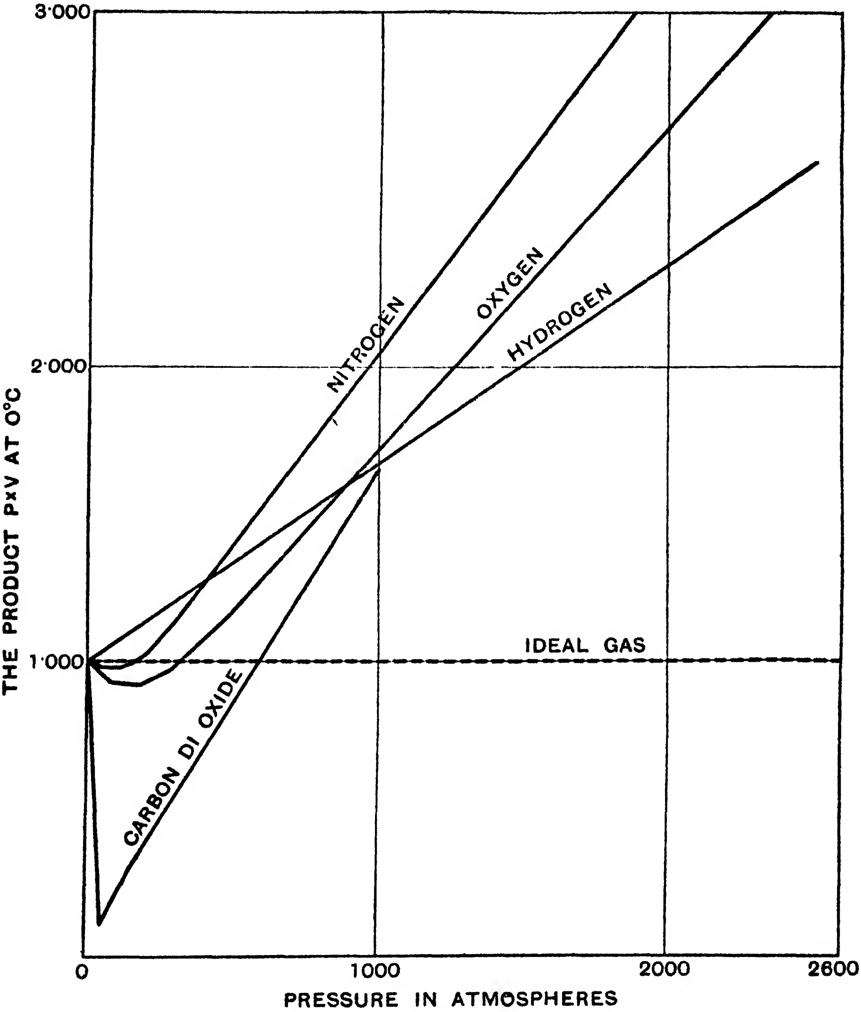


FIG. 5.—The Compressibilities of Oxygen, Nitrogen, Hydrogen and Carbon Dioxide at 0° C. (Amagat, 1893).

The pressures employed in the second series of experiments rose as high as 3000 atmospheres, being measured by a mechanical device in an apparatus based on the principle of the hydraulic press.

In addition to the five gases already mentioned, Amagat also investigated the behaviour of methane and ethylene. Some of his results are included in the following table, these being shown graphically in fig. 5. The data for carbon dioxide from 100 to 1000 atmospheres relate entirely to the liquid.

Relation between Pressure and Volume.

(Amagat, 1893.)

Pressure in Atm.	PV at 0° C. (Oxygen).	PV at 0° C. (Nitrogen).	PV at 0° C. (Hydrogen).	PV at 0° C. (Carbon Dioxide).	PV at 0° C. (Air).
1	1·0000	1·0000	1·0000	1·0000	1·0000
100	0·9265	0·9910	1·0690	0·202	0·9730
200	0·9140	1·0390	1·1380	0·385	1·0100
500	1·1570	1·3900	1·3565	0·891	1·3400
1000	1·7360	2·0700	1·7250	1·656	1·9990
2500	3·3238	3·9200	2·6950	..	3·7913

The results both confirmed and very considerably extended Regnault's observations, hydrogen standing alone as a gas less compressible than expected, all the others being more compressible than according to Boyle's Law, when only a comparatively limited range of pressure was employed. When still higher pressures were applied, the value of the product PV reached a minimum, as shown in the table, and thereafter steadily increased, just as with hydrogen.

The most convenient method of representing the facts graphically is to plot, not simply the pressure against volume, but the product PV against the pressure P, and in the curves (figs. 5 and 6) this method is adopted. Fig. 5 indicates the general types of curves obtained by Amagat, together with that which should be obtained if Boyle's Law were exact—namely, a horizontal straight line. Oxygen and air are similar in behaviour to nitrogen, while the curve for ethylene has a deep minimum point, like that for carbon dioxide, thus illustrating the fact that the more easily liquefiable a gas is, the more it tends to deviate from the gas laws. Modern work has shown that the curves for helium and neon resemble that for hydrogen ; these gases are therefore ultra-perfect. It will be observed that air gives results intermediate between those of oxygen and nitrogen, as is to be expected from a mixture of the two gases.

As the temperature falls, air shows a steadily increasing tendency to deviate from Boyle's Law. This is evident from the curves in fig. 6. As the temperature rises towards 100° C. air behaves more and more like a perfect gas. The same is generally true for carbon dioxide, as shown in fig. 7. As the temperature rises the initial fall in the value for PV becomes less pronounced. At the ordinary temperature, the curves for hydrogen, helium and neon do not exhibit minima and it is necessary to cool these gases to a low temperature before curves of this type are obtained.

Boyle's Law, for pressures less than atmospheric, has also been the subject of many investigations. Reference may be made to those of Lord Rayleigh (1901 to 1905). Three ranges of pressure were used—namely, 1 to 0·5 atmosphere, 150 mm. to 75 mm., and 1·5 mm. to 0·01 mm. The results obtained between one atmosphere and half an atmosphere pressure are recorded in the following table, the value of pv referring to 0·5 atmosphere and that of PV to 1 atmosphere. At

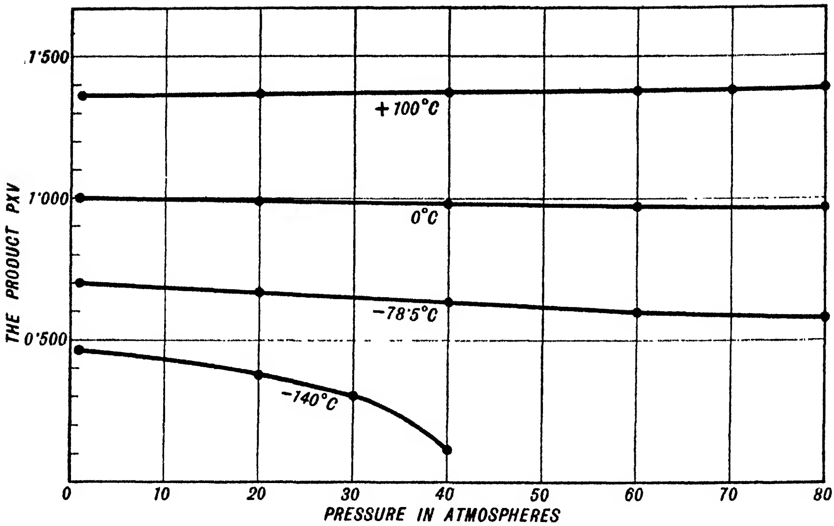


Fig. 6.—The Compressibilities of Air at Various Temperatures (Witkowski, 1896).

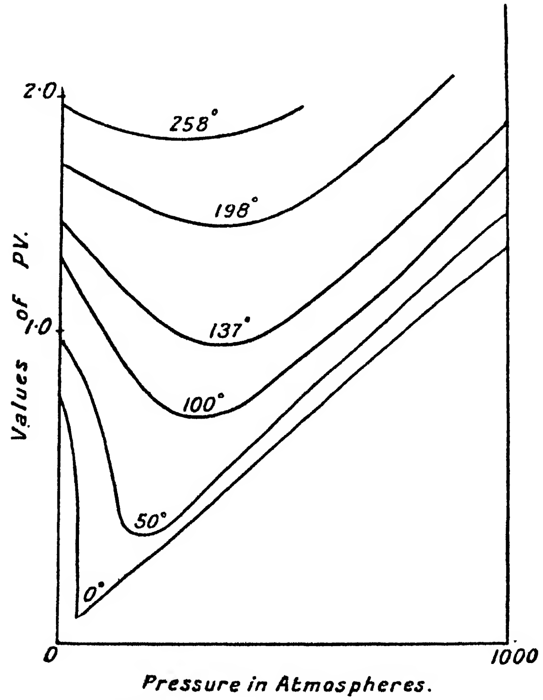


Fig. 7.—The Compressibilities of Carbon Dioxide at Various Temperatures (Amagat, 1896).

Gas.	Temperature, °C.	$\frac{pv}{PV}$.	Boiling Point, °C.
H_2	10·7	0·99974	−252·7
N_2	14·9	1·00015	−195·8
Air	11·4	1·00023	c. −193·0
CO	13·8	1·00026	−190·0
O_2	11·2	1·00038	−183·0
N_2O	11·0	1·00327	− 88·7
NH_3	9·7	1·00632	− 38·5

these pressures, then, just as at higher pressures, the gases most readily capable of liquefaction are those which depart to the greatest extent from Boyle's Law, the so-called permanent gases showing little deviation. Over the second range, 150 mm. to 75 mm., the easily liquefiable gases were found still to deviate slightly from the law, whereas the values of PV for nitrogen, air and hydrogen remained practically constant; but at low pressures, 1·5 mm. to 0·01 mm., all the gases appeared to obey Boyle's Law. Data obtained at very low pressures, however, are unreliable on account of the tendency of gases to condense on the walls of the containing vessels. At ordinary pressures the percentage error thus introduced may be negligible, but at very low pressures it may be considerable (see Chapter XXI).

The question of the absolute validity of Boyle's Law under extremely small pressures, then, cannot be decided from the experiments that have been made up to the present time. The error incurred by assuming the validity of Boyle's Law between two pressures p_1 and p_2 is best expressed by a coefficient $A_{p_1}^{p_2}$ defined by the equation

$$1 - \frac{p_2 v_2}{p_1 v_1} = A_{p_1}^{p_2}(p_2 - p_1) = A_0 \quad . \quad . \quad . \quad (9)$$

where A_0 is the **mean deviation** of the gas from Boyle's Law between 0 and 1 atmosphere. If Boyle's Law is accurate under extremely small pressures, then when p_1 and p_2 are very close to one another and each is almost nil, the coefficient $A_{p_1}^{p_2}$ should equal zero. Although experiment so far is unable to decide whether this is so or not, it is considered by many that such is *not* the case. This conclusion is readily deduced from van der Waals' equation (*vide infra*), and seems to be in accordance with the experimental evidence; for example, in the case of oxygen the deviation from Boyle's Law is as pronounced at 156 mm. as at 800 mm. pressure (Gray and Burt, 1909).

There is then, in general, at any fixed temperature, only one pressure in the immediate neighbourhood of which Boyle's Law is strictly true. This is the pressure at which PV is a minimum.

Deviations from Avogadro's Hypothesis.—It may be assumed that

at the same temperature and under a common, indefinitely small pressure, all gases have exactly the same gramme-molecular volume.

Since, however, as we have seen, gases do not rigidly obey either Boyle's Law or the Law of Charles, and no two gases deviate from these laws by exactly the same amount, it is obvious that, on raising the pressure to one atmosphere, the volumes occupied by gramme-molecules of two different gases will not now be the same. Ordinarily, therefore, Avogadro's hypothesis cannot be strictly true. As a result, Gay-Lussac's **Law of Combining Volumes** cannot be strictly true either, and we have already had occasion to point out (p. 44) that gases do not ordinarily combine together in ratios expressed exactly by whole numbers. Probably at indefinitely low pressures Gay-Lussac's Law would be obeyed exactly.

THE KINETIC THEORY OF MATTER.

We have already seen that the early Grecian philosophers believed that—

(i) matter was discontinuous, being composed of exceedingly minute particles, which we to-day call molecules, and

(ii) that these particles were always in motion.

If to these two hypotheses we add a third, namely,

(iii) that heat is a manifestation of molecular motion,

we have outlined the foundations of the modern kinetic theory of matter. This theory aims at interpreting thermal phenomena in mechanical terms.

In a **solid** the molecules are assumed to be very close together as compared with their distances in a gas. Since a solid normally offers great resistance both to tension and to compression, it would appear that whilst the molecules attract one another when situated certain distances apart, the force of attraction is changed to one of repulsion if the contact becomes too intimate. A compact solid may therefore be regarded as a vast number of molecules held closely together in an equilibrium configuration and almost entirely devoid of translatory movement.

It is convenient, though probably not quite correct, to assume that at the absolute zero of temperature (p. 39) the molecules are at rest. If any thermal energy is now absorbed it takes the form of vibrational movement, with possibly some rotational movement and certainly a little translational movement also. These movements manifest themselves as **heat**, and when they become increasingly pronounced we say that the **temperature** of the solid is rising.

That some of the molecules of a solid body do possess a certain amount of translational energy is indicated by the results of diffusion experiments. Thus Roberts-Austen (1896) stood cylinders of lead upon cylinders of gold and allowed them to remain in a cellar at 18° C. for four years. After this time it was found that some of the gold had diffused upwards into the lead. As the temperature is raised, the rate of diffusion is increased. At 197° C. gold has been found to diffuse into lead to a depth of 2·5 cm. in the course of 54 days (Ostrand, 1916), whilst copper and zinc cylinders placed in contact and warmed up to about 250° C. unite after a few hours, a thin layer of brass being formed at the joint. As zinc melts at 419° C., and both brass and copper at still higher temperatures (brass at 800° to 1000° C., copper at 1083° C.), it is evident the diffusion must have taken place whilst the metals were solid (Spring, 1900). This is a special case of what is known as **solid solution,** which subject is dealt with in further detail in a later chapter (p. 375). On the other hand, metals incapable of dissolving in each other do not diffuse in this manner. Zinc and lead, and bismuth and lead, are examples.

If our solid body continues to absorb thermal energy, the energy of vibration will continue to increase until eventually, provided no chemical change takes place to interfere with the normal course of things, the molecules acquire so much energy that their forces of attraction are unable to hold them in position. It is usually supposed that this is the case when **the amplitude of vibration of the molecules equals the distance between them.** The molecules then break away and we say that the substance melts, or acquires the **liquid state.** The molecules of a liquid thus certainly possess translational energy, and may possess other forms as well. On supplying further thermal energy to the liquid, again assuming no chemical change intervenes, a stage is ultimately reached when the translational energy of the molecules is so great that they dash away from each other with high velocities which their cohesive forces are entirely unable to control. The liquid is then said to boil, and to pass into the **vapour state.**

Such, in essence, is the kinetic theory of matter.

The Kinetic Theory of Gases.—Of the three forms of matter, gases are the most suitable for studying the kinetic theory. Gassendi, in 1658, appears to have been the first philosopher of the Christian era to suggest that the motion of the molecules of a substance might account for many phenomena, such as melting and boiling, for the explanation of which separate hypotheses had been advanced. In 1738 Bernouilli pointed out that the pressure exerted by a gas on the walls of a containing vessel may be caused by the impacts of the molecules. During the nineteenth century a large number of investigators took up the subject, including Clausius (1857), Maxwell (1859), and others whose names will be mentioned as occasion serves.

Before the kinetic theory was established, a *static theory* of gases was largely held. This theory, due largely to Sir Isaac Newton (1687), postulated that when a gas was nominally at rest, all its constituent molecules were likewise at rest, in static equilibrium, in consequence of their mutual repulsion. This repulsion was believed to account for the pressure exerted by a gas, and for the expansiveness. The increase of pressure observed on reducing the volume of a gas was explained on the very plausible ground that the nearer the molecules approached one another, the greater became the force of repulsion between them. For many years this static theory was a formidable rival to the kinetic theory, but was gradually discarded with the general acceptance of the latter between 1857 and 1870.

That the molecules in a gas do not repel one another may be illustrated as follows (Dunoyer, 1911): A vertical cylindrical tube is divided by two partitions A and B (fig. 8) into three compartments. Each partition is pierced at the centre with a small circular hole. Sodium is placed in the lowest compartment, the whole evacuated, and the sodium then vaporised by heating. The sodium molecules escape rapidly in every direction, the majority being deposited on the walls of the lowest compartment. Some pass through the hole in B and remain as a deposit in the middle compartment; a few pass through to the third compartment and form a deposit on the roof of the cylinder, the deposit coinciding with the projection of the hole in A formed by radii drawn from the hole in B. If the sodium molecules exerted a repulsive action upon one another they would expand in the second and third compartments and not follow rectilinear paths.

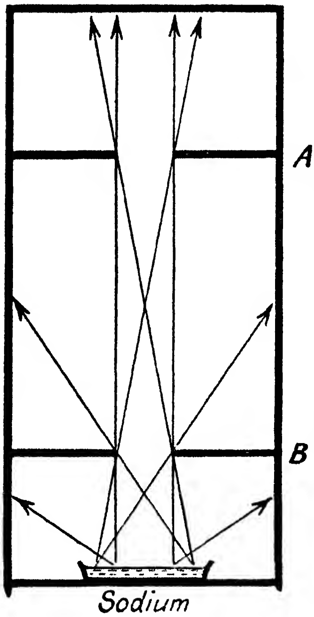


FIG. 8.

Size and Number of Molecules.—Gas molecules are regarded, for purposes of the kinetic theory, as perfectly elastic spheres, which, since they are in rapid motion, repeatedly collide with one another or with the walls of the containing vessel, and rebound unchanged and uninjured after each collision, no energy being dissipated as heat. We now know that molecules are complex structures (Vol. II), but if the interior structure remains unaltered after collision, we may, for mathematical purposes, regard molecules as elastic spheres. The volume actually occupied by the molecules themselves is small compared with the space they inhabit, so that, except during collision, the individual molecules are relatively free from each other's influence. Thus, for example, 1 c.c. of water when turned into steam at 100° C. occupies a volume of approximately 1700 c.c. under atmospheric pressure, so that the molecules in the steam are approximately $\sqrt[3]{1700}$ or 12 times as far apart as in the liquid.

The number of molecules in a gramme-molecule, that is to say in 22·4 litres, of gas at N.T.P. is inconceivably great, amounting to $6{\cdot}064 \times 10^{23}$. This is known as **Avogadro's Number**, and is denoted by N. The number of molecules in 1 c.c. of gas at N.T.P. is denoted by n, and is occasionally called **Löschmidt's Number.** The immensity of the value of N is indicated by the statement that if an ordinary evacuated electric light bulb were pierced with an aperture so that one million molecules of air could enter per second, 100 million years would elapse before the air inside the bulb could attain to the ordinary pressure of the atmosphere (Aston, 1924).

It is obvious that the molecules must be very minute when so vast a crowd can inhabit so small a volume, and in the accompanying table are given the effective diameters of the molecules of several typical gases, together with the **mean free paths,** λ, at N.T.P., by which expression we mean the average distance travelled by a molecule between two successive collisions with other molecules. In the solid and liquid states the mean free paths are of much the same order as the molecular diameters themselves.

The close similarity of the data for carbon dioxide and nitrous oxide, and for nitrogen and carbon monoxide, is noteworthy, and an explanation by the theory of the cubical atom is given in the sequel (Vol. II).

Molecular Data.

Gas.	Formula.	Molecular Diameter, cm.	Velocity * in Cm. per Second, u.	Mean Free Path at N.T.P. in Cm., λ.	Number of Collisions per Second, u/λ.
Hydrogen	H_2	$2{\cdot}17 \times 10^{-8}$	183,800	$17{\cdot}8 \times 10^{-6}$	10330×10^{6}
Oxygen	O_2	2·71 ,,	46,100	10·2 ,,	4520 ,,
Nitrogen	N_2	2·95 ,,	49,300	9·5 ,,	5190 ,,
Carbon monoxide	CO	2·74 ,,	49,300	9·5 ,,	5190 ,,
Nitric oxide	NO	2·59 ,,	47,700	9·4 ,,	5070 ,,
Carbon dioxide	CO_2	2·90 ,,	39,300	6·5 ,,	6050 ,,
Nitrous oxide	N_2O	3·33 ,,	39,300	6·5 ,,	6050 ,,
Sulphur dioxide	SO_2	..	32,600	4·7 ,,	6940 ,,
Water vapour	H_2O	2·27 ,,	61,500	7·2 ,,	8540 ,,

The knowledge of Avogadro's Number gives us a method of calculating the **mean mass of the molecules** when the gramme-molecular weight is known. Thus, for example, the gramme-molecular weight of oxygen is 32. The mass (m) of any single molecule is therefore

$$\frac{32}{6{\cdot}064 \times 10^{23}} = 5{\cdot}28 \times 10^{-23} \text{ gramme.}$$

Velocity of Gas Molecules.—Just as in a crowded city street all the people constituting the crowd are not moving with the same velocity, so there is a difference in the velocities of the molecules in a gas. Even if, at any one instant, all the molecules did possess the same velocity, a moment later they would differ widely again in this respect, since their energies change on collision. We may assume, however, that the resultant action of the impacts which each molecule suffers over a protracted time interval, with its kinetic energy continually changing, equals that which would result if all the impacts occurred with the same uniform mean kinetic energy, $\frac{1}{2}mu^2$, where m is the mass of each molecule and u is defined as that velocity which gives to the expression $\frac{1}{2}mu^2$ the value equivalent to the mean energy of motion of the molecules. This is equivalent to saying that if all the molecules possessed the same velocity u, the gas would have the same kinetic energy as it possesses with its random distribution of velocities.

The value thus obtained for u is not the arithmetic mean or average velocity, c, which is evaluated by adding all the velocities at a given moment together and dividing by the number of molecules, n. It is clearly the **square root of the mean square** of the molecular velocities divided by n, and may be expressed mathematically as

$$u = \frac{1}{n}\sqrt{c_1^2 + c_2^2 + \ldots} \quad . \quad . \quad . \quad . \quad (10)$$

---

* Square root of mean square molecular velocity at 0° C. calculated from equation (16), p. 56.

It can be shown (Maxwell, 1860) that

$$c=\sqrt{\frac{8u^2}{3\pi}}=0{\cdot}9213u \quad . \quad . \quad . \quad . \quad (11)$$

or

$$u=1{\cdot}0855c.$$

The number of collisions per second undergone by an individual molecule in a gas at N.T.P. is termed the **collision frequency**, and data for a few gases are given in the table (p. 53).

✓**Kinetic Explanation of Gas Pressure.**—During the intervals between successive collisions gas molecules may be regarded as travelling in straight lines, the effect of gravity being too minute to cause appreciable deviation. Owing to collision, both the velocity and the direction of motion are continually altering, and for the present the time occupied by a collision may be regarded as negligible.✓ We shall refer to this point again later (p. 65). Suppose, now, we consider a cubical vessel, the length of whose edge is l cm. (fig. 9). The vessel is filled with gas at N.T.P. and contains n molecules, each of mass m, the square root of the mean square of the velocities being u. In future we shall refer to this simply as the velocity, and assume that each molecule moves with this particular velocity.

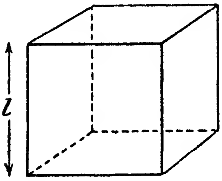


Fig. 9.

A molecule will not necessarily be moving in a direction at right angles to any wall of the containing vessel. We may, however, regard its velocity as made up of three component velocities u_1, u_2 and u_3, parallel to the edges of the cube, these components being related to the actual velocity as indicated by the equation

$$u^2=u_1^2+u_2^2+u_3^2 \quad . \quad . \quad . \quad . \quad (12)$$

Consider an individual molecule, moving with velocity u_1 and striking one of the faces of the cube perpendicularly. As it is perfectly elastic and the wall of the cube is also perfectly elastic, the molecule will rebound along its own path towards the opposite face of the cube. Before collision the momentum of the molecule was mu_1; after collision its momentum is numerically the same, but in the opposite direction. Hence the change in momentum during collision is $2mu_1$.

It is these impacts on the walls of the containing vessel that cause the effect which we call pressure. This can be calculated, since change in momentum equals impulsive force. The distance between the two parallel faces of the cube is l, so that assuming the molecule is unhindered by collision with other molecules, it will strike the opposite face in l/u_1 seconds, only to rebound again. The total number of collisions on the two parallel walls made by this molecule per second will thus be u_1/l, so that the total change of momentum per second, or in other words the force exerted by the molecule on the two faces, is

$$\begin{aligned}&2mu_1 \times u_1/l\\&=2mu_1^2/l.\end{aligned}$$

We have, however, only considered the velocity component u_1. It is obvious that on all six sides of the cube the total force exerted by our single molecule is

$$\frac{2m}{l}(u_1^2+u_2^2+u_3^2)$$
$$=\frac{2mu^2}{l}.$$

For the n molecules present in the cube the effect is

$$2nmu^2/l.$$

As this force is distributed over the six faces of the cube, the force per unit area, that is, the pressure, P, is given by

$$P=\frac{2nmu^2}{l}\cdot\frac{1}{6l^2}$$
$$=\tfrac{1}{3}nmu^2/l^3,$$

or, since l^3 is the volume, we may write

$$PV=\tfrac{1}{3}nmu^2$$

or

$$P=\tfrac{1}{3}\frac{nm}{V}\cdot u^2=\tfrac{1}{3}du^2 \quad . \quad . \quad . \quad (13)$$

where d is the density, given by mn/V.

The Kinetic Theory and the Gas Laws.—If a gas is maintained at constant temperature in a closed vessel, it neither gains nor loses energy; u, therefore, is constant, and since n and m are constant, it follows that

$$PV=\tfrac{1}{3}nmu^2$$
$$=\text{constant}.$$

This is **Boyle's Law.**

The total average kinetic energy, E, of the molecules in a gramme-molecule of gas is $\tfrac{1}{2}Nmu^2$.

Now

$$RT=PV,$$

where V is the gramme-molecular volume or 22·4 litres (p. 32); and

$$PV=\tfrac{1}{3}Nmu^2$$
$$=\tfrac{2}{3}\cdot\tfrac{1}{2}Nmu^2$$
$$=\tfrac{2}{3}E,$$

whence

$$E=\tfrac{3}{2}RT \quad . \quad . \quad . \quad . \quad . \quad (14)$$

That is, the mean kinetic energy of the gas molecules is proportional to the absolute temperature. This affords us another **method of expressing the temperature of a gas,** namely, in terms of the average kinetic energy of the molecules.

Let us now consider two gases under the same conditions of temperature and pressure. The product PV for the first gas may be written as $\tfrac{1}{3}N_1m_1u_1^2$ and for the second as $\tfrac{1}{3}N_2m_2u_2^2$. Whence

$$\tfrac{1}{3}N_1m_1u_1^2=PV$$
$$=\tfrac{1}{3}N_2m_2u_2^2.$$

Maxwell proved that when the gases are at the same temperature, the mean kinetic energies of their molecules must be the same, that is

$$\tfrac{1}{2}m_1u_1^2 = \tfrac{1}{2}m_2u_2^2,$$

and experiment shows that on mixing two chemically inert gases at the same temperature and pressure no change occurs in either of these factors.

From the two equations it is easy to derive that

$$N_1 = N_2.$$

This is **Avogadro's Hypothesis.**

Equation (13) may be written as

$$u = \sqrt{\frac{3PV}{nm}}$$

$$= \sqrt{3P/d} \quad . \quad . \quad . \quad . \quad (15)$$

since the density, d, of the gas is given by $\frac{mn}{V}$. If the pressure is kept constant, then

$$u \propto \frac{1}{\sqrt{d}}$$

which is **Graham's Law of Diffusion.**

Calculation of Molecular Velocities.—With the aid of equation (15) it is easy to calculate the mean velocity of gas molecules under specified conditions. Thus, for oxygen at N.T.P. :

$$P = 1 \text{ atmosphere,}$$
$$= 1{,}013{,}240 \text{ dynes per sq. cm.} \qquad \text{(p. 18),}$$

and

$$d = 1{\cdot}4290 \text{ grammes per litre,}$$
$$= 0{\cdot}001429 \text{ gramme per millilitre.}$$

Whence

$$u = \sqrt{\frac{3P}{d}}$$
$$= \sqrt{\frac{3 \times 1{,}013{,}240}{0{\cdot}001429}}$$
$$= 46{,}100 \text{ cm. per sec.,}$$
$$= 17 \text{ miles per minute (approx.).}$$

Since the density of a gas is proportional to the molecular weight, it is only necessary to know the molecular weight of a gas with reference to oxygen, as standard, in order to calculate the velocity of its molecules. Thus

$$u_{\text{gas}} : u_{\text{oxygen}} = \sqrt{d_{\text{oxygen}}} : \sqrt{d_{\text{gas}}}$$
$$= \sqrt{M_{\text{oxygen}}} : \sqrt{M_{\text{gas}}}$$

where M is the gramme-molecular weight. Whence

$$u_{\text{gas}} = u_{\text{oxygen}}\sqrt{\frac{M_{\text{oxygen}}}{M_{\text{gas}}}}$$

$$= \frac{261{,}000}{\sqrt{M_{\text{gas}}}} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

A few data, obtained in this way, are given in the table on p. 58. The magnitude of these velocities is surprising. Gravity cannot appreciably parabolise the paths of the molecules, but it does prevent the molecules from escaping to any appreciable extent, otherwise we should lose our atmosphere. To escape entirely from the earth, without returning, a molecule of oxygen, regarded purely from the point of view of a projectile, would require to move with a velocity of at least 1,100,000 cm. per second at the earth's surface, which is at least twenty times the velocity of the gas at 0° C. On the moon, however, whose diameter is only one-quarter that of the earth, the acceleration due to gravity is only about one-sixth that on the earth, and to escape entirely a molecule need on the foregoing hypothesis only move with a velocity of 240,000 cm. per second at the moon's surface. This is very little more than the mean value found for hydrogen, namely 183,800 cm. per second (Meyer, 1899).

In actual fact, however, the problem is not quite as simple as this. The earth appears to be surrounded by an **inner, convection,** or **adiabatic atmosphere,** beyond which is an **outer** or **isothermal atmosphere.** As regards the inner atmosphere, if it were at rest solely under the force of gravitation, its density would fall exponentially with the height, h, above the earth's surface at sea level. Actually, however, the air is continuously agitated and mechanical transference of the gases takes place from one point to another. The density, and hence the temperature, of each portion of air thus transported to a different level undergoes change, but before the new temperature has adjusted itself to its surroundings, transportation takes place to some other point. The relation between the pressure and volume is not that expressed by Boyle's Law, but conforms to the requirements of the adiabatic gas equation, namely

$$P = k \cdot \frac{1}{V^{\gamma}} = kd^{\gamma} \quad . \quad . \quad . \quad . \quad (3)$$

where d is the density.

The general equation of equilibrium of the air is

$$\frac{dP}{dh} = -gd. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

On coupling these two equations we obtain, upon integration,

$$\frac{k\gamma}{\gamma - 1}(d_0^{\gamma-1} - d^{\gamma-1}) = gh \quad . \quad . \quad . \quad (18)$$

where d_0 is the density at the earth's surface, and d that at height h.

Now the absolute temperature T is proportional to $d^{\gamma-1}$ (see p. 238), whence

$$\frac{T_0 - T}{h} = \text{constant},$$

where T_0 and T are the temperatures at the earth's surface and at a height h.

The temperature thus decreases with the altitude. If, now, in equation (18) we give a zero value to d, the height at which the density of the atmosphere is zero is given by

$$h = k \cdot \frac{\gamma d_0^{\gamma-1}}{g(\gamma-1)} \quad . \quad . \quad . \quad . \quad (19)$$

and by substituting numerical values we find that h is approximately 30 kilometres.

We cannot imagine, however, that there is an abrupt and absolute end to the earth's atmosphere at this height, for if such a free surface existed, molecules arriving at it from within with finite velocities would pass out into space much in the same way as molecules escape from a liquid during evaporation. Such molecules would form an outer atmosphere, of low density it is true, but of density greater than the zero postulated. Collisions would be rare, and although some molecules possessing greater velocities than usual might pass off into space and be lost in so far as the earth's atmosphere was concerned, the majority would undoubtedly describe orbits under the influence of the earth's gravitation and fall back again into the inner envelope. This outer layer would be isothermal in character.

The existence of these two atmospheres has been confirmed experimentally, though the average value for the height to which the adiabatic envelope extends appears to be considerably less than the 30 kilometres calculated from equation (19). It is regarded as probable that the adiabatic atmosphere extends up to an average height of about 10·5 kilometres, at which the pressure is one-quarter of a normal atmosphere, and the temperature 220° abs. or −53° C. Beyond this the atmosphere is in isothermal equilibrium (Jeans, 1916).

It was Dalton who first suggested that, since air is a mixture and not a compound, the proportion of nitrogen to oxygen ought to increase with the altitude, nitrogen being the lighter gas. In the inner atmosphere the composition of the air, owing to convection, remains fairly constant, although at high altitudes the percentage of oxygen does appear to be very slightly reduced. As is shown by the following results, at an altitude of 2060 metres on the Alps descending currents of air were found to contain nearly 0·2 per cent. less oxygen than did ascending currents on the succeeding day.

Mean Percentage of Oxygen in the Air.

(Leduc, 1893.)

Sorbonne	23·14 to 23·20 per cent.
Nice, Nîmes, Algiers	23·23 ,,
Alps (2060 metres)	
Descending air currents	23·05 ,,
Ascending air currents	23·23 ,,

In the outer isothermal atmosphere, however, the heavier gases tend to sink to the bottom, that is, to the outer surface of the inner adiabatic envelope, whilst the lighter ones, such as hydrogen, rise to the top. At about 100 kilometres from the earth's surface, or some 90 kilometres beyond the outer layer of the inner envelope, it is calculated that hydrogen will constitute 90 per cent. of the whole atmosphere, whilst at 800 kilometres hydrogen will constitute practically the whole of the atmosphere (Jeans, 1916). At this height the mean free path of the gas will be approximately 100 metres. At a height of 8000 kilometres the mean free path is relatively enormous and the chance of collision is negligible, although the air will still contain about 30,000 molecules per c.c. A few of these molecules will undoubtedly escape, but the number is negligibly small. The proportion of helium nowhere reaches any great value. At 100 kilometres it exceeds the nitrogen, but is even then only one-eightieth of the amount of hydrogen.

The application of the kinetic theory to the **planetary atmospheres** is of great interest, although we cannot enter into it here. It will suffice to say that Jupiter, Saturn, Uranus and Neptune may be expected, even more rigidly than the earth, to retain all atmospheric constituents, including helium and hydrogen. Venus should have an atmosphere not very different in composition from ours, whilst Mars ought to retain its water vapour and the heavier gases. Actually Mars appears practically to be destitute of an atmosphere, and it may be that its proximity to the sun accounts for this, the high temperature of the sun giving rise to increased molecular velocities in the Martian atmosphere and thus facilitating escape of the constituents.

If we pause to consider the enormous velocities possessed by the molecules of a gas, we may at first thought be surprised that gaseous diffusion should be such a relatively slow process. A drop of bromine allowed to fall in a corner of the room immediately vaporises, but if disturbing air currents are excluded, an appreciable time elapses before the bromine can be scented a short distance away. Even more remarkable is the poor conductivity manifested by gases for heat. If heat really consists, as we have urged, in rapid motion of molecules, then a rise in temperature at a given point ought to be detectable 400 metres away in a second or so, provided the molecular motion is rectilinear. It must be borne in mind, however, that the molecules are not free to move unchecked over very long paths owing to collision with other molecules, which results in zig-zagging, so that the effective movement in any one given direction may be comparatively slow. The molecules thus execute a motion analogous to that of grains of corn shaken about in a box which they very nearly fill (Meyer, 1899). We can, therefore, readily understand the slow rate at which vapours will diffuse or heat will be transmitted in any given direction.

Viscosity and Mean Free Path.—That particular property of a fluid, whether gaseous or liquid, which determines its rate of flow when acted upon by a given force is termed its **viscosity** or **internal friction.** The reciprocal of the viscosity is termed the **fluidity** of the substance. Viscosity is a shearing effect caused by layers of the fluid passing over one another, and is possessed by a perfect gas (p. 44), being quite distinct from the forces of molecular attraction which exist in ordinary gases and cause them to deviate to a greater or less extent from the gas laws.

The **coefficient of viscosity,** η, is expressed in dynes per square centimetre, and may be defined as :

the force per unit area exerted between two parallel layers, unit distance apart, when the velocity of streaming differs by unity in the two layers.

It may be deduced from the kinetic theory that

$$\eta = \tfrac{1}{3} d\lambda u \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where λ is the mean free path, as defined on p. 52.

Writing equation (15) in the form

$$u = \sqrt{\frac{3P}{d}}$$

and substituting this value for u in equation (20) we have

$$\lambda = \eta\sqrt{\frac{3}{Pd}} \quad . \quad . \quad . \quad . \quad (21)$$

This is an interesting equation as it gives us a convenient method of determining the mean free path of the molecules, and the **collision frequency,** which is given by u/λ. A few data obtained in this way are given in the table on p. 53.

Energy possessed by Gases.—The enormous amount of energy possessed by a gramme-molecule of gas in virtue of the motion of its molecules is surprising. We have already seen (equation (14)) that

$$E = \tfrac{3}{2}RT$$
$$= \tfrac{3}{2}PV.$$

Whence

$$E = \frac{3}{2} \times 1{,}013{,}240 \times 22{,}400$$
$$= 34 \times 10^9 \text{ ergs.}$$

Suppose, therefore, it were possible for us to stop all the molecules contained in 22·4 litres of any gas at 0° C. and under atmospheric pressure; the work done by the stoppage would be 34,000,000,000 ergs, sufficient, for example, to raise 350 kilograms through 1 metre, or approximately 1·1 tons through 1 foot. The temperature of the gas would then, of course, have fallen to the absolute zero.

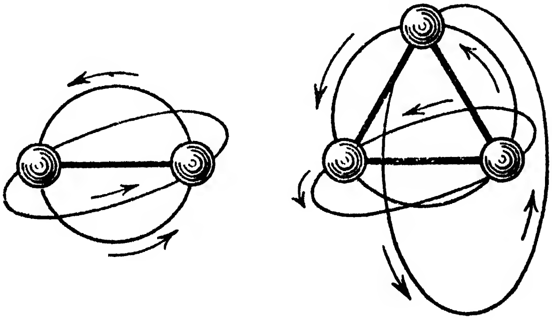


FIG. 10.

Degree of Freedom.—By this term is meant **a possible mode or direction of motion.** Consider, for example, a gas molecule; whether it is monatomic or polyatomic it possesses translational movement which may be resolved into three components at right angles to each other. We therefore say that the molecule possesses three degrees of translational freedom. In the case of a monatomic molecule these appear to be the sum total of its degrees of freedom, rotary and vibrational movement apparently being of no account.

It may be supposed that a diatomic molecule possesses rotary movement as well as translational. As the two atoms must necessarily lie linearly disposed, they are probably capable of rotating in two ways only, as shown in fig. 10, namely, around horizontal and vertical axes. They therefore possess but two degrees of rotational freedom. In addition the molecule possesses vibratory movement in one direction, namely that of the line joining the centres of the atoms, the atoms approaching or retreating from each other along this line as indicated in fig. 11.

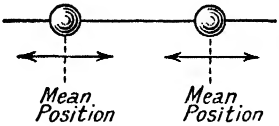


FIG. 11.

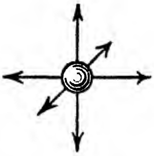


FIG. 12.

A triatomic molecule will possess three degrees of rotational freedom and an equal number of degrees of vibrational freedom; and so on.

In the following table are given the number of degrees of freedom which molecules containing up to four atoms are believed to possess.

No. of Atoms in Molecule.	Degrees of Freedom.		
	Translational.	Rotational.	Vibrational.
1	3	0	0
2	3	2	1
3	3	3	3
4	3	3	6

Considerable uncertainty exists as to the numbers of degrees of freedom that may be assigned to the molecules of liquids. Certainly the molecules will possess three translational degrees of freedom, but exactly how many in respect of rotation and vibration we do not know. Where solids are concerned, the molecules are believed to possess vibrational degrees of freedom only. In a monatomic solid, such as the solid inert gases and the metals, each atom can vibrate along three axes (fig. 12), and thus has three degrees of freedom. It is difficult to conceive the molecules of solids as possessing any free translational energy, otherwise their crystalline form could hardly be retained.

Boltzmann's Theorem of the Equipartition of Energy postulates that

> *The total kinetic energy of a system is equally distributed between the various degrees of freedom.*

To illustrate this, let us take the case of a monatomic gas, the molecules of which possess three degrees of freedom. The kinetic energy of a gramme-molecule of the gas is $\frac{3}{2}RT$ calories. This is presumed to be distributed equally between the three degrees of freedom, so that the kinetic energy of each degree is $\frac{1}{2}RT$ or approximately T calories, since R is 1·985.

The Radiometer.—This piece of apparatus was invented by Crookes and beautifully illustrates the motion produced by the unequal bombardment of surfaces by gas molecules. It consists of a glass bulb containing four mica vanes attached to the four arms of a cross, pivoted to move with but very slight friction about the centre, like a small paddle-wheel (fig. 13). Each vane is polished on one face and lamp-blacked on the other, the lamp-blacked faces being so placed that they all simultaneously move backward or forward. The gas-pressure inside the bulb is then greatly reduced and the vessel sealed.

When exposed to radiation, as, for example, sunlight, the vanes rotate in such a manner that their black faces recede from the source of radiation. The complete explanation is by no means simple, but an attempt may be made to convey an idea to the reader as to what is occurring. The black surfaces absorb the radiant heat more effectively than the polished surfaces, and the gas molecules in contact with the lamp-black receive, in consequence, more kinetic energy than those in contact with the polished surfaces. This extra energy of the rebounding molecules is manifested as a greater pressure on the lamp-black surface, and this surface of the vane recedes. This excess of pressure, however, will quickly die off from the general surface of the vane, for the rebounding molecules from the black surfaces will share their additional energy with other molecules by collision; a uniform temperature gradient outwards from each vane will become established and the decrease in density, resulting in fewer molecules coming up from the hot side, will compensate the extra energy of each collision, so that the pressure becomes the same on both sides, and the vanes would cease to move if this were the whole story. Near the edges, however, compensation will not be complete, for the impinging molecules come from a less restricted area, and the change in temperature and velocity at impact is greater. By using curved vanes, blackened on the convex side, there would be a wider distribution of the molecules from the black side, and the excess of pressure would be greater than with a plane vane.

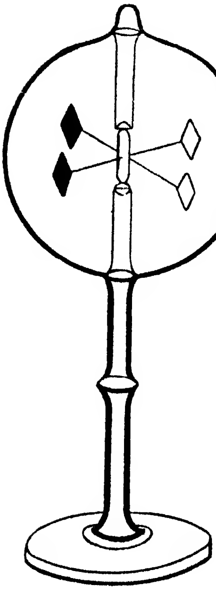


FIG. 13.—The Radiometer.

If the exhaustion of the glass globe is only partial, the vanes move in the opposite direction, namely with their blackened faces towards the source of radiation. This is supposed to be due to the heated molecules, after collision with the hot surface, colliding with and beating back the approaching, cooler molecules, thus causing a reduction in pressure in front of the vanes.

Hirn's Equation, 1865.—We have already seen that at high pressures the gas laws are not rigidly obeyed. In deriving these laws from the kinetic theory we have tacitly made two assumptions, neither of which is quite correct. These are :

i. That the volume of the molecules themselves is negligibly small compared with the space they inhabit; and
ii. That the molecules are devoid of cohesion and therefore exert no attractive force on each other.

At very low pressures and high temperatures these factors are in general negligibly small, but as the pressure increases we cannot afford to ignore them.

Hirn argued, therefore, that, in the equation

$$PV = RT,$$

instead of considering the volume V actually inhabited by the molecules, we ought to consider the available free or unoccupied space of that inhabited volume, namely $V - b$, where b represents some function of the *effective* volume of the molecules themselves, though not the *actual* volume.

The equation thus becomes

$$P(V - b) = RT \quad . \quad . \quad . \quad . \quad (22)$$

Hirn also introduced a correction for the second factor, to allow for the fact that molecules are not entirely without influence on one another. Joule and Thomson (Lord Kelvin) proved in 1854 that when a highly compressed gas is allowed to expand into a region of low pressure in such a manner that no work is done against external pressure, it nevertheless becomes slightly colder than before. This phenomenon, which was true for all gases examined except hydrogen (helium and neon must now be included), is explained by the assumption that at high pressures considerable attraction exists between the molecules of a gas ; expenditure of energy is necessary to overcome this attraction when expansion occurs, and consequently a cooling effect is the result. At the centre of a mass of gas, a molecule will be attracted equally in all directions, so that in effect the attractive forces neutralise one another. But near the sides of the containing vessel, the molecules must be on the whole attracted backwards towards the centre of the mass, and for this reason, the velocity with which they strike the sides will be somewhat diminished. The observed pressure is therefore less than would be measured if the molecules were without attractive influence on one another.

The attractive forces between the molecules are only effective over small ranges of the order of 10^{-7} or 10^{-8} cm., which is known as **the range of molecular attraction.**

Instead, therefore, of the observed pressure P, Hirn wrote $P + P_i$, where P_i represents the **internal** or **intrinsic pressure** of the gas. **Hirn's equation** (1865) thus becomes

$$(P + P_i)(V - b) = RT \quad . \quad . \quad . \quad . \quad (23)$$

Van der Waals' Equation, 1873.—This is similar to Hirn's equation, but instead of writing $P + P_i$ for the pressure, van der Waals assumed that the attractive force between two molecules was proportional to the product of their masses—that is, to the square of the density of the gas—or, in turn, to $\frac{1}{V^2}$, where V is the volume. This factor may accordingly be written in the form a/V^2, where a is a constant depending on the nature of the gas. If P represents the observed pressure of a gas whose volume is V, the true pressure, that is to say the pressure if no attraction occurred, would be $P + a/V^2$. Introducing this into Hirn's equation we obtain the modified form known as van der Waals' equation:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad . \quad . \quad . \quad (24)$$

This equation expresses the behaviour of a gas over a wide range of temperature and pressure with much greater accuracy than does the ordinary gas equation. This is well shown by the data in the following table, in which are given the values of PV for ethylene at various pressures as obtained experimentally by Amagat at 20° C. and the values calculated from equation (24), the volume being taken as unity under atmospheric pressure, the constant a being 0·00786 and b 0·0024.

Pressure (Atmospheres).	1000 PV Observed.	1000 PV Calculated.
1	1000	1000
46	781	782
110	454	446
282	941	940
400	1248	1254

Using the ordinary gas equation

$$PV = RT,$$

the value calculated for 1000 PV would of course have been 1000 for each pressure.

Let us endeavour to obtain a clearer insight into the meaning of the constants a and b in van der Waals' equation. Taking the latter first, we are considering the correction that must be introduced because molecules are not mere mathematical points, but have definite volumes of their own, the effect of which will be made clear by the following consideration. If a sphere of 1 cm. diameter starts to roll by the shortest possible path from one side of a box to the other, 100 cm. away, it will strike the farther side after moving over 99 cm., whilst a sphere of 2 cm. diameter would need to cover only 98 cm. If, further, two such spheres move backwards and forwards with the same velocity, it is clear that the larger sphere will make the greater number of impacts per second, since it has the shorter distance to travel. Hence, the fact that a molecule is of finite size means that the number of impacts made, and therefore the pressure set up, is greater than if it were indefinitely small; and this difference is most marked when the space through which the molecule is required to move before impact is much reduced, as when a gas is subjected to a high pressure. Evidently, then, the actual pressure measured is greater than if the molecules were indefinitely small. Van der Waals found that this increase in pressure was equivalent to a reduction of the volume available for compression in the ratio $V : (V - b)$, where b is dependent on, although not equal to, the space occupied by the molecules.

If r is the effective radius of the molecule, supposed spherical, the volume occupied by the molecules is $\frac{4}{3}\pi r^3 N$, where N is Avogadro's

Number, and the space available for compression is reduced by some function of this amount, which may be written as $f.\,\frac{4}{3}\pi r^3 N$ per gramme-molecule where f is a constant. In a total volume of V gramme-molecules, the loss of space is thus

$$f.\,\tfrac{4}{3}\pi r^3 N V = b.$$

Whence

$$\frac{\text{Total volume}}{\text{Available volume}} = \frac{V}{V - f.\,\frac{4}{3}\pi r^3 N V} = \frac{V}{V-b}.$$

Van der Waals calculated that $f=4$, on the assumption that the molecules are spherical. Had any other shape been assumed, a different factor would have been necessary. Other investigators give the value $4\sqrt{2}$ or 5·66.

The significance of b is that, no matter how great the applied pressure may be, the volume of the gas can never be made smaller than b (theoretically). This volume is frequently termed the **co-volume.**

Now let us consider the constant a. On collision, a molecule changes its velocity; on approach, there is a fall in velocity, followed, on separation, by an acceleration. Each collision, therefore, may be regarded as causing a certain loss of time, θ, which gives a measure of the attraction of the molecules for each other, that is, of the internal pressure P_i. The time lost in traversing a path involving x collisions will thus be $x\theta$, and a molecule will thus return less frequently to the walls of the containing vessel than if no collisions took place in the proportion of

$$1 : 1 + x\theta.$$

The pressure is thus reduced in the same proportion, so that if P is the observed pressure, the ideal pressure in the absence of molecular attraction would be

$$P(1 + x\theta).$$

Now

$$x \propto u \text{ (velocity)}$$

and

$$x \propto d \text{ (density)},$$

i.e.

$$x = kud$$

where k is a constant. Whence

$$\begin{aligned} Px\theta &= Pkud\theta \\ &= \tfrac{1}{3}\frac{Nmu^2}{V}.\,kud\theta, \quad \text{since } PV = \tfrac{1}{3}Nmu^2 \text{ (p. 55)} \\ &= \tfrac{1}{3}du^2 kud\theta \\ &= \text{constant} \times d^2 \\ &= \frac{a}{V^2} \end{aligned}$$

where a is a constant. Whence

$$P(1 + x\theta) = P + \frac{a}{V^2}$$

and

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT. \quad . \quad . \quad . \quad (24)$$

The assumption that a is constant is based on the constancy of $u^3k\theta$, and stands or falls with this. We have no data to confirm or contradict this, and herein lies a weakness in the theory.

The replacement of P by $\left(P+\frac{a}{V^2}\right)$ is a much more fundamental change than the replacement of V by $V-b$. It converts a simple equation into a cubic one, which may have either one or three real roots, and we shall see very shortly how this fits in with experimental data.

Van der Waals himself realised that his equation must not be pushed to extreme limits, and that the replacements given in the foregoing can only be accurate when their effect is small, that is under conditions in which the gas departs but slightly from the ideal. For example, suppose V were reduced to a lower value than b, which is physically possible; the equation predicts that either the pressure must be negative or the temperature must fall below the absolute zero and be negative too. Again, the equation may be used in connection with temperatures somewhat higher than the ordinary atmospheric temperature, but we shall see later that when it is strained to calculate values near the critical points (p. 103), the data diverge appreciably from experimental values.

Dieterici's Equation, 1899.—By the term a/V^2 van der Waals corrected for the molecular attraction or cohesive force between the main body of the gas and its outermost layers in contact with the containing vessel, on the assumption that the gas density in the outermost layer was the same as that elsewhere. This will not be the case under high pressures, when the force of attraction is comparable with the gas pressure. On multiplying P of the ordinary gas equation by the factor $e^{a/RT}$, where e is the base of natural logarithms and a and R have the same significance as before, we allow for this variation in the cohesive force. Equation (24) then becomes

$$Pe^{a/RT}(V-b)=RT$$

or, more usually

$$P(V-b)=RTe^{-a/RT} \quad . \quad . \quad . \quad . \quad (25)$$

Dieterici found, however, that a was not constant, but depended upon V. He therefore substituted a/V for a, so that his equation now became

$$P(V-b)=RTe^{-a/RTV} \quad . \quad . \quad . \quad . \quad (26)$$

or

$$\log_e\frac{RT}{P(V-b)}=\frac{a}{RTV} \quad . \quad . \quad . \quad . \quad (27)$$

b having the same significance as in van der Waals' equation.

When V is very large, b may be neglected in comparison, and $e^{-a/RTV}$ becomes practically equal to unity, so that equation (26) simplifies to the ordinary gas equation, namely

$$PV=RT.$$

Dieterici's equation coincides with that of van der Waals over small ranges of pressure; when the pressure is very high, however, results calculated by the two equations differ appreciably, and in general those of Dieterici agree more closely with experimental data.

Derivation of van der Waals' Equation from that of Dieterici.—This is easily effected if we put

$$e^{a/RTV} = 1 + \frac{a}{RTV}$$

and neglect square terms, for then

$$P(V-b) = RT \Big/ \left(1 + \frac{a}{RTV}\right)$$

$$= RT \Big/ \left(1 + \frac{a}{PV^2}\right) \qquad \text{(since } PV = RT\text{)}.$$

Whence

$$P\left(1 + \frac{a}{PV^2}\right)(V-b) = RT,$$

or

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT.$$

The Equation of Clausius.—The temperature over which van der Waals compared values calculated from his equation with experimental data was very limited, and the constancy of a was never in doubt. But when Amagat's extensive series of observations on carbon dioxide became available (1881), Clausius compared his data with the corresponding values calculated from the equation, and observed that a varied with the temperature. He therefore modified the equation as follows:

$$\left(P + \frac{a}{T(V+c)^2}\right)(V-b) = RT,$$

where c is a constant, and a is made to vary inversely as the absolute temperature. This equation gives satisfactory results with carbon dioxide, and agrees fairly well with the data obtained for oxygen, nitrogen and ethylene; but it is less successful with certain other gases, and, like the original van der Waals' equation, is merely an approximation to the truth. It will be observed that Clausius' equation is still cubic with respect to V.

CHAPTER IV.

VAPOUR PRESSURES OF SOLIDS.

All solid substances give off vapour and exert a distinct vapour tension at a fixed temperature. The odour which some solid substances emit is proof of the existence of a vapour pressure. Camphor is a case in point. Its odour, which is characteristic, is due to volatilisation of the solid at the ordinary temperature without passing through the liquid stage. In many cases—for example those of the metals, metallic oxides and salts—the vapour pressure must be exceedingly small at the ordinary temperature, but the fact that many metals have been sublimed under low pressures at temperatures far below their melting points affords evidence of the existence of a perceptible vapour pressure even at ordinary temperatures. Zenghelis (1905) found that a piece of silver foil exposed for some months at the ordinary temperature in a closed vessel containing a metal, or one of its oxides or salts, became alloyed with the metal present in the substance employed.

In the process of **Dry Galvanising** or **Sherardising**, as it is often termed, advantage is taken commercially of the vaporisation of zinc at temperatures below the melting point to effect the superficial alloying of iron with zinc in order to protect the former from corrosion. The cleaned iron (or steel) articles are placed in boxes packed with zinc filings and warmed to a temperature that is kept well below the melting point of the zinc (420° C.). The zinc vapour gradually unites with the iron to produce a closely adherent protective coat. This process enjoys one very distinct advantage over the dipping or wet galvanising process more generally employed, in that crevices or sharp patterns which by the latter process would become filled in or obliterated, by the former process are less seriously affected.

Even ice evaporates slowly, and the gradual disappearance of snow exposed to cold, dry winds at too low a temperature to allow of melting, is due to slow volatilisation. Ice crystals may be formed directly by cooling water vapour, without the intervention of liquid water, this process being the exact reverse of volatilisation.

A solid substance which passes off as vapour in this manner without liquefaction is said to **volatilise**. By cooling the vapours so formed, condensation to the solid state is again obtained; the whole process of volatilisation and condensation is known as **sublimation**, a process which is thus analogous to distillation, in which case liquid and vapour instead of solid and vapour alone are concerned. Thus certain ammonium salts, *e.g.* the chloride, arsenious oxide and iodine (if heated in a wide vessel), pass off wholly as vapour when heated at atmospheric pressure, and may be purified by the process of sublimation. The explanation of this phenomenon lies in the fact that the melting and boiling points lie close together. Increase of pressure, which raises the boiling point considerably, but has little effect on the melting point, will increase the range of temperature between the fusion and boiling points and bring about liquefaction.

At the sublimation point the **heat of volatilisation** of the solid is equal to the sum of the heats of fusion and of vaporisation. For every temperature there is a corresponding maximum vapour pressure or tension for any particular solid; this is known as the **sublimation pressure.** If we draw a curve connecting this sublimation pressure or tension and the temperature, a diagram is obtained like that shown in fig. 14, on which ST represents what is termed the **sublimation curve.** The lower limit of this curve is the absolute zero, provided, of course, no other phase separates out in the meantime, and the continuation of TS cuts the abscissa axis there, indicating zero tension. The upper limit of the curve, namely the point T, is the temperature at which the substance melts in contact with its own vapour. This is not the "true" melting point, since the latter is defined as the temperature at which the substance liquefies under the ordinary atmospheric pressure; but numerically the difference is very minute. For example, ice melts at 0° C. under atmospheric pressure. This is the **true melting point** and is, of course, one of the fixed points in thermometry. But *in vacuo,* in contact only with its own vapour, the temperature at which ice melts is +0·0076° C. This is known as the **triple point,** since at this temperature ice, liquid water and water vapour, that is, the three "states" of water, co-exist in equilibrium. Generally speaking, then, the upper limit of the sublimation curve is the triple point, although the possibility of the existence of a superheated solid ought not to be overlooked. The sublimation curve does not coincide with the vaporisation curve CT of the supercooled liquid, but is always lower, and cuts the curve CTL, which is continuous, at an angle. The difference between the vapour pressures of ice and supercooled water at the same temperatures is illustrated by the following data:

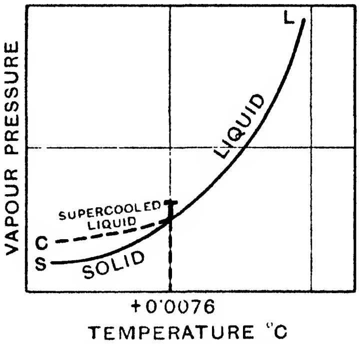


FIG. 14.—Vapour Pressure Curves of Solid and Liquid Water.

Vapour Pressures of Supercooled Water and of Ice.

(Scheel and Heuse, 1909.)

Temp., °C. . .	0	−2	−4	−8	−12	−15
Ice (mm.) . .	4·579	3·885	3·288	2·337	1·644	1·253
Supercooled water (mm.) . .	4·579	3·958	3·418	2·525	1·843	1·445

At the absolute zero these vapour pressures would correspond to the prolongations of the curves TS and TC cutting the abscissa axis at

−273° C., assuming, of course, the supercooled water did not solidify before then.

If we reduce the external pressure sufficiently we can reduce the boiling point of a substance to the neighbourhood of the melting point and thus induce sublimation of substances that normally do not sublime. Thus ice, which readily melts under atmospheric pressure, may be sublimed under reduced pressure from one part of a vessel to another part by keeping that second part cooler than the first. The ice then vaporises and condenses as ice again without intermediate liquid water formation. Carnelley observed this in 1880, and found that at exceedingly low pressures ice could not be melted on heating, but rapidly volatilised. He thought the temperature must rise above 0° C.

Beautiful crystals of white phosphorus may be obtained by sealing a little of the ordinary white substance in an evacuated tube, very gently warming to cause the element to melt and collect in one end of the tube. The other end is wrapped round with a wet cloth to keep it cool, and the whole is kept in the dark. After a few hours or days, according to the circumstances, crystals of phosphorus will have collected in the cooler end, the element having sublimed from the warmer end. It is essential to keep the tube dark, as light destroys the crystals.

The **volatilisation of filaments** in electric glow lamps is a phenomenon that has received much attention on account of its commercial importance. Tungsten is ordinarily used in the preparation of the filaments because of its high melting point (approx. 3267° C.) and comparative non-volatility at high temperatures. In the ordinary evacuated tungsten lamp a temperature of about 2130° C. may be attained with safety, but at higher temperatures the tungsten shows appreciable volatilisation and sublimes as a black deposit on the glass, thus reducing the efficiency of the lamp. By coating the filament with a layer of certain salts, such as sodium chloride or phosphate, calcium fluoride or potassium cyanide, this darkening may be overcome, for on passing the current the salt sublimes as well as the tungsten and condenses on the glass. The tungsten appears to dissolve in this deposit, yielding an almost colourless solid solution which absorbs the light much less than a coherent metal film. The volatilisation of the tungsten may also be reduced by filling the lamp with an inert gas such as argon, under diminished pressure, usually about half an atmosphere. Higher temperatures may then be realised with safety, and very powerful illumination obtained.

Velocity of Volatilisation and Sublimation.—Condensation in a vacuum is determined by the temperature of the vapour and of the surfaces upon which deposition tends to occur. It appears that the vapour of a metal, upon encountering a surface of the same substance, will always adhere, but if it encounters the surface of a different substance, its molecules will only adhere if the temperature of that surface is below a certain critical value (Knudsen, 1916). For glass and mercury the critical temperature is about −135° C., and for glass and silver it is above 575° C. If, therefore, mercury vapour is brought into contact with a glass surface below −135° C. its molecules will adhere, a sublimate of solid mercury being obtained ; but above this temperature the molecules of mercury will be completely reflected.

The fraction of the molecules which condenses on impact with the solid surface is called by Knudsen the **accommodation coefficient,** and denoted by α. If r is the fraction reflected, then

$$\alpha = 1 - r.$$

On the assumption that r is negligibly small, and hence that practically every molecule of vapour condenses on striking the surface of the walls of the containing vessel, the velocity of volatilisation or sublimation of a metal in a uniformly heated system admits of easy calculation.

It is obvious that if $\alpha = 0$, that is, if every molecule on striking the walls of the containing vessel were reflected, none being retained, the vapour pressure of the heated metal would reach a maximum for any particular temperature, a dynamic equilibrium being attained such that as many molecules return to the metal in unit time as evaporate from its surface.

Let us consider 1 centimetre cube of metal vapour, one face of which is bounded by the metal. The metal molecules are ejected *in vacuo* in straight lines, and half the molecules in our cube will be moving away from the metal, whilst the other half are moving towards it. If d is the vapour density, the mass of gas moving towards the metal is $d/2$.

If c is the mean arithmetical velocity of the molecules, the average component in any direction is $c/2$, so that the mean mass m of the metal molecules striking the surface of the metal is given by

$$m = \frac{d}{2} \times \frac{c}{2} = \tfrac{1}{4}dc \quad . \quad . \quad . \quad . \quad (1)$$

But, from the kinetic theory, it follows that

$$d = \frac{PM}{RT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P is the pressure, M the molecular weight and R the gas constant.

We have already seen (equation (11), p. 54) that

$$\begin{aligned} c^2 &= \frac{8u^2}{3\pi} \\ &= \frac{8}{\pi} \cdot \frac{P}{d} \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

since $P = \tfrac{1}{3}du^2$ (p. 55).

Inserting the value for the ratio d/P from equation (2), we have

$$c = \sqrt{\frac{8RT}{\pi M}} \quad . \quad . \quad . \quad . \quad (4)$$

Whence, from equation (1)

$$m = \sqrt{\frac{MP^2}{2\pi RT}} \quad . \quad . \quad . \quad . \quad (5)$$

where m is expressed in grammes per sq. cm. per second. This equation, then, gives the relation between the vapour tension, P, and the rate of volatilisation, m, of a metal *in vacuo*. It is a general equation and applies also to solids other than metals.

Determination of the Vapour Pressures of Solids.—This may be effected either statically or dynamically. The **static method** is of value when the solid has an appreciable vapour pressure. For example, the vapour pressure of ice at various temperatures may be obtained by introducing water into the Torricellian vacuum of a barometer tube over mercury, cooling to convert to ice and noting the depression of the mercury column compared with a standard barometer. The **dynamic method** consists in determining the loss of weight which the substance sustains when a known volume of air or other substance is passed slowly over its surface.

Influence of Temperature on Vapour Pressure.—As the temperature rises the vapour pressure increases, as indicated by the curve in fig. 14. Several complicated formulæ have been suggested to give mathematically the connection between vapour pressure and temperature. The formula

$$\log P = -\frac{a}{T} + b \quad . \quad . \quad . \quad . \quad (6)$$

where a and b are constants, applies to solids yielding monatomic vapours, such as most metals and the inert gases of Group 0 of the Periodic Table (Egerton, 1924). The following values for a and b are typical :

	a.	b.
Zinc . . .	6170	8·107
Lead . . .	10265	8·3165
Cæsium . . .	3753	7·256
Argon . . .	408·8	7·5811

This formula is identical in type with that given on p. 90 for liquids.

CHAPTER V.

VAPOUR PRESSURES OF LIQUIDS.

EVERY liquid exhibits a tendency to evaporate or pass into a state of vapour. If a liquid is sealed in a tube from which air has been removed, evaporation will occur until, for any one temperature, a state of equilibrium is reached between the vapour escaping and that re-entering the liquid. In this condition the pressure which the vapour exerts, called its **vapour pressure,** counterbalances and is therefore equal to the **vapour tension,** or tendency of the liquid to evaporate. The vapour tension and vapour pressure increase with rise of temperature, and, in order that the actual value of the vapour tension may be measured, liquid must be present as such. Since under these conditions the vapour pressure is a measure of the vapour tension, the two terms are often employed indiscriminately.

On plotting the vapour pressure against the temperature, a curve of the general form indicated in fig. 14 is obtained. Its lower limit is normally the melting point of the solid, or rather the triple point (see p. 69), but since a liquid can be supercooled, the vapour pressure curve can be extended below the melting point; the upper limit is the critical temperature (*vide infra,* p. 96). The vapour pressure of a supercooled liquid is always greater than that of the solid of the same composition at the same temperature. The data for supercooled water and ice down to −15° C. have already been given (p. 69) and illustrate this point.

The following figures represent the vapour pressure (in millimetres of mercury) of water at various temperatures:

°C.	mm.	°C.	mm.	°C.	mm.	°C.	mm.
−20	0·960	15	12·728	90	526·0	250	29,951
−10	2·159	20	17·406	100	760·0	300	67,620
0	4·579	25	23·546	120	1,503·0	350	126,924
5	6·528	50	92·17	150	3,578·0	360	141,865
10	9·179	75	289·32	200	11,625·0	364·3	147,904

The above figures represent not only the vapour pressure curve, but also, as will be evident from the dynamical method of measuring vapour pressures, the curve indicating the relationship between boiling point and pressure.

The **boiling point** of a liquid is defined as *the highest temperature attainable by a liquid under a given pressure of its own vapour when heat is applied externally and evaporation occurs freely from the surface.*

Thus, from the foregoing data, it is clear that the boiling point of water at 760 mm. pressure is 100° C., at 1503 mm. 120° C., and so on.

Experiment shows that the pressure of vapour in equilibrium with its liquid is reduced by the presence of an indifferent gas. This is contrary to Dalton's Law of Partial Pressures, but, as is mentioned later, this law is not strictly true (p. 343). It is for this reason that, in accurate work, the boiling point of a liquid is determined under a given pressure of its own vapour in the entire absence of any other gas or vapour. Except in special cases, such as molecular weight determinations, which are discussed in a later chapter (Chapter XX.), the temperature of the vapour issuing from a boiling liquid is measured, and not the temperature of the liquid itself.

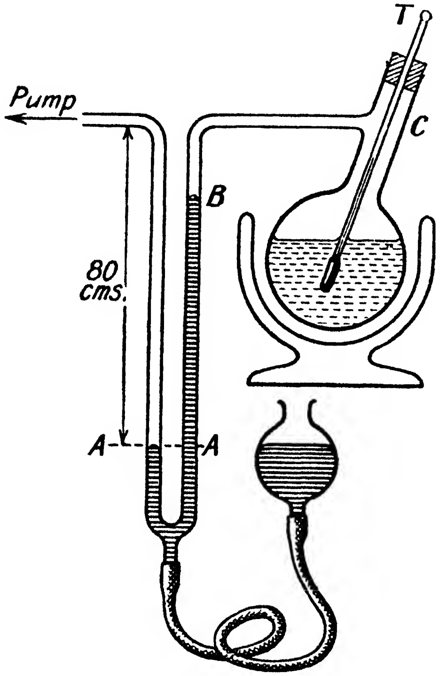


FIG. 15.—Apparatus for Determining Vapour Pressure of Carbonyl Chloride at Temperatures below 18° C.

Two methods are available for the **determination of vapour pressures**, namely :

(i) The so-called **static** method, in which the depression of the barometer column caused by the evaporation of the liquid above the mercury is measured.

(ii) The **dynamic** method, which consists in causing the liquid to boil under a definite pressure and measuring the temperature of the vapour.

By way of illustration of the former of these methods, the apparatus used in determining the vapour pressure of carbonyl chloride or phosgene, $COCl_2$, between $-183°$ and $+18°$ C. may be described briefly (Atkinson, Heycock and Pope, 1920). The pure chloride was distilled into the flask C (fig. 15), fitted with a thermocouple or thermometer, T, by means of which the temperature of the liquid could be determined with great accuracy. The flask was attached to a differential manometer, AB, placed in front of a silvered mirror on which a millimetre scale was engraved to avoid parallax. The mercury was run out of the manometer and the whole apparatus thoroughly exhausted in order to remove every trace of air. The mercury was then brought back into the manometer, and the vapour pressures determined when the liquid in C was maintained at various temperatures by subtracting the length of the column AB from the barometric height at the time of the experiment.

As liquid phosgene boils at 8·2° C. under normal atmospheric pressure, it was necessary to employ a different kind of apparatus in order to determine the vapour pressures at temperatures above about 18° C. This consisted of a sealed tube A (fig. 16), containing liquid carbonyl chloride, and a special manometer M, the top portion of which was graduated, silvered internally and filled with dry air. The tube A had been pumped free from air prior to sealing, so that the space above the liquid phosgene contained vapour only, the pressure of which was indicated by the height of the mercury in M. The whole was warmed to the desired temperature in a water bath, the mercury being forced by the increasing vapour pressure in the tube further up into the manometer. As it rose the mercury dissolved the silver from the glass, and at the end of the experiment it was easy to determine the height to which the mercury column had penetrated, and hence the pressure.

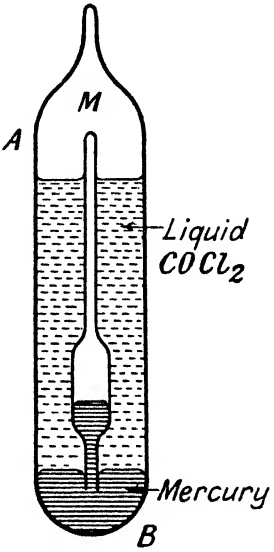


Fig. 16.—Apparatus for Determining Vapour Pressure of Carbonyl Chloride above 18° C.

A differential method for the measurement of the vapour pressure of a liquid has been devised (Jolly and Briscoe, 1926) which consists in sealing up the liquid free from gas in a simple U-tube and then observing the difference of level between the liquid in the two limbs maintained at different but constant temperatures, and repeating the observations for successive temperature intervals. One must, of course, know, for reference purposes, the absolute value of the vapour pressure at one temperature, but once that has been ascertained it is easy to derive from differential measurements the absolute vapour pressures at any other temperatures.

Determination of the Boiling Point.—Let us first consider the boiling point of a pure liquid. When placed in a long-necked flask and gently heated some of the liquid turns into vapour and expels a portion of the air from the flask. As the temperature rises, the rate of evaporation of the liquid increases until ultimately vapour is evolved very rapidly, the temperature of the liquid remains constant, and we say that boiling or ebullition has commenced. The air in the flask is fairly quickly expelled and the liquid surface is thus ultimately in contact with its own vapour phase only.

So far all is straightforward and clear, and if we insert a thermometer into the flask with its bulb in the boiling liquid we get an approximate value for the boiling point.

If, however, an accurate and readily reproducible value for the boiling point of the liquid is desired, we must take a number of points into consideration. Assuming the heat is applied to the bottom of the flask, it will be evident that, before a bubble of vapour can form at the bottom, not only must it overcome the pressure of the vapour above the liquid, and the pressure of the liquid itself, but it must also overcome the force of attraction of the liquid molecules for themselves and for the walls of the containing vessel. If the containing vessel is very clean and smooth, and if the liquid is free from dissolved gases, the temperature of the liquid may be raised very appreciably above the true boiling point before a bubble of vapour is formed. We say then that the liquid is **superheated.** When eventually a bubble of vapour does form, it is superheated and tends to expand very rapidly, often with explosive violence, its temperature falling and approaching the true boiling temperature. The temperature of the liquid falls likewise, only to rise again if no further bubbles are formed, until the process is repeated. Under these conditions the liquid is said to "bump," and its temperature thus depends partly on the pressure and partly on the ease with which bubbles of vapour are formed within it. For this reason it is not usual in practice, when accurate data are required, to determine the boiling point of a pure liquid by inserting the thermometer into the liquid.

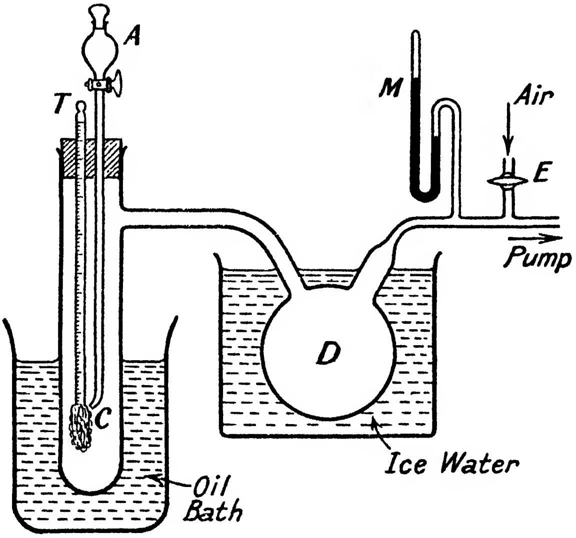


FIG. 17.—Apparatus for Determining Boiling Point of a Pure Liquid.

Now as regards the vapour; this, as we have seen, may or may not be superheated when it leaves the liquid. But it soon cools and condenses, and its temperature of condensation in the presence of its own liquid phase depends only on its pressure, and is thus identical with the true boiling point of the liquid. In practice, therefore, it is usual to determine the boiling point of a pure liquid by immersing the thermometer bulb in the vapour of the boiling liquid, or by surrounding the thermometer bulb with liquid under such conditions that this evaporates freely under the influence of external heat, but cannot "boil" in the accepted sense of the term. A suitable apparatus is shown in fig. 17. This is partially or completely exhausted, as the case may be, and a little liquid from the reservoir A is allowed to flow on to the cotton wool C, surrounding the bulb of the delicate thermometer T. The temperature of the oil bath is maintained at some 20° C. above that of the thermometer. The liquid evaporates and expels the air from around C, and as more liquid is admitted it is soon surrounded by its own vapour, free from air, and thus attains its true boiling point. The pressure is registered by the manometer M, whilst D is kept at constant temperature in an ice or water bath. Air may now be admitted through E, thus altering the pressure, and the boiling point is again determined under this new pressure; and so on. Under these conditions superheating is impossible.

Sometimes, however, it is necessary to ascertain the temperature of the boiling liquid, and not that of the vapour. This is the case, for example, in molecular weight determinations by ebullioscopic methods (p. 421), and when it is desired to know the temperature at which certain solutions boil, for, as we shall see later, the boiling point of a liquid is altered by the presence of dissolved substances. To eliminate superheating, pieces of granite, porous porcelain or, best of all, platinum tetrahedra are added. Whatever the method of heating, however, a bubble of vapour formed at the bottom of a mass of liquid is under a pressure not only of the vapour, but of the liquid column also, so that when boiling occurs, the temperature at the bottom will be slightly greater than that of the surface layer. Sometimes superheating is eliminated by allowing air from a capillary tube to enter the liquid. This introduces a very slight error, which, however, in most cases may be neglected. The error is due to the fact that the true boiling point depends on the pressure of the vapour and not necessarily on the total pressure of vapour plus air to which the liquid may be exposed.

At high temperatures, boiling point determinations are effected by measuring, either by thermocouples, platinum resistance thermometers, optical pyrometers or some other suitable means, the temperatures at which vigorous ebullition of the liquids occurs. In Greenwood's measurements (1909) of the boiling points of metals, the latter were heated, either in a carbon tube crucible or in one of graphite lined with magnesia, by an electrical resistance furnace, and when vigorous ebullition occurred the temperature was noted by an optical pyrometer directed against the bottom of the crucible.

For the standardisation of thermometers the following boiling points have been recommended:

	B.pt. (760 mm.).
Naphthalene	217·96 °C.
Benzoic acid	250·05 „
Phthalic anhydride . . .	285·10 „
Benzophenone	305·9 „
Anthracene	339·9 „
Anthraquinone	376·85 „

It is more usual, however, to use melting and transition temperatures, as these are not affected by small changes in the pressure of the atmosphere (p. 135).

The Spheroidal State.—Everyone is familiar with the fact that water, splashed on to a hot metal sheet, assumes the spheroidal state. Small spheres of the water roll about on the surface of the metal, gradually becoming smaller through evaporation, until they disappear. The temperature of the water does not attain the boiling point, the reason being that the water is separated from the plate by a cushion of steam, more or less admixed with air, so that it can take up the heat only slowly; further, it is elsewhere surrounded by steam largely admixed with air, so that the partial pressure of the water vapour is considerably below the atmospheric pressure. The result is that the water evaporates away, but never boils. If the plate is allowed to cool, a temperature is ultimately reached at which the globule of water flattens out and boils away rapidly.

A similar phenomenon is observed when a pellet of sodium is thrown on to water. At first hydrogen is evolved, and a molten globule of sodium hydroxide at a high temperature is ultimately left floating about on the surface of the water, but not actually in contact with it, being separated by a cushion of steam. As the globule cools, however, a temperature is eventually reached at which it comes into direct contact with the water and bursts with a slight report, rapidly passing into solution.

A striking illustration of the same kind of thing is afforded by pouring some liquid sulphur dioxide (b.pt. - 10·0° C.) into a red hot platinum crucible. It immediately assumes the spheroidal condition, and, upon adding a little water, the latter is frozen and a block of ice is obtained on inverting the crucible. Similarly, by the use of liquid nitrous oxide (b.pt. -88·7° C.) solid mercury can be obtained in a red hot crucible. If a ball of platinum is heated to bright redness and suspended in a beaker of water, the latter recedes from it, leaving an envelope of vapour round the metal. The platinum thus remains red hot for several seconds and cushioned off from the water until its temperature has fallen to about 150° C. Contact then takes place and the water boils vigorously.

Pressure and the Boiling Point.—By means of the Clausius-Clapeyron Equation we are able to calculate the effect of changes of pressure on the boiling point. The equation (Vol. II) may be written in the form

$$\frac{dP}{dT}=\frac{L}{T(V-V_1)} \quad . \quad . \quad . \quad . \quad (1)$$

where L is the molecular latent heat, and V_1 and V are the volumes of the liquid and vapour respectively at the boiling temperature T on the absolute scale.

As is well known, water, under a normal pressure of 760 mm. of mercury, boils at 100° C. Let us then calculate the pressure under which water would boil at 102° C. :

Since the volume of steam is very much greater than that of the water from which it is obtained, V_1 may be neglected, and equation (1) may be simplified to

$$\frac{dP}{dT}=\frac{L}{TV} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Assuming that steam obeys the ordinary gas laws under the conditions of the experiment, we may write

$$PV=RT$$

or

$$V=\frac{RT}{P}.$$

Inserting this value for V into equation (2) we have

$$\frac{dP}{dT}=\frac{LP}{RT^2} \quad . \quad . \quad . \quad . \quad (3)$$

The pressure may be expressed in terms of millimetres of mercury ; the latent heat of steam is 539 gramme-calories per gramme ; the molecular weight of water is 18·016 ; and, finally, for the gas constant, *R*, we may write 1·985 gramme-calories. Equation (3) thus becomes

$$dP = dT\frac{LP}{RT^2}$$

$$= \frac{2 \times 539 \times 18{\cdot}016 \times 760}{1{\cdot}985 \times 373 \times 373}$$

$$= 53{\cdot}4 \text{ mm.}$$

The total pressure is thus 760 + 53·4 or 813·4 mm. of mercury. The experimental value is 815·9 mm.

The boiling temperatures of water under various pressures ranging from 720 to 778 mm., based on the observations of Regnault, are given in the following table :

Variation of the Boiling Point of Water with Pressure.

Pressure, mm. Hg.	Temperature, °C.	Pressure, mm. Hg.	Temperature, °C.	Pressure, mm. Hg.	Temperature, °C.
720	98·493	740	99·255	760	100·000
722	98·570	742	99·331	762	100·074
724	98·647	744	99·406	764	100·147
726	98·724	746	99·481	766	100·220
728	98·800	748	99·555	768	100·293
730	98·877	750	99·630	770	100·366
732	98·953	752	99·704	772	100·439
734	99·029	754	99·778	774	100·511
736	99·104	756	99·852	776	100·584
738	99·180	758	99·926	778	100·656

The **hypsometer** is a small portable piece of apparatus which enables the boiling point of water to be determined at any place. The water is placed in a small tube or boiler and is heated by means of a spirit flame beneath, whilst the vapour in its passage to the open air heats a delicate thermometer. The instrument is sometimes used for determining the altitude of a place, since the boiling point of water falls through 1° C. for every 1000 feet rise above sea level. A more general expression is that of Soret, namely

$$h = 295(100 - t)$$

where h is the height above sea level expressed in metres, and t the ebullition temperature.

Ramsay and Young's Rule, 1885.—Experiment shows that the absolute boiling points of two closely related substances under equal pressures frequently bear a simple relationship to each other, which may be expressed mathematically as

$$\frac{T_1}{T_2} = \frac{T_1'}{T_2'} = \text{constant} \quad . \quad . \quad . \quad . \qquad (4)$$

where T_1 and T_2 are the boiling points of the two substances under a pressure p, and T_1' and T_2' those under a pressure p'. As examples of closely related substances may be mentioned methyl and ethyl acetates, ethyl bromide and iodide, chloro- and bromo-benzenes.

For less closely related substances, and indeed for widely different substances, the following formula is found to apply :

$$\frac{T_1'}{T_2'}=\frac{T_1}{T_2}+k(T_2'-T_2) \quad . \quad . \quad . \quad . \quad (5)$$

The value for k is usually small, vanishingly so for closely related substances, but for more widely different substances it is progressively greater. In the case of methyl acetate and benzene, for example, it is 0·000141.

As the above formula applies from very low pressures up to the critical point (p. 96), it has several useful features. To begin with, it will be obvious that if the boiling points of a pure substance are known over a wide range of pressures, those of a second pure substance can readily be calculated over the same pressure range provided k is known. For this purpose it is only necessary to determine the boiling points of the second substance at two or three pressures sufficiently removed from one another ; k is then calculated from equation (5), and for any intermediate pressures T_1' is then determined by the relationship

$$T_1'=T_2'\left\{\frac{T_1}{T_2}+k(T_2'-T_2)\right\} \quad . \quad . \quad . \quad (6)$$

A second point of interest lies in the observation that on plotting T_1'/T_2' against $(T_2'-T_2)$ a straight line AB (fig. 18) should be obtained. If it is not, k cannot be constant. This might be due to experimental error in the vapour pressure determinations, in which case the Rule is a useful check on such work. On the other hand it may be the result of abnormal behaviour of one of the substances, consequent upon dissociation in the vapour state or association in the liquid state. In the case of substances containing the hydroxyl group, such as water, the alcohols and oxy-acids, the value for k is not quite constant, and this is usually attributed to association.

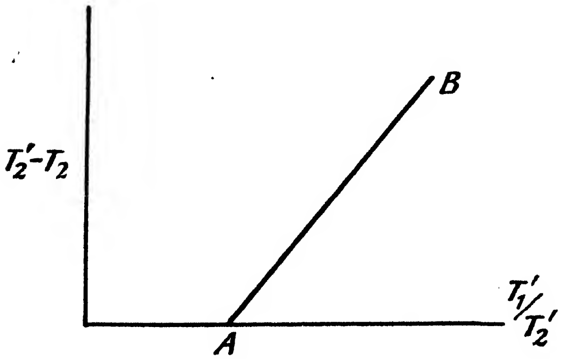


FIG. 18.

In order to calculate the boiling point of a substance under normal pressure, when its observed boiling point is $t°$ C. under a pressure p mm., we may make use of the equation

$$\delta t=c(760-p)(273+t) \quad . \quad . \quad . \quad (7)$$

where c is a constant and δt is the number of degrees on the centigrade scale to be added to $t°$.

The value of c has been calculated for many substances (Young, 1902) and ranges from 0·000146 to 0·000091. A few values are given in the following table :

Substance.	c.	Substance.	c.
Benzene . .	0·000122	Methyl alcohol .	0·000100
Toluene . .	0·000120	Ethyl alcohol .	0·000094
Naphthalene .	0·000119	Acetic acid . .	0·000107
Anthracene .	0·000108	Phenol . .	0·000107
m-Xylene . .	0·000115	Water . . .	0·000100
Ethyl ether. .	0·000121	Carbon disulphide .	0·000127
Acetone . .	0·000115	Carbon tetrachloride	0·000123
Ethyl acetate .	0·000114	Chloroform . .	0·000119

Now c is given by the relationship

$$c=\frac{dt}{dp}\cdot\frac{1}{T}$$

and may be calculated in several ways. The ratio dt/dp represents the rate of change of the boiling temperature with the pressure. The data in the table refer to a normal pressure of 760 mm. Using these data, therefore, equation (7) can only give accurate results when applied to pressures not far removed from the normal.

One method of calculating c is with the aid of the Clausius-Clapeyron equation, which we may write in the form

$$c=\frac{dt}{Tdp}=\frac{V-V_1}{L}=\frac{RT}{Lp}$$

in which the symbols have the same significance as on p. 78. In the case of water, therefore, we have

$$c=\frac{1{\cdot}985\times373}{539\times18{\cdot}016\times760}=0{\cdot}000100.$$

It will be observed that the value of c for groups of similar substances tends to fall with increasing molecular complexity. Thus benzene gives a higher value than anthracene or *m*-xylene, and methyl alcohol than ethyl alcohol. Associated liquids give low values for c, as witness the alcohols, acetic acid, phenol and water, all of which contain the hydroxyl group.

In order to illustrate the method of using equation (7) let us calculate the normal boiling point of water from the observation that under a pressure of 740 mm. water boils at 99·255° C.

Writing equation (7) as

$$\delta t=0{\cdot}0001(760-740)\,(273+99{\cdot}255)$$

we find that :

$$\delta t=0{\cdot}745°.$$

So that the boiling point of water under 760 mm. pressure is 99·255° + 0·745° or 100·000° C.

Latent Heat of Vaporisation.—It is well known that when heat is put into a pure liquid at its boiling point there is no rise in temperature; the liquid turns into vapour at the same temperature, and the absorbed heat is utilised in effecting this change of state. The number of calories absorbed per gramme of liquid under these conditions is termed the latent heat of vaporisation (or evaporation) of the liquid, or simply the latent heat of the vapour (Latin *latere*, to be hidden), since its presence cannot be detected with a thermometer. Exactly the same quantity of heat is liberated when one gramme of the vapour at the boiling point condenses to liquid at the same temperature. The **molecular latent heat** is the product of the latent heat per gramme and the molecular weight of the substance.

The latent heat of vaporisation may be determined in a variety of ways. *Berthelot's apparatus* (fig. 19) is very convenient. It consists of a flask A containing the liquid under examination, which is heated by a ring burner at B or by some simple electrical device. The vapour passes down the central exit tube C and condenses in the coil D, which rests in a shielded calorimeter containing water, the temperature of which is registered by the thermometer T.

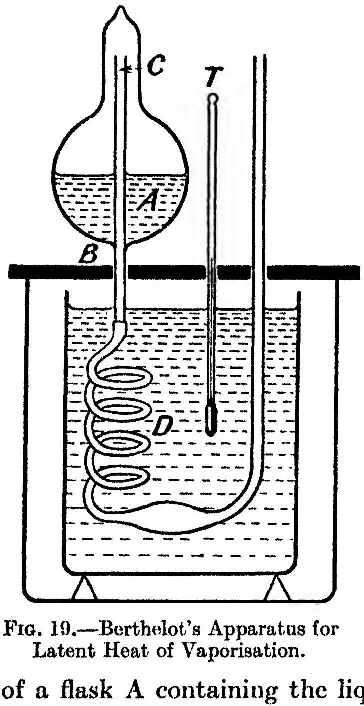


Fig. 19.—Berthelot's Apparatus for Latent Heat of Vaporisation.

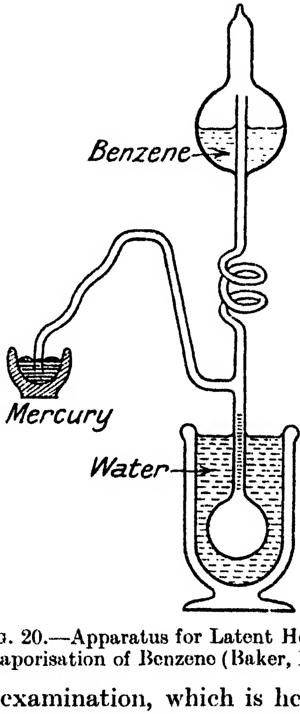


Fig. 20.—Apparatus for Latent Heat of Vaporisation of Benzene (Baker, 1928).

A modified form of Berthelot's apparatus was used by Baker (1928) in determining the latent heat of benzene which had been thoroughly dried for several years by exposure to phosphorus pentoxide and could not therefore be brought into contact with the open air without injuring its properties (see Vol. II). The benzene was contained in the upper bulb (fig. 20) and was distilled by means of a ring burner into the lower graduated tube immersed in a known weight of water contained in a Dewar vessel. From the volume of liquid distilled and the rise in temperature of the water the latent heat was calculated.

Brown's apparatus (1903) is shown in fig. 21. It consists of a flask A with an expanded neck into which is placed a cylindrical boiler B containing a platinum spiral, the terminals of which dip into mercury in C and D. The boiler has a small opening at its upper end, and is covered by a shield E which is also pierced at its top. A second over-all shield F is connected to a condenser through the side-tube G. The liquid to be tested is poured into A and B. A blank experiment is first carried out, the liquid in A being boiled, thereby raising the remainder of the apparatus to the boiling temperature, at which it is maintained for a given time, say 20 minutes. B is removed and weighed and the small loss in weight due to evaporation through the orifice *b* is noted, and is the correction that must be made in the experiment proper. B is replaced, the apparatus again heated until all is at the boiling temperature, and the electric current then switched on. This heats the spiral, and the liquid in B, already at the boiling point, now boils vigorously and the vapour escapes at *b*. The current used is noted at regular intervals. When the apparatus has been working for the same length of time as in the blank test, B is removed and weighed. The loss in weight, corrected for the slight additional loss determined in the blank test, gives the mass of vaporised liquid. The latent heat of vaporisation, *l*, is readily determined as follows :

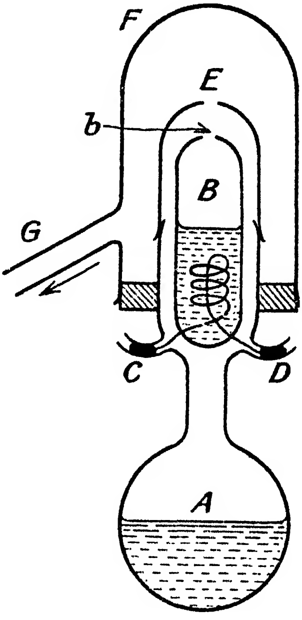


FIG. 21.—Brown's Apparatus for Latent Heat of Vaporisation.

By Joule's Law (1841) the number of calories of heat, H, equivalent to the electrical energy supplied through the spiral, is given by

$$H = \frac{A^2 R\theta}{4{\cdot}184} \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

where A is the current in ampères, R the resistance in ohms and θ the duration of the test in seconds. Whence, if m is the mass of the vaporised liquid,

$$l = \frac{H}{m} = \frac{A^2 R\theta}{4{\cdot}184 m} \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

The latent heats of liquefied gases may be determined by dropping mercury or pieces of solid metal into the liquid and measuring the volume of gas evolved. The essential features of the apparatus used by Dewar (1895) are shown in fig. 22. Mercury in A is allowed to fall into the liquefied gas B contained in a Dewar flask D and the gas evolved is collected through C. D is immersed in a larger Dewar flask E containing also a supply of the same liquefied gas. Provided the mass, specific heat and, in the case of very low temperatures, the latent heat of fusion of the mercury are known, it is easy to calculate the latent heat of vaporisation of the liquid if the latter is already at its boiling point when the experiment begins. This latter condition is easily arranged by allowing the liquid in E to remain at the boiling point.

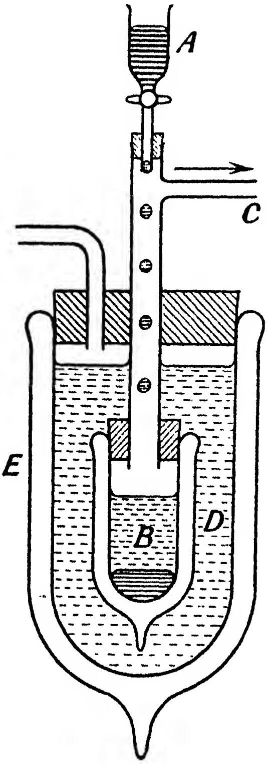


FIG. 22.—Dewar's Apparatus for Latent Heat of Liquefied Gases.

The latent heats of vaporisation of a number of substances are given in the table on p. 88. It will be observed that the value for water, namely 539 calories per gramme, is very much greater than for other liquids.

Nature of Latent Heat.—The heat absorbed when a liquid at the boiling point is converted into vapour is the sum of two factors, namely the heat required to separate the molecules and that required to overcome the pressure of the atmosphere and thus make room, so to speak, for the newly formed vapour, the volume of which is very much greater than the original volume of the liquid. We may therefore write

$$L = L_i + L_e \quad . \quad . \quad (10)$$

where L represents the total molecular heat of vaporisation, L_i that portion of it required for doing internal work, and L_e that required in doing external work.

It is easy to calculate L_e. Assuming the gas laws are obeyed, the work done against the atmosphere is the product of the pressure of the atmosphere, P, and the increase in volume, V. Whence

$$\begin{aligned} L_e &= PV \\ &= RT \\ &= 1{\cdot}985T \end{aligned}$$

where T is the absolute temperature of boiling. For water, T is 373° C., whence

$$L_e = 740 \text{ gramme-calories per gramme-molecule}$$

or

$$l_e = \frac{740}{18} = 41 \text{ gramme-calories per gramme.}$$

Since the latent heat of vaporisation of water is 539 calories per gramme,

$$\begin{aligned} L &= 539 \times 18 \\ &= 9702. \end{aligned}$$

Whence

$$\begin{aligned} L_i &= L - L_e \\ &= 8962 \text{ gramme-calories per gramme-molecule} \end{aligned}$$

or

$$\begin{aligned} l_i &= l - l_e \\ &= 539 - 41 \\ &= 498 \text{ gramme-calories per gramme.} \end{aligned}$$

Under ordinary conditions of boiling, therefore, more than 90 per cent. of the heat absorbed is used up in overcoming molecular attraction, less than 10 per cent. being required to overcome the pressure of the atmosphere.

Latent Heat and the Boiling Point.—The value of the latent heat usually falls as the temperature rises, as is illustrated by the following data :

Temperature, °C.	Latent Heat, l (gramme-calories per gramme).			
	Water.	Ethyl Alcohol.	Benzene.	Acetic Acid.
40	574	215	101·0	92
60	563	210	97·5	93
80	552	203	94·0	94
100	539	194	90·6	95
120	526	182	87·0	97
140	512	170	83·0	94
160	496	155	78·0	91

The latent heats of steam and benzene fall almost linearly with the temperature. Acetic acid is unusual ; its latent heat rises linearly to a maximum at its normal boiling point, namely 118·3° C., and then steadily falls (see fig. 23).

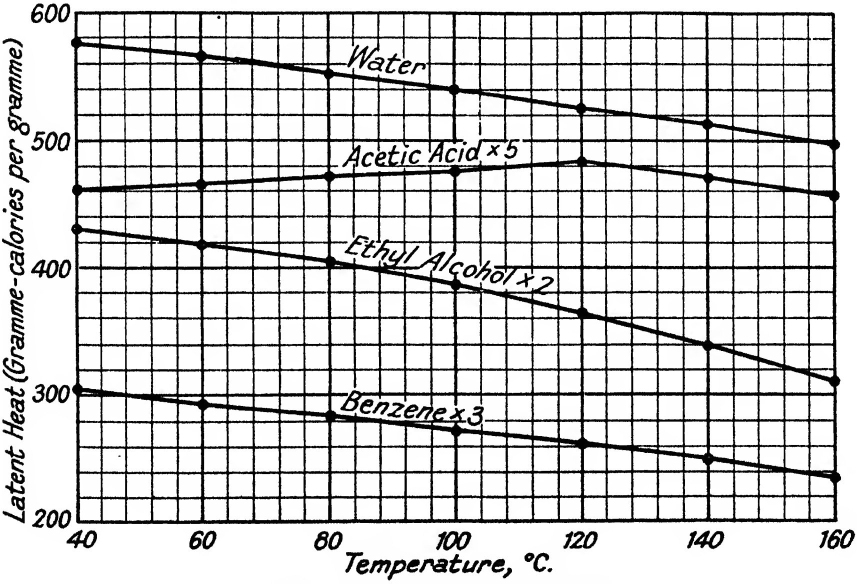


FIG. 23.—Latent Heat and Temperature.

Several equations have been suggested giving the mathematical connection between the latent heat of steam and the temperature.

One of the best of these (Henning, 1906), based on experimental data, is

$$l = 599{\cdot}4 - 0{\cdot}60t,$$

but its range is limited.

Latent Heat and the Clausius-Clapeyron Equation.—We have already had occasion to use the Clausius-Clapeyron equation (p. 78) to calculate the relationship between the pressure and boiling point of a liquid. We may write the equation in the form

$$Ml = L = \frac{dP}{dT} \cdot T(V - V_1) \quad . \quad . \quad . \quad (11)$$

from which it is evident that the latent heat of vaporisation of a liquid can be calculated provided we know the rate of change of vapour pressure with the temperature and the change in volume involved.

Let us, by way of example, employ this equation to determine the latent heat of steam. At 99° C. the vapour pressure of water is 733·24 mm., and at 101° C. it is 787·57 mm., so that the mean rate of change of vapour pressure with the temperature at 100° C., that is, at 373° abs., is

$$\frac{787{\cdot}57 - 733{\cdot}24}{2}$$
$$= 27{\cdot}165 \text{ mm.}$$
$$= 0{\cdot}0357 \text{ atmosphere per degree.}$$

Experiment shows that a gramme-molecule of steam at 100° C. occupies 30·159 litres under normal pressure, whilst a gramme-molecule of water occupies only 18 c.c. Whence

$$l = \frac{L}{M} = 0{\cdot}0357 \times \frac{373(30{\cdot}159 - 0{\cdot}018)}{18{\cdot}016}$$
$$= 22{\cdot}276 \text{ litre-atmospheres.}$$
$$= 22{\cdot}276 \times 24{\cdot}24 \text{ gramme-calories} \quad \text{(p. 20)}$$
$$= 539{\cdot}97 \text{ gramme-calories.}$$

The agreement with the experimental value of 539 calories (p. 88) is sufficiently close.

In general we can neglect the volume of liquid, V_1, in comparison with that of the vapour, so that equation (11) simplifies to

$$l = \frac{L}{M} = \frac{dP}{dT} \cdot \frac{TV}{M} \quad . \quad . \quad . \quad . \quad (12)$$

If, further, we assume the gas laws to hold for the vapour, we may write

$$V = \frac{RT}{P}$$

whence

$$l = \frac{L}{M} = \frac{dP}{dT} \cdot \frac{RT^2}{PM}$$
$$= \frac{RT^2}{M} \frac{d \log_e P}{dT}.$$

Upon integration

$$l = \frac{RT_1T_2}{M(T_2 - T_1)} \log_e \frac{P_2}{P_1} \quad . \quad . \quad . \quad (13)$$

where P_1 and P_2 are the vapour pressures at the absolute temperatures T_1 and T_2.

This relationship is only strictly true when L remains constant over the range studied. We have already learned, however, that the latent heat varies with the temperature, so that equation (13) is only approximately correct. If, however, the range of temperature is small, the error will be negligibly small for most purposes.

Upon conversion to common logarithms and replacing R by 1·985 calories (p. 40), equation (13) becomes

$$l=\frac{L}{M}=1{\cdot}985\times2{\cdot}303\times\frac{T_1T_2}{M(T_2-T_1)}\log_{10}\frac{P_2}{P_1}\quad.\qquad.\qquad(14)$$

If, therefore, we know the vapour pressures of a liquid at two different temperatures, we can by means of equation (14) calculate the mean latent heat of vaporisation of the liquid over that temperature interval.

Let us take the case of water again, using the same data for the vapour pressures. We have

$$l=\frac{1{\cdot}985\times2{\cdot}303}{18{\cdot}016}\times\frac{372\times374}{2}\log_{10}\frac{787{\cdot}57}{733{\cdot}24}$$
$$=546{\cdot}3\text{ gramme-calories.}$$

This value, which is the mean for the temperature range of 99° to 101° C., is somewhat too high. The main source of error lies in the assumption that the vapour obeys the gas laws rigidly, according to which one gramme-molecule of steam at 100° C. occupies a volume given by

$$V=\frac{22{\cdot}4\times373}{273}$$
$$=30{\cdot}60\text{ litres,}$$

whereas the experimental value, as given on p. 86, is 30·159 litres. In substituting the value for V in equation (12) it would therefore have been more correct to have written

$$V=\frac{30{\cdot}159}{30{\cdot}60}\cdot\frac{RT}{P}=0{\cdot}9856\frac{RT}{P}$$

and the value for the latent heat of steam as obtained from equation (14), when multiplied by this factor, gives

$$l=546{\cdot}3\times0{\cdot}9856$$
$$=538{\cdot}4$$

which closely approaches the experimental value.

Trouton's Rule.—It was pointed out by Depretz in 1823 that if v_1 and v are the specific volumes of a liquid and its vapour respectively at the boiling temperature, then

$$\frac{l}{v-v_1}=\text{constant.}$$

This is **Depretz' Rule.** Since v_1 is usually very small compared with v, we may neglect it, and say that l/v is approximately constant. If M is the molecular weight of the liquid, it is clear that the volume of the vapour is given by

$$v = \frac{22\cdot4}{M} \cdot \frac{T}{273} \text{ litres per gramme}$$

$$= \text{constant} \times \frac{T}{M} \text{ litres}$$

under atmospheric pressure.

Substituting this value for v in Depretz' equation we have

$$\text{constant} = \frac{l}{v} = \frac{Ml}{T} \quad . \quad . \quad . \quad . \quad (15)$$

This is **Trouton's Rule,** data illustrating which are given in the following table:

Trouton's Rule.

Substance.	Formula.	Molecular Weight, M.	Latent Heat, l.	Boiling Point, °C.	$\frac{Ml}{T}$.
Water . .	H_2O	18	539	100	26·0
Ammonia . .	NH_3	17	327	− 38·5	23·7
Oxygen . .	O_2	32	58	−183·0	20·6
Nitrogen . .	N_2	28	50	−195·8	18·1
Hydrogen fluoride	HF	20	361	19·4	24·7
Hydrogen chloride	HCl	36·5	106	− 85·0	20·6
Methane . .	CH_4	16	138	−161·4	19·8
Hexane . .	C_6H_{14}	84	79	69·0	19·4
Benzene . .	C_6H_6	78	95·5	79·6	21·1
Methyl alcohol .	CH_3OH	32	269	64·5	25·6
Ethyl alcohol .	C_2H_5OH	46	206	78·5	27·0
Propyl alcohol .	C_3H_7OH	60	164	97·8	26·5
Formic acid .	$HCOOH$	46	120	100·5	14·8
Acetic acid .	CH_3COOH	60	97	118·1	14·9
Propionic acid .	C_2H_5COOH	74	129	141·1	23·1
Butyric acid .	C_3H_7COOH	88	114	163·5	23·0
Methyl acetate .	CH_3COOCH_3	74	98	57·1	22·0
Ethyl acetate .	$CH_3COOC_2H_5$	88	88	77·1	22·1

At best the rule is only approximate. It holds fairly well for groups of closely allied substances. Hydrocarbons, esters and many inorganic substances yield values for the constant of about 20 to 22. For associated substances such as water, the alcohols and liquid ammonia, the constant is higher. This is explained by assuming that when a liquid is associated, but yields a normal vapour, a certain amount of heat is absorbed in breaking down the association, so that the normal heat of vaporisation is increased. Acetic acid gives a low value, and this is attributed to molecular association in the vapour state. From vapour density determinations the mean molecular weight of acetic acid vapour at the normal boiling point is approximately 100. If this value is employed for M, Trouton's constant becomes 24·8, and thus more nearly approaches the value found for propionic and other higher fatty acids.

Hildebrand's Rule (1915).—The latent heat of vaporisation varies, as we have seen, with the pressure, and as the pressure of the atmosphere is purely an arbitrary unit, there is no special significance, other than that of convenience, in choosing this for a comparison of the latent heats. We may with equal reason select any other pressure or function of the pressure and temperature for this purpose.

Although under atmospheric pressure the total pressure at the boiling point is the same for all liquids, we know from a consideration of the simple gas laws that the number of molecules of vapour in unit volume is not the same, but varies with the temperature; the lower the boiling point, the greater the number of vapour molecules; the higher the boiling point, the fewer the vapour molecules. Hildebrand therefore suggests that the latent heats should be compared *at such temperatures that unit volume of the different vapours shall contain the same number of molecules*; in other words, when the liquids are evaporated to similar concentrations of vapour. When this is done the value for Ml/T for normal liquids exhibits greater constancy. A few data are given in the following table, referring to a concentration of 0·005 gramme-molecule of vapour per litre:

Hildebrand's Rule (1915).

Substance.	Abs. Temp., T.	$\frac{Ml}{T}$.	Substance.	Abs. Temp., T.	$\frac{Ml}{T}$.
Nitrogen	55	27·6	Mercury	560	26·2
Oxygen	75	27·6	Cadmium	988	26·4
Chlorine	194	27·8	Zinc	1130	26·4
Pentane	256	27·0	Ammonia	200	32·4
Hexane	286	27·2	Water	325	32·0
Benzene	298	27·4	Ethyl alcohol	307	33·4

For non-associated substances the variation in the constant is small; the three typically associated liquids, namely ammonia, water and ethyl alcohol, give distinctly higher values, as we should expect.

Nernst's Formula.—Nernst has shown that the value of Trouton's constant depends on the boiling point of the substance, and tends to increase as the boiling point rises. When the substance is normal the following relationship holds:

$$\frac{Ml}{T} = 9{\cdot}5 \log_{10} T - 0{\cdot}007T \quad . \quad . \quad . \quad (16)$$

but if the substance is associated, then

$$\frac{Ml}{T} > 9{\cdot}5 \log_{10} T - 0{\cdot}007T.$$

Variation of Vapour Pressure with Temperature.—We may write equation (13) in the form

$$\begin{aligned}\log_e P &= -\frac{L}{RT} + \text{constant}\\ &= -\frac{A}{T} + B \quad . \quad . \quad . \quad . \quad . \quad (17)\end{aligned}$$

where A and B are constants. This is a very useful equation when only small differences in temperature are concerned. But since L, and therefore A, vary with the temperature, the equation is restricted in its application. A more exact equation is obtained by regarding L as a linear function of T, namely

$$L = L_0 + aT,$$

where a is a constant and L_0 is the latent heat at zero temperature. Then

$$\begin{aligned}\log_e P &= \int \frac{L_0 + aT}{RT^2} dT = -\frac{L}{RT} + \frac{a}{R}\log_e T + \text{const.}\\ &= -\frac{A}{T} + B \log_e T + C \quad . \quad . \quad . \quad . \quad . \quad (18)\end{aligned}$$

where A, B and C are constants. This is **Kirchhoff's equation** (1858), and applies with considerable accuracy to many substances even up to the critical temperature.

Boiling Points of the Elements.—The boiling points of the elements under atmospheric pressure are given in the table on p. 92. In fig. 24 the boiling points are plotted against the atomic numbers, and an interesting periodicity is at once discernible, closely resembling that manifested by the melting points, as discussed on p. 148. The inert gases of Group 0 of the Periodic Table occupy the troughs of the curves; the ascending slopes contain the alkali and alkaline earth metals; the non-metals of the Fifth, Sixth and Seventh Groups lie on the descending slopes, whilst Group IV and the transitional elements of Group VIII lie near or at the summits. It will be observed also that the boiling points of the alkali metals and of the beryllium subdivision of Group II fall with rise of atomic number. The reverse is the case for the non-metals of Groups V, VI, VII and 0.

Boiling Points and Chemical Constitution.—Hermann Kopp in 1842 investigated the relations between boiling point and chemical composition, and at first concluded that the boiling temperature is an **additive** property, so that a given change in composition is always to be followed by the same change in boiling point. This is known as **Kopp's Rule.** We now know, however, that this is only a part of the truth, for the boiling temperature is also in part **constitutive,** that is, it depends also upon the constitution of the substance. This is clearly proved by the very varying boiling points of many different isomerides, some of which we shall have occasion to study in succeeding pages.

Boiling Points of Homologous Series.—The addition of a methylene group, namely CH_2, to an organic compound tends to raise

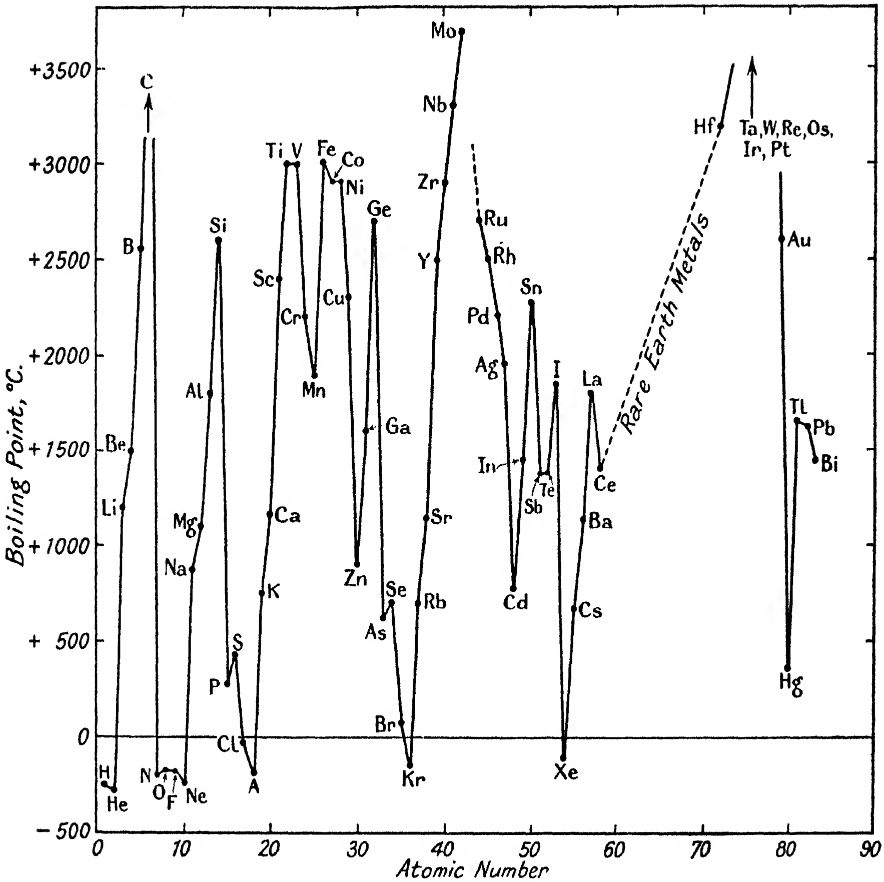


Fig. 24.—Boiling Point and Atomic Number.

the boiling point. The rise in temperature is not regular; it varies with the class of compound investigated, and even in the same homologous series the effect of each CH_2 falls off continuously as the series is ascended. These points are well illustrated by the data given in the table on p. 93.

Many attempts have been made to derive mathematically the boiling points of successive members of homologous series. A simple formula, given by Walker (1894), namely

$$T = aM^b,$$

gives very fair results, where T is the boiling point on the absolute scale, M the molecular weight, whilst a and b are constant for any homologous series.

If we logarise the above equation and apply the result to two members, not necessarily successive, of a homologous series, we have

$$\log T_1 = \log a + b \log M_1$$
$$\log T_2 = \log a + b \log M_2,$$

Melting and Boiling Points of the Elements.

Element.	Melting Point, °C.	Boiling Point, 760 mm., °C.	Element.	Melting Point, °C.	Boiling Point, 760 mm., °C.
Aluminium	658·7	1800	Niobium	1950	3300
Antimony	630·5	1380	Nitrogen	– 209·9	– 195·8
Argon	– 189·2	– 185·7	Osmium	2700	5300
Arsenic	814 *	615 †	Oxygen	– 218·4	– 183
Barium	850	1140	Ozone	– 251	– 112
Beryllium	1350	1500	Palladium	1551·5	2200
Bismuth	271	1450	Phosphorus		
Boron	2300	2550	(white)	44·1	280
Bromine	– 7·2	58·8	Platinum	1755	4300
Cadmium	320·9	767	Potassium	62·3	760
Cæsium	26	670	Praseodymium	940	. .
Calcium	810	1170	Radium	960	1140
Carbon	3500	4200	Radon	– 71	– 61·8
Cerium	640	1400	Rhenium	*c.* 3000	. .
Chlorine	– 101·6	– 34·6	Rhodium	1955	2500
Chromium	1615	2200	Rubidium	38·5	700
Cobalt	1480	2900	Ruthenium	2450	2700
Copper	1083	2300	Samarium	1300	. .
Fluorine	– 223	– 187	Scandium	1200	2400
Gallium	29·8	1600	Selenium	220	688
Germanium	958·5	2700	Silicon	1420	2600
Gold	1062·6	2600	Silver	960·5	1950
Hafnium	*c.* 1700	3200	Sodium	97·5	880
Helium	– 272·2	– 268·9	Strontium	800	1150
Hydrogen	– 259·14	– 252·7	Sulphur		
Indium	155	1450	(rhombic)	112·8	444·6
Iodine	113·5	184·4	Sulphur		
Iridium	2350	4800	(monoclinic)	119·0	
Iron	1535	3000	Tantalum	2850	4100
Krypton	– 169	– 151·8	Tellurium	452	1390
Lanthanum	826	1800	Thallium	303·5	1650
Lead	327·3	1620	Thorium	1845	3000
Lithium	186	1200	Tin (tetragonal)	231·85	2260
Magnesium	651	1110	Titanium	1800	3000
Manganese	1260	1900	Tungsten	3267	5900
Masurium	*c.* 2300	. .	Uranium	1850	. .
Mercury	– 38·87	356·9	Vanadium	1710	3000
Molybdenum	2620	3700	Xenon	– 140	– 109·1
Neodymium	840	. .	Yttrium	1490	2500
Neon	– 248·7	– 245·9	Zinc	419·4	907
Nickel	1452	2900	Zirconium	1700	2900

* Under 36 atmospheres. † Sublimation.

whence

$$b = \log\frac{T_1}{T_2} \div \log\frac{M_1}{M_2} \quad . \quad . \quad . \quad . \quad (19)$$

that is, the logarithm of the ratio of the absolute boiling points of any two members of a homologous series, divided by the logarithm of the ratio of the molecular weights, is constant.

Substance.	Formula.	Boiling Point, °C.	Rise per CH_2.
Methane	CH_4	-161·4	73·1
Ethane	C_2H_6	- 88·3	43·8
Propane	C_3H_8	- 44·5	45·1
Butane	C_4H_{10}	+ 0·6	35·6
Pentane	C_5H_{12}	36·2	
Acetaldehyde	CH_3CHO	20·2	28·6
Propionic aldehyde . .	C_2H_5CHO	48·8	26·9
Butyric ,, . .	C_3H_7CHO	75·7	27·7
Valeric ,, . .	C_4H_9CHO	103·4	25·6
Caproic ,, . .	$C_5H_{11}CHO$	129·0	
Methyl bromide	CH_3Br	4·6	33·4
Ethyl ,, ...	C_2H_5Br	38·0	32·9
Propyl ,, ...	C_3H_7Br	70·9	30·7
Butyl ,, ...	C_4H_9Br	101·6	26·3
Amyl ,, ...	$C_5H_{11}Br$	127·9	

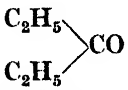
In Young's formula the rise in the boiling temperature of a substance due to addition of CH_2 is expressed as a function of the absolute temperature. Thus

$$\delta t = \frac{144\cdot86}{T^{0\cdot0148\sqrt{T}}} \quad . \quad . \quad . \quad . \quad (20)$$

where T is the boiling point of, say, a paraffin hydrocarbon, and $T + \delta t$ the boiling point of its next higher homologue. When 5 or more carbon atoms are present in the molecule the calculated results agree very satisfactorily with the observed boiling temperatures. Similar results are in general obtained with other homologous series in which association does not occur. Young's formula may therefore be used to calculate the boiling points of non-associated organic liquids containing more than 4 carbon atoms provided the boiling points of the adjacent homologues are known.

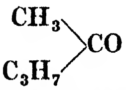
Boiling Points of Isomerides.—If Kopp's Rule were always obeyed, isomerides would possess identical boiling points. This, however, is approximately true only when the isomerides possess closely similar structures, for, as we have explained, the boiling point is a structural or constitutive, as well as an additive, property.

As examples of similar isomerides we have



$$\begin{matrix} C_2H_5 \diagdown \\ \quad\quad CO \\ C_2H_5 \diagup \end{matrix}$$

Diethyl ketone,
B.pt. 101·7° C.



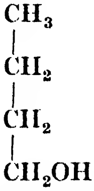
$$\begin{matrix} CH_3 \diagdown \\ \quad\quad CO \\ C_3H_7 \diagup \end{matrix}$$

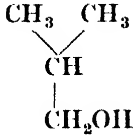
Methyl propyl ketone,
B.pt. 101·7° C.

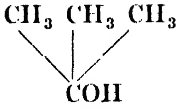
On the other hand

$CH_3.CH_2OH$ Ethyl alcohol, B.pt. 78·5° C.	$CH_3—O—CH_3$ Dimethyl ether, B.pt. -24·9° C.

Branching of chains tends to lower the boiling point. Thus :


n-Butyl alcohol,
B.pt. 117·7° C.


*Iso*butyl alcohol,
B.pt. 108° C.


Tertiary butyl alcohol,
B.pt. 82·8° C.

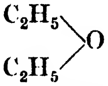
In general, the more closely two oxygen atoms or two halogens approach each other in a molecule, the lower is the boiling point. Thus

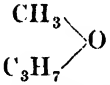
$CH_3.CO.CO.C_2H_5$ Methylethyl α-diketone, B.pt. 108° C.	$CH_3.CO.CH_2.CO.CH_3$ Acetylacetone, B.pt. 137° C.

and

$CH_3.CCl_2.CH_3$ 2 : 2-Dichloropropane, B.pt. 69·7° C.	$CH_2Cl.CH_2.CH_2Cl$ 1 : 3-Dichloropropane, B.pt. 125° C.

It frequently happens also, but not invariably, that symmetrical molecules have a lower boiling point than their less symmetrical isomerides. Thus


Diethyl ether,
B.pt. 34·5° C.


Methyl propyl ether,
B.pt. 38·9° C.

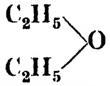
In the case of acetylacetone mentioned above, the effect of separating the oxygen atoms in the molecule has more than counterbalanced the influence of symmetry ; the boiling point of acetylacetone is thus higher than that of its less symmetrical isomeride.

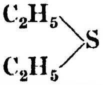
Ring Formation is usually accompanied by rise in boiling point.

Effect of Replacements.—The replacement of one or more atoms of hydrogen in an organic compound by other elements or groups of elements invariably effects a rise in the boiling point. Thus :

		Boiling Point, °C.
Methane . . .	CH_4	-161·4
Methyl chloride . .	CH_3Cl	- 23·7
Methylene chloride .	CH_2Cl_2	+ 40·1
Chloroform . . .	$CHCl_3$	61·2
Carbon tetrachloride .	CCl_4	76·8

When successive elements in a vertical group in the Periodic Table replace one another in organic compounds, there is usually a steady rise or fall in the boiling points. If, in any special case, this rule is not obeyed, or there is an abnormal rise in the boiling point, association is usually suspected. When an atom of oxygen is replaced by one of sulphur, the boiling point usually rises. Thus :


Diethyl ether,
B.pt. 34·5° C.


Diethyl sulphide,
B.pt. 91·6° C.

In the case of the alcohols, however, the thio-derivatives have lower boiling points. Thus :

C_2H_5OH
Ethyl alcohol,
B.pt. 78·5° C.

C_2H_5SH
Ethyl mercaptan,
B.pt. 34·7° C.

The alcohol, as is generally the case with substances containing the OH-group, is associated. That water is associated is indicated in a similar manner. Thus, when the boiling points of the hydrides of sulphur, selenium and tellurium are compared, it is evident that the boiling point rises steadily with the molecular weight:

Substance . .	H_2S	H_2Se	H_2Te	H_2O
Boiling point, °C. .	−60·2	−42	−1·8	+100

Water, therefore, if it conforms to the general rule, must have a molecular weight greater than that of tellurium hydride. This suggests very appreciable association, although, as we shall see later (Vol. II), this is not the only explanation of the high boiling point.

If the halides of hydrogen are compared, their boiling points are also seen to rise with the molecular weight. Thus :

Substance . .	HCl	HBr	HI	HF
Boiling point, °C. .	−85	−67	−35·5	+19·4

Hydrogen fluoride, therefore, if it conforms to the general rule, must have a greater molecular weight than hydrogen iodide, which suggests considerable association.

CHAPTER VI.

CRITICAL PHENOMENA.

All gases when sufficiently cooled and submitted to pressure may be reduced to the liquid state. Of the two factors involved, namely temperature and pressure, the former is by far the more important, since it is possible to liquefy a gas and even to solidify it at the ordinary atmospheric pressure by lowering its temperature sufficiently. Thus, at the temperature of boiling helium, namely −268·9° C., all other gases pass into the solid state. On the other hand it is seldom that a pressure as great as 100 atmospheres is required to effect liquefaction. The uselessness of very high pressures is due to the fact that for each gas there is a temperature above which it cannot be liquefied. This is called the **critical temperature** and is denoted by T_c or t_c, according as it is expressed on the absolute or on the centigrade scale. The pressure necessary to effect liquefaction at this temperature is termed the **critical pressure,** P_c, and is the highest pressure ever required to cause liquefaction of the particular gas. The volume occupied by the gas at the critical point is known as the **critical volume** and may be expressed in one of three ways, namely, as cubic centimetres per gramme, as the volume of one gramme-molecule of the gas, or as the ratio of the volume at the critical point to that occupied by the gas under normal conditions of temperature and pressure.

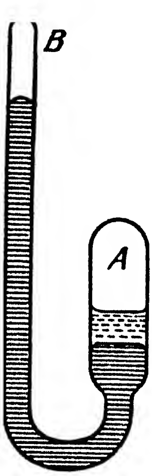


Fig. 25.—Cagniard's Apparatus for showing Existence of Critical Temperature.

The existence of the critical temperature was first noticed by Cagniard de la Tour in 1822 for a number of volatile liquids such as ether, although the significance of his results was not appreciated at the time. Cagniard sealed his volatile liquid in one end A (fig. 25) of a glass tube over mercury, the other end B also being sealed, but enclosing air, so that, by the application of Boyle's Law any change of pressure could be determined. On heating A he found that a temperature was reached ultimately at which it became impossible to differentiate between the liquid and vapour phases. This was the critical temperature of the substance, and represented the upper limit of the liquid state.

Andrews' Experiments.—The reverse change to that studied by Cagniard, namely the condensation of a gas to the liquid state, was studied by Andrews, who commenced his classic researches on carbon dioxide in 1861. The essential features of Andrews' apparatus are shown in fig. 26. The glass tube AB containing the gas was fitted into a strong copper tube containing water, the gas being sealed off from the water by a globule of mercury. (The tube was much narrower than indicated in the diagram, so that the mercury was kept in position by capillary force.) A second precisely similar vessel, but containing air in the glass tube, was attached at C. This served as a manometer and enabled the pressure to be determined. The pressure was obtained by screwing the steel screw into the water and was distributed immediately through the interior of both vessels, being applied through the movable columns of mercury to the two gases to be compressed. A pressure of 400 atmospheres could be attained by this method.

Andrews found that at temperatures above 31·1° C. no sensible liquefaction of carbon dioxide takes place. This temperature, therefore, is the critical temperature, and represents the lower limit of the gaseous state. Below this temperature liquid is formed at some definite pressure.

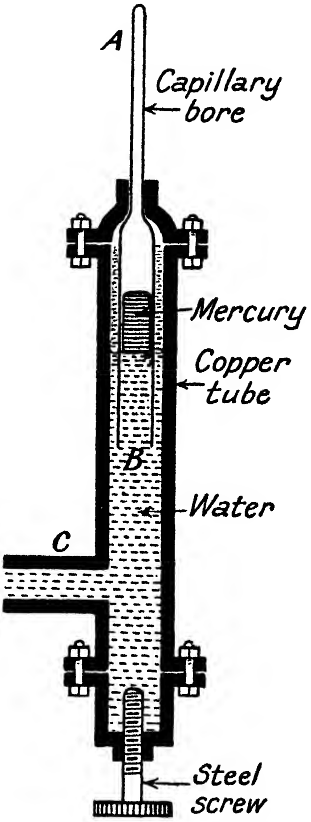


Fig. 26.—Andrews' Apparatus.

Isotherms of Carbon Dioxide.—The results obtained with carbon dioxide may be shown graphically by plotting the volume against the pressure for unit mass of gas at any particular temperature. The curve obtained is known as an isotherm (Greek *isos* equal, *thermos* warm). When a series of isotherms is drawn for different temperatures, as shown in fig. 27, several interesting features present themselves. For a perfect gas the product pv is constant provided the temperature is constant; hence the isotherm of a perfect gas is a rectangular hyperbola. Such is very nearly the case for carbon dioxide at about 50° C. and above. As the temperature falls the isotherm deviates increasingly from the hyperbolic, the maximum deviation occurring at 31·1° C., which is the critical temperature. Below this point the curve breaks into three parts, the middle portion being horizontal, and an abrupt change of gradient occurring on passing from the horizontal part to the other portions of the isotherm. The significance of this may be explained with reference to the isotherm for 21° C. The portion AB represents the compression of vapour. At B liquefaction commences; the volume diminishes as more and more vapour condenses, but the pressure remains constant and equal to the vapour pressure of liquid carbon dioxide at this particular temperature. At C all the vapour has disappeared and CD rises very steeply, indicating that the liquid is only very slightly compressible. The horizontal portion grows with fall of temperature, but decreases with rise of temperature, ultimately vanishing at the critical point F.

Now let us consider the critical isotherm EFG. EF represents the compression of the vapour or gaseous phase, for this isotherm marks the boundary between gas and vapour. Below the critical temperature the gaseous phase is termed **vapour**; above this temperature it is regarded as **gas**. F is the critical point, and marks the critical pressure and volume respectively. At this point the liquid and saturated vapour become identical. Curve FG represents the compression of the liquid.

At temperatures above the critical value, the isotherms exhibit no abrupt change of gradient and no portion of them corresponds with an equilibrium between liquid and vapour; indeed, at these temperatures all distinctions between the liquid and gaseous states has disappeared.

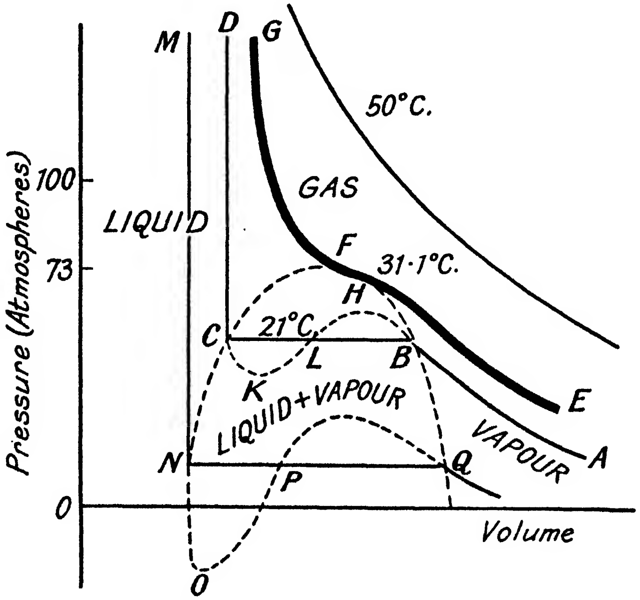


FIG. 27.—Isotherms of CO_2 at Different Temperatures.

The critical phenomena observed by Andrews in connection with carbon dioxide and nitrous oxide may be observed with all substances that can be obtained as gases and liquids. A few critical data are given in the accompanying table (p. 99).

Law of Cailletet and Mathias (1886).—It is not a very difficult matter in many cases to determine the critical temperature and pressure of a substance. The latter can be ascertained with the aid of apparatus similar to that shown in fig. 25, the former by heating in a suitable bath a sealed tube containing the liquid and its vapour only and noting the temperature at which the liquid surface just disappears. It is much more difficult to measure directly the critical volume, for a small change in pressure at the critical temperature causes a large change in volume. We can, however, arrive at a solution of our problem indirectly by applying the Law of Cailletet and Mathias, according to which:

The mean values of the densities of liquid and saturated vapour for any stable substance are a rectilinear function of the temperature.

Critical Data.

Substance.	Critical Temperature, T_c (abs.).	Critical Pressure, P_c (atm.).	Critical Volume,* V_c (litres per gramme-molecule).	$\frac{RT_c}{P_cV_c}$.†
Hydrogen	34	12·8	0·064	3·41
Nitrogen	126	33·5	0·087	3·52
Oxygen	154	49·7	0·074	3·44
Carbon dioxide	304	73·0	0·096	3·56
Carbon tetrachloride	556	45·0	0·276	3·67
Benzene	561	47·7	0·256	3·77
Chlorobenzene	632	44·6	0·308	3·78
Water	647	217·7	0·056	4·36
Methyl alcohol	513	78·7	0·117	4·58
Acetic acid	594·6	57·2	0·171	4·99

This is shown graphically in fig. 28. The densities of the liquid and saturated vapour are plotted against the temperature to points as near the critical temperature as possible, giving a curve that is roughly parabolic when complete. The mean densities lie on the **rectilinear diameter** AB, which is extended to T, which marks the critical temperature. The point of intersection gives the critical density, from which the volume is readily determined. The law holds with considerable accuracy for a great number of substances. Normal pentane is an excellent example, as it obeys the law with great exactness from 0° C. up to its critical temperature of 197·2° C. In most cases, however, the law is not absolutely obeyed, the diameter AB proving slightly curved; but the error involved is usually small.

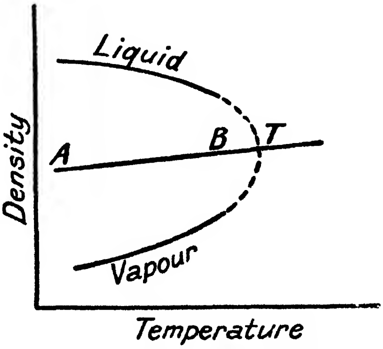


FIG. 28.—Illustrating Law of Cailletet and Mathias.

This method was used in 1925 for determining the critical density of helium, the value 0·0693 gramme per c.c. being obtained at the critical temperature of 5·19° abs. The critical volume is thus 1 ÷ 0·0693 or 14·4 c.c. per gramme.

Continuity of State.—The liquid and vapour phases become identical at the critical temperature. The curved surface of a liquid

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[*] That is, numerically, the molecular weight divided by the critical density in grammes per c.c.

[†] R is taken as 0·0821 (p. 40).

in contact with its vapour, generally known as its *meniscus* (Greek *mēniskos*, crescent), which is well-defined at lower temperatures, gradually flattens out as the critical temperature is approached, since the surface tension (p. 263) of the liquid is rapidly falling. Ultimately a point is reached where the liquid boundary becomes unsteady, for the surface tension has become so very feeble that but little work has to be done to increase the boundary surface. If the temperature is now raised a very little more, the meniscus disappears entirely as the critical point is reached; and when it is passed, the liquid and vapour have been transformed to gas. On cooling, the changes take place in the reverse order. In neither case is any physical change involved such as marks the abrupt transition from liquid to vapour at lower temperatures, and the phenomenon is termed **continuity of state.**

Supercooled or Supersaturated Vapour.—It is well known that a vapour saturated at a certain temperature may be cooled to a lower temperature, at any rate for a short time, in the absence of the liquid phase and of dust particles that might serve as nuclei, without deposition of liquid. If, however, a drop of the liquid or nuclei of dust are present, a certain amount of condensation occurs and the vapour pressure falls to the value normally obtained when the liquid is maintained at that lower temperature. Prior to the deposition of liquid the vapour has been supercooled and is supersaturated, its pressure being greater than normally corresponds to the lower temperature. The vapour is thus in a " meta-stable " condition.

Suppose, for example, the saturated vapour of carbon dioxide was originally at 22° C., and we cool it to 21° C. It is now supersaturated and its condition may be represented by a point lying on the prolongation of the isothermal curve AB, that is, somewhere on the broken line BH (fig. 27). We could arrive at the same point, theoretically at any rate, by starting with a supply of unsaturated vapour at 21° C. and gradually compressing it isothermally until the point B is reached. If condensation does not take place, increase of pressure will decrease the volume in accordance with the broken line BH until the point H is reached, when condensation must take place, for the system is now excessively unstable.

Superheated Liquid.—It is not usually a difficult matter to raise the temperature of a liquid somewhat above the boiling point without the occurrence of ebullition. Thus the temperature of pure water, free from dissolved gases and contained in a well-cleaned vessel, may be raised appreciably above 100° C. under atmospheric pressure without boiling. When at length boiling does occur, it does so with almost explosive violence, a phenomenon frequently known as " bumping " ; the temperature falls to 100° C. and the extra heat energy is utilised in converting a portion of the liquid rapidly into vapour. Drops of water have been heated in a mixture of oil of cloves and linseed oil up to 178° C. before ebullition has taken place.

Suppose, now, we start with liquid carbon dioxide at 21° C. and steadily reduce the pressure isothermally until the boiling point, represented by C in fig. 27, is reached. It is possible to reduce the pressure still further without ebullition taking place. The condition of the system is then represented by some point on the broken line CK, which is a continuation of the curve DC. At length the system will become so very unstable that ebullition takes place.

Lest it should be thought that experimental evidence of this kind of change is lacking, it may be mentioned that pure methyl formate, boiling normally at 31·9° C., was heated by Young under pressure to 80° C. The pressure was then gradually lowered to approximately atmospheric without ebullition taking place, although the liquid was more than 45° C. above its boiling point under this lower pressure. When ebullition did take place eventually, it was explosively violent.

Boyle's Law Defied.—The broken line KH has never been realised experimentally. It will be observed that the volume and the pressure increase simultaneously.

The Tensile Strength of Liquids.—It is frequently but quite erroneously imagined that liquids possess no tensile strength. A cylinder of water flowing steadily out of a burette soon breaks up into drops which fall apart. But if we could arrange to support the sides of the cylinder we should easily be able to show that water resists any attempt to increase its volume; in other words, it possesses great tensile strength. This was demonstrated by Worthington (1892), who sealed some air-free water in a tube in such a manner that the water did not quite fill the tube, the " empty " space above being occupied by pure water vapour only. On warming, the liquid expanded and completely filled the tube. On cooling, the bubble of vapour did not reappear. The liquid continued to fill the tube until a large negative pressure was reached, which sometimes was so great as to cause the thick-walled glass tube to collapse.

We are now in a position to understand the curve MNOPQ (fig. 27). On reducing the pressure from M to N isothermally, the boiling point N of the liquid is reached. If ebullition is avoided, the pressure may be reduced below the zero line, when it becomes negative pressure, or a tension, and we travel in the direction of O along the broken line. Normally, long before O is reached the liquid will boil and the system change to a stable condition represented by some point along the line NP.

Application of van der Waals' Equation.—It was suggested by James Thomson in 1871 that the true form of the isothermal curves below the critical temperature is the continuous curve represented, in the case of carbon dioxide at 21° C., by the curve DCKLHBA, and not the discontinuous lines DC, CB, BA. We have already considered a certain amount of experimental evidence in favour of this view. If such is the case it is obvious that, at any temperature below the critical, there may be three volumes capable of existing in equilibrium with a single pressure. At 21° C. the three volumes represented by the points C, L and B are theoretically in equilibrium with the same pressure. It is interesting to note that van der Waals' equation (p. 64) is in complete harmony with this, for it is a cubic equation with respect to V. Thus, instead of in the more usual form, namely

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \quad . \quad . \quad . \quad (1)$$

the equation may be written as

$$V^3-\left(b+\frac{RT}{P}\right)V^2+\frac{a}{P}V-\frac{ab}{P}=0 \quad . \quad . \quad . \quad (2)$$

from which it is obvious that V may have three values. If the three roots are x, y and z, respectively, the equation may be written

$$(V-x)(V-y)(V-z)=0 \quad . \quad . \quad . \quad (3)$$

a, b and R are constants, and by inserting the appropriate data and plotting the results we obtain curves similar to DCKLHBA in fig. 27, the loops CKL and LHB having equal areas. Points C, L and B correspond to the three values of V for the particular pressure. At a lower pressure these values for V are more widely different and the loop areas are larger ; as the temperature rises, the values for V become more nearly alike, and finally become identical at the critical temperature. This is the case at F in fig. 27. At higher temperatures still, three values for V are mathematically possible, but of these only one is real, the others being imaginary and having no physical significance. ✓ At the critical temperature, T_c, the three values for the volume, V, at the critical pressure, P_c, are identical, that is to say, the three roots of van der Waals' equation are equal, and constitute the critical volume, V_c, so that

$$x=y=z=V_c.$$

Equation (3) thus simplifies to

$$(V-V_c)^3=0 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Expanding this equation we obtain

$$V^3-3V_cV^2+3V_c^2V-V_c^3=0 \quad . \quad . \quad . \quad . \quad (5)$$

Comparing this with equation (2) we see that

$$3V_c=\frac{RT_c}{P_c}+b \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$3V_c^2=\frac{a}{P_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$V_c^3=\frac{ab}{P_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From equations (7) and (8) it follows that

$$V_c=3b \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If, therefore, van der Waals' equation is trustworthy up to the critical point, equation (9) gives us a method of calculating the critical volume, which volume, as we have already mentioned (p. 98), is very difficult to determine directly with accuracy. If, on the other hand, V_c has been measured or calculated with the aid of the Law of Cailletet and Mathias, one-third of this value gives van der Waals' constant b.

From equations (7) and (9) we can deduce an expression defining the critical pressure in terms of the constants a and b, namely

$$P_c=\frac{a}{27b^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Similarly, from equations (6), (9) and (10) we find

$$T_c=\frac{8a}{27Rb} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which defines the critical temperature in terms of van der Waals' constants a and b and the gas constant R.

On the other hand, since P_c and T_c may often be determined with comparative ease, their values may be employed to calculate a and b, since from the foregoing equations it is easy to show that

$$a = 3P_cV_c^2 \tag{12}$$

$$b = \frac{V_c}{3} = \frac{RT_c}{8P_c} \tag{13}$$

and

$$R = \frac{8}{3} \cdot \frac{P_cV_c}{T_c} \tag{14}$$

Unfortunately, however, van der Waals' equation does not represent accurately the condition of a gas near the critical point. The values for a and b are readily calculated from equation (1) by inserting the observed volumes and pressures at a series of temperatures; but the critical data calculated from these values with the aid of equations (9), (10) and (11) do not agree very closely with the observed values.

From equation (14) we see that

$$V_c = \frac{3}{8} \cdot \frac{RT_c}{P_c} = \frac{3}{8} \cdot \frac{RT}{P} = \frac{3}{8} V \tag{15}$$

that is, the critical volume as calculated from van der Waals' equation is three-eighths of the critical volume calculated for a gas on the assumption that the ordinary gas equation, namely $PV = RT$, were to hold; or, conversely

$$V = \frac{8}{3} V_c = 2{\cdot}667\, V_c \tag{16}$$

We may write equation (14) as

$$\frac{RT_c}{P_cV_c} = \frac{8}{3} = 2{\cdot}667 \tag{17}$$

Values found experimentally for the expression RT_c/P_cV_c are given for several substances in the table on p. 99. It will be observed that they approach more nearly to a mean value of 3·6.

Corresponding States.—If we insert the values obtained for a, b and R in equations (12), (13) and (14) into equation (1) we have

$$\left(P + \frac{3P_cV_c^2}{V^2}\right)\left(V - \frac{V_c}{3}\right) = \frac{8}{3}\frac{P_cV_c}{T_c}T.$$

Dividing this by $\frac{P_cV_c}{3}$, we obtain

$$\left(\frac{P}{P_c} + \frac{3V_c^2}{V^2}\right)\left(3\frac{V}{V_c} - 1\right) = 8\frac{T}{T_c} \tag{18}$$

Writing

$$\pi = \frac{P}{P_c}, \qquad \phi = \frac{V}{V_c} \qquad \text{and} \qquad \theta = \frac{T}{T_c}$$

equation (18) becomes

$$\left(\pi+\frac{3}{\phi^2}\right)(3\phi-1)=8\theta\,. \qquad (19)$$

This is a **fundamental equation** known as the **reduced equation of state** of van der Waals. It applies to all substances, for it possesses no constants peculiar to any one substance, a and b having been eliminated, as also P_c, V_c and T_c. This has been effected by expressing the pressure, temperature and volume, not in arbitrary units such as atmospheres, degrees absolute and litres, but as fractions of the critical values for the substances concerned. π is thus known as the **reduced** or **corresponding pressure,** and ϕ and θ as the **reduced** or **corresponding volume** and **temperature** respectively.

When two or more substances are at the same reduced temperature and pressure they are said to be in **corresponding states,** a term that explains itself. Under these conditions, if equation (19) is correct, the volumes of all the substances will be the same fraction of their critical volumes. This is called the **Law of Corresponding States.** That it is at any rate approximately true is indicated in the following table:

Corresponding States ($\pi=0\cdot08846$).
(Young and Thomas, 1893.)

Substance.	θ.	ϕ (Liquid).	ϕ (Saturated Vapour).
Methyl formate	0·7348	0·4007	29·4
Ethyl formate	0·7385	0·4004	29·6
Methyl alcohol	0·7734	0·3949	34·2
Ethyl alcohol	0·7794	0·4047	32·1
Propyl alcohol	0·7736	0·4028	31·1
Benzene	0·7282	0·4053	28·2
Carbon tetrachloride	0·7251	0·4072	27·4
Stannic chloride	0·7357	0·4021	28·1

The ratios of the volumes of liquid to the critical volume show very close agreement; for the saturated vapours the agreement is less good.

Application of Dieterici's Equation.—At low pressures, as we have already seen (p. 66), Dieterici's equation is practically identical with that of van der Waals; but at higher pressures it is mathematically a more perfect conception of the condition of a gas, in that it takes into account the difference in density between the outermost layer and the main body of the gas, to which difference reference has already been made. At the critical point Dieterici's equation predicts that

$$\frac{RT_c}{P_cV_c}=\tfrac{1}{2}e^2=3\cdot695.$$

This agrees much better with the values observed (see Table, p. 99).

On the other hand, Dieterici's equation does not give with equal success the numerical values for the individual factors of the foregoing equation, namely T_c, P_c and V_c. Thus, for example, the ratio V_c/b should be the same for all gases, namely 2, according to Dieterici's equation, and 3, according to van der Waals' equation. Nevertheless the following figures are obtained :

	V_c/b.
Hydrogen	2·80
Carbon dioxide . . .	1·86
Argon	1·41

It must be admitted, therefore, that as yet our equations are only approximations to the truth. It may well be that the factors involved are so complex that no relatively simple equation can ever be more than an approximation.

Boiling Points as Corresponding Temperatures.—In 1890 Guldberg pointed out that the boiling point of a substance at atmospheric pressure is approximately two-thirds of the critical temperature when the absolute scale is used in both cases as a basis of comparison. The boiling point is thus approximately a reduced or corresponding temperature. This is usually known as the **Guldberg-Guye Rule.** In the following table are given a few data illustrating the Rule:

Guldberg-Guye Rule (1890).

Substance.	Boiling Point, T_b.	Critical Temperature, T_c.	T_b/T_c.
Sulphur dioxide . .	263·0	430·5	0·611
Carbon dioxide . .	194·5	304	0·640
n-Pentane . . .	309·0	470	0·658
Diethyl ether . . .	307·5	467	0·658
Carbon tetrachloride .	350·0	556	0·630
Benzene	352·6	561	0·629
Chlorobenzene . .	405·0	632	0·641
Water	373·0	647	0·577
Ammonia	234·5	404	0·580
Chlorine	238·4	417	0·572
Ethane	184·7	305	0·600
Carbon disulphide . .	319·3	550·7	0·577

It should be noted, however, that many substances deviate appreciably from the Rule.

Connection between T_m, T_b and T_c.—It is interesting to note that in some cases the critical temperature is approximately given by the sum of the melting and boiling temperatures, all measured on the absolute scale. This is illustrated by the following data :

Substance.	T_m.	T_b.	T_m+T_b.	T_c.
Hydrogen . .	13·9	20·3	34·2	34
Chlorine . . .	171·4	238·4	409·8	417
Oxygen . . .	54·6	90·0	144·6	154
Hydrogen sulphide .	190·0	213·0	403·0	373
Water . . .	273·0	373·0	646·0	647
Ammonia . . .	196·0	234·5	430·5	404
Carbon dioxide . .	216·0	194·5	410·5	304
Carbon disulphide .	160·0	319·0	479·0	551
Benzene . . .	278·5	352·6	631·1	561

It is evident, however, that some substances do not conform at all closely to this regularity. If the melting (see p. 142) and boiling temperatures of substances were true reduced temperatures, the rule would be exceedingly useful.

CHAPTER VII.

LIQUEFACTION OF GASES.

Historical.—All gases can be liquefied provided the temperature is reduced sufficiently. The first gas to be condensed was sulphur dioxide (Monge and Clouet, *c.* 1800); liquefaction is readily effected by passage of the gas through a tube cooled below - 10° C. in a freezing mixture of, say, salt and ice. Commercially, however, the gas is at the present time liquefied by compression. In 1805 to 1806 Northmore liquefied chlorine, hydrogen chloride and sulphur dioxide by compression; with carbon dioxide his apparatus burst.

The first systematic investigation of the liquefaction of gases is due to Faraday (1823), who employed both pressure and cold. He sealed up the materials necessary to prepare the gas in one limb of a bent tube, cooled the other limb in a freezing mixture of ice and salt, and generated the gas within the closed tube by mixing and warming the materials. For example, chlorine hydrate was used in obtaining chlorine, and the ammoniate of silver chloride in obtaining ammonia. It was only necessary to warm these. In other cases the gases were generated by mixing two reagents and then warming. In this way the following gases were liquefied: Chlorine, sulphur dioxide, hydrogen sulphide, "euchlorine," cyanogen, ammonia, carbon dioxide and nitrous oxide. The method was rather dangerous, frequent explosions occurring in the experiments on the last two gases. (On one occasion thirteen fragments of glass entered Faraday's eye.)

Bussy (1824) prepared liquid sulphur dioxide, and by rapidly evaporating it under reduced pressure he attained a temperature of - 65° C. As a result he was able to liquefy chlorine and ammonia, and solidify cyanogen, through the agency of cold alone.

Ten years later Thilorier liquefied carbon dioxide on a large scale in a wrought-iron cylinder by the combined application of pressure and cold. He made solid carbon dioxide or carbon dioxide "snow" by allowing the liquid to evaporate rapidly in a box provided with hollow wooden handles through which the vapour escaped. He also discovered that when the solid was mixed with ether an extremely convenient cooling medium was obtained, capable of yielding temperatures below - 100° C. when rapidly evaporated. The mixture is known as **Thilorier's mixture.**

Faraday resumed his work on the liquefaction of gases in 1845. He applied pressure by means of two air-pumps, and availed himself of "Thilorier's mixture" in order to obtain low temperatures. By evaporating this liquid under reduced pressure, a temperature of - 110° C., measured by an alcohol thermometer, was reached, and the following gases were liquefied: Ethylene, silicon fluoride, phosphine and boron trifluoride, whilst hydrogen bromide, hydrogen iodide, "euchlorine," cyanogen, ammonia, sulphur dioxide, hydrogen sulphide and nitrous oxide were solidified.

Faraday was unable to liquefy hydrogen, nitrogen, oxygen, nitric oxide or carbon monoxide, and these gases came to be known as the "permanent gases." We now know the reason for this. In the preceding chapter we learned that a gas cannot be liquefied at temperatures above the critical point, no matter how great the pressure. In the following table are given the boiling points and critical temperatures of some gases, and it will be noted that Faraday's "permanent gases" have very low critical temperatures. At the present time we term **permanent gases** those gases whose critical points lie below the ordinary temperature of the air, that is to say, those gases that cannot be liquefied by pressure alone.

Gas.	Boiling Point, °C.	Critical Point, °C.	Gas.	Boiling Point, °C.	Critical Point, °C.
Helium	− 268·9	− 268	Ethane	− 88·3	+ 32
Hydrogen	− 252·7	− 239	Carbon dioxide	− 78·5	31·1
Nitrogen	− 195·8	− 147	Nitrous oxide	− 88·7	36·5
Carbon monoxide	− 192·0	− 139	Hydrogen chloride	− 85·0	51·4
Argon	− 185·7	− 122	Hydrogen sulphide	− 60·0	100
Oxygen	− 183·0	− 119	Ammonia	− 38·5	131
Nitric oxide	− 150·0	− 92·9	Chlorine	− 34·6	144
Methane	− 161·4	− 82·5	Sulphur dioxide	− 10·0	157·5
Ethylene	− 103·8	+ 9·7	Nitrogen tetroxide	+ 22·0	158·2

Carbon dioxide is on the border line between the "permanent" and the more easily liquefiable gases. Its critical temperature is 31·1° C., which is several degrees above our average summer temperature, so that cylinders of the compressed gas when freshly filled contain liquid as well as vapour. The pressure in the cylinder thus corresponds to the normal vapour pressure of the liquid, namely

Temperature, °C.	0	10	15	20	25
Pressure (atmos.)	35	46	52	59	66

Success in liquefying some of the permanent gases was first achieved in 1877, almost simultaneously by Cailletet in France and by Pictet in Switzerland. Pictet employed what is known as the **cascade method.** He first of all prepared a considerable quantity of liquid sulphur dioxide. By boiling this under reduced pressure a temperature of − 65° C. was attained, and used to liquefy carbon dioxide at a pressure of 4 to 6 atmospheres. This liquid in its turn was boiled under reduced pressure, and temperatures varying from − 120° to − 140° C. were thereby obtained. The liquid carbon dioxide was used to cool highly compressed oxygen, which condensed to the liquid state.

Cailletet introduced the method of **adiabatic expansion** with the performance of external work. The sudden adiabatic expansion of a gas against an external pressure causes external work to be performed by the gas, which accordingly suffers a diminution in its internal energy, and falls in temperature. The lowering of temperature obtained in this way may be very great. Cailletet compressed the gas confined over mercury in a capillary glass tube to pressures of several hundred atmospheres, cooled it to between 0° and $-20°$ C., and then suddenly released the pressure. In this way he succeeded in liquefying acetylene, nitric oxide, methane, oxygen, carbon monoxide, air and nitrogen (the first two gases yielded to cold and pressure alone, without any necessity for expansion), and also obtained indications of the liquefaction of hydrogen. The process, as carried out by Cailletet, was of no use commercially, for the permanent gases were only converted to a mist of small globules, and it was not until many years later that the method of cooling by adiabatic expansion was successfully worked on a large scale.

Cailletet prepared large quantities of liquid ethylene, which he recommended as a valuable refrigerant, and, employing this liquid, boiling under reduced pressure, as a cooling bath, he succeeded in obtaining liquid methane and oxygen as static liquids. The employment of the same cooling medium by Wroblewski and Olszewski led subsequently to the production of considerable quantities of liquid oxygen, carbon monoxide and nitrogen, and the solidification of nitrogen and carbon monoxide, temperatures as low as $-200°$ C. being reached. The rapid evaporation of liquid ethylene *in vacuo* leads to a temperature of $-152°$ C. The utility of liquid ethylene as a refrigerant was also recognised by Dewar (1886), who prepared liquid air and oxygen in large quantities by its aid.

Production of Liquid Air.—The methods for the production of liquid air are divisible into two classes according to whether the cooling of the gases is due to the **external** or **internal** work performed by them.

The former method is based on the principle that the sudden adiabatic expansion of gases against an external pressure causes external work to be done by them, accompanied by a proportional diminution in their own internal energy, manifested by a reduction in their temperature. Although this method was introduced by Cailletet in 1877 and was, as already stated, successfully applied by him to the liquefaction of oxygen, nitrogen and air, it was not until 1905 that it was successfully applied on a commercial scale, namely, in the **Claude Process.**

The difficulty of lubrication appears to have been mainly responsible for the failure of previous attempts, and this was first overcome by the employment of petroleum ether, which does not solidify, but merely becomes viscous at such low temperatures as $-140°$ to $-160°$ C. Later, however, it was found that leather retains its ordinary properties at these low temperatures, and in 1912 leather stampings were fitted to the working parts of the machinery to the entire exclusion of lubricants. Claude's apparatus is shown diagrammatically in fig. 29.

Air, compressed to 40 atmospheres, passes along the inner tube T_1 of the usual concentric system to the branched tube B, where it is in connection with a "liquefier," whilst much of it passes on through the expansion machine. Cooled by its loss of energy during expansion, it proceeds to the tubes inside the liquefier, and finally passes along the outer of the concentric tubes, thus cooling the oncoming air, which reaches the expansion machine at $-100°$ C. So cold does the expanded gas become that the compressed air in the liquefier finally condenses and is tapped off periodically, whilst the gas, after exerting this cooling effect, flows from the tubes of the liquefier into the outer tube T_2 and reduces to approximately −100° C. the temperature of the air passing through T_1.

The liquid air is usually collected and stored in Dewar vacuum flasks. These are double-walled glass vessels, the space between the walls being completely evacuated, so that the liquid in the flask is vacuum-jacketed. The heat conveyed by radiation across the vacuous space is only about one-sixth of that which would reach the liquid by conduction and convection if the space were filled with air, and this can be reduced to one-thirtieth by silvering the interior of the jacket. This latter procedure, however, is impracticable if for any purpose it is necessary to observe the contents of the flask.

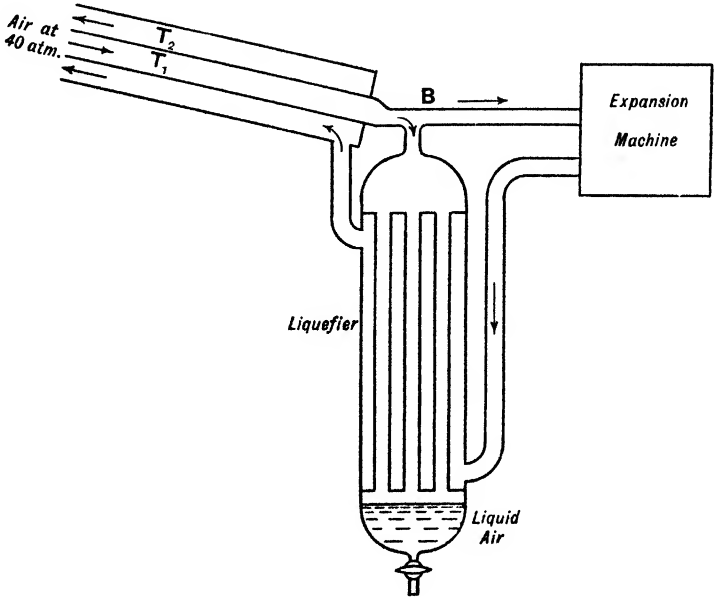


FIG. 29.—Claude's Apparatus for Production of Liquid Air.

The Joule-Kelvin Effect.—Reference has already been made to the fact, observed by Joule and Thomson (Lord Kelvin) in 1854, that when a highly compressed gas is allowed to expand into a region of low pressure in such a manner that no work is done against external pressure, the gas in general becomes slightly cooler. This is known as the Joule-Kelvin effect and is attributable to the fact that the molecules possess a certain amount of attraction for each other, which is sometimes referred to as **internal or intrinsic pressure** (p. 63). The work done in separating the molecules is carried out at the expense of the sensible heat of the gas, and is greater the lower the temperature. It would not exist in the case of a perfect gas upon free expansion, namely into a vacuum, and must be carefully distinguished from the cooling already considered as the result of adiabatic expansion against the external atmospheric pressure, and utilised in the Claude Process.

This thermal effect was studied first by Joule and Thomson. The method of experiment consisted in passing a steady stream of gas through a copper spiral immersed in a water bath at constant temperature. The gas was allowed to escape through a porous plug of cotton wool, which prevented it from leaving with any appreciable kinetic energy. The initial and final temperatures of the gas were noted. In the following table are given the observed changes in temperature per atmosphere:

The Joule-Kelvin Effect.

Gas.	Temperature, °C.	Alteration in Temperature, °C. per Atmos.
Air	0	−0·276
Oxygen . . .	0	−0·366
,, ...	20	−0·328
,, ...	100	−0·193
Nitrogen . . .	0	−0·333
,, ...	20	−0·291
Carbon dioxide . .	0	−1·382
Hydrogen . . .	0	+0·013
,, ...	20	+0·018
,, ...	100	+0·039

As is seen from the table, the thermal effect is quite small, and for most gases falls with rise of temperature, becoming *nil* if the temperature is raised sufficiently to what is termed the **inversion temperature.** Above this temperature heat is evolved on expansion. In the case of the air the thermal effect may be calculated from the expression

$$(t_1 - t_2) = 0{\cdot}276(p_1 - p_2)\left(\frac{273}{T}\right)^2$$

where p_1 is the initial high pressure, p_2 the final low pressure, in atmospheres, and T the initial absolute temperature, the cooling being expressed in degrees centigrade. By employing high pressures the cooling effect is proportionately enhanced. Thus, if a pressure difference of 100 atmospheres is employed, working at 0° C., the fall in temperature is 27·6 centigrade degrees in the case of air.

By allowing air to expand suddenly at ordinary temperatures a certain cooling is thus produced, and by applying this cooled gas to the reduction of the temperature of yet unexpanded gas, the latter after expansion will attain a still lower temperature. In this way it is possible to make the cooling effect cumulative, so that at last the temperature of the air is reduced to the liquefying point. The Linde, Dewar and Hampson liquefiers are based on this principle.

A diagrammatic representation of the Linde machine is given in fig. 80. Air compressed to 200 atmospheres passes through the steel bottle B, where it deposits its moisture, and thence proceeds to the worm surrounded by a refrigerating medium. Here the temperature is reduced to −50° C. and the last traces of water-vapour are removed. The gas then passes down the innermost of the concentric copper tubes T, by way of which it reaches the needle-valve V, where it expands to a pressure of 40 atmospheres. This limited expansion affords the major portion of the Joule-Kelvin effect, and at the same time reduces the subsequent necessary work of compression. The cooled expanded gas returns through the second concentric tube to the compressor, cooling the oncoming air as it passes. As this process is continued, the air reaching V steadily falls in temperature until at last it begins to condense to the liquid state, when the liquid is allowed periodically to pass through the valve Y where, on account of the further decrease of pressure to one atmosphere, it evaporates vigorously until its temperature falls to its normal boiling point for this pressure; the cold gas from the evaporation passes away through the outermost concentric tube and so assists in cooling the compressed air, whilst the liquid air collects in the receiver R and can be drawn off as required by the tap C. The apparatus is enclosed in a packing of non-conducting material such as wool and is supported externally by a wooden or metallic case. In the earlier forms of this type of liquefier the process was somewhat simpler, because the pressure was allowed to fall directly to the ordinary external atmospheric pressure by one expansion only. Machines of the more modern type have been constructed to yield over 50 litres of liquid air per hour.

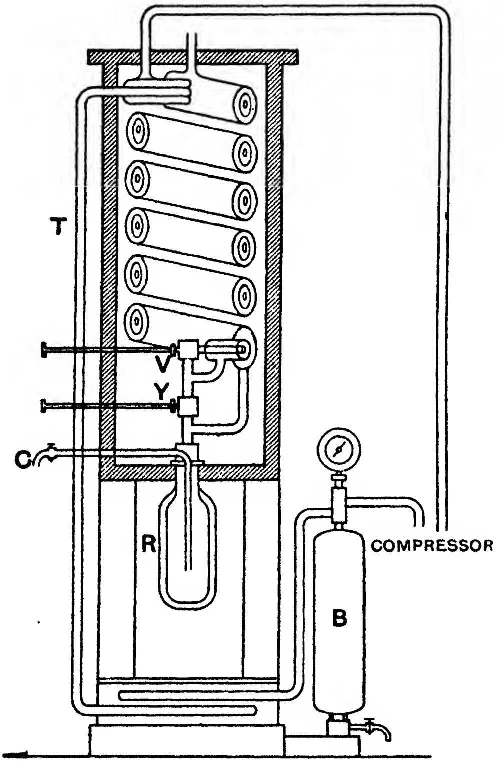


Fig. 30.—The Linde Liquid Air Machine.

The application of this method to the liquefaction of hydrogen at first sight seems out of the question, since a slight rise in temperature is observed with this gas after passage through the aforementioned plug, as though the molecules actually repel one another. Helium is similar. These two gases are thus " over-perfect " or " ultra-perfect " (p. 45). The heating effect in the case of hydrogen is seen to fall with fall in the temperature, and if the gas is cooled below −80·5° C. before passing through the plug, a cooling effect is observed as with ordinary gases. In 1898 Dewar succeeded in liquefying hydrogen for the first time in bulk by making use of this fact. The gas was first cooled by liquid air, and then further cooled by adiabatic expansion. Helium proved even more difficult to liquefy than hydrogen, but its liquefaction was at length accomplished by Kamerlingh Onnes in 1908 by the self-intensifying process, as outlined above, after initially cooling the gas to the temperature of liquid hydrogen. Keesom in 1926 succeeded in obtaining solid helium at 1·1° abs. as a homogeneous transparent mass of refractive index closely similar to that of the liquid.

Production of Liquid Oxygen.—On account of the great importance of oxygen and the increasing importance of nitrogen for industrial and other purposes, the liquid mixture of these elements (liquid air) provides a promising field for a successful process for the production of the individual gases on a large scale.

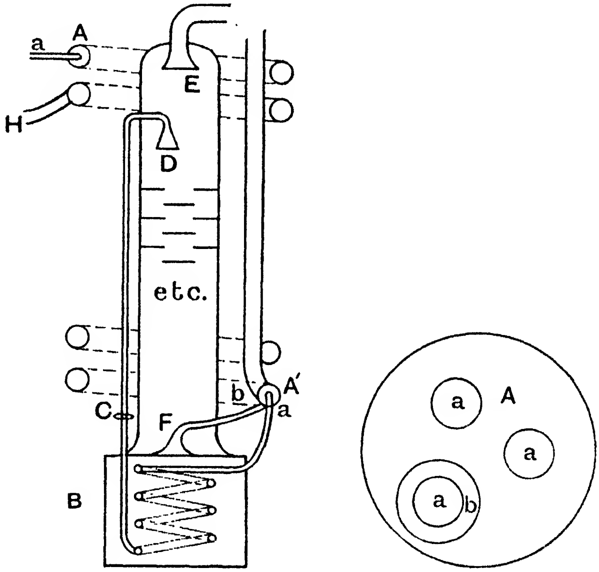


FIG. 31.—The Linde Oxygen Plant.

The vapour of boiling liquid air is richer in nitrogen than is the liquid; hence careful fractional distillation or evaporation should finally yield the oxygen in a pure condition, because the boiling point rises steadily as the percentage of oxygen increases.

Several forms of apparatus have been proposed. One of the earlier forms, suggested by Linde, consisted of a modification of the apparatus represented in fig. 30; this was supplied with only one valve, which allowed immediate expansion to atmospheric pressure, the liquid air produced by the cooling being collected in a suitable receiver. The compressed gas, before reaching the valve, was made to circulate through a copper coil actually inside the receiver, so as to be covered by the liquid air already formed. The relative warmth of this gas caused an evaporation of the more volatile nitrogen, the liquid lost by evaporation being replaced by fresh liquid air produced by the expansion of the cooled gas. Proceeding in this way, the receiver soon contained fairly pure liquid oxygen, which could be drawn off as necessary, and transported, in the form of compressed gas, in steel cylinders. As the gaseous nitrogen which passes away from the apparatus is formed by the evaporation of a liquid containing at least 21 per cent. of oxygen, the nitrogen is not pure, but contains at least 7 per cent. of oxygen. A more recent form of the **Linde oxygen plant** is shown in fig. 31.

Prior to admission to the plant, the air is compressed to 135 atmospheres (2000 lb. per square inch) and cooled to −20° C. in an ordinary refrigerating apparatus. This serves to freeze out atmospheric moisture. Carbon dioxide is removed by passage through a slaked lime purifier. Thus treated, the air is admitted to the Linde plant at the mouth of the regenerator spiral AA′ through three small pipes *a*, one of which is surrounded by a wider concentric pipe *b*, as indicated in fig. 31. These small pipes, inside AA′, encircle the rectifying column D, and emerge into the smaller spiral surrounded by liquid oxygen in B. The air on its passage becomes increasingly cooler, and escapes by way of the throttle-valve C to the top of the rectifying column D, a fall in temperature occurring at C owing to the Joule-Thomson effect. Ultimately a liquid rich in oxygen collects in B, whilst gas rich in nitrogen and containing only about 7 per cent. of oxygen escapes at E and leaves the apparatus through the regenerator spiral AA′, cooling in its passage, by conduction, the incoming air in *a*. The oxygen at F leaves through the tube *b* passing up inside A′A.

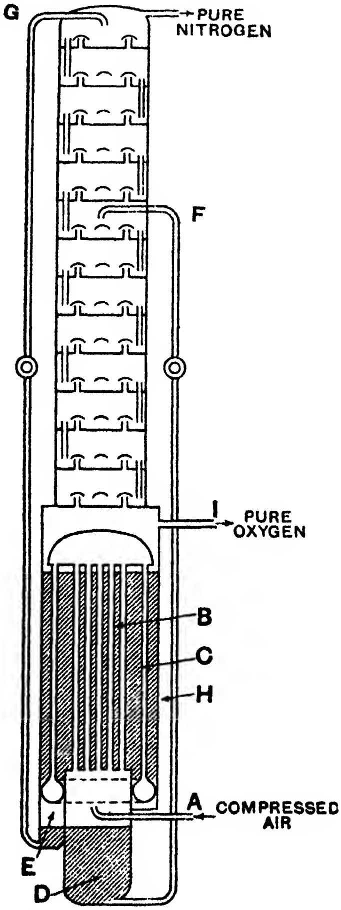


Fig. 32.—The Claude Separator.

When the apparatus has been at work a sufficient time to become steady, the liquid in B is continuously evaporated by the warmer air passing through the spiral, and the vapours escaping from B are rich in nitrogen, whilst the liquid remaining is rich in oxygen. The rectifying tower, with its baffle plates, reduces the amount of oxygen in the vapours escaping at E to about 7 per cent., for the ascending gases are constantly meeting liquids whose temperatures farther up the rectifying column are increasingly lower. The oxygen thus condenses and joins the descending liquid stream. On the other hand, the nitrogen in that stream meets increasingly warmer gases as it falls, and having a lower boiling point than the oxygen, it evaporates away and escapes at E. Liquid oxygen of 98 to 99 per cent. purity collects in B and is finally drawn off at H through *b*.

The efficiency of the apparatus depends upon the temperature gradient between D and F, and this is controlled by the throttle-valve C. In practice it is found that a pressure of 50 to 60 atmospheres is sufficient, when the plant is in steady running, the temperature of the entering liquid air at D being −192° C., and at F −181·5° C.

In **Claude's process** compressed air, cooled by passage through a coil surrounded by the cold gases issuing from other parts of the apparatus, enters the lower portion of the apparatus (fig. 32) at A, whence it reaches the inner part of the tubular vessel B of annular cross-section; this vessel is surrounded by liquid oxygen. During its ascent through B, the air becomes partially condensed to a liquid which will contain up to 47 per cent. of oxygen. If the pressure of the incoming gas is correctly adjusted, the residual gas will consist of almost pure nitrogen, which will pass over into the external tubular space C, where it becomes entirely liquefied. The liquids condensed in D and E are therefore greatly enriched in oxygen and nitrogen respectively before admission to the "still" proper. The liquid collecting in D is caused by its pressure to rise through a regulating-valve into the fractionating column at F, and, overflowing downwards, meets the ascending gases from the liquid oxygen in H. On account of the contact between these two currents, the descending liquid grows steadily richer in oxygen until it reaches the vessel H, which is in connection with the tubes in B, as liquid oxygen. The gases rising up the column beyond F become submitted to further "scrubbing" by the liquid nitrogen reaching G from E, the effect of this being to condense any oxygen still remaining in the gas so that it returns to scrub the ascending gases in the lower portion of the column, whilst the gas issuing at the top is reduced to pure nitrogen. Gaseous oxygen can be drawn from I above the condensed liquid. Thus almost pure oxygen and nitrogen are produced simultaneously.

Commercial liquid oxygen, however, contains a small percentage of argon, the bulk of the argon from the original air being concentrated in the oxygen fraction.

CHAPTER VIII.

DENSITIES AND MOLECULAR WEIGHTS OF GASES AND VAPOURS.

Density has already been defined as the mass of unit volume (p. 11). For solids and liquids the cubic centimetre is usually chosen as the unit of volume, but in the case of gases the mass of 1 c.c. would be an inconveniently small amount to deal with, and the litre is therefore usually chosen as the unit of volume. For purposes of comparison, where great accuracy is required, the density may be calculated for the **normal litre,** that is to say, for a litre of the gas measured at 0° C. under a pressure of 1 atmosphere at sea level and at a latitude of 45° (p. 14).

In the table on p. 122 are given the **normal densities** (L) of a few typical permanent gases.

Relative Density.—It is frequently convenient to express the density of a solid or liquid relatively to that of water. The ratio obtained is known as the relative density or specific gravity. Similarly we often find it convenient to express the density of a gas or vapour relatively to that of some other gas. Air is frequently chosen as the standard, particularly for vapour densities where great accuracy is not essential ; but for very accurate work the choice is not good unless the composition of the air is also given, since the composition varies slightly from time to time at the same place, and from locality to locality ; this is reflected in changes of the air density, which normally varies between the limits 1·2927 and 1·2933. At the present time oxygen is chosen as the standard, but, as we have already seen (p. 34), even this gas is not altogether free from objection, as three isotopes are known to exist, of atomic weights 16, 17 and 18 respectively. Unless these are always present in exactly the same proportions in our samples of the gas, the mean density of the latter must vary. Fortunately we have every reason to believe that no appreciable variation occurs, but theoretically the position is disturbing.

According to Avogadro's Hypothesis the molecular weights of gases are proportional to their relative densities. If, therefore, D_O represents the gas or vapour density compared with that of oxygen taken as 16, and M is the molecular weight of the substance, it follows that

$$M : 32 = D_O : 16$$

or

$$M = 2D_O \quad . \quad . \quad . \quad . \quad . \quad (1)$$

that is to say, the molecular weight is numerically equal to twice the density. If hydrogen or air be taken as standards, our equation becomes

$$M = 2{\cdot}016 D_{\mathrm{H}}$$

or

$$M = 28{\cdot}88 D_{\mathrm{air}}$$

respectively.

The methods available for the experimental determination of the densities of gases and vapours fall into two classes, according as they are capable of yielding exact or merely approximate results. Exact determinations are possible only when the substances are gaseous at ordinary temperatures. Liquid and solid substances have to be vaporised, and the gas laws do not accurately describe the behaviour of vapours.

THE EXACT DETERMINATION OF GAS DENSITIES.

1. The Globe Method.—This was first adapted to accurate work by Regnault (1845); it is comparatively simple to carry out, permits of several experiments being conducted simultaneously, and furnishes results little, if at all, inferior to those obtained by the volumeter method. It is not necessary to employ very large globes, the results obtained with quite small globes being at least as concordant among themselves as those obtained with 8- to 10-litre globes. Lord Rayleigh's accurate experiments were carried out with a globe the volume of which was about 1·8 litres, while the density of nitric oxide was measured by Gray using a globe of only 0·267 litre capacity.

A small globe possesses the advantage that the correction necessary on account of its contraction when evacuated is proportionally less than that for a large globe. In fact, the only error that is augmented by employing a small globe is that due to **adsorption** of gas on the surface of the glass (Chapter XXI).

The procedure is as follows: A glass globe of known capacity is carefully cleaned, dried, evacuated and weighed. To obtain accurate results it is absolutely necessary to have the interior of the globe perfectly dry, and to ensure this, after first filling the globe repeatedly with pure air dried by phosphoric anhydride, it is necessary to fill it repeatedly with the pure, dry gas, and evacuate. Successive density determinations then give concordant results, provided care is taken to maintain the globe vacuous between the experiments. After weighing, the globe is filled with the pure gas, at an observed pressure p and temperature t, and reweighed. The value of p is usually about 760 mm., and the value of t is almost invariably 0° C. During the weighings the globe is counterbalanced by a dummy globe made of the same kind of glass and being as nearly as possible of the same weight and external volume as the experimental globe. The surfaces of the two globes are always treated in precisely the same manner. In this way errors due to the hygroscopic nature of glass and to changes in the temperature and pressure of the air in the balance room are avoided.

In order to explain the method of calculation, suppose that the excess weight of the evacuated globe over that of its counterpoise is w_1 grammes, and that of the globe plus gas is w_2 grammes. The approximate weight of gas is then $(w_2 - w_1)$ or w grammes, say. It may be supposed that t is 0° C. and that p is approximately 760 mm.

Now, the glass globe, being elastic, responds to pressure, so that the volume of the evacuated globe is a trifle smaller than that of the globe when filled with gas. Let this diminution in volume of the globe, due to evacuation, be e c.c. A correction to the weight w is clearly necessary. Assuming that 1 c.c. of air under laboratory conditions weighs a grammes, the upward force of the atmosphere on the globe, when filled at atmospheric pressure, exceeds that on the exhausted globe by ae grammes. The corrected weight of the gas is therefore $w + ae$ grammes.

The contraction undergone by a globe when evacuated may be measured by the following method (Travers, 1901): The globe is supported in the interior of a large desiccator, its stem passing through one of the holes in a stopper in the desiccator lid. Through the other hole a calibrated vertical capillary tube is passed. The desiccator is filled with water and immersed in a constant temperature bath, and the contraction of the globe is obtained by observing how far the level of the water falls in the capillary tube when the globe is evacuated.

The volume of the globe is deduced from the weight of water that the globe holds. If the apparent weight of water (corrected if necessary for the weight of air displaced by the water) filling the globe at 0° C. is W grammes, and d is the density of water at 0° C., the volume of the globe at 0° C. is W/d c.c. = V litres, say.

Hence, assuming the validity of Boyle's Law, the weight of 1 litre of gas at 0° C. and 760 mm. is given by—

$$\frac{760(w+ae)}{PV} \text{ grammes} \quad . \quad . \quad . \quad . \qquad (2)$$

In order to deduce the weight of a "normal litre," L, *i.e.* the weight of 1 litre of the gas at 0° C. and 760 mm. pressure, and at sea level in lat. 45°, the above expression must be divided by—

$$(1 - 0{\cdot}0026 \cos 2\lambda - 0{\cdot}000000196h) \quad . \quad . \qquad (3)$$

where λ is the latitude of the laboratory and h the height in metres above sea level.

The value thus obtained is still subject to correction for at least two further sources of error, namely:

(i) Adsorption.—This is a surface phenomenon, and refers to the tendency for a layer of gas molecules to condense on the inner surface of the glass globe. This causes the result to be too high, but for the permanent gases, which are difficult to liquefy, the effect is small and may in general be ignored.

(ii) The assumption that Boyle's Law is valid. If the globe is filled with gas at a pressure which differs from 760 mm. by only a few millimetres the error involved is negligible. Otherwise a correction is necessary and can be applied readily if the compressibility of the gas is known.

It will be noticed that no allowance has been made for the weight of air displaced by the *weights* employed. This is not necessary if the relative values assigned to the various pieces are correct *in air*; if, however, in the calibration of the weights, all results had been reduced to the vacuum standard before the relative values of the pieces were calculated, the correction for air displaced by the weights would become necessary.

2. The Volumeter Method.—By this method it is possible to deal with large quantities of gas, since the apparatus for measuring the volume need not be portable. The weight of the gas may be determined in two ways, either by disengaging the gas from an apparatus which only allows pure, dry gas to escape, and determining the loss in weight of the apparatus, or by removing the gas from the volumeter after its volume, temperature and pressure have been determined, absorbing it by suitable means, and determining the increase in weight of the absorption apparatus and contents.

The arrangement adopted by Guye and Pintza for determining the density of nitrogen is shown in fig. 33. The globes A and B were calibrated by determining the weight of water at 0° C. that filled them to the marks *a* and *b*. Their combined volumes amounted to 3502·63 c.c. The "dead space" extending from these marks to the tap L in one direction, and the zero-point *n* of the mercury manometer in the other, was separately determined, as also was the space between the taps H, I and L.

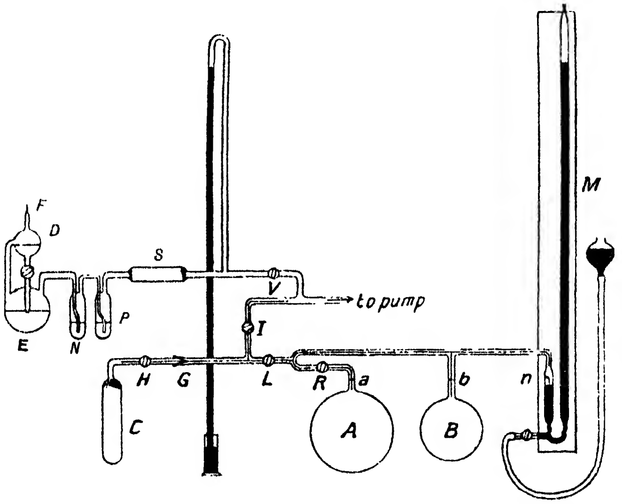


FIG. 33.—Guye and Pintza's Apparatus for Density of Nitrogen.

In conducting an experiment, the absorption tube C, containing coconut charcoal, was evacuated, weighed and attached to the apparatus as shown. The apparatus, which had previously been rinsed out several times with the pure, dry gas, was evacuated, and then slowly filled with the gas until the pressure was about atmospheric. The globes were surrounded by melting ice, and when the temperature of the gas had reached 0° C., the taps I and L were closed, the mercury adjusted to the mark *n*, and the initial pressure of the gas accurately observed. The space H I L was next evacuated, the tap I closed, and then, by suitably manipulating the taps H, L and R, the gas was absorbed in the charcoal contained in the tube C; this tube was cooled in a bath of ether and solid carbon dioxide. After most of the gas had been absorbed, the taps H and L were closed, and the pressure of the residual gas in the globes determined. The gas contained between H, I and L was pumped out and measured, and the absorption tube removed and reweighed.

In calculating the results, the difference between the initial and final pressures was taken, and the densities deduced according to the method given on p. 118, the correction for elasticity of the glass being, however, unnecessary. Due allowance was made for the fact that the temperature of the gas in the "dead space" was not 0° C., and the results were corrected for the known deviations of the gases from Boyle's Law.

The terms **molecule** and **molecular weight** have already been defined in the second chapter. Although much evidence of the reality of molecules now exists, no methods of measurement have yet been devised for the accurate determination of their absolute masses. In chemistry, however, one is concerned almost exclusively with the comparison of molecular weights. Accepting Avogadro's Hypothesis as a fundamental principle, this comparison can be accomplished readily by methods which were indicated by Avogadro and finally established through the clear exposition of the hypothesis by Cannizzaro (p. 32).

The determination of molecular weights is a necessary preliminary to a knowledge of the atomic weights of the elements, but only in the cases of substances gaseous at the ordinary temperature can exact molecular weights be directly determined. In the majority of cases it is necessary to determine approximate molecular weights of elements and compounds, and also the accurate chemical equivalents of the elements. From these two sets of data the accurate atomic weights of the elements and the molecular formulæ of the elements and compounds can be deduced. Exact molecular weights are then derived by adding together for each substance the relative weights of the atoms present in the molecule.

Calculation of Exact Molecular Weights from the Normal Densities of Gases.

In an earlier chapter (p. 32) we saw that Cannizzaro's system of determining atomic weights consisted in ascertaining first the molecular weights of gases or volatile substances on the assumption, implied in Avogadro's Hypothesis, that the relative masses of the molecules of the gases are proportional to the gaseous densities (p. 32). The product of the gramme-molecular volume of a gas and its density will therefore give its gramme-molecular weight. Avogadro's Hypothesis assumes that the gramme-molecular volume is the same for all gases, and on this basis the molecular weights of several gases have been calculated (see Table, p. 122). But these molecular weights cannot rigidly be true, for, as we have seen, Avogadro's Hypothesis itself is only an approximation to the truth under ordinary conditions. We believe, however, that **under a common, indefinitely small pressure, all gases have exactly the same gramme-molecular volume, provided the temperature is the same.** If, therefore, we can by any means determine the mean deviation of a gas from Boyle's Law between 0 and 1 atmosphere (p. 49), we can calculate its molecular weight by the method of **limiting densities.** The procedure is as follows (D. Berthelot, 1898):

Let the common molecular volume of two gases be V_0 at 0° C. and under the infinitesimal pressure P_0. Their volumes will be different, V and V' say, at a pressure of 1 atmosphere, P_1. Now the deviations of the gases from Boyle's Law may be expressed conveniently as follows:

$$1 - \frac{P_1 V_1}{P_0 V_0} = A\frac{P_1}{P_0}(P_1 - P_0) = A_0^1 \quad . \quad . \quad . \quad (4)$$

and

$$1 - \frac{P_1 V'_1}{P_0 V_0} = A'\frac{P_1}{P_0}(P_1 - P_0) = A'^1_0$$

in which A_0^1 and A'^1_0 represent the mean deviations of the gases from Boyle's Law between 0 and 1 atmosphere. Hence

$$P_1 V_1 = (1 - A_0^1) P_0 V_0,$$
$$P_1 V'_1 = (1 - A'^1_0) P_0 V_0,$$

and therefore

$$\frac{V_1}{V'_1} = \frac{1 - A_0^1}{1 - A'^1_0} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If, then, the "normal" densities (*i.e.* masses in grammes of a "normal" litre) of the gases are L and L' respectively, their molecular weights M and M' satisfy the equation

$$\frac{M}{M'} = \frac{(1 - A_0^1)L}{(1 - A'^1_0)L'}$$

which, if M', L' and A'^1_0 refer to oxygen, may be written—

$$M = 32 \cdot \frac{L}{L_{O_2}} \cdot \frac{(1 - A)}{(1 - A_{O_2})} \quad . \quad . \quad . \quad . \quad (6)$$

the limits zero and 1 atmosphere between which A is determined being understood. This equation expresses the molecular weight of a gas in terms of its density and compressibility and the corresponding values for oxygen.

Since the values of L and A for oxygen are 1·42897 and 0·00096 respectively, equation (6) becomes

$$M = 22{\cdot}4L(1 - A) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The determination of A_0^1 involves an extrapolation, but this is easily carried out in the case of gases that are difficult to liquefy, since, over the range of pressure from 1 to 2 or 3 atmospheres the relationship between PV and P is linear. Moreover, the numerical values of A_0^1 for these gases are very small, and a very high order of accuracy in their measurement is not necessary. With gases such as carbon dioxide, hydrogen chloride, etc., that are readily liquefied, the values of A_0^1 are much greater and require to be determined with a considerable degree of precision. At the present time it cannot be said that such measurements have been accomplished. The relation between PV and P in these cases is not linear, the graph showing a slight, but decided curvature, and the most satisfactory method of deducing A_0^1 consists in measuring accurately the values of PV from $P = 1$ atmosphere downwards as far as it is possible to obtain exact measurements; graphic extrapolation then furnishes the limiting value $P_0 V_0$.

The following table gives the results obtained for the gramme-molecular weights of several gases with the aid of equation (4). Under Σ Atomic Weights are given the corresponding molecular weights calculated as the sum of the atomic weights from the table on pp. 35, 36. It will be observed that the agreement is very close.

Gas.	Formula.	Normal Density, L.	Boiling Point, °Abs.	A.	M.	Σ Atomic Weights.
Hydrogen . .	H_2	0·08987	20·5	− 0·00056	2·0156	2·0156
Nitrogen . .	N_2	1·25036	77	+ 0·00044	28·015	28·016
Carbon monoxide .	CO	1·25011	83	+ 0·00060	28·009	28·00
Nitric oxide . .	NO	1·3402	123	+ 0·00114	30·006	30·008
Hydrogen chloride .	HCl	1·6392	188	+ 0·00743	36·469	36·465
Carbon dioxide .	CO_2	1·9768	194 *	+ 0·00676	44·009	44·00
Nitrous oxide .	N_2O	1·9777	184	+ 0·00739	44·002	44·016
Methane . .	CH_4	0·7168	112	+ 0·00175	16·039	16·031
Ethane . . .	C_2H_6	1·3562	185	+ 0·01194	30·037	30·054

* Sublimation temperature.

The value for A rises with the boiling point. For hydrogen it is negative, but we have already seen that this gas is "ultra-perfect."

It is easy to deduce from the foregoing table the atomic weights of the elements concerned, and the mean values are in good agreement with those obtained by gravimetric analysis and other methods, as given in the table on pp. 35, 36.

This method is the only one by which we can determine with accuracy the molecular weights of the **inert gases** of Group 0 of the Periodic Table. These gases are believed to be monatomic, since the ratio of their specific heats at constant pressure and constant volume respectively is approximately 1·66, a value which is characteristic for monatomic vapours, as we shall see later (Chapter XII). The inert gases do not yield definite compounds suitable for accurate analysis, so that their atomic weights cannot be determined in the usual chemical manner. Their atomic weights, which are identical with their molecular weights, are therefore determined from their densities in the foregoing manner.

Another method of calculating exact molecular weights is that known as the **Reduction of Critical Constants Method** (Guye, 1905). It is as follows:

Van der Waals' equation (p. 64)

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad . \quad . \quad . \quad (8)$$

becomes, when P is expressed in atmospheres, and the unit of volume is taken as the volume occupied by a gramme-molecule of the gas at N.T.P.:

$$\left(P+\frac{a}{V^2}\right)(V-b)=\frac{(1+a)(1-b)}{273}T \quad . \quad . \quad (9)$$

From this it has been deduced that the relative molecular volumes of different gases at N.T.P. are proportional to

$$\frac{1}{(1+a)(1-b)},\quad \frac{1}{(1+a')(1-b')},\quad \frac{1}{(1+a'')(1-b'')},\ \text{etc.}$$

Hence,

$$M=\frac{KL}{(1+a)(1-b)},$$

where K is a constant for all gases, and is obviously the volume in litres occupied by a gramme-molecule of a perfect gas at N.T.P. For K, Guye adopts the value 22·412. Hence,

$$M=\frac{22{\cdot}412L}{(1+a)(1-b)} \quad . \quad . \quad . \quad . \quad (10)$$

The values of a and b may be calculated from the equations (p. 102)

$$T_c=8a/27bR, \qquad P_c=a/27b^2,$$

in which, as has been already found above,

$$R=(1+a)(1-b)/273.$$

Now van der Waals' equation is only approximately correct, and in order to obtain a more accurate representation of the behaviour of gases, it is necessary to assume that a and b vary with the temperature. For this purpose Guye employs the following empirical formulæ to deduce the values of a_0 and b_0, the values of a and b at 0° C.:

$$a_0=a\left(\frac{T_c}{T}\right)^{3/2}, \qquad b_0=b\left(1+\frac{T_c-T}{T_c}\right)\left(1-\beta\frac{P_c}{P}\right) \quad . \quad (11)$$

The value of β, deduced from the critical constants, density and molecular weight of carbon dioxide, is 0·0032229. The molecular weight M is then given by the formula

$$M=\frac{22{\cdot}412L}{(1+a_0)(1-b_0)}.$$

A simpler method of calculation suffices for the difficultly liquefiable gases. The relations (11) above are not necessary, the equation

$$\frac{M}{L}(1+a)(1-b)=22{\cdot}412+mT_c \quad . \quad . \quad . \quad (12)$$

being sufficiently accurate. The value of m, obtained by substituting the known data for oxygen, is 0·0000623.

This method is an empirical method, and being based upon van der Waals' equation, it would be expected to break down for gases that are at all associated at the critical temperature. The following table illustrates the nature of the results it yields:

Gas.	*L.*	Molecular Weight.	Sum of Atomic Weights (pp. 35, 36).
H_2	0·08987	2·015	2·0156
N_2	1·25036	28·013	28·016
CO	1·25011	28·003	28·000
NO	1·3402	30·009	30·008
CH_4	0·7168	16·034	16·031
N_2O	1·9777	44·012	44·016

The agreement between the data in the last two columns is exceedingly close.

APPROXIMATE DETERMINATION OF GAS AND VAPOUR DENSITIES.

Quartz Microbalance Method.—This method was used by Aston (1913) when determining the densities of different fractions of neon in an attempt to separate its isotopes. The balance consists of a light, evacuated quartz bulb B (fig. 34), of about 0·3 c.c. capacity, attached to one end of a lever, fitted with a suitable fulcrum F, the whole being in a glass case. The other end of the lever is kept in position between two stirrups. The vessel is first evacuated, then the gas under test is admitted until A rests at an arbitrary zero on a telescope scale. The pressure p_1 is noted. The gas is now removed and oxygen admitted until the lever again rests at the same zero. The pressure is again noted, p_2. Low pressures are used, of the order of 8 cm., and under these conditions the temperatures quickly adjust themselves to constancy. The density of the gas is given by the ratio

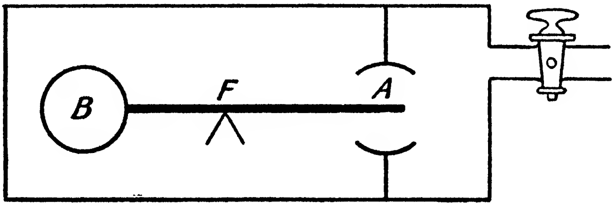


FIG. 34.—Quartz Microbalance.

$$d_{\text{gas}} : d_{\text{oxygen}} = p_2 : p_1$$

with an accuracy of about 0·1 per cent. Not more than 0·5 c.c. of gas need be used, and the experiment can be completed in about 10 minutes.

Bunsen's Effusion Method.—This method was introduced by Bunsen (1857) to determine approximately the density of a gas when only a few c.c. were available. An account of the method has already been given (p. 43).

For the determination of the vapour densities of substances that exist normally as liquids or solids, the following methods are available:

Dumas' Method (1826).—The substance to be volatilised is introduced into a weighed round, pear-shaped or cylindrical bulb, the neck of which is drawn out to a point. The bulb is heated by means of a constant temperature bath, maintained at 20° to 30° C. above the boiling point of the substance under investigation, until the air has been swept out and all excess of the material also removed. The end of the neck is then quickly sealed, the temperature and barometric pressure noted, the bulb allowed to cool and then weighed. After the weight has been recorded, the bulb is immersed in air-free distilled water at the laboratory temperature, or in mercury, and the point of the neck nipped off. The weight of liquid filling the bulb is then obtained, the weight of the air contained in the bulb when originally weighed being neglected, as it is small in comparison with the weight of the liquid.

The vapour density of the substance may now be calculated. If w_1 is the weight of the bulb filled with air, w_2 the weight when filled with the vapour, and w_3 the weight when filled with water, then $w_3 - w_1$ = weight of water filling the bulb (neglecting weight of air, as already mentioned). If the weight is expressed in grammes, the number, so far as an approximate determination is concerned, expresses also the capacity of the bulb in c.c. If, then, d be the density of the air in grammes per c.c., the weight of air which the bulb contained is $(w_3 - w_1)d$, and the weight of the bulb itself $w_1 - (w_3 - w_1)d$. Hence the weight of the vapour is $w_2 - [w_1 - (w_3 - w_1)d]$. The weight of the vapour and its volume now are known, and the density can be deduced.

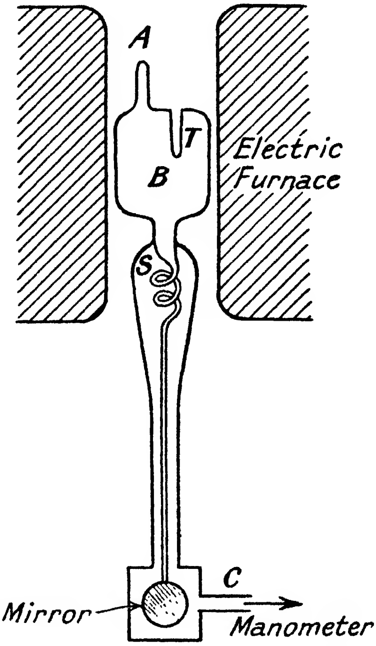


FIG. 35.—Apparatus for Determining Vapour Densities at Various Pressures.

A more accurate development of Dumas' method permits of the determination of vapour densities at various pressures according to the amount of substance initially taken. The apparatus consists of a glass (or quartz) vaporisation bulb, B, of known capacity, fused into which is a flattened spiral tube, S (fig. 35), which ends in a quartz thread carrying a small mirror. Increase of the internal pressure causes the spiral to distend, and this can be countered by raising the external pressure through the tube C. The internal pressure can clearly be determined by adjusting the external pressure, the deflections being observed by means of the small mirror. After the introduction of the material, the bulb is evacuated and sealed at A, and a thermocouple inserted into the tubulure T gives the temperature. Upon raising the temperature the pressure observed is that due to the vaporised material.

Hofmann's Method (1868).—In this method a known weight of the substance is volatilised in the space above the mercury in a calibrated barometer column, jacketed with a vapour tube at some constant temperature. The amount of the substance required is small and is passed to the surface of the mercury column in a small glass-stoppered tube, in such quantity as to leave no portion unvolatilised. Fig. 36 shows the form of apparatus used by Young (1895). By means of this apparatus a series of readings can be made at different temperatures by varying the pressure on the vapour contained in the jacket, and by connecting the closed mercury reservoir to a second pump the pressure on the vaporised substance in the barometer tube can likewise be altered at will.

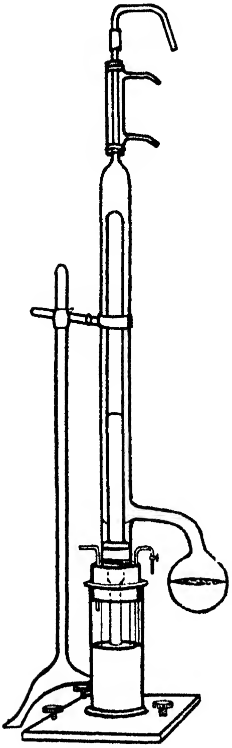


FIG. 36.—Young's Modification of Hofmann's Vapour Density Apparatus.

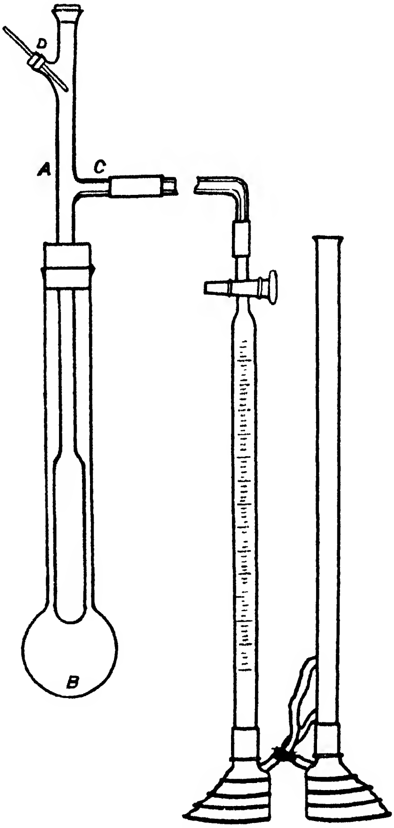


FIG. 37.—Victor Meyer's Vapour Density Apparatus.

In any case, the material is volatilised at a pressure less than atmospheric, and, in consequence of the lower temperature, substances which undergo decomposition when heated at atmospheric pressure can be investigated by this method. If the barometric pressure is P mm., and the height of the mercury column (corrected for temperature) h mm., then the pressure at which the vapour exists is $P - h$ mm. The volume is read on the calibrated barometer tube.

The process requires much smaller quantities of material than that of

Dumas, but cannot be used at temperatures over 250° C. owing to the vapour tension of mercury then becoming considerable. Above 100° C. a correction for the mercury vapour present should be made.

Victor Meyer's Method.—The method most widely used in modern investigations is that due to Victor Meyer (1878), which is not only very convenient in manipulation, but also offers a wide range of temperature. The apparatus (fig. 37) consists essentially of the vaporisation tube A, closed at the top by a stopper, and terminating in a cylindrical bulb at the lower end. Outside the heating jacket B, a side tube C is attached to A, connecting it with a gas burette or eudiometer tube. A glass rod, fitted through a side tube in the head of the apparatus, serves as a support for the small capsule, glass bulb or stoppered bottle containing a weight of the substance sufficient to give 20 to 30 c.c. of vapour. Constant temperature is maintained in the cylindrical bulb by the vapour of a suitable liquid boiled in B, and when once obtained, as shown by a constant reading in the gas burette, the glass rod at D is drawn back and the vessel containing the substance allowed to fall on to a pad of sand or asbestos at the bottom of the bulb. Rapid vaporisation occurs, and, owing to the length of the bulb and narrowness of the tube, air is expelled instead of vapour through C, this being collected and measured at the temperature of the gas burette, the pressure being the barometric, corrected for the vapour tension of the water in the collecting tube. The temperature is ascertained by suspending a thermometer in contact with the gas-collecting apparatus or in the water jacket with which it is best to surround the measuring apparatus to preserve constancy of temperature.

If w is the weight in grammes of substance vaporised, v the volume in c.c. of gas observed, p the barometric pressure in mm., f the vapour tension of water at t° C. (the temperature of the experiment), the vapour density relative to hydrogen and oxygen is given by the following expressions :

(*a*) Relative to hydrogen, $$\frac{w \times (273 + t) \times 760}{v \times (p - f) \times 273 \times 0{\cdot}0000899}$$

(*b*) Relative to oxygen, $$\frac{w \times (273 + t) \times 760}{v \times (p - f) \times 273 \times 0{\cdot}001429}.$$

These formulæ hold when the air initially present in the apparatus is dry. If, however, the pressure of aqueous vapour in the initial air was x per cent. of the pressure of saturated aqueous vapour at t°, the factor $(p - f)$ should be replaced by $\left(p - \frac{100 - x}{100} f\right)$.

It is necessary that vaporisation of the substance shall occur at a rapid rate, otherwise the vapour will, by slow diffusion, find its way up the vaporisation tube, be carried forward with the air expelled, and condense when cooled, thus reducing the volume of air which ought to be obtained in the burette. To obtain rapid vaporisation, the bulb should be maintained at a temperature not less than 30° C. above the boiling point of the substance. Thus, if steam is the heating medium in the jacket, a successful determination could be easily carried out with carbon disulphide (B.pt. 46° C.), but probably not with ethyl alcohol (B.pt. 78·5° C.).

A very convenient and accurate method of determining the density of a saturated vapour consists in introducing into A (fig. 38) a known mass of the volatile liquid, and into B a somewhat larger quantity of the same liquid, both vessels having previously been evacuated. The mercury level in A is slightly above that in B, since B contains a greater depth of liquid. On warming, so long as any liquid remains in A, the difference of level in the two vessels remains constant. The moment all the liquid in A has evaporated, however, the mercury level within it begins to rise; the temperature is taken at this point, for at this temperature the known mass of saturated vapour fills A to the mercury level.

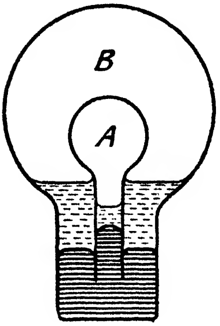


FIG. 38.—Apparatus for Determining Density of a Saturated Vapour.

Determination of Vapour Density at High Temperatures.—Both the Dumas and the V. Meyer methods may be used at high temperatures. In the former, porcelain may be substituted for glass, and for the latter, which is the more useful method, modifications are described below.

Up to 600° C., constant temperatures can be maintained by a vapour bath, for which purpose aniline (B.pt. 184° C.), diphenylamine (B.pt. 310° C.), sulphur (B.pt. 445° C.), phosphorus pentasulphide (B.pt. 518° C.) and stannous chloride (B.pt. 606° C.) are all available. For still higher temperatures an electric furnace may advantageously be employed. Up to about 1700° C. a porcelain vaporisation tube is useful, but at this temperature it begins to soften and must be protected by a platinum covering. For higher temperatures an iridium bulb is used, coated inside and outside with a glaze of fused magnesia and magnesium chloride to render it impervious to gases.

Air cannot be used to fill the apparatus in any case where the substance readily undergoes oxidation, and, as a rule, is not used at high temperatures. Nitrogen or hydrogen is generally employed, and sometimes argon.

Since in Meyer's method the gas expelled is measured at the ordinary temperature, the temperature of evaporation need not be ascertained. But as many substances change their molecular state, and hence their density, as the temperature changes, it is obviously of interest to record the temperature. For low temperatures this is an easy matter. For very high temperatures photometric methods may be used. These consist in comparing the light emitted by the heated bulb with that from a standard source of light.

MOLECULAR STATE OF GASES AND VAPOURS.

Having ascertained the density of a gas or vapour relatively to oxygen by any of the preceding methods, the molecular weight is calculated with the aid of equation (1) (p. 116). The value obtained does not always coincide with the simplest possible formula; sometimes it is greater, as in the case of the majority of the non-metallic elements, but sometimes it is less, as in the case of certain compounds which undergo dissociation when vaporised.

The state of aggregation is not dependent upon the temperature only; it is affected also by the pressure. For this reason the results obtained by the methods of Dumas and Victor Meyer with the same substance at the same temperatures are not necessarily identical. **Aluminium chloride** furnishes us with an excellent example of this. The results obtained at atmospheric pressure and varying temperatures by Dumas' method are shown by crosses in fig. 39, air being taken as the standard. The asterisks in the same figure represent the values obtained by the method of Victor Meyer, in which the aluminium chloride is vaporised in an inert gas, so that its mean partial pressure is considerably less than 1 atmosphere, but has no definite value throughout a series of experiments. From 200° to 400° C. the density, as obtained by Dumas' method, indicates a molecular formula of Al_2Cl_6. Above 400° C. dissociation takes place, becoming increasingly pronounced with rise of temperature, until it reaches completion in Victor Meyer's apparatus at about 800° C., the molecules of vapour then corresponding to $AlCl_3$ (p. 131). It is advisable, therefore, when stating vapour density data, to mention also the conditions under which those data have been obtained.

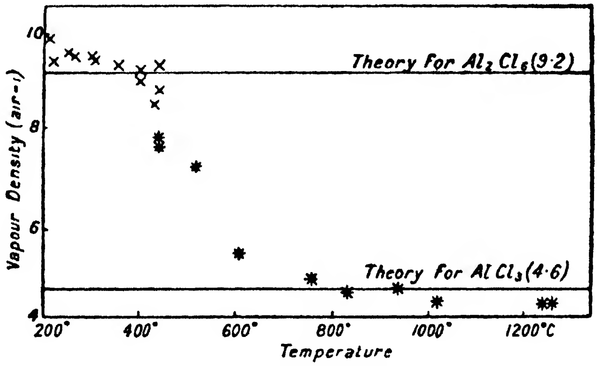


Fig. 39.—Vapour Density of Aluminium Chloride.

The inert gases of Group 0 are, as we have already seen, monatomic in the gaseous state. In addition to these, many **metals** are definitely recognised as monatomic in the vapour state. This is the case with the following metals at the temperatures stated: Sodium (700° C.), mercury (900° C.), thallium (1300° C.), zinc (1400° C.), lead (1600° C.), cadmium (1700° C.), bismuth (2040° C.) and antimony (2070° C.). At lower temperatures both bismuth and antimony associate to form larger molecules.

Vapour density determinations of the alkali metals are difficult to arrange on account of the corroding action of the vapours on the containing vessel. By volatilising sodium in argon, however, Rodebush (1930) successfully determined its vapour density. The apparatus used is shown in fig. 40. A and B are nickel tubes fixed horizontally in the electric furnace F, the temperature being registered by the thermocouple T. Argon was admitted through the open end of B, passed over sodium in the nickel boat C and, when saturated with the sodium vapour, escaped through the small perforation O. The sodium deposited on the cooler portions of A was estimated by titration. The vapour density of the sodium was calculated from the equation

$$M = \frac{Pw_s}{P_s n} - \frac{w_s}{n}$$

where M is the molecular weight of the sodium, P and P_s the total pressure of the system and the partial pressure of the sodium respectively, w_s the mass in grammes of sodium vapour which saturated n gramme-molecules of argon. The results indicated very slight association at 570° and 706° C., the molecular weights being 25·1 and 24·1 respectively, suggesting the existence of a few Na_2 molecules, the value at 570° C. being in fair agreement with the value calculated from spectroscopic data (see Vol. II).

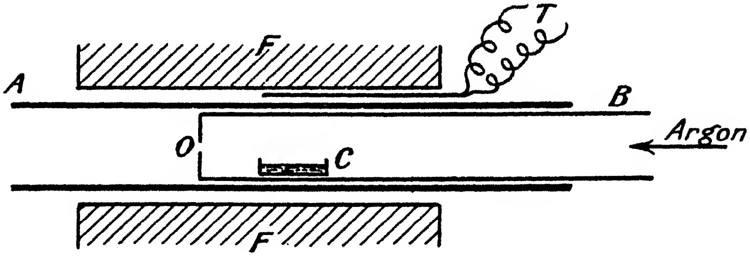


FIG. 40.—Rodebush's Apparatus for Vapour Density of Sodium.

In general, the non-metals (other than the inert gases) and the metalloids are polyatomic in the vapour state. Thus oxygen, nitrogen and the halogens are diatomic. The halogens, particularly iodine and, to a less extent, bromine, tend to dissociate into atoms at high temperatures, thus illustrating the rule that molecules of high molecular weight are more readily decomposed than those of low weight. Phosphorus and arsenic are tetratomic, both more or less dissociating at high temperatures, arsenic becoming diatomic at 1700° C., and phosphorus partially so. The maximum known molecular complexity occurs with sulphur and selenium, as the following data indicate :

	Temperature, °C.	Probable Composition of Vapour.
Sulphur . .	445	S_8 mainly
	900	S_2
	2000	$S_2 + S$
Selenium . .	<900	$Se_6 + Se_2$
	c. 900	Se_2
	>900	$Se_2 + Se$

Tellurium is diatomic in the vapour state.

Many non-metallic compounds are associated in the vapour state; thus, at 30° C. hydrogen fluoride is H_2F_2. In the solid state nitrogen dioxide exists as the tetroxide, N_2O_4; the liquid contains some NO_2 molecules, the number of which rises with the temperature, until the vapour, at 140° C., consists entirely of dioxide molecules. Other familiar cases are phosphorous oxide, P_4O_6 ; phosphoric oxide, P_4O_{10} at 1400° C. ; arsenious oxide, As_4O_6 below 800° C. ; and antimonious oxide, Sb_4O_6 at 1560° C.

At relatively low temperatures the vapour densities of many **metallic halides** indicate association to double molecules which is, in some cases, complete, and in others only partial. Rise of temperature invariably results in dissociation to simpler molecules. A few of the best known examples are given in the following table :

Halide.	Simplest Formula.	Method.	Temp., °C.	Apparent Degree of Association.	Probable Composition of Vapour.
Cuprous chloride .	$CuCl$	V. Meyer	1650	1·9	Cu_2Cl_2
Beryllium chloride	$BeCl_2$	V. Meyer	500	2·0	Be_2Cl_4
		,,	1500	1·0	$BeCl_2$
Aluminium chloride	$AlCl_3$	Dumas	440	2·0	Al_2Cl_6
		V. Meyer	440	1·6	$Al_2Cl_6 + AlCl_3$
		,,	1100	0·9	$AlCl_3$
Gallium chloride .	$GaCl_3$	Dumas	< 280	2·0	Ga_2Cl_6
Aluminium bromide	$AlBr_3$	,,	444	2·0	Al_2Br_6
Aluminium iodide	AlI_3	,,	444	2·0	Al_2I_6
Stannous chloride	$SnCl_2$	V. Meyer	600	1·3	$SnCl_2 + Sn_2Cl_4$
		,,	1110	1·0	$SnCl_2$
Chromic chloride .	$CrCl_3$	V. Meyer	1065	1·1	$CrCl_3 + Cr_2Cl_6$
		,,	1375	0·8	$CrCl_3 + CrCl_2$
Chromous chloride	$CrCl_2$	V. Meyer	1550	1·5	$CrCl_2 + Cr_2Cl_4$
Ferrous chloride .	$FeCl_2$	V. Meyer	Yellow heat	1·5	$Fe_2Cl_4 + FeCl_2$
		,,	1350	1·0	$FeCl_2$
Ferric chloride .	$FeCl_3$	Dumas	440	2·0	Fe_2Cl_6
		V. Meyer	750	1·0	$FeCl_3$ (with traces of $FeCl_2$)

The following chlorides present points of special interest :

Mercurous Chloride.—Early determinations of the vapour density of mercurous chloride agreed with that required for the simple formula $HgCl$; but in 1850 Odling showed that if a piece of gold leaf were suspended in the vapour it became amalgamated, showing that free mercury was present. It was evident, therefore, that dissociation had taken place, presumably in accordance with the scheme

$$Hg_2Cl_2 \rightleftharpoons HgCl_2 + Hg$$

since a residue of mercuric chloride was left. This was confirmed by Baker in 1900, who found that the vapour density of thoroughly dry mercurous chloride corresponded approximately to that required for the double formula Hg_2Cl_2, and that no amalgamation of gold leaf took place. With the moist vapour, however, the earlier observations were confirmed.

Chlorides of Indium.—These are of historical interest. Vapour density determinations by Victor Meyer's method showed that three such chlorides could exist in the vapour state, namely $InCl$, $InCl_2$ and

$InCl_3$ (Nilson and Pettersson, 1888). This was the first case to be proved definitely in which an element could manifest three grades of valency. The result was of special value at the time since it clinched the argument, already supported by specific heat measurements (p. 222), that indium should be classed in the Periodic Table in Group III along with aluminium, and not in Group II along with zinc, with which it occurs associated in Nature and which in many ways it resembles.

Zirconium Tetrachloride.—The valency of zirconium was for many years a vexed problem. Berzelius isolated the metal and studied many of its compounds in a series of researches between 1824 and 1835, determining its combining weight as 22·37. He first formulated its oxide as ZrO_3, but later altered this to Zr_2O_3, thus making it analogous to Al_2O_3. Gmelin wrote ZrO, thus comparing zirconia with MgO and BeO. In 1857, however, the vapour density of the chloride was determined at the boiling point of sulphur by Deville and Troost, using Dumas' method, and found to be approximately 8·16 (air = 1); its molecular weight was therefore 8·16 × 28·88 or 236. There were thus 4 Cl-atoms in the molecule, and the formula for the chloride might thus be Zr_2Cl_4, analogous to Fe_2Cl_4, or $ZrCl_4$, analogous to $SnCl_4$, but certainly not $ZrCl_3$. The zirconium was assumed to be tetravalent, and the assumption was confirmed in subsequent years by the application of Dulong and Petit's Law (p. 222) and Mitscherlich's Law of Isomorphism (p. 193).

CHAPTER IX.

CHANGE OF STATE FROM SOLID TO LIQUID.

THE familiar phenomenon of the passage of a crystalline substance from the solid to the liquid state occurs at a definite temperature known as the melting point. More accurately defined the **normal melting point** is *the temperature at which the solid and liquid phases can exist in equilibrium in dry air under a given pressure—usually the pressure of the atmosphere.*

It is generally assumed that, when a substance melts, the amplitude of vibration of the molecules around their positions of rest is approximately equal to the mean distance between them, so that the resulting collisions destroy the crystalline form. Looked at from another point of view, the melting point may be regarded as the temperature at which the probability of attachment of a molecule to the crystal surface is equal to the probability of its detachment (Garner, 1931).

Most crystalline substances melt sharply, and if the liquid phase has the same composition as the solid, and will re-solidify without change of temperature or composition, the melting point is termed the **true** or **congruent melting point.** Examples are ice and calcium chloride hexahydrate, $CaCl_2.6H_2O$, which melt at 0° C. and 30·2° C. respectively.

Some crystalline substances melt sharply at a definite temperature, but the liquid phase has not the same composition as the solid. Sodium sulphate decahydrate, $Na_2SO_4.10H_2O$, is a case in point. At 32·4° C. partial fusion takes place, but whilst the liquid obtained is a saturated solution of the salt in water, the solid phase consists of anhydrous sodium sulphate admixed with more or less decahydrate. Although the vapour pressure and temperature remain constant, this is not a true melting point; it is really a transition point (p. 179), and is frequently termed an **incongruent melting point.**

Determination of the Melting Point.—Various processes are available for the determination of melting points. The first which may be mentioned depends on finding the freezing point of the liquid, for when certain precautions are taken, the freezing point and melting point are identical. The precautions are due to the fact that when a liquid is slowly cooled without agitation, or even, in some cases, when slowly and regularly stirred, the temperature falls below the melting point, or normal freezing point, and the liquid becomes supercooled. This supercooled condition can be removed by the addition of a trace of the solid phase (a minute amount of ice if the liquid is water) or by the production of the solid phase by agitating the liquid. Both these methods are followed in practice, the latter the more frequently. When crystals once appear in the liquid, freezing rapidly takes place, and the temperature, provided the degree of supercooling was only small, rises rapidly to the equilibrium temperature of the solid-liquid mixture, that is, to the melting point. The Beckmann apparatus is very suitable for the purpose of the determination (see p. 405).

Another accurate process consists in surrounding the bulb of a thermometer with the finely divided material in a wide tube and raising the temperature slowly by means of a bath maintained at a point only slightly higher than the contents of the tube, until melting has begun. The mixture of liquid and solid is then stirred thoroughly, though not rapidly, the constant temperature registered being the melting point.

For substances of high melting point, such as metals, a variety of methods has been adopted :

1. The substance is heated to its point of fusion in a crucible or porcelain tube, a current of hydrogen or of some inert gas being passed over the surface of the metal, and the temperature noted by inserting the protected ends of a thermocouple.
2. The substance is inserted in the form of a wire into the thermo-element, and its temperature raised until fusion occurs and breaks the circuit.
3. The metal wire forms part of a circuit and is heated up in a porcelain tube together with the bulb of an air thermometer, the temperature being noted when fusion breaks the electric circuit.

Standardisation of Thermometers.—For this purpose it is usual to choose as fixed points the melting temperatures of certain metals which can readily be obtained in a very pure condition, and which give sharp melting points which are easily reproducible. There is a further advantage in using metals for this purpose, namely, that owing to their high thermal conductivity there is less danger of local overheating, which would lead to conflicting results. The following metals are frequently used for high temperature work :

	M.pt.
Lead	327·3 °C.
Zinc	419·4 ,,
Aluminium	658·7 ,,
Gold	1062·6 ,,
Palladium	1551·5 ,,

There are occasions, however, when it is inconvenient or even impossible to use metals directly for calibrating a thermometer in its everyday working condition. For low temperature work, mercury is the only suitable metal available, and we have to fall back upon such relatively poor conductors of heat as *iso*pentane and carbon disulphide. For higher temperatures the transition or melting points of salts may be used. As we shall presently see, it is essential that the salts should be free from all traces of impurity, and in view of their low conductivity for heat, care must be taken to avoid local overheating.

The zero point on the centigrade scale is, of course, the melting point of ice under atmospheric pressure. For very accurate work the ice should be prepared from de-aerated water *in vacuo*, as dissolved gases affect its melting point. The following points have been determined with great accuracy, and may be used for calibration purposes. Together with the five melting points given above, they are an attempt to reproduce the thermodynamic temperature scale which, as explained in Vol. II, is closely similar to the gas scale.

Substance.	Formula.	Phenomenon.	Temperature, °C.
*Iso*pentane	C_5H_{12}	Freezing	− 159·6
Carbon disulphide	CS_2	,,	− 111·6
Toluene	$C_6H_5CH_3$	,,	− 95·1
Chloroform	$CHCl_3$	,,	− 63·5
Mercury	Hg	,,	− 38·87
ICE	H_2O	Melting	0·000
Benzene	C_6H_6	,,	5·493
Acetic acid	CH_3COOH	,,	16·60
Acetophenone	$CH_3COC_6H_5$	,,	19·655
Sodium sulphate decahydrate	$Na_2SO_4.10H_2O$	Transition	32·384
Benzophenone	$C_6H_5COC_6H_5$	Melting	47·85
Naphthalene	$C_{10}H_8$	,,	80·22
Benzoic acid	C_6H_5COOH	,,	122·45
Phthalic anhydride	$C_6H_4(CO)_2O$	,,	131·60
Anthracene	$C_6H_4(CH)_2C_6H_4$	,,	216·05
Anthraquinone	$C_6H_4(CO)_2C_6H_4$	,,	284·84
Potassium dichromate	$K_2Cr_2O_7$	,,	397·5
Potassium sulphate	K_2SO_4	Transition	583
Potassium chloride	KCl	Melting	770·3
Sodium chloride	$NaCl$	,,	800·4
Sodium sulphate	Na_2SO_4	,,	884·7
Potassium sulphate	K_2SO_4	,,	1069·1

Structure of Liquids.—It is generally assumed that liquids possess little or no definite structure at temperatures somewhat removed from their freezing points. The molecules are regarded as free to move in every direction, so that any particular arrangement obtaining at a given moment would not be likely to persist for long. There is a good deal of evidence, however, both direct and indirect, in favour of the view that, at temperatures slightly above the melting point, fragments of the solid structure or lattice persist in the liquid, and only disappear as the temperature rises (p. 248). Water affords an interesting example of indirect evidence for this. The irregularities in the specific heat and density of water at various temperatures, and particularly the contraction observed when water is warmed from 0° to 4° C., has led to the view that water is a ternary mixture containing molecules of "ice," molecules of "water" and molecules of "steam" in equilibrium. Thus:

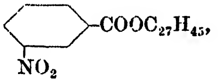
$$\underset{\substack{\text{Trihydrol or}\\ \text{“ ice ” molecule.}}}{(H_2O)_3} \rightleftharpoons \underset{\substack{\text{Dihydrol or}\\ \text{“ water ”}\\ \text{molecule.}}}{(H_2O)_2} \rightleftharpoons \underset{\substack{\text{Monohydrol}\\ \text{or “ steam ”}\\ \text{molecule.}}}{H_2O}$$

The "ice" molecules are presumed to have a more complex structure, but to be less dense, than the " water " molecules. Hence, when water at 0° C. is warmed, the equilibrium at 0° is displaced in the direction left to right, some " ice " molecules melting to the more dense " water " molecules. The contraction thereby at first resulting more than counteracts the normal thermal expansion of the liquid with rise of temperature, so that the density of the liquid increases to a maximum at approximately 4° C., and then continuously falls with further rise of temperature as the bulky " steam " molecules increase in number.

The various so-called **liquid crystals** are of great interest in this connection as affording more direct evidence of structure in the liquid state. When, for example, *p*-azoxyanisol,

is warmed, it melts sharply at 118·3° C. yielding a turbid, doubly refracting liquid, which gives interference colours when examined by polarised light. At 135·9° C. the liquid turns clear, and ceases to be doubly refracting. On cooling this clear liquid turbidity is assumed again at 135·9° C. and solidification occurs at 118·3° C., supercooling of course being excluded. The turbid liquid appears to be perfectly homogeneous, and no separation of a second phase, whether liquid or solid, has ever been effected, so that the probability of its being a suspension or an emulsion appears to be ruled out. The molecular weight, as determined from the surface tension (p. 268), is the same for the turbid as for the clear liquid. X-ray analysis of the turbid liquid has, however, yielded faint indications of structure, indicating that the turbid liquid is an intermediate stage between the true crystal and the true liquid.

Cholesteryl *m*-nitrobenzoate,



melts to a turbid liquid at 137° C. and becomes clear at 170° C. On cooling, a beautiful play of colours is observed--violet, green, red and orange (Dorée and Orange, 1916).

Volume Changes on Melting.—When a substance melts at constant temperature it invariably undergoes a change in volume. Usually expansion occurs, but sometimes contraction. The change in volume may be calculated if the densities of the solid and liquid phases at the melting point are known. Let us take water as a familiar example :

Mean density of ice at 0° C.. . . . 0·9168 gramme per c.c.,
∴ Volume of 1 gramme of ice . . 1·09075 c.c.
Density of water at 0° C. . . . . 0·999868 gramme per c.c.,
∴ Volume of 1 gramme of water . 1·00013 c.c.
∴ Contraction of 1 gramme of ice on melting =0·09062 c.c.

$$\therefore \text{ Percentage volume change of ice on melting} = -\frac{0{\cdot}09062 \times 100}{1{\cdot}09075} = -8{\cdot}31.$$

Volume change is sometimes determined by direct measurement.

The method employed by Endo (1923) consisted in suspending a silica crucible, C, from one arm of a silica beam, AB, whose coefficient of expansion with rise of temperature is negligibly small (see fig. 41).

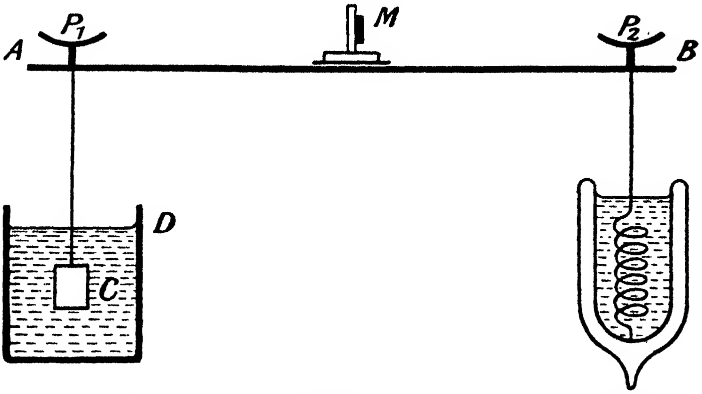


Fig. 41.—Endo's Apparatus for Measuring Volume Change on Melting.

The solid to be tested is placed in C, which hangs in a suitable liquid medium in the vessel D, the temperature of which can be raised electrically. From B a weak spiral hangs, with its lower end fixed to the bottom of a Dewar flask containing cotton-seed oil. This serves as a damping arrangement. Small deflections of the beam AB are indicated by the mirror M, which is observed through a telescope, using an arbitrary scale, so that the apparatus lends itself to accurate adjustment. The scale pans P_1 and P_2 are utilised in the preliminary rough adjustment, and in calibrating the arbitrary scale. The solid in C is raised to a temperature within a few degrees of its melting point, after which, as the temperature rises, the deflection of the beam is continuously observed. As shown by AB in fig. 42, which indicates

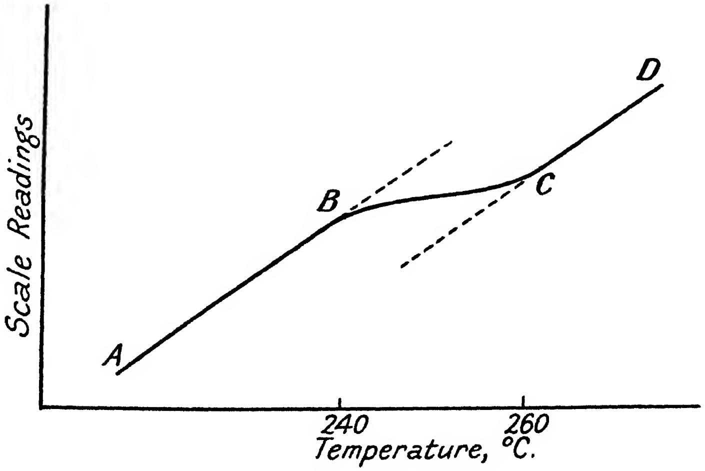


Fig. 42.—Endo's Results for Tin.

the results obtained when pure tin was heated in C, the relation between the deflection and the temperature is linear. When the metal begins to melt, its volume rapidly expands, its buoyancy increases, and the deflection of the scale is proportionately affected. After the metal has completely fused, the beam undergoes steady deflection CD with rise of temperature, as before. The actual change in volume of the metal can easily be calculated provided we know the density of the liquid medium at the melting point of the metal and the mean coefficient of expansion of the metal with rise of temperature.

If δV_m is the change in volume of the metal during melting, and ρ the density of the liquid medium at the melting point of the metal, it is obvious that

$$\rho\delta V_m = \delta m$$

where δm is the apparent change in mass caused by the increased buoyancy of the metal upon expansion during melting.

Hence, if V_m is the volume at the melting point, the percentage change in volume is given by

$$\frac{100\delta V_m}{V_m} = \frac{100\delta m}{\rho V_m}.$$

The volume V_m can be deduced from the volume V at the room temperature, $t°$ C., by the equation

$$V_m = V\{1 + a(t_m - t)\}$$

where a is the mean coefficient of cubical expansion of the metal.

The volume change may also be obtained by calculation with the aid of the Clausius-Clapeyron equation (p. 78). This equation may be written in the form

$$V_2 - V_1 = \frac{l}{T} \cdot \frac{dT}{dP}.$$

The latent heat of fusion, l, of ice is 79·7 calories, whilst $\frac{dT}{dP}$ is $-0{\cdot}0075°$ C. per atmosphere; that is to say, by increasing the pressure on ice by 1 atmosphere the melting point is lowered by 0·0075° C. Converting these into the proper units we have

$$V_2 - V_1 = \frac{79{\cdot}7 \times 4{\cdot}19 \times 10^7}{273} \times \frac{0{\cdot}0075}{1{,}013{,}240}$$
$$= 0{\cdot}09054 \text{ c.c.}$$

The increase in specific volume upon melting, that is, the increase in volume per gramme, or $\delta V/w$, where w is the number of grammes of metal taken, is given by

$$\frac{\delta V}{w} = \frac{\delta V}{Vd}$$

where d is the density of the solid at its melting point.

A few results obtained by various methods are given in the following table:

Percentage Changes in Volume on Melting.

Substance.	Melting Point, °C.	$\frac{100\delta V_m}{V_m}$.	Substance.	Melting Point, °C.	$\frac{100\delta V_m}{V_m}$.
Sodium .	97·5	2·53	Gallium .	29·8	− 1·812
Copper .	1083·0	4·05	Bismuth .	271·0	− 3·32
Magnesium	651·0	4·20			
Zinc . .	419·4	6·5	Ice . .	0·0	− 8·31
Tin . .	231·85	2·80	Formic acid	8·3	2·06
Lead . .	327·3	3·44	Acetic acid	16·7	20·1
Silver .	960·5	5·00	Benzene .	5·4	13·07
Gold . .	1062·6	5·17	Naphthalene	80·0	19·4

The great majority of solids expand on melting, and with many organic substances, such as acetic acid and naphthalene, the expansion is very considerable. As we have already seen ice is exceptional, since it contracts by 8·31 per cent. on melting. The reverse change, namely the expansion of water on freezing, is of great importance in Nature, being one of the main factors concerned in the disintegration of rocks and the pulverising of the soil in agriculture, to say nothing of domestic misfortunes to water pipes during winter. Most of the metals expand on melting. This is so for copper, silver and gold. Were it otherwise, and the liquid metals expanded like water on solidification, they would readily yield sharp castings. Gallium and bismuth are exceptional in that they contract on melting.

Influence of Size of Particle.—Undoubtedly the size of the solid particles or, what is substantially the same, the specific surface of the solid, exerts an influence on the melting temperature. The greater the specific surface, the lower the melting point. The actual mathematical connection between the two factors, however, appears to be involved, and not readily expressible in a simple formula.

Influence of Pressure.—If a solid expands on melting, an increase of pressure will render the change more difficult; in other words, a higher temperature is necessary, so that the melting point is raised. This is a logical consequence of Le Chatelier's theorem (p. 23). On the other hand, when a solid contracts on melting, an increase in the pressure will facilitate the change, the melting point being lowered. This is the case with ice.

That such ought to be the case was first realised by James Thomson, who, in 1849, showed that from theoretical considerations a connection must exist between the melting point of a solid and the pressure. The following year this was experimentally demonstrated by his brother W. Thomson (Lord Kelvin), who found that under a pressure of 8·1 atmospheres the melting point of ice was lowered by 0·059° C., equivalent to a fall of 0·0073° per atmosphere. The more accurate determinations of Tammann are given below, the third column giving the results calculated in terms of atmospheres.

Depression of the Melting Point of Ice under Pressure.

(Tammann, 1899.)

Melting Point, °C.	Pressure in Kilograms per sq. cm.	Pressure in Atmospheres.	Depression in Melting Point per Atmosphere.
0	1	0·968	..
− 2·5	336	325	0·0077
− 5	615	595	0·0084
−10	1155	1118	0·0089
−15	1625	1573	0·0095
−20	2042	1977	0·0100

As examples of the elevation of the melting point with increase of pressure, the following may be cited (Pushin, 1924):

p-Nitrotoluene.

Pressure, kilograms per cm.^{2} .	1	900	2080	3110
Melting point, °C. . . .	51·5	75	100	125

m-Dinitrobenzene.

Pressure, kilograms per cm.^{2} . .	1	1000	2000
Melting point, °C.	89·8	114·8	138

In these cases the effect of the pressure is more pronounced than with water.

By means of the Clausius-Clapeyron equation (p. 78) we can calculate the effect of pressure upon the melting point of a substance, provided we know the latent heat of fusion, *l*, and the change of volume involved in the melting. Let us consider ice, for example. We may write the Clausius-Clapeyron equation as

$$\frac{dP}{dT}=\frac{l}{T(V_2-V_1)}$$

where l is the latent heat, and V_2-V_1 gives the volume change per gramme of ice on melting. Taking l as 79·7 gramme-calories, or $79{\cdot}7\times4{\cdot}19\times10^7$ ergs, and V_2-V_1 as $-0{\cdot}0906$ c.c., we have

$$\frac{dP}{dT}=-\frac{79{\cdot}7\times4{\cdot}19\times10^7}{273\times0{\cdot}0906}\text{ dynes per cm.}^2$$

$$=-\frac{79{\cdot}7\times4{\cdot}19\times10^7}{1{,}013{,}240\times273\times0{\cdot}0906}\text{ atmospheres}$$

$$=-\mathbf{133{\cdot}3\ atmospheres};$$

that is, in order to lower the melting point of ice by 1° C. a pressure of 133·3 atmospheres must be applied. Conversely, a pressure of 1 atmosphere will lower the melting point by 1/133·3 or 0·0075° C. This value agrees sufficiently closely with that found by Tammann, as given in the foregoing table. The temperature at which ice would melt *in vacuo*, therefore, is +0·0075° C.

The effect of pressure upon the melting point of glacial acetic acid has been studied with the aid of the apparatus shown in fig. 43, termed by de Visser a **manocryometer** (Greek *manos*, rare; *kryos*, ice). On maintaining in a thermostat at constant temperature, the relative amounts of solid and liquid acetic acid in bulb C adjust themselves to the pressure, which is measured by noting the mercury level in the closed manometer AB. On raising the temperature by a fraction of a degree, some of the solid melts. The expansion thus caused compresses the air in AB until equilibrium is again restored, and the new pressure is noted. It will be observed that, with this apparatus, the pressure corresponding to any particular melting temperature is obtained directly, and not the temperature of melting for any given pressure. In this way it was found that, for glacial acetic acid,

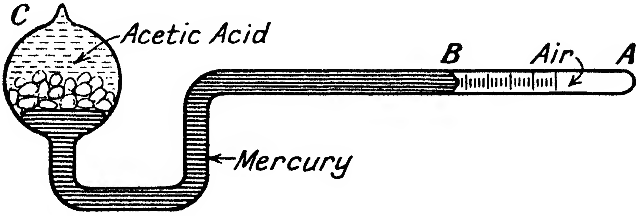


FIG. 43.—The Manocryometer (de Visser).

$$\frac{dT}{dP} = 0{\cdot}02435^\circ \text{ C. per atmosphere,}$$

the calculated value being +0·0242° C.

According to Damien (1891) the effect of pressure on the melting point of a substance may be calculated from the formula

$$t = t_0 + a(p-1) - b(p-1)^2$$

where t_0 and t are the melting points under a pressure of 1 and p atmospheres respectively, a and b being constants. If b is smaller than a the melting point will rise to a maximum and then fall with further rise of pressure. This has been experimentally realised in the case of α-naphthylamine:

	M.pt.
At 1 atm. pressure . . .	49·750 °C.
,, 81 ,, ,, . . .	50·543 ,,
,, 173 ,, ,, . . .	49·646 ,,

The effect of **intensive desiccation** on a number of substances is to raise their melting points. This is discussed in greater detail in Volume II.

Influence of Foreign Substances.—The addition of a foreign body to a substance tends to affect the melting temperature of that substance. This is a feature of very great importance when accurate data are required for calibration purposes.

In order to determine the melting point of a substance which melts at high temperatures a thermocouple may be embedded centrally in a crucible containing the substance and the whole steadily heated in a furnace the temperature of which is raised by, say, 5° C. per minute. The temperature registered by the thermocouple is noted at definite intervals, and the results are plotted as a time-temperature curve (fig. 44.)

If the substance undergoes no physical change, a continuous curve is obtained, the rise in temperature being proportional to the time.

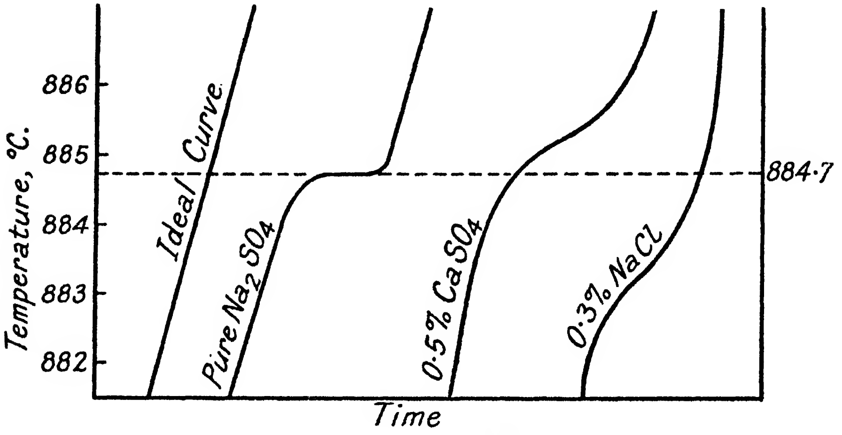


FIG. 44.—Illustrating Influence of Impurities on Melting Point of Sodium Sulphate (Roberts, 1924).

If the substance is chemically pure, a sharp break may be looked for at the melting point. This in the case of pure anhydrous sodium sulphate is given at 884·7° C. The temperature remains constant for an appreciable time owing to the absorption of heat during the change of state. The time-temperature curve thus becomes horizontal. When all the salt has melted the temperature begins to rise again. The presence of small quantities of impurity not only alters the melting point, but renders it less certain by reducing its sharpness. Thus, addition of 0·5 per cent. of $CaSO_4$ raises the melting point of sodium sulphate by approximately 1° C., whilst 0·3 per cent. of sodium chloride lowers it by about 2° C. The curve in both cases shows a deviation from its regular course, but the horizontal portion has lost its sharpness.

Melting Points as Corresponding Temperatures.—It was pointed out by Clark in 1896 that, for many substances, the following relationship between the critical and melting temperatures on the absolute scale is approximately true :

$$\begin{aligned} T_c/T_m &= \text{constant} \\ &= 2 \text{ approx.} \end{aligned}$$

This means that the melting temperature may be expressed as a fraction of the critical temperature, and is thus a "corresponding" or "reduced" temperature. The data in the following table illustrate this rule and also indicate the extent to which some substances depart from it:

Substance.	Formula.	T_c.	T_m.	T_c/T_m.
Nitrogen	N_2	126	63	2·0
Bromine	Br_2	575	266	2·2
Carbon monoxide	CO	132	66	2·0
Ammonia	NH_3	404	196	2·0
Methane	CH_4	177·5	89	2·0
Benzene	C_6H_6	561	278	2·0
Oxygen	O_2	154	54·6	2·8
Water	H_2O	647	273	2·3
Ethane	C_2H_6	305	102	3·0
Toluene	$C_6H_5CH_3$	594	176	3·4
Ethyl acetate	$CH_3COOC_2H_5$	523	189	2·8
Nitric oxide	NO	177	112	1·58

It is evident that the rule is not universally true.

Latent Heat of Fusion.—It is well known that when heat is put into a solid at its melting point there is no rise in temperature until the whole of the solid has melted. The absorbed heat has been utilised in changing the state of the solid, and the number of calories absorbed per gramme of substance is therefore termed the latent heat of fusion of that substance (Latin *latēre*, to be hidden), since its presence cannot be detected with a thermometer. This quantity represents the work done on the molecules in overcoming the forces that hold them rigidly together. Exactly the same quantity of heat is liberated when 1 gramme of the liquid at the melting point freezes to solid at the same temperature.

The latent heat of fusion per gramme of substance, denoted by l, is frequently calculated with the aid of van 't Hoff's equation (p. 407):

$$D = 0{\cdot}01985T^2/l$$

where D represents the depression of the freezing point of the molten substance when a gramme-molecule of a second undissociated substance is dissolved in 100 grammes of it, and T is the melting point on the absolute scale.

A convenient and accurate method of determining the latent heat of fusion experimentally is that devised by Partington (1922). The essential features of the apparatus are shown in fig. 45. A weighed quantity, m, of the solid substance is placed in A, which is surrounded by an outer vessel B containing the same substance partly in the molten condition and therefore at its melting point. The whole is surrounded by insulating material in such a manner as to protect it from draughts and changes of temperature. An electric heating coil is placed in A, and when the whole apparatus has attained the melting temperature of the substance, current is passed through the heating coil until the solid in A has completely melted, being subjected to suitable stirring to avoid local overheating. When this has taken place the temperature begins to rise. The latent heat per gramme of the substance, l, is readily obtained by calculation, since, as shown on p. 83,

$$l = A^2R\theta/4{\cdot}19m$$

where R is the resistance in ohms, θ the time in seconds during which the current was passed, and A the current measured in ampères. This method is exceedingly neat and simple. No corrections for cooling are necessary, neither do we require to know the specific heats of the solid and liquid substance, nor even its exact melting point.

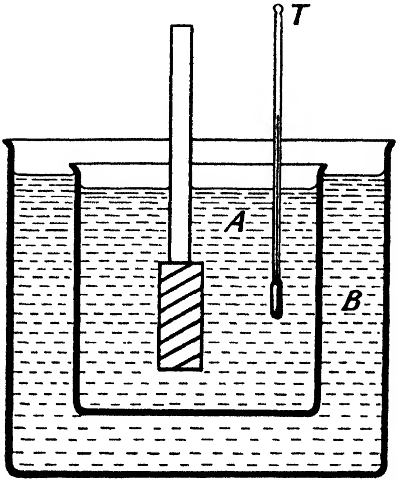


FIG. 45.—Partington's Apparatus for Latent Heat of Fusion.

In the table on p. 145 are given the latent heats of fusion per gramme, l_m, of a number of substances, together with the melting points on the absolute scale, T_m.

Trouton's Rule (p. 88) has been applied by Walden (1908) to substances at the melting point. The value found for Ml_m/T_m in the case of unassociated organic substances approximates to 13·5. This is illustrated by the data in the table on p. 145. The value obtained with associated substances is lower, since the actual molecular weight of the associated molecule is greater than that corresponding to the simple formula, and too small a value has therefore been used in calculating the constant. To arrive at the true constant, therefore, the full molecular weight of the associated substance must be used. If this is not known the rule gives us an approximate method of determining it. Thus, if M is the molecular weight of the unassociated molecule, and M' that of the associated one, it follows that

$$\frac{M'}{M} = \frac{13{\cdot}5}{\text{observed value}} = a.$$

a is termed the **association factor** and gives the degree of association of the substance in question.

Thus, taking the case of water as a typical example, M, corresponding to H_2O, is 18. Whence

$$\frac{Ml_m}{T_m} = \frac{18 \times 79{\cdot}7}{273} = 5{\cdot}3.$$

Dividing this into 13·5 we find a is 2·55; that is, on the average, 2·55 simple molecules have united to form one large or associated molecule, so that the mean or average molecular weight of the water is not 18 but 18 × 2·55 or 46 at the melting point. This agrees, qualitatively at any rate, with the conclusion arrived at from many other independent sources (see pp. 135, 227) that water at its melting point consists of a mixture of trihydrol, $(H_2O)_3$, and dihydrol, $(H_2O)_2$, molecules.

Supercooling.—Although on steadily raising the temperature of a crystalline substance, such as ice or sodium sulphate decahydrate, melting ultimately takes place at a definite fixed and easily reproducible temperature, it is not equally true to say that on cooling the liquids

Latent Heats of Fusion.

Substance.	Formula.	Molecular Weight, M.	T_m.	l_m.	$\frac{Ml_m}{T_m}$.	Association Factor, a.
p-Dibromobenzene	$C_6H_4Br_2$	236	360	20·6	13·5	. .
p-Dichlorobenzene	$C_6H_4Cl_2$	147	326	29·9	13·5	. .
Aniline	$C_6H_5NH_2$	93	267	39·9	13·9	. .
p-Xylene	$C_6H_4(CH_3)_2$	106	288	38·8	14·3	. .
Naphthalene	$C_{10}H_8$	128	353	34·7	12·6	. .
Anthracene	$C_6H_4(CH)_2C_6H_4$	178	489	38·7	14·1	. .
Diphenylmethane	$CH_2(C_6H_5)_2$	168	300	25·2	14·1	. .
Benzophenone	$C_6H_5COC_6H_5$	182	321	21·7	12·3	. .
Triphenylmethane	$CH(C_6H_5)_3$	244	365	17·8	11·9	. .
p-Toluidine	$C_6H_4NH_2CH_3$	107	317	39·0	13·2	. .
Water	H_2O	18	273	79·7	5·3	2·55
Carbon disulphide	CS_2	76	163	8·7	4·1	3·30
Ethyl alcohol	C_2H_5OH	46	161	14·1	4·0	3·38
Formic acid	$HCOOH$	46	281	66·0	10·8	1·28
Acetic acid	CH_3COOH	60	290	43·7	9·0	1·50
Acetone	CH_3COCH_3	58	178	22·4	7·3	1·85
Chloroform	$CHCl_3$	119·5	203	17·4	10·2	1·32
Benzene	C_6H_6	78	278	29·9	8·4	1·60

they will necessarily freeze or solidify at the same definite temperatures. If, for example, water is cooled, separation of ice may not occur immediately a temperature of 0° C. is reached, and under suitable conditions it is possible to reduce the temperature many degrees below 0° without freezing taking place. This was first observed by Fahrenheit who, in 1724, succeeded in cooling water in cleaned tubes down to 15° F. or $-9·4°$ C. without solidification occurring. A convenient method of effecting this consists in preparing a mixture of chloroform and olive oil in such proportions that the product has the same density as water. Drops of water suspended in this mixture may be cooled down to very low temperatures (*c.* $-20°$ C.) without freezing. Such water is termed **supercooled** or **superfused,** and is stable only so long as the solid phase is absent. It is therefore said to be **metastable.** The water will usually solidify immediately upon exposure to air or dust, or on the introduction of some foreign material. Even the act of scratching the inside wall of the containing vessel will suffice to induce crystallisation. If the supercooling is carried beyond a certain amount, the water becomes **unstable,** and solidification takes place spontaneously without the introduction of the solid phase or foreign material. In either case the temperature rises to 0° C. and remains there until solidification is complete.

We have already seen (p. 69) that the vapour pressure of supercooled water is always greater than that of ice at the same temperature, and this explains why supercooled water is stable only so long as the solid phase is absent. If a piece of ice is introduced into the same closed vessel, the vapour is supersaturated with regard to the ice, and a portion condenses. But this leads to a vapour unsaturated with respect to the supercooled liquid, which, in consequence, vaporises to a corresponding amount. The condensation on the ice and vaporisation of the liquid continue until the whole of the latter has disappeared, leaving only ice and vapour.

Supercooling is a very general phenomenon, but some substances show it to a more marked degree than others. Hydrogen peroxide is a case in point. The pure oxide, 99·93 per cent. pure anhydrous liquid, readily assumes a supercooled condition (Maass and Hatcher, 1920), and may refuse to crystallise even at temperatures as low as −30° C., although its melting point is −1·70° C. If, however, a small quantity be solidified by strongly cooling, *e.g.* with a mixture of solid carbon dioxide and ether, the product can be used as a nucleus to induce crystallisation at temperatures just below the melting point. The solid then separates in prismatic crystals, and fractional crystallisation may be applied as an effective method of final purification. In the absence of the solid phase liquid gallium possesses to an extraordinary degree the power of remaining in a superfused state.

In all cases the presence of the solid phase will prevent supercooling, just as the presence of the solid solute will prevent supersaturation in solutions. The question as to the minimum quantity of solid phase that must be introduced into a system to destroy supercooling was studied by Ostwald (1897), who found that 10^{-7} gramme of "salol" or phenyl salicylate, $HOC_6H_4COOC_6H_5$, was sufficient to initiate crystallisation in the supercooled liquid. A nucleus of an isomorphous substance, shock, and mechanical agitation, are also able individually to initiate crystallisation.

In most supercooled liquids nuclei appear on standing, and once these have formed, crystallisation tends to spread. There is thus more chance of keeping a liquid in the superfused condition if its bulk is small, as the chance of nucleus-formation will increase with the volume of liquid under consideration. The number of nuclei forming in a given time increases with the degree of superfusion, but as the temperature drops still further crystallisation is hindered by the increase in viscosity. Sudden, intense cooling gives what is termed a "gel" or glassy mass of great viscosity. There is then little tendency for nuclei to be formed, and the mass, though really only metastable, may exhibit great stability, even in contact with the crystalline solid. Ordinary glass is a good example of this. When heated it sometimes tends to devitrify or crystallise, as every glass-blower knows, and it is then useless for ordinary purposes.

Velocity of Crystallisation.—The velocity of crystallisation of supercooled liquids is usually determined by enclosing them in narrow glass tubes and noting the time required for crystallisation to proceed over a given length. The following results were obtained with supercooled water in a tube 1 metre in length and 0·7 cm. in diameter (Walton and Judd, 1914):

Temperature, °C. .	−2·00	−4·67	−6·18	−7·50	−9·07
Velocity, cm./min. .	31·6	71·4	114·7	308	684

The maximum velocity of crystallisation evidently lies below −9·07° C., but, owing to spontaneous solidification of the water, it was not found possible to make determinations at lower temperatures.

It is interesting to note that whereas ice produced with a cooling temperature within one or two degrees of the melting point is usually clear, the product obtained with stronger cooling is milky in appearance on account of the inclusion of minute bubbles of air which was previously in solution.

In general it is found that the velocity of crystallisation is constant for any one substance for any given degree of supercooling. It increases to a maximum usually some 20 to 30 degrees below the normal melting point, and may remain fairly constant at this maximum over a considerable range of temperature. Eventually the velocity of crystallisation falls off as the glassy, highly stable condition referred to above is reached.

Foreign bodies are found to reduce the velocity of crystallisation at temperatures above that of the maximum velocity, and in some cases the reduction in velocity is the same for equimolecular quantities of different foreign bodies. This suggests a method of determining molecular weights, and is referred to at a later stage (Vol. II). The rule, however, is not universal and cannot be widely applied.

Capillary Action.—When contained in capillary tubes, water offers very great resistance to freezing, unless it is in contact with ice. Thus Sorby, in 1859, found that no congelation took place, even upon shaking, when water was cooled to −15° C. in glass tubes of diameter 0·008 to 0·013 cm. The temperature could even be reduced to −16° C. if the tubes were kept very quiet, although at −17° C. the water froze immediately. In a tube of diameter approximately 0·025 cm. the water froze at −13° C. but not at −11° C. In contact with ice, however, water freezes readily in capillary tubes, and ice thaws as usual at 0° C. when in tubes in which water will not congeal in the absence of the solid phase above −16° C.

Filter paper moistened with distilled water freezes at −0·1° C., whilst a clay sphere, under similar conditions, has been found to freeze at −0·7° C. These observations refer to the actual freezing points under the conditions named, and are quite apart from supercooling effects, which, as already shown, may be extended to much lower temperatures.

The presence of finely divided particles of solid materials, such as ferric hydroxide, alumina, etc., causes an appreciable depression of the freezing point. This is, of course, quite distinct from the depression of the freezing point caused by soluble substances, which is studied in Chapter XIX.

The low temperature required to freeze capillary water has suggested a method of distinguishing between combined and capillary water in hydrated precipitates, such as ferric hydroxide (Foote and Saxton, 1916). The hydroxide is cooled to a low temperature and the quantity of water physically attached to it is calculated by observing dilatometrically the change in volume undergone in consequence of the expansion of this water in forming ice. Subtraction of this from the total amount of water, as determined by heating to redness and weighing the anhydrous ferric oxide, gives a maximum value for the amount of water chemically combined. In this way it is found that ferric hydroxide contains

(*a*) Water, very loosely attached, which freezes out at about −5° C.

(*b*) Capillary water, intimately associated with the precipitate, requiring a temperature of the order of −30° C. to effect its complete removal by freezing.

(c) Water which is presumed to be chemically combined, and which does not in amount exceed that required for the formula $Fe_2O_3.4{\cdot}25H_2O$. This is obviously the *maximum* possible quantity of combined water, for there is no guarantee that *all* the capillary water has been accounted for.

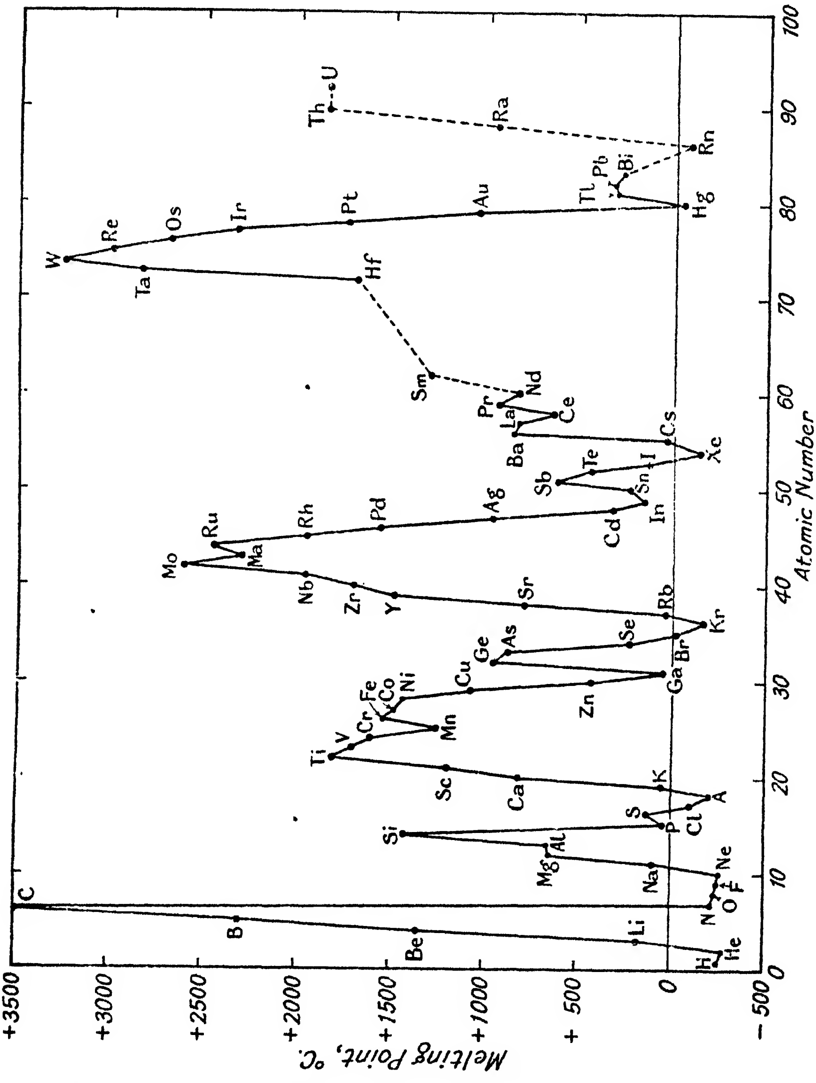


Fig. 46.—Melting Point/Atomic Number.

Melting Points of the Elements.—The melting points of the elements, generally under atmospheric pressure, are given in the table on p. 92. In fig. 46 the melting points are plotted against the atomic numbers, and an interesting periodicity is readily discernible. The inert gases of Group 0 of the Periodic Table occupy the troughs of the curves. The ascending slopes contain the alkali and alkaline earth metals; the descending slopes contain the non-metals of the Fifth, Sixth and Seventh Groups and the metals of Group VIII; whilst Groups IV and VI occupy the summits.

There are also interesting connections observable between the melting points of the elements and their atomic volumes (p. 157). Reference to fig. 52 shows that the easily fusible and volatile elements occupy the crests or upper portions of the slopes of the curves, whilst the more difficultly fusible elements occupy the troughs and lower portions of the slopes.

Considering now the elements in vertical groups of the Periodic Table, it will be observed that the melting points, like the boiling points (p. 91), of the alkali metals and of the beryllium subdivision of Group II fall with rise of atomic number. This is clearly shown in fig. 47. The reverse is the case for the non-metals in Groups V, VI, VII and 0. In this connection Group V is of special interest; as we pass from arsenic to antimony and bismuth the metallic properties of the elements become increasingly pronounced, and the slope of the atomic number-melting point curve is reversed.

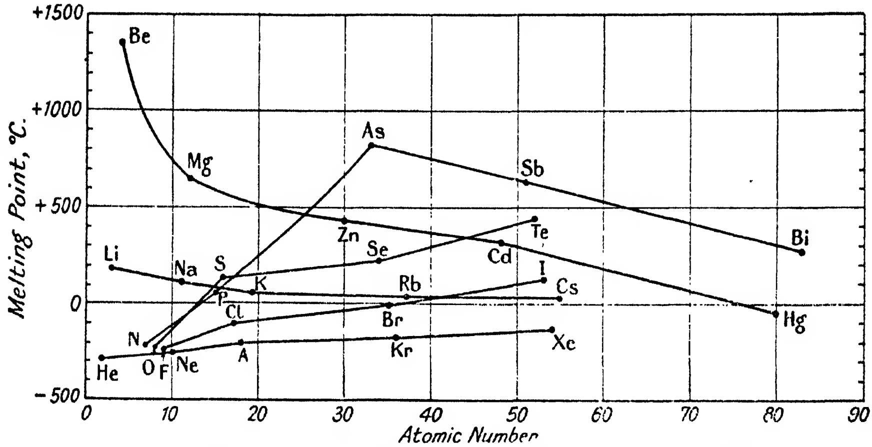


FIG. 47.—Melting Point/Atomic Number for Vertical Groups of Periodic Table.

Melting Points of Homologous Series.—In general the melting points of successive members in a homologous series tend to rise with the molecular weight. The rise for each added CH_2 group is not usually regular, and the effect falls off as the higher members are reached.

Homologous series may be divided roughly into two groups, namely, those in which the properties vary continuously with successive increases in the methylene groups, and those in which the properties alternate according as an odd or even number of carbon atoms is present in the molecule. Examples of the continuous series are afforded by alcohols, ketones and the amides of the fatty acids. In the following table (p. 150) are given data for a few alcohols.

Examples of the alternating series are afforded by the normal paraffins, monobasic and dibasic fatty acids, diamines and glycols.

Alcohol.	Formula.	Melting Point, °C.	Rise per CH_2.
Methyl	CH_3OH	− 97·8	
Ethyl	CH_3CH_2OH	−117·3	−19·5
n-Propyl	$CH_3CH_2CH_2OH$	−127·0	− 9·7
n-Butyl	$CH_3(CH_2)_2CH_2OH$	− 89·8	+37·2
n-Amyl	$CH_3(CH_2)_3CH_2OH$	− 78·5	+11·3
n-Hexyl	$CH_3(CH_2)_4CH_2OH$	− 51·6	+26·9
n-Heptyl	$CH_3(CH_2)_5CH_2OH$	− 34·6	+17·0
n-Octyl	$CH_3(CH_2)_6CH_2OH$	− 16·3	+18·3
n-Nonyl	$CH_3(CH_2)_7CH_2OH$	− 5·0	+11·3
n-Decyl	$CH_3(CH_2)_8CH_2OH$	+ 7·0	+12·0

The effect is believed to be due mainly to differences in the crystal structure of the solid bodies. The fatty acids have been made the subject of much study in this connection (Garner and coworkers, 1924 to 1931), and it has been observed that the " odd " series of acids, that is those containing an odd number of carbon atoms, can exist in two enantiotropic (p. 178) forms or isomerides. In the following table are given the melting points, or, more correctly, the " setting points," of the liquid acids, together with their molar heats of crystallisation, that is, the heat evolved when a gramme-molecule of the liquid at its melting point sets to a solid at the same temperature. The molar heat of crystallisation is thus numerically equal to the molar latent heat.

Acid.	Formula.	No. of Carbon Atoms.	Setting Points, °C.	Molar Heat of Crystallisation, Gramme-calories.
Formic	$HCOOH$	1	+ 8·5	2,520
Propionic	CH_3CH_2COOH	3	−22·0	2,260
Valeric	$CH_3(CH_2)_3COOH$	5	−20·0	. .
Heptoic	$CH_3(CH_2)_5COOH$	7	−11·2	3,580
Nonoic	$CH_3(CH_2)_7COOH$	9	+12·5	4,850
Undecoic	$CH_3(CH_2)_9COOH$	11	28·3	5,990
Tridecoic	$CH_3(CH_2)_{11}COOH$	13	41·1	8,020
Acetic	CH_3COOH	2	+16·5	2,770
Butyric	$CH_3(CH_2)_2COOH$	4	− 3·0	2,640
Caproic	$CH_3(CH_2)_4COOH$	6	− 1·5	3,600
Octoic	$CH_3(CH_2)_6COOH$	8	+16·5	5,100
Decoic	$CH_3(CH_2)_8COOH$	10	31·2	6,690
Lauric	$CH_3(CH_2)_{10}COOH$	12	43·8	8,750
Myristic	$CH_3(CH_2)_{12}COOH$	14	53·7	10,740

When these data are plotted in the manner shown in fig. 48, the alternating character of both the setting points and the molar heats of crystallisation, Q, become apparent, and there is evidently a close connection between these two properties. The ratio Q/T, where T is the setting temperature on the absolute scale, gives a continuous curve.

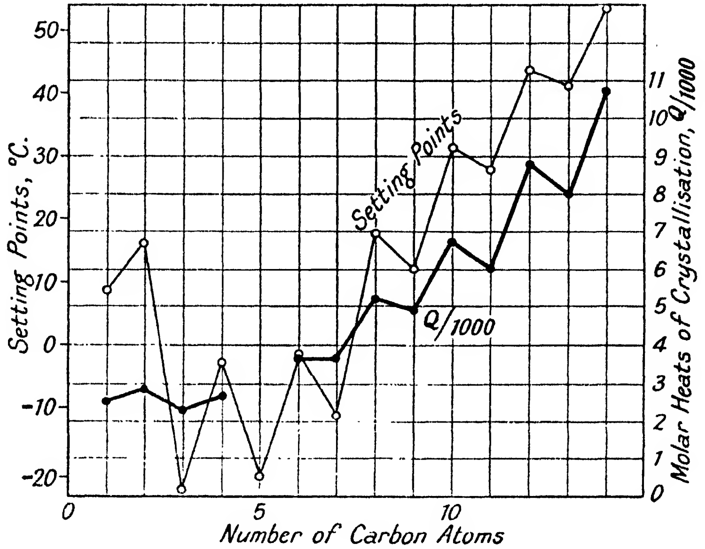


FIG. 48.—Showing Alternating Character of Setting Points and Molar Heats of Crystallisation of Fatty Acids (Garner).

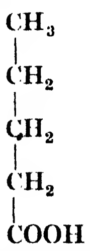
It is noteworthy that both Q and T in each series yield a minimum value, with 3 and 4 carbon atoms respectively.

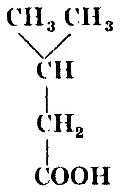
Melting Points of Isomerides.—In so far as **structural** isomerides are concerned, it usually happens that the highest melting point is possessed by the isomeride which is most symmetrical in structure. Thus:

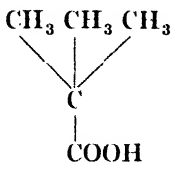
$C_2H_5.CO.C_2H_5$
Diethyl ketone,
M.pt. −42·0° C.

$CH_3.CO.C_3H_7$
Methylpropyl ketone,
M.pt. −77·8° C.

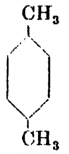
Branching of chains tends to raise the melting point. Thus:


n-Valeric acid,
M.pt. −59° C.

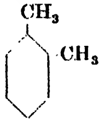

*iso*Valeric acid,
M.pt. −37·6° C.


Trimethyl
acetic acid,
M.pt. +35·5° C.

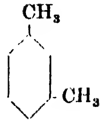
Amongst aromatic substances, *para* di-substituted derivatives usually have higher melting points than the *ortho-* and *meta*-derivatives. A good example is afforded by the xylenes:



p-Xylene,
M.pt. + 13·2° C.

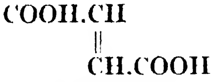


o-Xylene,
M.pt. – 27·1° C.



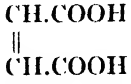
m-Xylene,
M.pt. – 53·6° C.

Amongst the **ethylenic** isomerides, those possessing the fumaroid structure are the more symmetrical and have the higher melting points. Thus :



$$\begin{array}{l} COOH.CH \\ \quad\| \\ \quad CH.COOH \end{array}$$

Fumaric acid,
M.pt. 287° C.



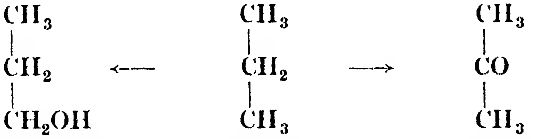
$$\begin{array}{l} CH.COOH \\ \| \\ CH.COOH \end{array}$$

Maleic acid,
M.pt. 130·5° C.

For **optical isomerides** no simple rule appears to apply.

Effect of Replacements.—The replacement of one or more atoms of hydrogen in an organic compound by oxygen invariably causes a rise in the melting point, and addition of oxygen has in general the same effect. Thus :

$$\underset{\substack{\text{Methane,} \\ \text{M.pt.} - 184^\circ\text{ C.}}}{CH_4} \longrightarrow \underset{\substack{\text{Methyl alcohol,} \\ \text{M.pt.} - 97{\cdot}8^\circ\text{ C.}}}{CH_3OH} \longrightarrow \underset{\substack{\text{Formic acid,} \\ \text{M.pt. } 8{\cdot}4^\circ\text{ C.}}}{HCOOH}$$



$$\begin{array}{ccccc} CH_3 & & CH_3 & & CH_3 \\ | & & | & & | \\ CH_2 & \longleftarrow & CH_2 & \longrightarrow & CO \\ | & & | & & | \\ CH_2OH & & CH_3 & & CH_3 \end{array}$$

Propyl alcohol, M.pt. – 127° C. Propane, M.pt. – 189·9° C. Acetone, M.pt. – 94·3° C.

When successive elements in a vertical group in the Periodic Table replace one another in organic compounds there is usually a steady rise or fall in the melting point. This is illustrated by the following data :

	M.pt. °C.		M.pt. °C.		M.pt. °C.
$(C_6H_5)_4C$	285	$(C_6H_5)_3N$	126·5	CF_4	– 80
Si	233	P	79	CCl_4	– 23
Ge	225	As	60	$CBr_4(\alpha)$	+ 48·4
Sn	223	Sb	48	CI_4	Solid, decomposing on melting.
Pb	227·7	Bi	78		

It will be observed that both the lead and bismuth derivatives break the regularity in their respective series.

It does not seem possible, however, to find any general quantitative relationships of universal applicability between the melting points, composition and constitution of substances. At the moment, therefore, we must remain content with the foregoing qualitative observations.

CHAPTER X.

VOLUME RELATIONSHIPS IN THE SOLID AND LIQUID STATES.

Density has already been defined (p. 11) as the **mass of unit volume.** In the c.g.s. system it is the mass in grammes of 1 c.c. of a substance. The inverse of this, namely the volume occupied by one gramme of a substance, is termed the **specific volume.** The product of the atomic or molecular weight of a substance and the specific volume is termed the **atomic** or **molecular volume** respectively.

The term **specific gravity** or **relative density** expresses a ratio and represents the number of times heavier a substance is than an equal volume of water at the same or at another specified temperature. Numerically the data for density and specific gravity are closely similar, but for accurate work it is necessary to distinguish between them. It is most important, therefore, to know as accurately as possible the density and specific volume of water at various temperatures. A few data are given in the following table:

Density and Specific Volume of Water between −10° and 100° C.

Temperature, °C.	Density, Grammes per c.c.	Specific Volume, c.c.	Temperature, °C.	Density, Grammes per c.c.	Specific Volume, c.c.
−10	0·99815	1·00186	15	0·99913	1·00087
− 5	0·99930	1·00070	20	0·99823	1·00177
			30	0·99567	1·00435
0	0·99987	1·00013	40	0·99224	1·00782
2	0·99997	1·00003	50	0·98807	1·01207
4	**1·00000**	**1·00000**	60	0·98324	1·01705
6	0·99997	1·00003	70	0·97781	1·02270
8	0·99988	1·00012	80	0·97183	1·02899
10	0·99973	1·00027	100	0·95838	1·04343

According to these data unit volume of water at 0° C. becomes 1·0433 volumes at 100° C.

Mention has already been made of the fact that ice at 0° C. contracts on melting to water at the same temperature, and a steady but slight contraction continues to take place as the temperature is raised to 3·98° C. This is the point of maximum density of water under atmospheric pressure, and further rise in temperature results in expansion.

On cooling below 0° C. the expansion of supercooled liquid water continues with fall of temperature, but, once ice has formed, further cooling of the ice is accompanied by contraction. The explanation for these anomalies has already been given.

Increase of pressure reduces the temperature of maximum density, as we should expect from the theorem of Le Chatelier (p. 23), the two factors being connected by the expression

$$t_p = 3{\cdot}98 - 0{\cdot}0225(p - 1)$$

where t_p is the centigrade temperature of maximum density under a pressure of p atmospheres.

Dissolved salts depress the temperature of maximum density of water, the depression being directly proportional to the concentration of the solute. This is known as the **Law of Depretz, 1839.** There is, however, no simple connection between the quantitative depression of the maximum density and freezing temperatures of water on addition of soluble substances (p. 404), for whilst the depression of the freezing point depends only on the concentration of the solute, the depression of the point of maximum density depends also upon the nature of the solute. The effect produced by a salt is the sum of the depressions caused by the acid and metallic radicals respectively. Feebly ionised and non-ionisable substances, such as the alcohols, do not in general obey Depretz' Law. Indeed, both ethyl alcohol and *n*-propyl alcohol actually elevate the temperature of maximum density to 4·25° and 4·15° C. respectively.

Determination of Densities and Specific Volumes.—For liquids of which sufficient supplies are available it is frequently convenient to apply some method depending upon the application of Archimedes' Principle. A body of known volume is suspended in the liquid and its "weight" determined. The difference between this and its "weight" in air or, preferably, *in vacuo*, gives the mass of the same volume of liquid, from which the liquid density and specific volume can readily be calculated.

The **Westphal Balance** is a very suitable instrument to employ, and if the float is made of silica, which has a negligibly small coefficient of expansion, the density of the liquid may be determined directly at various temperatures without the necessity of correcting for varying volume of the float.

More usually, where very accurate results are required, liquid densities are determined by weighing some form of density bottle or pyknometer (Greek *puknos*, dense) filled with the liquid at a given temperature. The volume of the pyknometer itself is determined in the usual manner by weighing in air both empty and filled with water or mercury, from the known densities of which liquids the volume can readily be calculated. If the pyknometer is made of silica only a very minute change will occur in its capacity with rise of temperature, and for most purposes this may be neglected.

The foregoing method, of course, gives the density in air; if the absolute density *in vacuo* is required, it can be calculated from the formula:

$$D_4^t = \frac{m}{V}(1 - 0{\cdot}0012/d) + 0{\cdot}0012$$

where m is the apparent mass of the liquid in air, V is the volume of the pyknometer, d the density of water, all at $t°$ C., and 0·0012 the mean density of the air. This formula is readily derived from first principles, and the student is recommended to check it for himself.

Glass floats are sometimes used for determining the densities of liquids which cannot for some reason or other be exposed to the air. Silicon tetrachloride is a case in point, and Robinson and Smith in 1926 used this method in order to determine the comparative densities of various samples of silicon tetrachloride with a very high degree of accuracy. In brief, the method involves the preparation of two sets of floats of the shape shown in fig. 49, with densities slightly above and slightly below the density of the liquid under examination at the proposed temperature of measurement. The densities of the floats, ten in all, were determined by ascertaining with great care the flotation temperature of each float in bromobenzene, the density of which was ascertained with great exactness pyknometrically over the temperature range of about 25° to 33° C. The procedure consisted in introducing the floats into a cylindrical vessel containing the bromobenzene, and varying the temperature of the latter in order to make each float rise or fall. The mean of the last closely-agreeing pair of readings was taken as the flotation temperature of that float. Knowing the densities of the floats at these temperatures, their densities at other temperatures could readily be calculated when the coefficient of cubical expansion of the glass was once known. The experiments could now be repeated, using silicon tetrachloride as the flotation liquid, the flotation temperatures being ascertained in a similar manner, and hence the densities of the liquid at the corresponding temperatures.

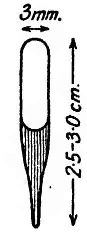


FIG. 49.—Float for Determining Densities of Liquids.

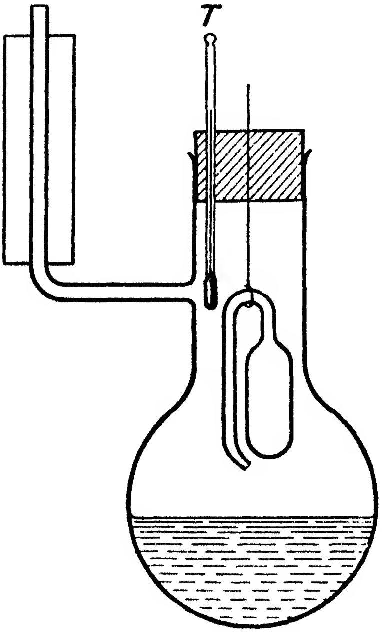


FIG. 50.—Pyknometer Method for Density at Boiling Point.

The density at the boiling point may be determined by suspending a pyknometer (fig. 50) filled with the liquid in a flask containing a further supply of the liquid. The latter is kept on the boil until the pyknometer and its contents have reached the same temperature. When this is the case no more liquid is expelled from the tip of the pyknometer. The pyknometer is then removed, quickly cooled so that the liquid in the capillary is drawn into the bulb, and weighed.

The specific volumes of compact solids may be determined by weighing in air and again when suspended in some suitable liquid of known density, and applying Archimedes' Principle.

Small pieces of solid may be examined by flotation methods. These are particularly useful when the solid is too hygroscopic to bear exposure to the atmosphere. This method was used by Briscoe, Robinson and Stephenson (1926) in determining with great exactness the densities of various specimens of boric oxide. Beads of the oxide were sealed in tubes containing dry, inert organic liquids of suitable density, and their flotation temperatures were ascertained. For powders pyknometric methods are largely used.

Density and Chemical Composition.—Determination of the density of a powder containing two different substances sometimes affords a convenient and rapid method of estimating the relative proportions of the ingredients. A mixture of zirconia, ZrO_2, and hafnia, HfO_2, is very difficult to analyse chemically, as the two oxides very closely resemble each other, as do also corresponding salts of zirconium and hafnium. Fortunately, however, the densities of the oxides differ appreciably, that of zirconia at 20° C. being 5·73, that of hafnia 9·67. If *d* is the density of a mixture of the two, the percentage, *x*, of hafnia present is given by

$$x = \frac{d - 5{\cdot}73}{0{\cdot}0394}.$$

When separating hafnium from zirconium, therefore, by fractional crystallisation or precipitation by any of the recognised methods, the process can readily be controlled by series of density measurements (Hevesy and Berglund, 1924).

Influence of Temperature.—Unless a change of state or some polymorphic transformation occurs, a rise in temperature is invariably accompanied by a fall in density, and on plotting the density against the temperature a continuous curve is obtained. If a break occurs, and this frequently happens with solids, some allotropic or polymorphic change is to be anticipated. Usually in the case of metals the change in density is practically a rectilinear function of the temperature over a considerable range, and it is frequently determined indirectly by noting the coefficient of linear expansion. A suitable apparatus for this purpose is shown in fig. 51. The metal, in the form of a bar or rod, M, some 50 cm. in length, rests on a quartz block A and is kept vertical by the washer W. On the upper end of M rests a fused silica rod B, which slides vertically through the glass tube C, its upper end supporting the gauge G. Fused silica is chosen for A and B as its coefficient of expansion with rise of temperature is negligibly small (see p. 157). Steam or other vapour is passed through the outer jacket, and when a constant temperature has been attained

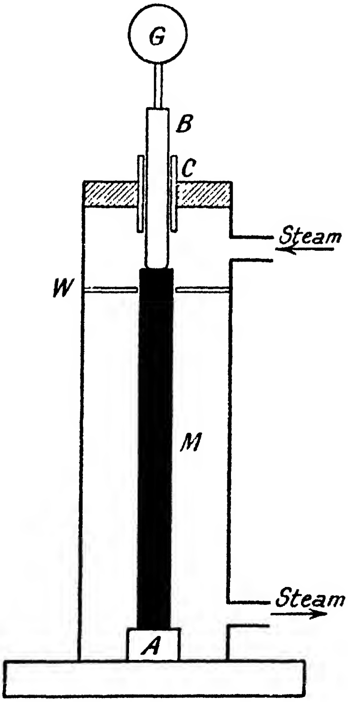


FIG. 51.—Apparatus for Linear Coefficient of Expansion.

the reading on the gauge is taken. If, for example, the initial and final temperatures were 0° and 100° C., the initial length L and the final length $L+l$ cm., the **coefficient,** α, **of linear expansion** over the given range of temperature is given by

$$\alpha = \frac{l}{100L}.$$

The change in volume undergone by unit volume of the metal when its temperature is raised by one degree is clearly

$$(1+\alpha)^3 - 1.$$

Neglecting squares and powers of α, since α is very small, this is equal to 3α, which is termed the **coefficient of cubical expansion.**

The coefficients of linear expansion of a few typical substances are as follows :

	α.
Aluminium	0·0000255
Silver	0·0000188
Copper	0·0000169
Gold	0·0000139
Platinum	0·0000089
Flint Glass	0·0000078
Silica (Fused)	0·0000005

The extremely small value of α for fused silica has already been mentioned. Since glass and platinum expand by closely similar amounts, platinum wire is largely used in making electrical connections through glass.

The change in volume of small pieces of solid with rise of temperature is frequently determined dilatometrically. This is particularly the case when transition temperatures are being sought (see p. 185).

Usually in the case of liquids the curve connecting density and rise of temperature is continuous. The curve for nitrobenzene, however, sometimes shows a distinct break at 9·5° C., indicating the existence of two forms of this body, which are mutually transformable at this temperature (p. 187).

Atomic Volumes.—It was first pointed out by Lothar Meyer, *circa* 1864, that the atomic volumes of the elements are a periodic function of the atomic weights. By atomic volumes are here understood the volumes of the gramme-atoms of the elements in the solid state. This relationship is clearly shown in fig. 52, in which the atomic volumes are expressed as ordinates and the atomic weights as abscissæ. The atomic volumes in the liquid state have been used in the case of elements, such as hydrogen and helium, that are gaseous at ordinary temperatures. The properties of the elements appear to be determined by the positions on these curves. With the exception of lithium, the alkali metals occupy the summits, and the heavy metals the troughs. Lithium and the alkaline earth metals lie on the descending arms, and the non-metals and metalloids on the ascending portions of the curves.

As a general rule, in any given vertical group in the Periodic Table, the atomic volume rises with the atomic weight. There are, however, a few exceptions, the most notable being helium and neon, and zirconium and hafnium.

Although of considerable interest, this systematic arrangement of

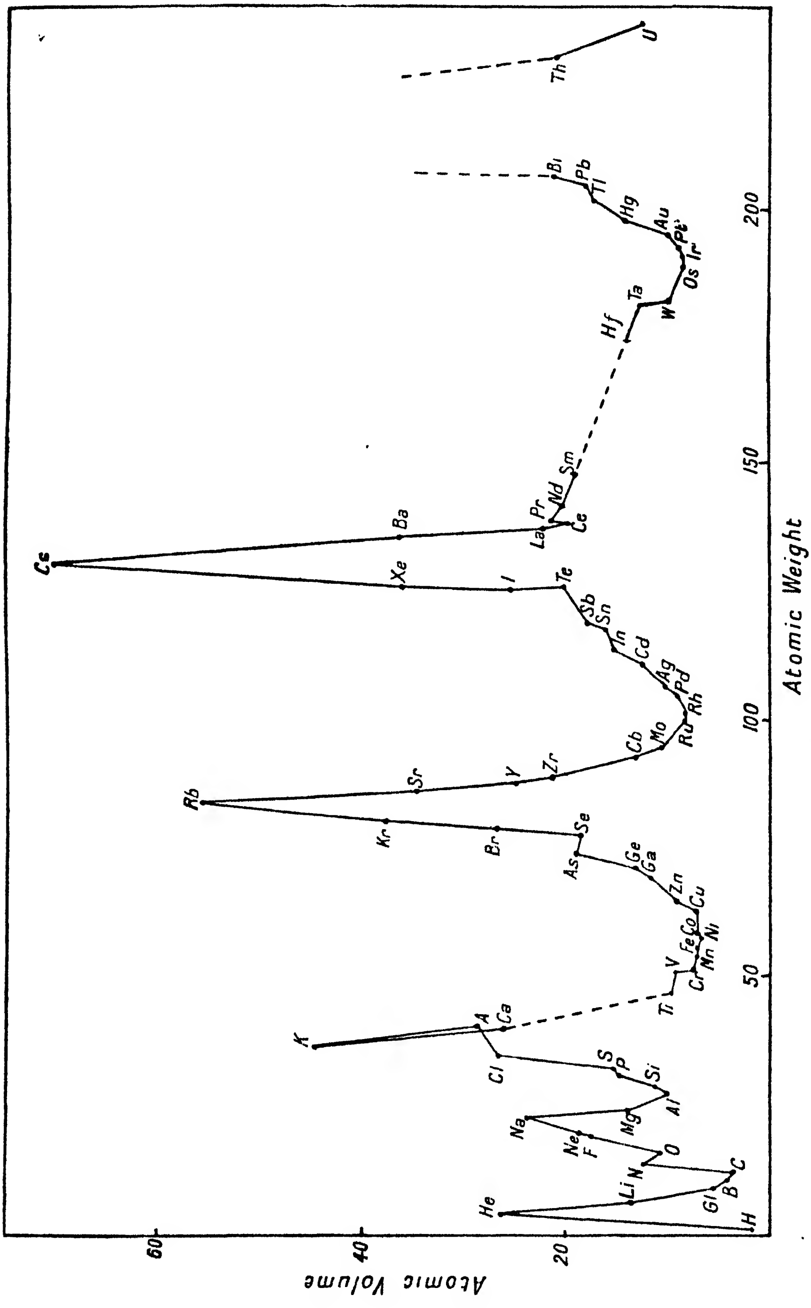


FIG. 52.—Lothar Meyer's Atomic Volume Curve.

the elements is inferior to what is known as the Periodic Classification, which is discussed later (p. 330). It does not indicate clearly when each curve is complete, consequently it has afforded but little help either in the search for fresh elements or in the attempt to correct atomic weight values that were open to doubt.

Molecular Volumes of Solids.—The enunciation of Gay-Lussac's Law of Combining Volumes of Gases in 1808 (p. 30) stimulated chemists to search for similar relationships amongst solid bodies. The results, however, have on the whole been disappointing, owing to their lack of general applicability.

In certain cases the molecular volume is found to be additive. Thus, for example, on comparing the molecular volumes of the halides of sodium and potassium, the differences in volume caused by substituting potassium for sodium are the same in all three cases. Similar remarks apply to the halogens. This is well shown in the following table:

Salt.	Molecular Volume, c.c.	Difference.	Salt.	Molecular Volume, c.c.	Difference.
NaCl	27·1	10·4	NaCl	27·1	6·7
KCl	37·5		NaBr	33·8	
NaBr	33·8	10·5	KCl	37·5	6·8
KBr	44·3		KBr	44·3	
NaI	43·5	10·5	NaCl	27·1	16·4
KI	54·0		NaI	43·5	
			KCl	37·5	16·5
			KI	54·0	

It has also been observed that the densities of many solid substances are 3·5 times their critical densities.

One further item of interest may be mentioned. **Water of hydration** may either be attached to the cationic portion of a salt or to the anion. Thus, for example, in zinc sulphate the six relatively loosely attached water molecules are cationic; the last molecule of water is more firmly attached and is anionic. The molecular volume of cationic water is 14·6 c.c., which is the same as that calculated for ice at the absolute zero of temperature. On the other hand, the molecular volume of anionic water is 10·0 c.c., and is the same as that observed when water unites with acid anhydrides to form acids or with basic oxides to form hydroxides.

Molecular Volumes of Liquids.—In 1855 Kopp turned his attention to organic liquids. As their coefficients of expansion with rise of temperature are, in general, much greater than those of solids, it is necessary to pay more attention to the temperature of measurement. Any arbitrary temperature such as 0° C. or 100° C. presents difficulties, for some "liquids" might be solid or gaseous at these respective temperatures. Kopp therefore employed the boiling points of the substances under atmospheric pressure. Under these conditions

the molecular volume of a liquid is approximately equal to the sum of the volumes of its constituent atoms.

This is known as **Kopp's Law.** It is not absolutely true; deviations amounting to several per cent. are known. Nevertheless the law presents many features of interest and in more recent years has been made the subject of exhaustive study by Le Bas and Traube.

In the following table are given the mean atomic or group volumes of several elements and groups as calculated by Kopp from the molecular volumes at the boiling point—the **boiling volumes**—of a large number of compounds:

Element or Group.	Calculated Volume, c.c.	Observed Volume of Free Liquid, c.c.
C	11·0	. .
O : (Keto). . .	12·2	14·1
·O·(Enol) . .	7·8	. .
H	5·5	. .
NO_2. . . .	31·5	32·0
Cl	22·7	22·7
Br	27·8	26·9
I	37·5	. .
S	22·6	. .
CN	28·9	28·9

It is interesting to note that the boiling volumes of such atoms or groups as can be determined experimentally in the free state agree very closely with those calculated from the molecular volumes of compounds containing these atoms or groups. It appears, therefore, that liquid elements and radicals possess the same volume whether free or chemically combined.

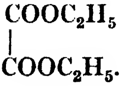
From the foregoing data it is easy to calculate the molecular volumes of many organic substances. Let us, for example, consider *acetone*, CH_3COCH_3.

3C give a volume of 11·0 × 3 = 33·0 c.c.
6H ,, ,, ,, 5·5 × 6 = 33·0 ,,
O : ,, ,, ,, 12·2 ,,

∴ Total volume = 78·2 c.c.

The observed boiling volume of acetone is 77·5 c.c. The agreement is thus distinctly good.

Now let us try *ethyl oxalate*,



$$\begin{array}{l}COOC_2H_5\\ \,|\\ COOC_2H_5.\end{array}$$

6C give a volume of 11·0 × 6 = 66·0 c.c.
2O : ,, ,, ,, 12·2 × 2 = 24·4 ,,
2 · O · ,, ,, ,, 7·8 × 2 = 15·6 ,,
10H ,, ,, ,, 5·5 × 10 = 55·0 ,,

∴ Total volume = 161·0 c.c.

The observed boiling volume of ethyl oxalate is 167 c.c. The agreement is not quite so close as before.

Kopp's Law is thus only approximately true, for the molecular volume is not only an **additive** property, but partly **constitutive** as well. Thus, for example, ring formation, such as the conversion of a paraffin to a cyclic hydrocarbon, leads to a contraction in the molecular volume. Furthermore, it is found that the volume of an atom varies with its degree of saturation ; an unsaturated carbon atom is found to have a larger volume than a saturated carbon atom.

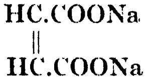
Isomerides.—If two or more isomerides possess a closely similar structure, their boiling volumes are practically identical. Thus

Methyl valerate, $C_4H_9COOCH_3$	149·2 c.c.
Ethyl butyrate, $C_3H_7COOC_2H_5$	149·3 ,,
Butyl acetate, $CH_3COOC_4H_9$	149·3 ,,

On the other hand, isomerides of widely different constitution have different boiling volumes. Thus

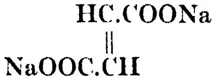
Aniline, $C_6H_5NH_2$	109·1 c.c.
Methyl pyridine, $C_5H_4(CH_3)N$	121·5 ,,

Even *geometrical isomerides* show decided differences in their boiling volumes. Thus



$$\begin{matrix} HC.COONa \\ \| \\ HC.COONa \end{matrix}$$

Sodium maleate,
Boiling volume 54·3 c.c.



$$\begin{matrix} HC.COONa \\ \| \\ NaOOC.CH \end{matrix}$$

Sodium fumarate,
Boiling volume 59·4 c.c.

Density at the Absolute Zero.—In 1894 van der Waals showed that

$$\sigma = \sigma_0(1 - \theta)^{6/5} \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where σ is the surface tension of a liquid at any absolute temperature T, θ is the corresponding temperature (p. 103) given by T/T_c, and σ_0 is a constant, presumably the surface tension at the absolute zero.

In 1923 Macleod showed that

$$\sigma = k(D - d)^4 \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where D and d are the densities of the liquid and saturated vapour respectively, k being a constant (p. 274).

By eliminating σ in equations (1) and (2) we obtain

$$D - d = D_0(1 - \theta)^{3/10} \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

D_0 is a constant, and represents the density of the supercooled liquid at the absolute zero, on the assumption that the equation is trustworthy down to such a low temperature (Sugden, 1927).

Between the freezing point and the critical point equation (3) has been found to give with great accuracy the relation between the density and temperature of unassociated liquids ; for associated liquids the equation holds over the lower part of the temperature range, and in some cases nearly to the critical point.

Dividing the molecular weight by D_0 gives the molecular volume V_0 at the absolute zero of temperature. This volume is termed for brevity the **zero volume.** As is evident from the data in the following table, the ratio V_0/V_c is practically constant, hydrogen alone giving an anomalous value. V_c is the **molecular critical volume.**

Zero and Critical Volumes.

(Sugden, 1927.)

Substance.	V_0 c.c.	V_c c.c.	V_0/V_c
Hydrogen	22·0	64·0	0·344
Ethyl ether	77·1	281·9	0·273
Carbon tetrachloride . .	77·4	276·1	0·280
Ethyl acetate	76·4	286·3	0·267
n-Pentane	83·9	310·3	0·270
Benzene	71·2	256·1	0·278

V_0 is thus a corresponding volume.

Sugden has found that the zero volumes of substances bear a simple relation to their chemical composition. For example, ordinary isomerides have the same zero volumes. This is illustrated by

	V_0.
Methyl formate, $HCOOCH_3$	46·7 c.c.
Acetic acid, CH_3COOH	46·7 ,,

The zero volumes of substances can be calculated with the aid of the atomic and structural constants in a similar manner to the boiling volumes investigated by Kopp. The following table gives a selection from the constants which have been evaluated :

Atomic and Structural Constants.

(Sugden, 1927.)

Atomic Constants.	c.c.	Structural Constants.	c.c.
H	6·7	Non-polar double bond .	8·0
O	5·0	Semipolar double bond .	0·0
C	1·1	Triple bond . . .	15·5
N	3·6	3-Membered ring . .	4·8
Cl	19·3	6-Membered ring . .	0·6
S	14·3		
O (in alcohols) . .	3·0		
N (in amines) . .	0·0		

The difference between non-polar and semipolar double bonds will be explained fully in a subsequent chapter (see Vol. II), as a knowledge of atomic structure is essential to its understanding. For present purposes

it is sufficient to state that double bond union between C-atoms and between C-atoms and other atoms is non-polar, as for example C=C, C=O. Semipolar double bonds occur in many double bond unions between sulphur and oxygen, phosphorus and oxygen, and frequently between nitrogen and oxygen.

Let us take a few examples by way of illustration :

Ethylene, C_2H_4.

2C give a zero volume of $1{\cdot}1 \times 2 = 2{\cdot}2$ c.c.
4H ,, ,, ,, $6{\cdot}7 \times 4 = 26{\cdot}8$,,
Non-polar double bond $= 8{\cdot}0$,,
$\therefore$ Total V_0 $= 37{\cdot}0$ c.c.

The observed value, that is the figure obtained from equation (3) by insertion of experimental values, is 37·4 c.c.

Thionyl chloride, $SOCl_2$.

Zero volume of S	14·3 c.c.
,, ,, O	5·0 ,,
,, ,, 2Cl	38·6 ,,
Semipolar bond	0·0 ,,
$\therefore$ Total V_0	$= 57{\cdot}9$ c.c.

Observed value, 58·0 c.c.

For associated liquid acids the calculated values of V_0 are frequently somewhat too high. This is particularly so with formic, monochloracetic and dichloracetic acids, whilst for acetic acid itself the difference is negligible. Association in alcohols and amines appears to produce the opposite effect, the calculated values being too low ; in these cases the calculated values approach more closely to the observed values if the zero volume of oxygen is taken as 3·0 and that of nitrogen as 0·0 respectively, although even then methyl and ethyl alcohols remain exceptional, as well as ammonia and several amines.

The examples given in the following table (p. 164) will serve to illustrate the foregoing.

Compressibility.—The volume of a liquid at a given temperature and under a pressure equal to that of its own vapour is termed its **orthobaric volume.** Below its ordinary boiling point small differences in pressure have a very small influence upon the volume of a liquid, but near its critical point a liquid becomes more highly compressible. For this reason, as we have already seen (p. 98), it is extremely difficult to determine critical volumes with great accuracy.

The **coefficient of compressibility**, β, is defined as *the change in unit volume produced by unit pressure change*, and may be represented mathematically by the expression

$$\beta = \frac{V_0 - V_p}{V_0 p}$$

where V_0 and V_p are the initial and final volumes under a change of pressure p. The pressures are usually expressed either in atmospheres or in megabars (p. 17).

Observed and Calculated Zero Volumes.

(Sugden, 1927.)

Substance.	Formula.	V_0 Obs.	V_0 Calc.	Difference, per cent.
Benzene	C_6H_6	71·2	71·4	+0·3
Toluene	$C_6H_5CH_3$	86·7	85·9	−0·9
Carbon tetrachloride	CCl_4	77·4	78·3	+1·2
Ethyl ether	$(C_2H_5)_2O$	77·1	76·4	−0·9
Acetone	$(CH_3)_2CO$	56·0	56·5	+0·9
Acetic acid	CH_3COOH	46·7	47·0	+0·7
Carbon disulphide	CS_2	48·2	45·7	−5·1
Formic acid	$HCOOH$	30·7	32·5	+5·8
Methyl alcohol	CH_3OH	32·3	30·9	−4·3
Ammonia	NH_3	19·1	20·1	+5·0

In the following table are given the compressibilities of a few substances. In general, solids are less compressible than liquids. Thus ice is less compressible than water at the same temperature. The compressibilities of the majority of substances at constant pressure rise with the temperature. Ice has an abnormally high temperature coefficient. Water, however, is exceptional, its compressibility falling with rise of temperature, a minimum being reached at 50° C. This is usually attributed to the diminishing number of bulky, compressible "ice" molecules (p. 135) as the temperature rises from 0° to 50° C. At this latter temperature their number is negligibly small, and from this point onwards water behaves as a normal liquid. This is shown in the accompanying table.

Substance.	Temp., °C.	β per Megabar.	Substance.	Temp., °C.	β per Megabar.
Ice	0	$3·3 \times 10^{-5}$	Benzene	18	$9·08 \times 10^{-5}$
	−15	1·8 ,,	Carbon disulphide.	15·6	8·59 ,,
Water	0	$5·01 \times 10^{-5}$	Mercury	20	$3·88 \times 10^{-6}$
	20	4·59 ,,	Lead	18	2·2 ,,
	50	4·40 ,,	Tin	18	1·7 ,,
	80	4·57 ,,	Zinc	18	1·5 ,,
Sea water	17·5	4·36 ,,	Silver	18	0·84 ,,

As is evident from the following data β usually falls as the pressure rises :

Pressure range (megabars) .	0–100	200–300	400–500
β for water at 20° C. . .	$4{\cdot}52 \times 10^{-5}$	$4{\cdot}18 \times 10^{-5}$	$3{\cdot}94 \times 10^{-5}$
β for mercury at 20° C. .	$3{\cdot}88 \times 10^{-6}$	$3{\cdot}79 \times 10^{-6}$	$3{\cdot}71 \times 10^{-6}$

Incidentally it will be noted that water is more than ten times as compressible as mercury.

As a rule solutions are less compressible than the pure solvents; thus sea water is appreciably less compressible than fresh water.

Although the compressibilities of natural waters are thus exceedingly small, their effect upon the distribution of land and water on the surface of the earth is important. It has been calculated that, in consequence of the compressibility of sea water, the mean sea level is 116 feet lower than it would be if water were absolutely incompressible, with the result that two million square miles of land are now uncovered which would otherwise be submerged.

Amongst such elements as have been tested, their compressibilities appear to show a *periodic relation* with the atomic weight.

CHAPTER XI.

THE CRYSTALLINE STATE.

SUBSTANCES that ordinarily are classed as solids may be divided into two groups, namely (i) those in which the physical properties are the same in all directions, and (ii) those in which certain properties, such as expansion with rise of temperature, thermal conduction and various optical properties, have different values in different directions. Substances belonging to the first group are in general said to be **amorphous** (Greek *a*, without; *morphe*, form), that is, without any definite geometrical form. Substances belonging to the second group are **anisotropic** (Greek *anisos*, not equal) and **crystalline** (Greek *krystallos*, ice).

Historical.—Quartz was well known to the ancients and was given the name *krystallos*, which became Anglicised to **crystal**, from its clear, ice-like appearance. Indeed, Albertus Magnus (1250) regarded rock crystal as a form of ice so hardened by Alpine frosts that it refused to melt. Even to-day clear specimens of quartz are frequently referred to as crystal or rock crystal. When other minerals came to be recognised as occurring in definite geometrical shapes, the term "crystal" was extended to include these, and ultimately to embrace all such substances as are termed "crystalline" to-day. The scientific study of crystals dates back merely to the seventeenth century, when Nicolaus Steno (1669) enunciated the law of the constancy of crystal angles. This was followed in 1780 by the invention of the contact goniometer (Greek *gonia*, angle) by Carangeot of Paris, which enabled mineralogists to verify Steno's law, and thus the way was prepared for the Abbé Réné Just Haüy in 1784 to show that all the faces of natural crystals may be derived from a few simple forms.

Characteristics of a Crystal.—When a body passes from the liquid or gaseous state, or from solution, to the solid state, it assumes, under favourable conditions, a definite geometrical shape, and is said to **crystallise.** We now know that the outward form of a crystal is determined by the internal arrangement of the molecules, so that the science of crystallography, which was at one time mainly of interest to mineralogists, has now become a study of great importance to chemists and physicists. This aspect of the subject is dealt with in Vol. II.

In view of what has just been said we may define a crystal as *a homogeneous chemical substance, bounded by surfaces that are usually planar and arranged upon a definite plan which is an expression of the internal arrangement of the molecules.* The surfaces referred to in this definition are called **faces**, and may be curved, as in the diamond. Faces that have the same properties are termed "like" or "similar" faces; those with different properties, "unlike" faces. When two adjacent faces intersect an **edge** is formed, but a **solid angle** results when three or more edges intersect. The angle between the normals to two intersecting faces is termed the **interfacial angle.**

In addition to a well-defined geometrical shape, a crystal often shows a **plane fracture.** When struck by a heavy blow it breaks along **cleavage planes,** which are parallel to important crystal faces. Mica affords an excellent illustration of this; it has one very pronounced cleavage plane, so that it readily splits into thin sheets or laminæ.

Crystals have a **definite melting point,** so definite that the temperatures at which melting takes place in various crystalline substances are used as fixed points in thermometry (pp. 134, 135).

Finally it is found that various directions in a crystalline substance are equivalent, that is, in those directions the physical properties are the same, and equivalent directions are found to be arranged in space in a symmetrical manner. The symmetry of these arrangements is closely connected with the symmetry of the geometrical shapes of the crystals, and accordingly the latter are only the outward expression of the internal structures of crystalline substances.

When a crystal is composed of similar faces, like the cube (fig. 53) or octahedron (fig. 54), it is termed a **simple form.** More usually, however, a crystal consists of two or more simple forms, and is known as a **combination of forms.** A well-known example of the latter is afforded by galena, which commonly occurs as combinations of the cube and octahedron (fig. 55).

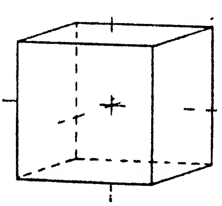


FIG. 53.—Cube.

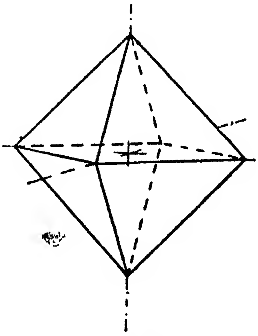


FIG. 54.—Octahedron.

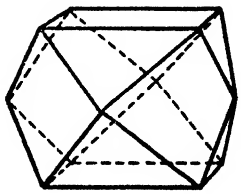


FIG. 55.—Crystal of Galena, showing Combination of Cube and Octahedron.

Characteristics of Amorphous Substances.—As their name implies amorphous substances have no definite crystalline form. They possess no cleavage planes, although they frequently exhibit conchoidal fractures (Latin *concha*, a mussel-shell). Examples are afforded by pitch, glass and flint. Again, amorphous substances have no sharp and decided melting point. They gradually soften and become pasty over a considerable range of temperature before being converted into typical liquids. Finally, the properties of amorphous substances are the same in all directions; the substances are therefore termed **isotropic** (Greek *isos*, equal; *tropos*, direction). This property, however, is not distinctive, for crystals belonging to the cubic system (p. 171) are also isotropic.

FUNDAMENTAL LAWS OF CRYSTALLOGRAPHY.

There are three fundamental laws of crystallography, the significance of which the student should attempt to grasp at the outset.

1. Steno's Law of the Constancy of Angles.—This refers to interfacial angles, and may be stated as follows :

Under the same physical conditions the angles between corresponding faces on various crystals of the same substance are constant.

Steno arrived at this law in 1669 as the result of a series of rough measurements on specimens of rock crystal from various localities. No accurate instruments for measuring angles were then available, and it was not until 1783 that Romé de l'Isle, in Paris, working with a contact goniometer, invented by his assistant Carangeot, was able to show that the law applies with accuracy to a large number of substances and is a general law of Nature.

Accurate crystal measurement is thus of very great importance, since crystalline form is one of the most distinctive and characteristic properties of a solid and offers an infallible method of establishing the identity of the substance. In this connection it is important to bear in mind that it is immaterial to what extent the shapes and appearances of the crystals may vary as a result of unequal development (fig. 56). In other words, the sizes of the faces on a crystal are not important, but only the inclinations of the faces to each other. Accordingly, whenever necessary, it is permissible to suppose the faces of a crystal to move parallel to their original positions, in order that like or similar faces shall be equal in size.

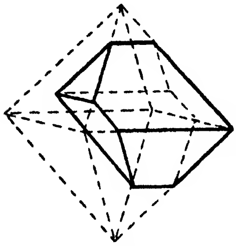


FIG. 56.—Octahedron Unequally Developed.

2. Haüy's Law of Rational Intercepts.—This remarkable law, enunciated by Haüy in 1784, is the foundation upon which is built our system of classification of crystals. It may be explained as follows :

Suppose any three edges of a crystal that meet at a point are taken as axes of co-ordinates. Any face of the crystal will intersect one or more of the axes, the face being extended if necessary. Choose *one* of the faces which intersects the *three* axes as the standard, and suppose the intercepts that this plane cuts off from the axes are a, b and c respectively, measured from the origin. It is only the ratio of these intercepts that matters. Now suppose that *any other face* of the crystal cuts off intercepts in the ratios of $x : y : z$ respectively. These intercepts may be expressed in terms of a, b and c as follows :

$$x : y : z : : \frac{a}{h} : \frac{b}{k} : \frac{c}{l}.$$

The remarkable feature is **that h, k and l are in the ratios of simple integers**, usually 1, 2, 3 or 4, rarely as large as six. We shall refer to this again presently.

3. Law of Constancy of Symmetry.—Before stating this law it is necessary to understand the specialised meaning given to the term " symmetry " as used by crystallographers.

Crystals may be symmetrical with respect to a point, a line, or a plane. When, for example, to each face of a crystal there corresponds a similar, parallel face, the crystal is said to possess a **centre of symmetry** or to exhibit **centrosymmetry.** This is illustrated clearly by figs. 53 and 54, which illustrate the cube and octahedron respectively. The centres of symmetry are indicated.

If on rotation about an axis a crystal presents exactly the same appearance n times in one complete revolution, the **axis** is said to be one of **n-fold symmetry.** It should be borne in mind that only the inclinations of the faces, not the sizes, are of consequence, for we are dealing with crystallographic, not geometrical, symmetry. The only values of n are two, three, four and six, giving rise to di-, tri-, tetra- and hexa-gonal axes of symmetry. The only angles between pairs of axes of symmetry are 30°, 45°, 60° and 90°. An axis of symmetry is always perpendicular to a possible crystal face and parallel to a possible interfacial crystal edge. From fig. 57 it is evident that the axis AB of a cube is one of fourfold symmetry, whereas the diagonal axis CD has threefold symmetry, and the axis EF only twofold symmetry.

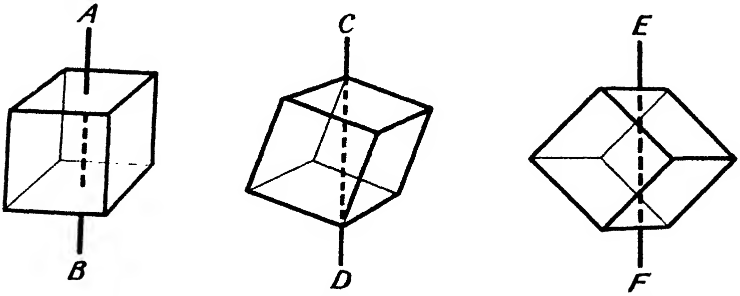


FIG. 57.—Axes of a Cube, showing Fourfold, Threefold and Twofold Symmetry, respectively.

A plane of symmetry divides a crystal into two symmetrical halves such that, if the plane were a mirror, one-half of the crystal would coincide with the reflected image of the other half. It may of course be necessary to move some of the faces parallel to themselves in order to preserve this coincidence, but such a procedure is admissible. In fig. 58 a plane of symmetry of a pyritohedron is illustrated.

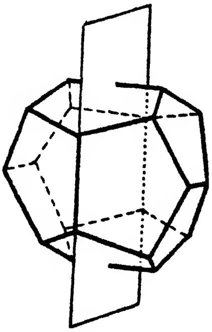


FIG. 58.—A Plane of Symmetry of a Pyritohedron.

Planes and axes of symmetry constitute the **elements of symmetry.** The centre of symmetry is not a true element of symmetry.

The **law of symmetry** states that

all crystals of any one substance have the same symmetry.

Crystal Elements.—In order to express briefly the various crystal forms, a symbolic method is employed, based upon the principles of co-ordinate geometry. A point within the crystal is taken as the origin of co-ordinates, and three **crystallographic axes** of co-ordinates are chosen, parallel to three crystal edges not lying in the same plane or parallel to one another. Taken two by two, these axes lie in three **axial planes,** dividing space into eight octants. Whenever possible, axes of symmetry are for simplicity chosen as co-ordinate axes, since they are always parallel to possible crystal edges; preferably, axes of more than twofold symmetry are selected.

A face that lies in the octant XOYZ (fig. 59) and cuts each of the axes, is chosen as the **fundamental face** or **parametral plane,** and the ratios of its intercepts on the axes are taken as the ratios of the units of length in terms of which measurements along the three axes are expressed. Hence, in general, measurements are made in three different scales, one for each axis. The axes are conventionally drawn, as shown in fig. 59, and the intercepts or **parameters** a, b and c of the fundamental face are always referred to in a standard order: firstly, a on the front to back axis; secondly, b on the left to right axis; and thirdly, c on the vertical axis. The ratios of the parameters or **axial ratios** $a : b : c$, together with the angles YOZ $= \alpha$, ZOX $= \beta$, XOY $= \gamma$, constitute the **crystallographic elements** of a crystal. The value of b is generally put equal to unity.

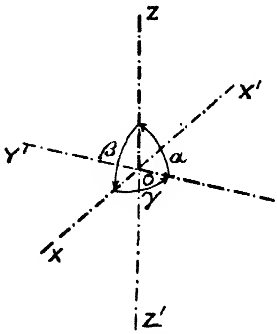


FIG. 59.—Crystallographic Axes.

Haüy's law of rational intercepts (p. 168) postulates that the intercepts x, y and z of any other face of a crystal are related to the axial ratios $a : b : c$ as follows:

$$x : y : z :: \frac{a}{h} : \frac{b}{k} : \frac{c}{l}$$

where h, k and l are in the ratios of simple integers. The face is therefore given the **symbol** (hkl), and h, k, l (expressed in their lowest terms) are called the **indices** of the face. This index system of notation is due to Miller (1839) and is almost universally adopted.

It will be noticed that the intercepts are inversely proportional to the indices of the face. As an example, the symbol (112) means that the crystal face cuts off intercepts on the axes the *lengths* of which are in the ratios of $\frac{1}{1} : \frac{1}{1} : \frac{1}{2}$, *i.e.* 2 : 2 : 1, the scales of measurement along the axes being in the ratios of $a : b : c$; hence the *absolute lengths* of the intercepts are in the ratios of $2a : 2b : c$. Whenever *zero* occurs as an index, it means that the corresponding intercept is infinitely great, *i.e.* that the plane is parallel to the axis.

To indicate that intercepts are measured along OX′, OY′, OZ′ (fig. 59) the corresponding indices are written with minus signs above them. When the symbol of a face is enclosed in brackets, *e.g.* $\{hkl\}$, it stands for all the faces belonging to the form of which (hkl) is one face. Usually the symbols for the various faces of a form only differ in the order of taking the same indices and in the signs attached to them; the eight faces of the octahedron, for example, are (111), $(1\bar{1}1)$, $(\bar{1}11)$, $(\bar{1}\bar{1}1)$, $(11\bar{1})$, $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$ and $(\bar{1}\bar{1}\bar{1})$. Four of these faces are shown in fig. 60.

Crystal forms are named as follows: **pyramids,** $\{hkl\}$, each face of which cuts all three axes; **prisms,** $\{hk0\}$, each face of which cuts the lateral axes and is parallel to the vertical axis ; **domes,** $\{h0l\}$ or $\{0kl\}$, each face of which cuts the vertical and one lateral axis, but is parallel to the other lateral axis ; and **pinacoids,** $\{h00\}$, $\{0k0\}$ or $\{00l\}$, in which each face cuts one axis and is parallel to the other two. The symbol for the fundamental (pyramid) face is obviously (111).

Those forms which present the full number of faces requisite to exhibit the maximum symmetry of a system are termed **holohedral** (Greek *holos*, whole ; *hedra*, base). Thus, for example, the cube and octahedron are two holohedral forms of the cubic system (below). **Hemihedral** (Greek *hemi* = Latin *semi*, half) forms possess only half the number of faces present in the corresponding holohedral forms. As an example quartz (p. 176) may be mentioned, since it consists of two hemihedral forms combined, alternate faces, only, being similar. When a form is represented by only a quarter of the holohedral number of faces it is termed **tetartohedral** (Greek *tetartos*, fourth).

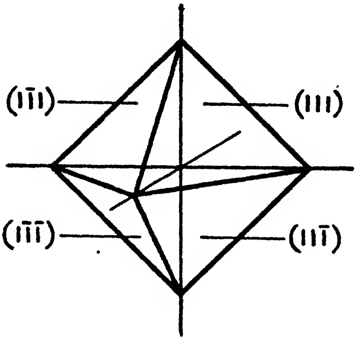


Fig. 60.—Four Faces of Octahedron.

Sometimes a group of crystals shows **parallel growth,** the edges and faces of the different crystals lying parallel to one another. This, for example, is frequent with quartz crystals. **Irregular aggregates,** however, in which there is no simple relation between the orientations of two or more crystals, are generally more common. When two crystals are united symmetrically about a plane which is a possible face of the crystals, or about an axis which is a possible crystal edge, a **twin crystal** results. Gypsum crystals (p. 174) frequently are twinned.

Crystallographic Systems.

The elements of symmetry may be associated in 31 different ways, so that, counting as one class those crystals which possess no symmetry whatever, crystals may be divided into 32 classes. These classes are grouped into seven systems, each system including all the crystal forms, whatever their symmetry, that can be referred to the same set of axes. Let us consider briefly each of these systems.

1. Cubic, Regular or Isometric System.—This system comprises five classes of crystals, all of which may be referred to three equal and interchangeable crystallographic axes, at right angles to each other. The axial ratios thus are $a : b : c = a : a : a$ or $1 : 1 : 1$, and need not therefore be mentioned. As the axes are interchangeable, the properties of the crystals are the same in all directions ; the crystals thus are isotropic (p. 167) and show no double refraction (p. 321).

A few well-known examples are as follows : Metallic sodium and potassium and many other metals often crystallise in cubes, whilst rock salt, sylvine, KCl, and fluorspar, CaF_2, occur in Nature as simple cubes. These are composed of six pinacoid faces, the form symbol being $\{001\}$. Galena, PbS, also occurs as cubes, but frequently as a combination of the cube and octahedron (fig. 55).

The octahedron $\{111\}$ is composed of eight pyramid faces. As examples the various alums may be mentioned (p. 190), also the diamond, spinel, $MgO.Al_2O_3$, and magnetite, $FeO.Fe_2O_3$.

Iron pyrites, FeS_2, usually occurs as striated cubes, pyritohedra (fig. 58), or as combinations of the pyritohedron with the cube, octahedron or diploid (fig. 61). A pyritohedron, it will be noted, is a solid bounded by twelve pentagonal faces, each face cutting two axes and lying parallel to the third. A diploid is bounded by twenty-four faces, grouped in pairs, each face being a trapezium.

Garnets crystallise in rhombic dodecahedra $\{110\}$ (fig. 62), trapezohedra $\{211\}$ (fig. 63), or in combinations of these (fig. 64).

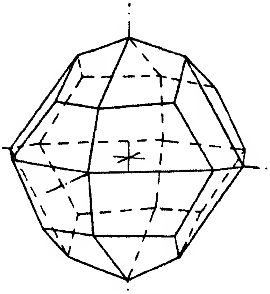


Fig. 61.—Diploid.

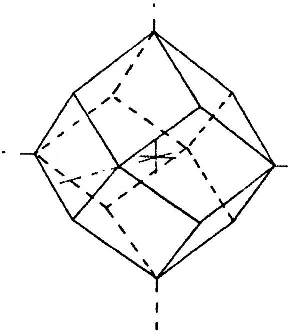


Fig. 62.—Rhombic Dodecahedron.

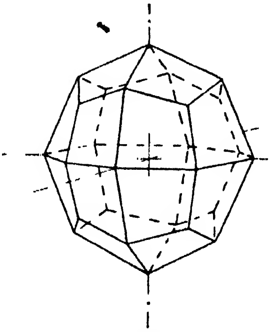


Fig. 63.—Trapezohedron.

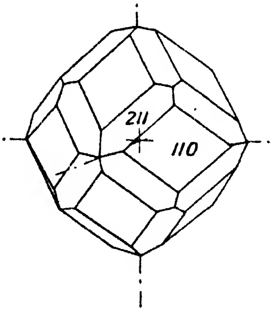


Fig. 64.—Combination of Rhombic Dodecahedron and Trapezohedron.

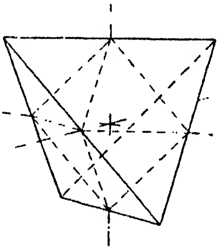


Fig. 65.—Positive Tetrahedron.

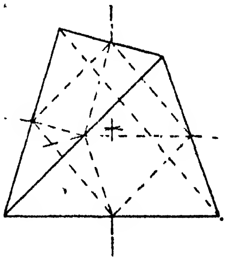


Fig. 66.—Negative Tetrahedron.

Zinc blende, ZnS, crystallises in tetrahedra. A tetrahedron, as its name implies, is a four-faced solid; each face cuts the axes at equal distances, so that the symbol of the form is $\{111\}$. As shown by figs. 65 and 66, two tetrahedra are possible, termed "positive" and "negative" respectively. They may occur singly or in combination, and are produced by developing the two sets of faces of the octahedron. Their geometrical relationship to the octahedron is indicated in the figures, the symbol of the positive form being $\{111\}$, that of the negative, $\{1\bar{1}1\}$.

2. Tetragonal or Quadratic System.—This system comprises seven classes of crystals, each class being characterised by a fourfold or tetragonal axis of symmetry, which is chosen for the vertical crystallographic axis. The other two axes of reference are chosen perpendicular to the vertical axis and to one another. A tetragonal crystal is therefore referred to three mutually perpendicular axes, two of which are equal to one another, but not to the third. The axial ratios thus are $a : b : c = a : a : c$ or $1 : 1 : c$. It is only necessary, therefore, to state the value of c when describing a tetragonal crystal.

The only tetragonal metals known are ordinary white tin and indium. The following minerals belong to this system: Cassiterite, SnO_2; rutile, TiO_2; anatase (TiO_2); zircon, $ZrSiO_4$ (fig. 67); thorite or orangite, $ThSiO_4$; scheelite, $CaWO_4$; and wulfenite, $PbMoO_4$.

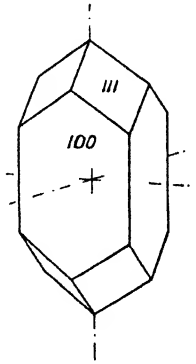


Fig. 67.—Zircon.

3. Orthorhombic or Rhombic System.—Three classes of crystals are included in this system, which is characterised by three rectangular but unequal crystallographic axes at right angles to each other. The vertical axis is one of twofold or digonal symmetry only. In no case is it possible for any crystal face to have two equal intercepts on the crystallographic axes; hence in specifying an orthorhombic crystal it is necessary to state the values of a and c, b being taken as unity, in the axial ratios $a : b : c$. Such a crystal is said to be referred to three mutually perpendicular but unequal axes.

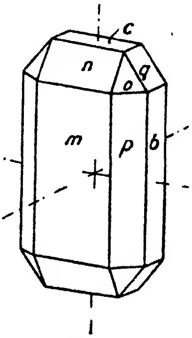


Fig. 68.—Olivine.

One of the best known examples of this system is rhombic sulphur, the axial ratios of which are:

$$a : b : c = 0{\cdot}8138 : 1 : 1{\cdot}9076.$$

Other well-known examples are: Potassium nitrate, chromate, sulphate (p. 179) and selenate; aragonite, $CaCO_3$, strontianite, $SrCO_3$, witherite, $BaCO_3$, and cerussite, $PbCO_3$; anhydrite, $CaSO_4$, celestine, $SrSO_4$, barytes, $BaSO_4$, and anglesite, $PbSO_4$; carnallite, $KCl.MgCl_2.6H_2O$, epsomite, $MgSO_4.7H_2O$, and olivine, Mg_2SiO_4 (fig. 68).

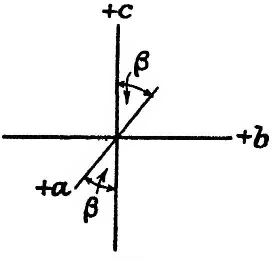


Fig. 69.—Monoclinic Crystallographic Axes.

4. Monoclinic, Oblique or Monosymmetric System.—This system comprises three classes of crystals, all of which possess three unequal crystallographic axes, of which one, the b-axis, is perpendicular to the other two. As usual the c-axis is the vertical one. At right angles to this is the left to right b-axis, known as the *ortho*-axis, whilst the a-axis is inclined at an angle β to the c-axis, and hence is known as the *clino*-axis. This is clearly shown by fig. 69. In no case is it possible for any crystal face to have two equal intercepts on the crystallographic axes. Hence in describing a monoclinic crystal it is necessary to state the values of a and c, b being taken as unity, in the axial ratios $a : b : c$. Further, the magnitude of the angle β must be given. Obviously both α and γ are equal to 90°. Monoclinic crystals therefore are said to be referred to three unequal axes, two of which are perpendicular to the third but not at right angles to each other. As an example the crystallographic elements of a crystal of monoclinic sulphur may be given. These are :

$$a : b : c = 0{\cdot}9958 : 1 : 0{\cdot}9998,$$
$$\beta = 84{\cdot}23^\circ.$$

To the monoclinic system belong large numbers of well-known minerals and other crystalline substances. Mention may be made of the isomorphous series of double sulphates, typified by ammonium ferrous sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$ (p. 189); Glauber's salts, $Na_2SO_4.10H_2O$; borax, $Na_2B_4O_7.10H_2O$; the vitriols, as typified by ferrous sulphate (p. 188), but not by magnesium sulphate or epsomite, $MgSO_4.7H_2O$, which is rhombic (p. 173); vivianite, $Fe_3(PO_4)_2.8H_2O$, and erythrite, $Co_3(AsO_4)_2.8H_2O$; cryolite, Na_3AlF_6; orthoclase, $KAlSi_3O_8$ (fig. 70), but not albite, $NaAlSi_3O_8$, which is triclinic (below), lepidolite or lithium mica. Gypsum or selenite, $CaSO_4.2H_2O$, is shown in fig. 71; twins are very frequent. Finally mention may be made of potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, and the tartaric acids (fig. 88), which latter are of special interest on account of their optical activity (p. 200).

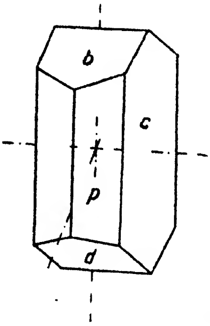


FIG. 70.—Orthoclase.

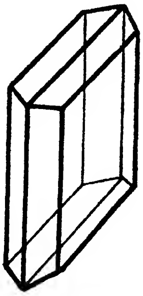


FIG. 71.—Gypsum.

5. Triclinic, Anorthic or Asymmetric System.—Two classes, only, are included in this system, one of which, the holohedral class, has a centre of symmetry only, whereas the other, the asymmetric class, has not even that. The system is characterised by three unequal crystallographic axes all inclined to each other, none of the angles being right-angles. There being no axes of symmetry the crystallographic axes are chosen parallel to three crystal edges. From the symmetry of the system no axial angle can equal 90° and no two intercepts of any face can be equal. Hence a triclinic crystal is said to be referred to three oblique and unequal axes, and in describing such a crystal it is necessary to state the values of a and c, b being taken as unity, in the axial ratios $a : b : c$. Further, the magnitudes of the angles α, β and γ must also be given. One axis is arbitrarily chosen as the vertical axis, and usually corresponds to a direction in which the crystal is well developed; of the other two axes the longer or *macro*-axis is placed from left to right as the b-axis, and the shorter or *brachy*-axis from front to back as the a-axis.

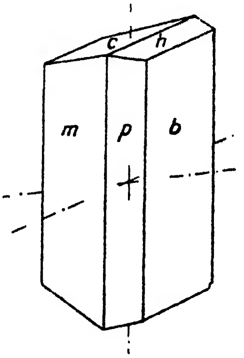


FIG. 72.—Potassium Dichromate.

An excellent example of the holohedral class is copper sulphate, $CuSO_4.5H_2O$, which possesses a centre of symmetry; a second is potassium dichromate, $K_2Cr_2O_7$ (fig. 72). Other examples of triclinic crystals are afforded by albite, $NaAlSi_3O_8$ (above); sassolite, H_3BO_3; calcium thiosulphate, $CaS_2O_3.6H_2O$.

6. Hexagonal System.—Each of the five classes included in this system is characterised by a crystallographic axis of sixfold symmetry which is chosen as the vertical crystallographic axis. Instead, however, of choosing two more axes of reference, three more are selected, arranged symmetrically about the vertical axis in a plane perpendicular to it. Their positive directions are regarded as being separated by 120°, as shown in fig. 73. The symbol of a face, therefore, contains four indices, which cannot, however, all be independent of one another. In fact, any lateral index can be calculated from the other two lateral indices, since the sum of the lateral indices is zero. The four indices are always cited in the order x, y, z, w of fig. 73.

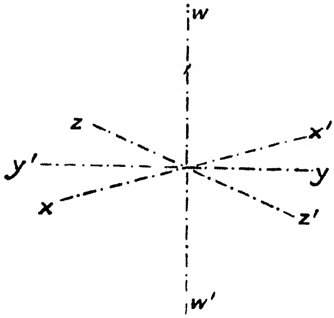


Fig. 73.—Hexagonal Crystallographic Axes.

The simplest pyramidal face in any class belonging to this system intercepts a on the x-axis, is parallel to the y-axis, intercepts $\bar{a}$ on the z-axis and c on the w-axis. Hence its symbol is $(10\bar{1}1)$. Each of the other faces of this form likewise cuts off intercepts numerically equal to a on the lateral axes and c on the vertical axis, c never being equal to a. Hexagonal crystals are therefore said to be referred to three equal lateral axes inclined to one another at 120°, and a vertical axis, perpendicular but not equal to the lateral axes. The ratio c/a is called the axial ratio, and must be given when describing a hexagonal crystal.

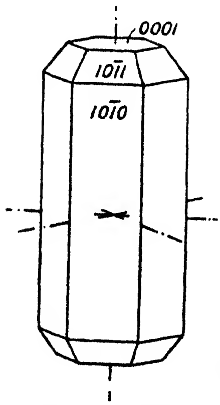


Fig. 74.—Beryl.

A typical example is the beryl, $3BeO.Al_2O_3.6SiO_2$, which frequently crystallises in a combination of the forms $\{10\bar{1}0\}$, $\{10\bar{1}1\}$ and $\{0001\}$, as shown in fig. 74. Other examples are apatite, $CaCl_2.3Ca_3(PO_4)_2$, and its isomorphs pyromorphite, $PbCl_2.3Pb_3(PO_4)_2$, mimetite, $PbCl_2.3Pb_3(AsO_4)_2$, and vanadinite, $PbCl_2.3Pb_3(VO_4)_2$; greenockite, CdS; spartalite or zincite, ZnO; and ice.

7. Trigonal or Rhombohedral System.—This system is sometimes regarded as part of the hexagonal system. It comprises seven classes, and may be referred to hexagonal axes of reference, the vertical axis, however, having only threefold symmetry. As an example of one of the classes, quartz may be chosen. This mineral commonly occurs in the form of a hexagonal prism capped by hexagonal pyramids at its ends (fig. 75). From its geometrical appearance one would imagine such a crystal to yield a vertical axis of hexagonal symmetry and thus to belong, like the beryl, to the hexagonal system. But etch-marks prove that all the pyramidal (or prism) faces are not of the same kind, so that the vertical crystallographic axis has only trigonal symmetry, alternate faces, only, being similar. A quartz crystal, therefore, really consists of two hemihedral forms combined.

Another feature of quartz crystals is the frequent presence of other small faces which lie between the prism and pyramid faces on alternate corners of the crystal. These small faces cause the crystals to appear asymmetric; there are two kinds of such crystals, related to one another as object and image or as right hand and left hand. The crystals therefore are said to be **enantiomorphous** (Greek *enantios*, opposite; *morphe*, form) and are conveniently termed right- and left-handed crystals, respectively (fig. 75).

Enantiomorphous crystals are known amongst organic compounds (p. 199), and are there associated with optical activity of the compounds, as, for example, in the case of the lactic and tartaric acids. Quartz, also, is optically active, for it rotates the plane of polarisation of a beam of polarised light passing through it in the direction of the vertical axis; the opposite crystals are opposite in their optical activity. In the case of organic compounds the optical activity is a molecular property which persists when the compound is in the state of fusion or in solution; in the case of quartz, however, optical activity is a property of the crystal rather than of the molecule of silica; it depends on the way in which the silica molecules are built up within the crystal. A section of quartz, 1 mm. thick, cut perpendicular to the vertical axis, rotates the plane of sodium D light (p. 321) through 22°. Such a section also shows interference colours in the polariscope.

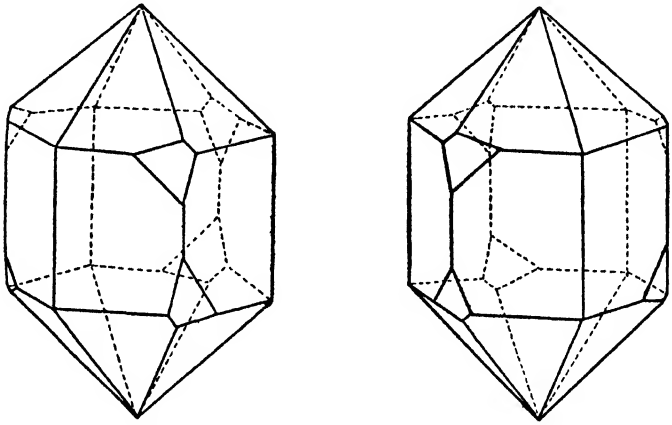


FIG. 75.—Enantiomorphous Quartz Crystals.

Cinnabar, HgS, is a second example of the quartz class.

Another class is represented by tourmaline, a complex borosilicate of aluminium and iron, which possesses peculiar optical and pyroelectric properties.

A third class is represented by calcite, $CaCO_3$, which crystallises in a variety of forms, notably as scalenohedra (fig. 76), in the dog-tooth variety, and as a combination of rhombohedron and prism in "nail-head spar." A pure, transparent form of calcite from Iceland is known as Iceland spar. It cleaves into remarkably perfect rhombohedra, the derivation of which from the hexagonal bipyramid is clearly shown in figs. 77 and 78. The spar exhibits double refraction to a marked degree and is used in the construction of the Nicol prism (p. 321).

Periodicity of Crystal Systems of Elements.—The crystalline forms of all the metals are not known, but when the systems of those that are known are entered on the Periodic Table (p. 336), several interesting regularities are observed. Thus, the elements of Group I, Group IV B, Group VI A and Group VIII (the cobalt and nickel sub-groups) are cubic. Group II B, Group IV A and Group V B are essentially hexagonal. In many cases metals forming homogeneous series of solid solutions crystallise in the same system (Haughton and Ford, 1922).

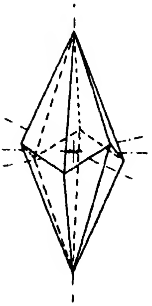


FIG. 76.—Scalenohedron.

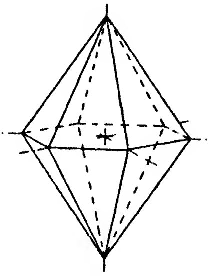


FIG. 77.—Hexagonal Bipyramid, First Order.

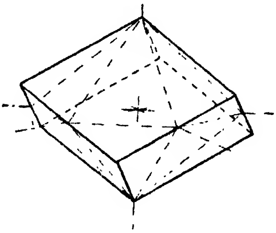


FIG. 78.—Positive Rhombohedron.

ALLOTROPY AND POLYMORPHISM.

If, upon examination, two substances prove to have exactly the same properties, physical and chemical, it is unhesitatingly assumed that they also have the same chemical composition. The converse is not true, however, for substances may be chemically identical although their physical properties are widely different.

When in Florence in 1814, Davy concentrated the rays of the sun on to a diamond with the aid of a large new lens then just obtained by the Cabinet of History and showed that carbon dioxide was the only product. He thus demonstrated what had hitherto been regarded as impossible, namely that two substances of the same composition may have entirely different physical properties. Other examples were soon discovered. In 1821 Mitscherlich showed that disodium hydrogen phosphate, $Na_2HPO_4.H_2O$, can exist in two distinct crystalline forms, and in 1823 he added sulphur to the list.

When an elementary substance can exist in more forms than one, it is said to exhibit **allotropy** (Greek *allos*, another; *tropos*, direction), the different varieties being termed the **allotropes** or **allotropic modifications**. Examples are furnished by sulphur, carbon, phosphorus, iron, tin, etc. In the case of compounds, however, the term **polymorphism** is used. A substance that can occur in two crystalline forms is said to be **dimorphous**, *e.g.* calcium carbonate; in three forms, **trimorphous**, *e.g.* metallic tin and thallous nitrate; in four forms, **tetramorphous**; in five forms, **pentamorphous**, *e.g.* ammonium nitrate; and so on. The term "polymorphism" is frequently used in connection with both elements and compounds in the crystalline state, but it does not include the allotropy of amorphous substances, such, for example, as that of ozone or of liquid sulphur.

When the different polymorphous forms of any one substance are examined, it is found that each exists under a definite set of conditions of temperature and pressure. The physical properties of metals, for example, are susceptible to alteration according to the treatment to which the metals have been subjected. Thus Beilby (1902) found that a metal can exist in two phases—namely, (1) the hardened or amorphous phase, (2) the annealed or crystalline phase. The former is convertible into the latter by heat, and the reverse change may be caused by pressure, producing mechanical flow. Again, it is well known that the density of a metal depends on the treatment to which the metal has been subjected, decreasing in many cases as the result of compression. Subsequent annealing of the specimens causes a renewed increase of density. It is also known that the heat of solution of a metal, and its behaviour in a voltaic cell, depend on the treatment which it has previously undergone. But whilst these may be regarded as examples of polymorphism, another explanation is possible, for it is very probable that any deformation of a metal is a manifestation of *melting* produced by unequal strain, and that with the removal of the strain the liquid portions do not immediately return to the crystalline, solid form.

In other more definite instances of polymorphism the different varieties are found to have distinct and different physical properties. Each possesses its own crystalline form, melting point, rate of expansion, conductivity for heat and electricity, colour, etc.; but although the chemical behaviour and reactivity are often dependent on the physical state of the substance, yet the ultimate products of chemical change are the same, as for example in the combustion of the various forms of carbon with oxygen.

Types of Allotropy or Polymorphism.

Three such types are known.

1. Enantiotropic Substances.—The different forms of many polymorphic substances can be transformed from one into the other at

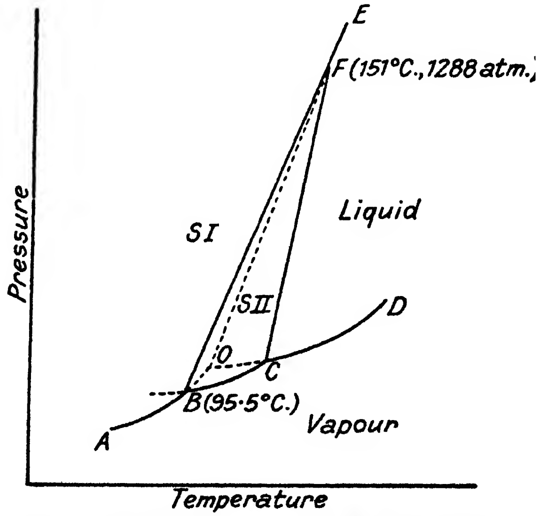


FIG. 79.—Pressure-Temperature Diagram for Sulphur.

definite temperatures and pressures representing the transition points, just as ice can be melted at 0° C. and water boiled at 100° C. under atmospheric pressure. In illustration of this the case of sulphur may be cited. This element can exist in a variety of different crystalline forms, of which the rhombic and monoclinic forms are the most important. At temperatures above 95·5° C. the latter is the stable variety, but when the temperature falls below 95·5° the monoclinic form commences to change into rhombic sulphur. 95·5° C. is therefore known as the **transition temperature,** and at this point the two polymorphous forms are mutually transformable. This type of polymorphism is termed *enantiotropism* (Greek *enantios*, opposite), inasmuch as the polymorphous forms are directly interconvertible and exhibit a transition point. The transition point B lies below the melting point of each form, O and C, as indicated in fig. 79, which gives the pressure-temperature diagram for sulphur. Rhombic sulphur melts at 112·8° C. (point O, fig. 79), monoclinic sulphur (point C) at 119·2° C. (p. 92).

The following is a list of well-marked cases of enantiotropic polymorphism among inorganic substances :

Substance.	Form.	Transition Point, °C.
Iron	$\alpha \rightleftharpoons \beta$	769·0
	$\beta \rightleftharpoons \gamma$	906·0
	$\gamma \rightleftharpoons \delta$	1404·0
Sulphur	Rhombic $\rightleftharpoons$ Monoclinic	95·5
Tin	Grey $\rightleftharpoons$ White (tetragonal)	13·0
	White $\rightleftharpoons$ Rhombic	*c.* 170
Zinc	$\alpha \rightleftharpoons \beta$	*c.* 174
	$\beta \rightleftharpoons \gamma$	322·0
Ammonium chloride	$\alpha \rightleftharpoons \beta$	184·5
Ammonium nitrate	α-Rhombic $\rightleftharpoons$ β-Rhombic	– 17·0
	β-Rhombic $\rightleftharpoons$ γ-Rhombic	32·1
	γ-Rhombic $\rightleftharpoons$ Rhombohedral	84·2
	Rhombohedral $\rightleftharpoons$ Regular	125·2
Mercuric iodide	Tetragonal $\rightleftharpoons$ Rhombic	127·0
Potassium nitrate	Rhombic $\rightleftharpoons$ Rhombohedral	129·5
Potassium sulphate	$\alpha \rightleftharpoons \beta$	583·0
Silver iodide	Hexagonal $\rightleftharpoons$ Regular	146·5
Silver nitrate	Rhombic $\rightleftharpoons$ Rhombohedral	159·5
Thallous nitrate	Rhombic $\rightleftharpoons$ Rhombohedral	72·8
	Rhombohedral $\rightleftharpoons$ Regular	142·5
Thallous picrate	Red $\rightleftharpoons$ Yellow	46·0

2. Monotropic Substances.—Some substances exist in two or more forms which are not directly interconvertible and do not exhibit a transition point.

In 1855 Gore observed that when a concentrated solution of antimony trichloride in hydrochloric acid is electrolysed, using a platinum wire as cathode and a piece of antimony as anode, a deposit of distinctly metallic appearance is formed on the cathode, which becomes strongly heated when scratched, the metal being converted into powder by a kind of explosion, whence the name "explosive antimony." This is due to the fact, established by Cohen, that antimony can exist in two varieties, termed α- and β- respectively. Of these the α-form is stable at ordinary temperatures, the β- being metastable. It is this β-variety that is formed during electrolysis and, upon mechanical excitation, it is transformed into the stable α-form with evolution of heat. The β-form contains some dissolved or occluded antimony trichloride, in consequence of its method of preparation, and the heat of transformation of the antimony causes this to vaporise suddenly, giving rise to the explosive effect.

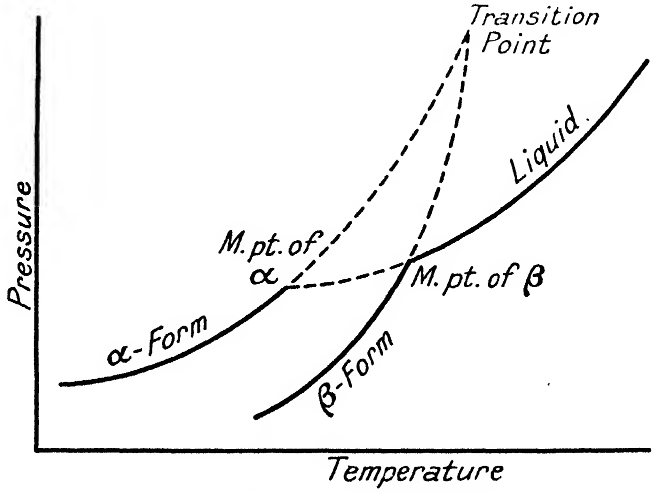


FIG. 80.—Showing Monotropic Polymorphism of Antimony.

The heat evolved in the transformation of β- to α-antimony is 20 gramme-calories per gramme. Taking the specific heat of antimony as 0·05, the theoretical rise in temperature would be 20÷0·05 or 400° C. In practice this is not attained, owing to loss of heat, mainly by conduction and radiation, but the temperature rises sufficiently to volatilise the enclosed antimony trichloride, which boils at 225° C. The reaction is not reversible, and it is assumed that the transition point lies above the melting points of the α- and β-forms, as shown in fig. 80.

In cases like this the polymorphism is said to be **monotropic** (Greek *monos*, one; *tropos*, direction). Many other examples are known. The two varieties of iodine monochloride may be mentioned; the stable α-ICl melts at 27·2° C., and the metastable β-ICl at 13·9° C. In addition to the two well-known enantiotropic forms of sulphur, several other varieties have been described which are not reversibly transformable. Two forms of phosphorus also are known, which are often placed in this category, namely red and white, the latter being metastable.

It is conceivable that by raising the pressure enantiotropy might be induced. In that case the same pair of polymorphs would exhibit monotropy or enantiotropy, according to the pressure obtaining at the time. It may, on the other hand, so happen that, in certain cases of presumed monotropy, the transition point lies very much below the melting point and has not been realised experimentally for this reason. Possibly this is the case with the two forms of phosphorus, and with graphite and diamond. This is termed **pseudomonotropy**, and is really a special case of enantiotropy.

3. Dynamic Allotropy.—In the two preceding cases of solid polymorphic forms, the various varieties cannot exist in contact (except at a transition point), one form always being stable, and the other, the metastable, tending to change into it. Quite different, however, is the behaviour of the three liquid forms of sulphur, known respectively as S_λ, S_μ and S_π, which exist together in equilibrium in definite proportions depending on the temperature. The phenomenon is known as dynamic allotropy.

These three forms of liquid sulphur, of which S_λ is yellow and mobile, and S_μ brown and viscous, are present in molten sulphur, the amount of S_μ being small near the melting point, but rising steadily with the temperature to a maximum of about 37 per cent. at the boiling point. The percentages of these allotropes present when equilibrium has been attained are as follows :

Temperature, °C.	120	140	180	220	445
S_λ	96·4	93·7	73·1	62·7	59·1
S_μ	0·1	1·3	20·4	32·0	36·9
S_π	3·5	5·0	6·5	5·3	4·0

The freezing point of sulphur accordingly varies with both the nature of the solid phase that separates and the percentage of S_μ and S_π in the liquid. Unless the liquid has been kept near the freezing point for a sufficient length of time to enable equilibrium to be established, the percentage of S_μ and S_π contained by it will vary according to circumstances. This type of allotropy is due to the existence of molecules of different complexity. Thus, in the case of sulphur, S_λ probably corresponds to the molecule S_8, S_μ to S_6, and S_π possibly to S_4.

Dynamic isomerism, or tautomerism, which is closely allied to dynamic allotropy, is discussed on p. 208.

Physically Pure Specimens.—Owing to the persistence of certain phases in regions outside their ordinary range of stability, a substance capable of exhibiting allotropy or polymorphism may not, at any one temperature, be physically pure. In the table on p. 179 reference is made to β-iron. At one time this was believed to be a definite allotropic form of iron. It is now usual to regard it as a solid solution of γ-iron in α-iron ; in other words, the assumption is made that when iron cools below what is known as the A_3 point (906° C.) the conversion of γ-iron into α-iron is not quite complete, some γ-molecules remaining dissolved until the A_2 point (769° C.) is reached, at which point the transformation is completed, α-iron alone remaining. Nevertheless it is found convenient to retain the name β-iron to indicate that particular phase of the metal between the A_2 and A_3 points.

E. Cohen (1929) has very usefully drawn attention to the difficulty of ensuring that specimens are physically pure, and points out how important this matter is for those engaged in the determination of physical constants. When α-silver iodide is converted to the β-form, there is a shrinkage in volume, which has been determined by many independent investigators, with widely differing results. These results differ far more than can be accounted for as due to errors of observation, the reason being that physically pure specimens were not being examined. A few observations are given below :

Observer.	Volume Change, c.c. per kilogram.
Rodwell, 1882 . . .	− 3·4
Mallard and Le Chatelier, 1884	−19·3
Tammann, 1911 . . .	−10·0
Benedicks, 1912 . . .	− 9·1
Bridgman, 1915 . . .	− 8·6
Cohen, 1928	− 9·4

The extreme variation is nearly 600 per cent.! Cohen examined what he believed to be a physically perfectly pure specimen.

Thallous picrate changes at 46° C. from the red to the yellow form. Now if the temperature of the supernatant liquid over the yellow crystals is allowed to fall somewhat below 40° C. red crystals separate out amongst the yellow. For many months these two types of crystals will remain together at the temperature of the room, the red being stable and the yellow metastable ; the rate of change of the yellow into the red is so small that the two forms appear to be stable.

Ordinary rhombic sulphur affords another example of the difficulty of obtaining a physically pure specimen. Even when obtained by crystallisation from carbon disulphide the octahedral crystals contain some γ- and π-sulphur in solid solution, and the observed slight variation in the crystallographic elements is attributable to this, as also the variation in the results obtained for the density of the crystals.

Some metals when quenched from a high temperature by plunging into water are found to remain for prolonged periods, sometimes several weeks, at a temperature very slightly above the normal. This has been shown by connecting a quenched and an annealed specimen with a thermo-element when kept in a thermostat. The difference in temperature may be as much as 0·1° C., several gramme-calories of heat being evolved per day in consequence of the quenched specimen being metastable and slowly changing, with heat evolution, into the stable form (Majorana, 1928). As a typical example consider a block of white tin weighing 300 grammes. On being wholly transformed into the grey variety at 0° C. it would evolve 1350 gramme-calories. If it lost 12 calories per day, which may be regarded as typical, it would take 1350÷12 days, or approximately 4 months, to transform completely.

Analogies between the Melting Point and the Transition Point.—The analogies between the melting point and the transition point may be stated as follows :

1. The transformation occurs at a perfectly definite temperature in

both cases, and marks a change of phase in either case. So definite is this temperature that transition points, like melting points, may be used as fixed points in thermometry. Potassium sulphate (p. 179) affords an example.

2. Both melting point and transition point depend on the pressure. An illustration of this has already been given in connection with the melting point. The following table provides a similar illustration of the effect of pressure on the transition point of rhombic and monoclinic sulphur:

Effect of Pressure on the Transition Point of Sulphur.
(Tammann, 1899.)

Transition Point.	Pressure.	Transition Point.	Pressure.
95·5° C.	1 atmosphere	120·01° C.	638 kilos. per sq. cm.
100·11° C.	123 kilos. per sq. cm.	140·1° C.	1108 ,, ,,
110·11° C.	391 ,, ,,	150·1° C.	1350 ,, ,,

The transition point is, like the melting point, either raised or lowered, according to circumstances. In the case of sulphur, iron, mercuric and silver iodides, which expand during transition, the transition point is raised by increasing the pressure. On the other hand, the transition point of γ-rhombic ammonium nitrate into the rhombohedral form is, like the melting point of ice, lowered by pressure, as contraction occurs during transition.

3. Heat is absorbed or evolved at the transition point according to the direction of the change. The form stable at the higher temperature always passes into that stable at the lower temperature with evolution of heat, in accordance with Le Chatelier's Theorem (p. 23), and the reverse change occurs during the heating process. Evidence of these facts is afforded by the horizontal portion always observed in the cooling curve. When β-iron passes into α-iron, a considerable amount of heat is disengaged, and the transition point is known widely as the "recalescence point." There is therefore a latent heat of transformation just as there is a latent heat of fusion.

4. Both melting point and transition point are affected by the presence of foreign substances, being lowered as a rule thereby. The presence of carbon in iron thus lowers the transition temperatures of (carbon) steels. Moreover, the extent of the depression depends on the number of foreign molecules present, and not on the kind.

Differences between Melting Point and Transition Point.—These may be summarised as follows:

1. Whilst the melting point involves a solid and a liquid phase, transition points usually are concerned with two solid phases, although examples of transition are known in a few cases amongst pure liquids (p. 187). Neglecting these latter, however, it is evident that the rate of transformation of one phase into another at the transition point will be slow compared with the rate at which melting takes place, as the molecules in the latter case are held together less rigidly.

2. It is well known that a liquid can be cooled considerably below its normal freezing point. In like manner, monoclinic sulphur may be preserved for some time at temperatures far below its transition point, and the same holds good for other substances, especially if cooled rapidly. But there is this difference that, whilst monoclinic sulphur may be kept for a prolonged period below its transition point without change occurring, rhombic sulphur may just as readily be maintained above the transition point without transformation into monoclinic sulphur commencing ; and this superheating is not peculiar to rhombic sulphur alone, but is exhibited by other substances. The superheating of a solid above its melting point, however, is of very rare occurrence.

Any substance cooled below its transition point remains for a time in what is known as the metastable state. Before the stable variety can be produced, the substance must pass through the unstable state, which can best be brought about by the addition of a trace of the form which is stable. The previously suspended transformation now begins immediately, for the metastable condition cannot be maintained in the presence of the stable phase of the substance. Transition from monoclinic to rhombic sulphur, on cooling, can be assisted therefore by the addition of a small amount of the rhombic form ; so also the transformation of white into grey tin, which otherwise occurs only very slowly at ordinary temperatures, by adding a trace of grey tin.

The Determination of Transition Points.

All methods proposed for the determination of transition points depend on the study of some particular physical property of the substance under investigation which undergoes a marked change when the transition point is reached.

1. **The Cooling Curve Method.**—If water be continuously cooled and the temperature be plotted against the time, the cooling curve so obtained will show a horizontal portion where freezing occurs, corresponding to the fact that the temperature remains constant during a change of phase.

Since at the transition point a change of phase also occurs, from one solid to another, a cooling curve of similar form may be expected, on which the horizontal portion will mark the transition temperature. When, for example, a piece of pure iron is allowed to cool from its melting point, 1535° C., to 0° C., its time-temperature cooling curve exhibits three breaks or arrests, designated by the symbols Ar_4, Ar_3 and Ar_2, respectively. If the iron contains carbon, preferably about 0·25 per cent., a fourth arrest is observed, designated Ar_1 on the cooling curve (and Ac_1 on the heating curve). Ar_1 occurs at approximately 600° C., and is generally recognised as due to a change in the condition of the carbide of iron, known as cementite, which, at higher temperatures, is held in solid solution, but at the Ar_1 point begins to separate out as a eutectic mixture of cementite and ferrite under the name of pearlite, owing to its pearly appearance under high magnifications. We are concerned at the moment, however, with the three arrest points Ar_4, Ar_3 and Ar_2, which are caused by the evolution of a small amount of heat consequent upon allotropic change taking place within the iron. At the Ar_3 point, which was the first to be discovered, the evolution of heat is sufficient to raise the temperature of the iron by an appreciable amount, causing it to glow more brightly. This phenomenon is termed **recalescence.** Similarly, on reheating the metal, three arrests due to heat absorption are observed at temperatures denoted by Ac_2, Ac_3 and Ac_4 (c = *chaud*, warm). The points occur approximately at the following temperatures:

Ac_2	770° C.	Ac_3	910° C.	Ac_4	1404° C.
Ar_2	760° C.	Ar_3	890° C.	Ar_4	1401° C.

The Ac points thus are slightly higher than the corresponding Ar points, but they are believed to be due to the same phenomena. The divergence is explained by assuming a certain amount of inertia or resistance to change exists, known as **lag,** which tends to lower the temperature of arrest during cooling and probably raise it slightly during heating. These results are taken to mean that iron exists in three allotropic forms, known as α-, γ- and δ-iron (or ferrite), the ranges of existence of which are given by the above scheme (fig. 81).

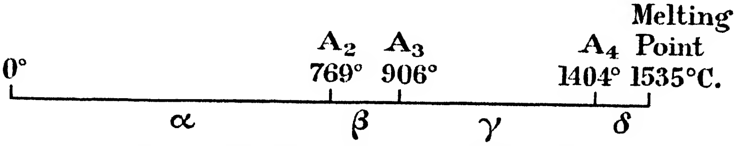


Fig. 81.—Illustrating the Allotropic Forms of Iron.

As we have seen already (p. 181), the β-form is believed to be a solid solution of γ- in α-ferrite. X-ray examination has confirmed the view that α-ferrite has a different structure from γ-ferrite, and that allotropy therefore exists.

The transition point of ammonium chloride was determined by Smith (1919) with the aid of the apparatus shown in fig. 82. The apparatus was exhausted and sealed. After standing for a prolonged period to ensure thorough desiccation, the tube containing the ammonium chloride was heated in a bath and from the heating curve the transition temperature was ascertained (184·5° C.). The result was the same with ordinarily dry ammonium chloride as for the highly desiccated material. Considerable lag was observed on cooling.

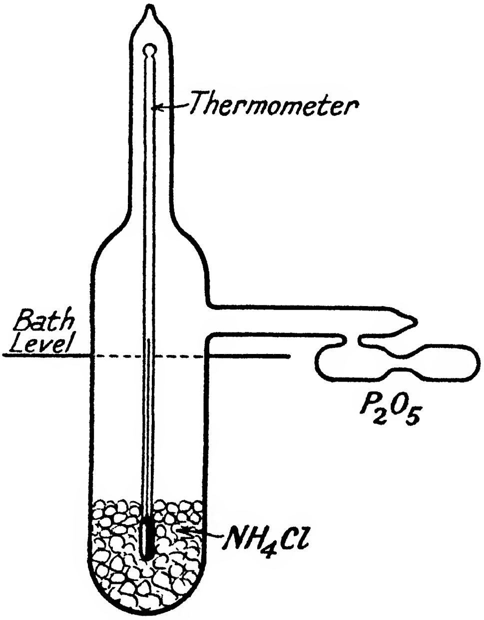


Fig. 82.—Smith's Apparatus for Transition Point of NH_4Cl.

2. The Dilatometric Method.—In this method the rate of expansion with temperature is noted. The substance is contained in a dilatometer (a glass bulb with a long capillary stem), and covered with a liquid in which it is relatively insoluble. The stem is calibrated, and the rate noted at which the liquid expands as the dilatometer is slowly heated. At the transition point there is a marked change in the rate of expansion, as indicated by the portion BC on the curve (fig. 83). Observations are repeated as the temperature slowly falls to the initial value.

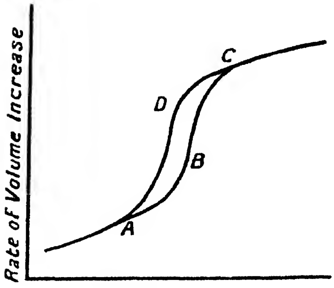


Fig. 83.—Illustrating Dilatometric Determination of Transition Point.

A lag in undergoing transformation is usually observed, due to superheating when the temperature is being raised, or to supercooling if the temperature is being lowered, so that two branches, ABC and CDA, are obtained, from which the mean value of the transition point is calculated.

Instead of observing the temperature at which a marked change in volume occurs, the method may be modified by introducing both allotropic or polymorphic forms into the dilatometer, and noting the temperature at which no volume change occurs. This method was adopted by Reicher (1884) when determining the transition temperature of rhombic to monoclinic sulphur. A mixture of carbon disulphide and turpentine was used as the indicating liquid, and both rhombic and monoclinic sulphur were introduced into the dilatometer bulb. At temperatures below 95·5° C. the liquid indicated a contraction in volume, as monoclinic sulphur changed into rhombic sulphur. Above 95·5° C. expansion occurred, indicating the reverse change. At 95·5° C. no alteration in volume took place; both phases were in equilibrium. This was taken as the transition temperature.

3. Electrical Methods.—If two pieces of the same metal in the same condition are immersed in an electrolyte and the metals connected together so as to form a closed circuit, no current passes, the E.M.F. of the cell being zero. If, however, the pieces of metal exist in different polymorphic forms, the cell has a definite, though small, E.M.F. At the transition point, however, where the two forms are in equilibrium, the difference of potential between each metal and the solution is the same, and, since the potentials act in opposite directions, they neutralise each other, the E.M.F. of the cell becoming zero.

Cohen and van Eyk (1899) determined in this manner the transition point of grey tin into the white or tetragonal variety. They employed a cell containing a strip of white tin and a strip of white tin whose surface had been transformed into grey tin, the electrolyte in the cell being ammonium stannic chloride. The cell was immersed in a bath the temperature of which was altered until the E.M.F. was zero. The transition temperature is 13° C., below which white tin dissolves in the electrolyte, being metastable. In very cold weather, therefore, there is a tendency for ordinary tin to change over into the grey variety; but unless the temperature is very low, the rate of change is exceedingly slow, reaching a maximum at about $-50°$ C. and then diminishing again (fig. 84).

Aristotle (B.C. 384 to 322) spoke of tin "melting" at low temperatures, and probably referred to this change. During the extremely severe winter of 1867 to 1868 in Russia, blocks of tin, which had been stored in the Customs House at Petrograd, were found to have crumbled and disintegrated into a grey tin. The change was not understood at the time. In our climate, for obvious reasons, this trouble, known variously as "tin pest" and "museum sickness," is not often encountered.

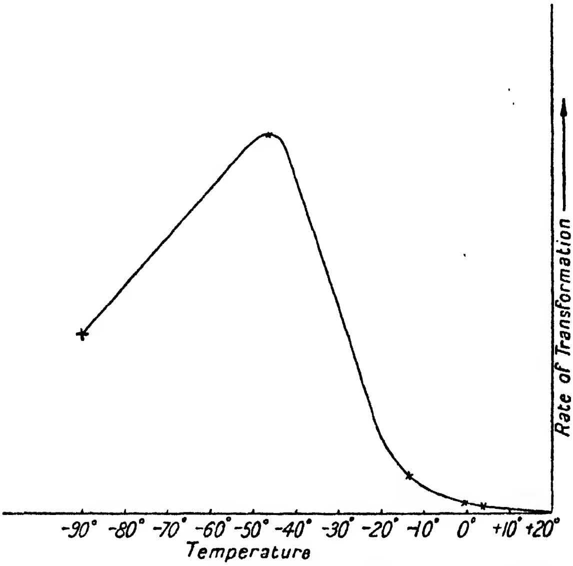


FIG. 84.—The Rate of Transformation of White Tin into Grey Tin (Cohen and van Eyk, 1899).

4. **Change in Solubility.**—This is often a convenient method of detecting polymorphic changes, although it does not give a very accurate indication of the exact transition point. The type of curve obtained is illustrated by that shown in fig. 146 (p. 367) for ammonium nitrate.

5. **Miscellaneous Methods.**—Other methods depend on noting any **change in colour,** as in the cases of silver and mercuric iodides and thallous picrate; watching under the microscope a **change in crystalline form** (the so-called "optical method"); measuring the **vapour pressure**; determining the **conductivity for heat** or **electricity**; noting changes in **viscosity** (p. 250) or **resistance to indentation.** This last-named method has been used to detect the transition of α- to β-zinc.

Transition Points in Pure Liquids.—It is not often that a pure liquid shows transition points, but an interesting example is afforded by nitrobenzene. When its density and dielectric constant are plotted against the temperature, breaks sometimes occur in the curves at 9·5° C., showing that the liquid can exist in two modifications, one of them stable below this temperature and one stable above. The cooling curve similarly shows discontinuity and points to the same conclusion (Mazur, 1930). So-called "liquid crystals" (p. 136) likewise show transition points.

CHEMICAL CRYSTALLOGRAPHY.

Isomorphism.—That different chemical entities frequently yield very similar kinds of crystals has been known for many years. Thus in 1772 Romé de l'Isle was aware that mixed solutions of copper and ferrous sulphates will crystallise after the same form as those of pure ferrous sulphate, whereas a pure copper sulphate solution yields crystals of quite a different shape. In 1784 Leblanc drew attention to the fact that crystals of potassium aluminium sulphate may contain considerable quantities of iron and yet retain the same crystalline form; and in 1816 Gay-Lussac made the remarkable observation that a crystal of potassium alum will grow readily in a solution of ammonium alum, from which he concluded that the molecules must have a similar form. In 1819 Eilhardt Mitscherlich, after a careful study of the arsenates and phosphates of certain metals, enunciated his famous **Law of Isomorphism,** according to which:

Substances possessing an equal number of atoms united in a similar manner exhibit identity of crystalline form.

This law was at variance with the current view, originated by Haüy in 1784, that every substance of definite chemical composition was distinguished by its own particular crystalline form, and it was soon found that Mitscherlich's law was only approximately true. Thus, for example, copperas, pisanite and boothite possess a similar constitution and are regarded as isomorphous, although their crystal elements show a small, but decided, fluctuation. These elements are as follows:

	$a : b : c.$	$\beta.$
Copperas, $FeSO_4.7H_2O$ . .	1·1828 : 1 : 1·5427	75° 44′
Pisanite, $(Fe, Cu)SO_4.7H_2O$.	1·1670 : 1 : 1·5195	75° 30′
Boothite, $CuSO_4.7H_2O$ . .	1·1622 : 1 : 1·5000	74° 24′

It has now been completely established, mainly through the extensive researches of Tutton, that Haüy's hypothesis is perfectly correct, and that all the so-called isomorphous substances exhibit definite differences, although in many cases these differences are relatively small. At the same time Mitscherlich's principle of isomorphism, with a not too rigid interpretation, has proved, as will be seen presently, of great value to chemistry.

Recognition of Isomorphism.—Had the early belief of Mitscherlich that isomorphous bodies possess identical crystalline form proved to be correct, the recognition of isomorphism would have been an easy task; but from what has been said it will be evident that a mere study of crystalline form cannot of itself determine isomorphism. Thus, the sulphates of copper and iron referred to above are regarded as isomorphous, although their characteristic angles exhibit a difference of more than one degree. On the other hand, sodium nitrate and calcite have nearly the same crystallographic elements, but are not regarded as isomorphous by some crystallographers. Similarly, substances crystallising in the regular system have the same crystallographic elements, but are not to be regarded as isomorphous unless, like the alums, they possess a similar chemical constitution.

Again, it does not follow that substances must contain the same number of atoms in their molecules in order to be isomorphous, as was postulated originally by Mitscherlich. The ammonium salts, which have been made the subject of careful study by Tutton, are cases in point, for the replacement of the two atoms of potassium by the ten atoms of the ammonium groups is accompanied by an effect comparable with that produced when two atoms of rubidium or cæsium are substituted for those of potassium. This is well illustrated by the monoclinic double sulphates $M_2SO_4.FeSO_4.6H_2O$, as the following data show :

Crystal Elements of Double Sulphates.

(Tutton, 1913.)

Sulphate.	Atomic Number of Alkali Metal.	*a* : *b* : *c*.	*β*.
Ferrous ammonium .	. .	0·7377 : 1 : 0·4960	106° 50′
,, potassium . .	19	0·7377 : 1 : 0·5020	104° 32′
,, rubidium . .	37	0·7377 : 1 : 0·5004	105° 44′
,, cæsium . .	55	0·7261 : 1 : 0·4953	106° 52′

The axial ratios for the rhombic sulphates of potassium, rubidium and cæsium are given by Tutton as follows :

Anhydrous Sulphate.	Atomic Number of Alkali Metal.	*a* : *b* : *c*.
K_2SO_4 . .	19	0·5727 : 1 : 0·7418
Rb_2SO_4 . .	37	0·5723 : 1 : 0·7485
Cs_2SO_4 . .	55	0·5712 : 1 : 0·7531

It will be noted that in both tables the order of the axial ratios is the same as that of the atomic numbers.

More recently the following groups of salts have been shown to be isomorphous :

(i) Rhombic (Curjel, 1929):

K_2BeF_4 and K_2SO_4.

(ii) Miscellaneous (Ray, 1930):

$NiSO_4.7H_2O$ and $NiPO_3F.7H_2O$.

$CuSO_4.5H_2O$ and $CuPO_3F.5H_2O$.

$CoSO_4.6H_2O$ and $CoPO_3F.6H_2O$.

(iii) Alums and

$K_2BeF_4.Al_2(SO_4)_3.24H_2O$,
$K_2ZnCl_4.Al_2(SO_4)_3.24H_2O$,
$(NH_4)_2PO_3F.Al_2(SO_4)_3.24H_2O$,
$(NH_4)_2PO_3F.Al_2(PO_3F)_3.24H_2O$.

(iv) Derivatives of heteropolyacids (Copaux, 1908). The following, for example, are hexagonal :

$6K_2O(3H_2O.24WO_3).36H_2O$,
$5K_2O(B_2O_3.24WO_3).36H_2O$,
$4K_2O(2SiO_2.24WO_3).36H_2O$.

What, then, is the criterion to be adopted in order to recognise isomorphism ? The evidence is cumulative.

1. The **crystal elements** should be closely similar numerically.

2. According to Kopp (1879) and Retgers (1889) two or more substances are to be regarded as isomorphous when they are capable of yielding **mixed crystals**—that is to say, crystals in which the components may be made to occur in varying proportions. It is not usually possible to obtain a complete series of " mixed crystals " of any two isomorphous substances, but it is often possible to obtain a limited series. This is the case with the chlorides of potassium and ammonium, " mixed crystals " being obtainable only when one of the components is in considerable excess of the other. The sulphates of potassium and ammonium, on the other hand, yield a very complete series of " mixed crystals," which is all the more remarkable inasmuch as in ammonium sulphate the ten atoms of the two ammonium groups are equivalent to the two potassium atoms in potassium sulphate.

The term " mixed crystals " is not a happy one. It does not mean a mechanical mixture of crystals such as would be obtained on mixing, for example, crystals of sodium chloride and potassium permanganate. The " mixed crystals " possess a homogeneous structure.

A close connection exists between the power to form " mixed crystals " and the molecular volumes of the substances, and it appears that in an isomorphous series of substances only those members yield " mixed crystals " the molecular volumes of which are closely similar. Evidently, therefore, it is possible to have, on the one hand, isomorphous substances incapable of yielding " mixed crystals " and, on the other hand, " mixed crystals " from substances that are not truly isomorphous. Exceptions, however, are very uncommon.

3. Mention has already been made of Gay-Lussac's observation that a crystal of potassium alum will readily grow in a saturated solution of ammonium alum and retain its same characteristic shape. This is known as **isomorphous overgrowth**, and was regarded by Kopp (1879) as a reliable test for the isomorphism of any two or more substances. Like the power of yielding " mixed crystals," however, that of exhibiting isomorphous overgrowth is possessed by bodies which are not necessarily isomorphous, but which have almost identical molecular volumes. Consequently this test is insufficient by itself, but exceptions are rare.

When the molecular volumes of two isomorphous substances are approximately equal, it is possible to obtain regular or " parallel " growths of one substance upon the other. For example, when a drop of a saturated solution of potassium permanganate is placed on a perfectly clean face of a crystal of potassium perchlorate and allowed to evaporate, numerous minute crystals of potassium permanganate are observed to form, having their corresponding edges arranged as nearly parallel to one another and to the corresponding edges of the perchlorate crystal as it is possible to expect when the slight angular differences between the permanganate and perchlorate are recalled.

4. The **removal of supersaturation** (p. 376) is frequently regarded as evidence of isomorphism, although this is not an infallible test.

Generally speaking, therefore, if two or more substances possess a similar or analogous chemical structure, are capable of yielding " mixed crystals," of exhibiting isomorphous overgrowth and of removing supersaturation, they may be regarded as isomorphous. As recognised in this way, isomorphism has in the past proved very helpful in determining atomic weights (*vide infra*). It is usually considered necessary that two substances should belong to the same crystal *system* before they can be regarded as isomorphous, but they need not of necessity belong to the same class. In exceptional cases, however, it is possible to make out a good case for the isomorphism of substances belonging to different systems.

Isopolymorphism.—Many substances are capable of existing in a variety of crystalline forms. Now, it frequently happens that two or more polymorphs of one substance are isomorphous with polymorphs of another substance. This phenomenon is known as isopolymorphism. When the number of isomeric polymorphs is two, the term **isodimorphism** is usually employed; if three, **isotrimorphism.** As might be expected, isodimorphism is the most usual type of isopolymorphism, and a good example of this is afforded by arsenious and antimonious oxides. For a long time these were known only in one form each, not isomorphous, the arsenious oxide occurring in octahedra as the mineral *arsenolite*, and the antimonious oxide in rhombic crystals as the mineral *valentinite.* In view of the close chemical similarity between the two oxides this appeared remarkable, and it was to be presumed that other varieties of the two oxides existed isomorphous with those then known. In 1832 Wöhler observed that arsenious oxide in the sublimate from a cobalt roasting furnace sometimes occurred as rhombic prisms, isomorphous with the usual rhombic antimonious oxide. Claudet likewise found the same modification in a Portuguese mineral, now known as *claudetite.* Finally, the mineral *senarmontite* was discovered, in which antimonious oxide occurs as octahedra, isomorphous with *arsenolite.* The two oxides are therefore isodimorphous. An example of isotrimorphism is afforded by the dioxides of tin and titanium. The three crystalline dioxides of tin, namely the natural tetragonal *cassiterite* and two other forms prepared artificially, are isomorphous with *rutile* (tetragonal), *brookite* (rhombic) and *anatase* (tetragonal), respectively, which are the corresponding natural dioxides of titanium.

Isomorphous Series.—Elements that replace one another isomorphously in their compounds are termed " isomorphous elements," although it often happens that the free elements themselves are not isomorphous. Adopting this convention, it is possible to arrange the elements into ten isomorphous series. The following is Arzruni's (1893) arrangement, with one or two additions :

I. H, K, Rb, Cs, (NH_4), Tl ; Na, Li, Ag.
II. Be, Zn, Cd, Mg, Mn, Fe, Os, Ru, Ni, Pd, Co, Pt, Cu, Ca, Sr, Ba, Pb.
III. La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, Bi.
IV. Al, Fe, Cr, Co, Mn, Ir, Rh, Ga, In, Tl.
V. Cu, Hg, Pb, Ag, Au.
VI. Si, Ti, Ge, Zr, Sn, Pb, Ce, Th, Mo, Mn, U, Ru, Rh, Ir, Os, Pd, Pt, Te (?).
VII. N, P, As, Sb, Bi, V.
VIII. Nb, Ta.
IX. S, Se, Cr, Mn, W ; Te (?), As, Sb.
X. F, Cl, Br, I, Mn, (CN).

It will be observed that all the best known elements are included in this classification, save oxygen, carbon, boron and scandium. Several of the elements appear in two or more series. Manganese is a case in point, occurring in Series II, IV, VI, IX and X, since its variable valency affords it special facilities for yielding different types of chemical compounds with correspondingly different crystalline structures. Thus, as divalent manganese in MnO we have isomorphism with CaO, FeO, etc. Trivalent manganese yields alums isomorphous with those containing aluminium and ferric iron, and so on. Further, the above grouping affords considerable support to the usually accepted periodic arrangement of the elements (see Chapter XVI). Thus, the inclusion of silver in the first group of the Periodic Table is supported by the isomorphism of the sulphates and selenates of sodium and silver ; the isomorphism of the chromates and sulphates of several metals justifies the inclusion of chromium in the sixth group along with sulphur ; and finally the isomorphous resemblance between $KClO_4$ and $KMnO_4$ indicates that manganese is correctly placed in the seventh group along with the halogens.

Applications of Mitscherlich's Law.—A study of isomorphism has frequently been of assistance in determining the atomic weight of an element when its equivalent weight has been known.

Selenium.—The occurrence of this element in Swedish pyrites led Berzelius to its discovery in 1817 in the deposit formed in the lead chambers of a sulphuric acid plant. Berzelius observed its close resemblance in chemical properties to tellurium. Mitscherlich concluded that potassium sulphate and potassium selenate are isomorphous, and application of his Law of Isomorphism indicates that, if K_2SO_4 represents the constitution of the former salt, K_2SeO_4 must indicate that of the latter. Now, simple analysis has shown that the selenate contains 28·92 per cent. of oxygen and 35·79 per cent. of selenium. Hence for every 64 parts of oxygen (4 atoms) it contains $64 \times \frac{35{\cdot}79}{28{\cdot}92} = 79{\cdot}2$ parts of selenium (one atom). Thus the atomic weight of selenium is 79·2.

Silver.—Prior to 1836 the atomic weight of silver was taken as 216, but that of copper as 63. In 1837 J. B. Dumas showed that chalcocite, Cu_2S, and acanthite, then written as AgS, were isomorphous, both being rhombic. If, therefore, the formula for chalcocite is correct, that for acanthite should be Ag_2S, the atomic weight of silver falling to 108.

Zirconium.—For many years zirconium was regarded as trivalent (p. 132), but the determination of the vapour density of its chloride in 1857 suggested its tetravalency. This was confirmed by Cleve, who showed that the following salts are isomorphous: K_2SnF_6, K_2SiF_6 and K_2ZrF_6. Zirconium, therefore, must be tetravalent like tin and silicon.

Vanadium.—Berzelius assumed in 1831 that vanadium, like sulphur, yielded an oxide VO_3, its atomic weight being approximately 6 × 10·2 or 61. In 1868 Roscoe pointed out that the following minerals had been shown by Rammelsberg (1856) to be isomorphous, but were not at that time represented by analogous formulæ:

Vanadinite,	$3Pb_3(VO_3)_2.PbCl_2$,
Mimetite,	$3Pb_3(AsO_4)_2.PbCl_2$,
Pyromorphite,	$3Pb_3(PO_4)_2.PbCl_2$.

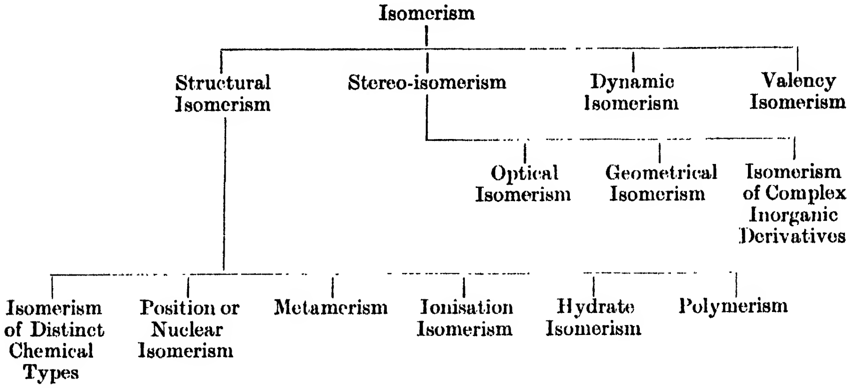
According to Mitscherlich's Law, the formula for vanadinite should be similar to those of the other minerals. The formula for vanadic anhydride should thus be V_2O_5, corresponding to As_2O_5 and P_2O_5, and not VO_3. Roscoe was able to show that such was definitely the case, and that the substance regarded by Berzelius as vanadium was in fact an oxide, VO. The formula for vanadinite thus becomes $3Pb_3(VO_4)_2.PbCl_2$ and the atomic weight of vanadium 5 × 10·2 or 51 (approx.).

Beryllium.—The difficulty of deciding whether beryllium is divalent or trivalent is referred to on p. 332. Mendeléeff assumed it to be divalent, as he could then find a suitable place for it in his Periodic Table. This was subsequently confirmed by a determination of the specific heat, and further confirmation was afforded when, in 1887, Mallard observed that crystallised beryllia is isomorphous with crystallised zinc oxide, ZnO, and must, therefore, have a similar structure.

An interesting illustration of the application of crystallographic data to determine the constitution of a mineral is afforded by **ilmenite,** or titanic iron ore. The mineral takes its name from the Ilmen Mountains. The formula may be written as $Fe_2O_3.Ti_2O_3$ or as $FeO.TiO_2$, and on account of the difficulty of determining the state of oxidation of the titanium it is not easy to decide, from chemical considerations alone, which formula is correct, although the balance of chemical evidence appears to favour the ferrous titanite formula, $FeO.TiO_2$. The mineral crystallises, however, in the trigonal system like hæmatite, Fe_2O_3, and artificial titanium sesquioxide, Ti_2O_3. But its axial ratio in no case lies between that of hæmatite, $c = 1·359$, and titanium sesquioxide, $c = 1·316$, as it might be expected to do if it were an isomorphous mixture of Fe_2O_3 and Ti_2O_3. This lends strong support to the view that the mineral is ferrous titanite, $FeTiO_3$.

ISOMERISM.

When two or more substances possess the same empirical composition, but differ in their physical and, usually, in their chemical properties, they are said to be **isomeric** (Greek *isos* equal, *meros* part). The substances themselves are called **isomerides** or simply **isomers.** Several different kinds of isomerism are known, and the following classification is usual :



Structural Isomerism of Distinct Chemical Types.—This occurs widely in the fields of both inorganic and organic chemistry. The first case to be recognised amongst inorganic substances was that of silver cyanate and silver fulminate (Liebig, 1823). The constitution of these salts is as follows :

$$\mathrm{C{=}N{-}O{-}Ag} \qquad\qquad \mathrm{Ag{-}N{=}C{=}O}$$

Silver fulminate.

Silver cyanate (*iso*-formula).

In the one case the silver is attached to oxygen, in the other to nitrogen direct.

A better known case is that of ammonium cyanate and urea. In 1828 Wöhler announced that merely on evaporating an aqueous solution of ammonium cyanate to dryness on the water bath, urea is produced (p. 27). This was an epoch-making discovery, for it showed that organic substances could be synthesised in the laboratory without the aid of a vital force such as had hitherto been postulated. Wöhler himself realised the great importance of his discovery and delayed publication for three years.

Organic isomerides are very numerous. Well-known examples are the aliphatic alcohols and the corresponding ethers. Thus

$$\mathrm{CH_3.CH_2.OH} \qquad\qquad \mathrm{CH_3.O.CH_3}$$

Ethyl alcohol, B.pt. 78·5° C.

Dimethyl ether, B.pt. $-$24·9° C.

Both physically and chemically these substances are widely different from each other, each behaving as a typical member of its own series.

Isomerism of this structural kind occurs in many complex metallic derivatives, as, for example, the cobaltammines. If aquopentammino-cobaltic chloride is treated with nitrous acid, a red, unstable nitrito-derivative is obtained which, on standing, changes to the brown, stable nitro-salt. Thus

$$[Co(NH_3)_5.H_2O]Cl_3 + HNO_2 \longrightarrow \underset{\text{Red, unstable.}}{[Co(NH_3)_5(ONO)]Cl_2} + HCl$$

$$\downarrow$$

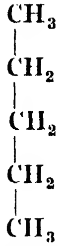
$$\underset{\text{Brown, stable.}}{[Co(NH_3)_5NO_2]Cl_2}$$

The nitrito-salts are easily decomposed by dilute acids; those containing the nitro-group, on the other hand, are stable towards acids.

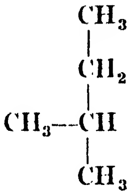
Position or Nuclear Isomerism.—Examples of this are afforded by

$$\underset{\substack{\alpha\text{-Chloropropane,}\\ \text{B.pt. } 44^\circ \text{ C.}}}{CH_3.CH_2.CH_2Cl} \quad \text{and} \quad \underset{\substack{\beta\text{-Chloropropane,}\\ \text{B.pt. } 36{\cdot}5^\circ \text{ C.}}}{CH_3.CHCl.CH_3}$$

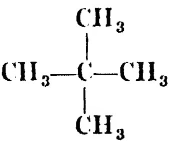
in which the positions of the two chlorine atoms in the hydrocarbon molecule are different. Other well-known examples are



n-Pentane,
B.pt. 36·2° C.



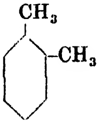
Dimethyl-
ethyl methane,
B.pt. 27·95° C.



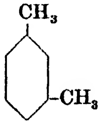
Tetramethyl
methane,
B.pt. 9·5° C.

These are somewhat similar in their general physical properties, but in their chemical reactions they exhibit certain marked divergences.

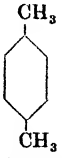
Amongst ring compounds isomerism is very prevalent. Consider, for example, the xylenes:



o-Xylene,
M.pt. − 27·1° C.
B.pt. 142·6° C.



m-Xylene,
M.pt. − 53·6° C.
B.pt. 139·8° C.



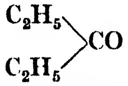
p-Xylene,
M.pt. + 13·2° C.
B.pt. 138° C.

These substances exhibit parallel properties with great uniformity. All three may be synthesised from the corresponding bromotoluenes; thus, using Fittig's reaction:

$$CH_3.C_6H_4Br + CH_3I + 2Na \longrightarrow CH_3.C_6H_4.CH_3 + NaBr + NaI.$$

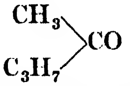
Oxidation converts them stepwise into the corresponding *o*-, *m*- and *p*-toluic acids and then into the *o*-, *iso*- and tere-phthalic acids respectively. Analogies of this kind are very usual amongst ring-compound isomerides.

Metamerism.—This term (Greek *meta* a change, *meros* part) was introduced by Berzelius to designate the metamorphosis of one isomer into the other, as for example the conversion of ammonium cyanate into urea. The term is not used now in that sense. At the present time the term metamer is employed to denote those isomers which consist of radicals attached to the same polyvalent element or group. As examples we have diethyl ketone and methylpropyl ketone :



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle CO$$

Diethyl ketone,
B.pt. 101·7° C.

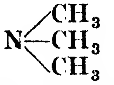


$$\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\rangle CO$$

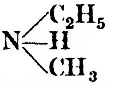
Methylpropyl ketone,
B.pt. 101·7° C.

These two ketones are very much alike physically and have the same boiling point. Chemically they behave as typical ketones and yield analogous reaction products.

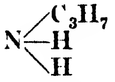
Other well-known examples are afforded by the alkylamines. Thus



Trimethylamine,
B.pt. 3·5° C.

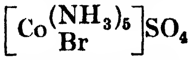


Ethylmethylamine,
..



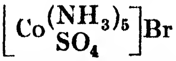
Propylamine,
B.pt. 49° C.

Ionisation Isomerism.—A variety of structural isomerism known as ionisation isomerism is very common amongst the metal-ammines. If two or more different acid radicals are present in a molecule of a metal-ammine, that is a metallic salt containing one or more NH_3 groups in its molecule, it was suggested by Werner that the acid radicals may be firmly fixed in what is known as the inner, undissociable zone, constituting the *co-ordination complex*, and thus closely attached to the central metal atom, as shown within the square brackets below, in accordance with Werner's notation, or they may be outside this complex and in the outer or dissociable zone. In this latter case they are easily ionised and easily liberated by other acids, whereas those within the brackets are not ionised and are difficult to liberate by means of other acids. This distribution of the acid radicals gives rise to isomerism. For example, two varieties of the compound represented by the empirical formula $Co(NH_3)_5Br(SO_4)$ are known, one of which is violet and the other red. In aqueous solution the violet modification gives SO_4-ions, which may be precipitated with barium chloride. The red variety yields no sulphate ions in aqueous solution and barium sulphate is not precipitated on addition of the chloride. The two isomerides thus have the following structures :



$$\left[Co\begin{matrix}(NH_3)_5\\Br\end{matrix}\right]SO_4$$

and



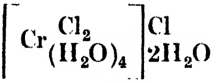
$$\left[Co\begin{matrix}(NH_3)_5\\SO_4\end{matrix}\right]Br$$

Bromo-pentammino-cobaltic sulphate.

Sulphato-pentammino-cobaltic bromide.

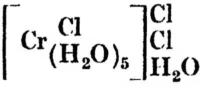
Similarly, chloro-pentaquo-chromic sulphate, $[Cr(H_2O)_5Cl]SO_4$, is isomeric with sulphato-pentaquo-chromic chloride, $[Cr(H_2O)_5SO_4]Cl$.

Hydrate Isomerism.—As its name implies, hydrate isomerism depends on the position of water in complex molecules. An example is afforded by the hexahydrate of chromic chloride, $CrCl_3.6H_2O$. This occurs in three forms, to which the following structures are assigned, in accordance with Werner's theory :



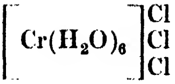
$$\left[Cr\begin{matrix}Cl_2\\(H_2O)_4\end{matrix}\right]\begin{matrix}Cl\\2H_2O\end{matrix}$$

Dark green,
Dichlor-tetraquo-
chromic chloride.



$$\left[Cr\begin{matrix}Cl\\(H_2O)_5\end{matrix}\right]\begin{matrix}Cl\\Cl\\H_2O\end{matrix}$$

Light green,
Monochlor-pent-
aquo-chromic
chloride.



$$\left[Cr(H_2O)_6\right]\begin{matrix}Cl\\Cl\\Cl\end{matrix}$$

Violet,
Hexaquo-chromic
chloride.

The *dark green* salt crystallises in the rhombic system. In dry air it readily loses two molecules of water from the outer zone, in other words, the so-called " water of crystallisation," yielding the tetrahydrate, $[CrCl_2(H_2O)_4]Cl$, which contains all its water within the undissociable zone, that is to say as water of constitution. From solution only one atom of chlorine is precipitable with silver nitrate.

In dilute solution the dark green hexahydrate changes rapidly to the *light green* salt, which can be isolated. Two-thirds of the chlorine of this salt are precipitable from aqueous solution with silver nitrate, and five molecules of water are contained within the inner zone as water of constitution; the sixth molecule of water is loosely combined as water of crystallisation and is removed by exposing the salt over concentrated sulphuric acid.

The light green salt gradually changes in solution to the *violet* salt, which can be crystallised out. The crystals, which are monoclinic, do not lose water when exposed over sulphuric acid, all the water being firmly fixed within the inner zone as water of constitution. In aqueous solution all three atoms of chlorine are precipitable with silver nitrate.

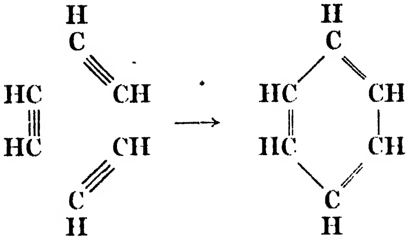
Polymerism.—Many unsaturated compounds exhibit a strong tendency to unite with themselves to form a more complex and more fully saturated substance. The product is called a **polymer** of the original substance.

Numerous examples of polymerisation are afforded by the lower members of the homologous series of fatty aldehydes and thioaldehydes. Let us, for instance, consider the case of acetaldehyde, CH_3CHO. It is a mobile liquid of characteristic odour, boiling at 20° C. When a few drops of concentrated sulphuric acid are added to the aldehyde at the ordinary temperature, heat is evolved, and the liquid rapidly changes, with contraction in volume, into the polymer **paraldehyde,** $(C_2H_4O)_3$. This is a colourless liquid, boiling at 124° C. Its vapour density corresponds to the formula given, and the depression of the freezing point of phenol by its addition (p. 404) leads to the same conclusion. Many of its properties are quite different from those of acetaldehyde. It is used in medicine as a soporific or sleep-producer. When distilled with dilute sulphuric acid, ordinary aldehyde is generated.

When gaseous hydrogen chloride is passed into acetaldehyde, a white crystalline solid is obtained called **metaldehyde,** the formula of which, as determined by vapour density and freezing point methods, is also $(C_2H_4O)_3$. It is thus an ordinary isomer of paraldehyde, but a polymer of acetaldehyde. It is insoluble in water, and is used as a solid fuel for spirit lamps under the name of " *meta.*"

In the presence of potassium carbonate solution, two molecules of acetaldehyde unite to form **aldol,** $(C_2H_4O)_2$ or $CH_3.CH(OH).CH_2.CHO$. This is termed the **aldol condensation** and is an example of the polymerisation of the aldehyde which is not reversible.

An interesting example is afforded by acetylene. When passed through a heated tube three molecules of acetylene condense to form one of benzene :



3 Molecules of Acetylene, B.pt. −83·6° C.

Benzene, B.pt. 79·6° C.

As benzene cannot easily be converted back to acetylene, this example of polymerisation differs from that of metaldehyde.

The polymer invariably has the higher boiling point. It should be noted that one substance is not necessarily a polymer of another because its molecule happens to contain an exact multiple of the same atoms. For example, the molecular formula of acetic acid is $C_2H_4O_2$ or $2CH_2O$; that of formaldehyde is CH_2O. But acetic acid is not a polymer of formaldehyde, for the latter cannot be converted into the former *directly*.

Polymerisation occurs also amongst the complex metal-ammines. The best-known example is that of triammino-trinitro-cobalt, $[Co(NH_3)_3(NO_2)_3]$, of which polymers have been prepared containing two, three, four and five such groups. Thus :

$$[Co(NH_3)_3(NO_2)_3]_2 \quad \text{or} \quad [Co(NH_3)_6][Co(NO_2)_6]$$

$$[Co(NH_3)_3(NO_2)_3]_3 \quad \text{or} \quad [Co(NO_2)(NH_3)_5][Co(NO_2)_4(NH_3)_2]_2$$

$$[Co(NH_3)_3(NO_2)_3]_4 \quad \text{or} \quad [Co(NH_3)_6][Co(NO_2)_4(NH_3)_2]_3$$

$$[Co(NH_3)_3(NO_2)_3]_5 \quad \text{or} \quad [Co(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$$

Polymers of chromium compounds of this type are also known. Thus, $[Cr(NH_3)_3(SCN)_3]$, which has been prepared up to pentamolecular form.

Optical Isomerism.—This type of isomerism is beautifully illustrated by lactic acid, $CH_3.CHOH.COOH$, three distinct varieties of which are known, which are alike chemically but differ in certain of their physical properties, notably in their action on polarised light. The nature of this action is explained in a subsequent chapter (see p. 321). Meanwhile it will suffice to state that substances which, either in the liquid state or in solution, are able to rotate the plane of polarisation of light are termed **optically active.** If the analyser must be rotated in a clockwise direction in order to obtain extinction the substance in the polarimeter is said to be **dextro-rotatory** ; if the analyser must be moved in an anticlockwise direction the substance is **lævo-rotatory.**

Turning now to the three lactic acids, we have

(i) *Ordinary lactic acid*, or the *lactic acid of fermentation*, discovered by Scheele in 1780 in sour milk. It melts at 18° C., and is optically inactive.
(ii) *Sarcolactic acid* (Greek *sarx*, flesh), found by Berzelius in 1808 in the juices of the muscles. It melts at 26° C., and is dextro-rotatory.
(iii) *Lævolactic acid* does not occur naturally, but is readily prepared in the laboratory. As its name implies, it is lævo-rotatory.

In order to explain the differences between these three acids, Le Bel and van't Hoff independently in 1874 put forward the same suggestion, namely that the four valencies of a carbon atom do not act in one plane, but at four equidistant points in space around the centre of the carbon atom. This is most easily visualised by picturing the carbon atom as a small sphere at the centre of a tetrahedron at the corners of which the four valencies act. This is shown diagrammatically in fig. 85. If the carbon atom has four different groups attached to it, the molecule thus obtained will possess no symmetry, that is, it cannot be divided into two similar halves, and if held to a mirror the image obtained by reflection is not identical with the original. This is clear from fig. 86, in which A, B, C and D represent four different groups attached to the carbon atom. A molecule of this character is termed **asymmetric.** Chemically two such molecules are identical; physically they are not, the difference being due to their spatial configurations. This type of isomerism is therefore frequently termed **spatial isomerism** or **stereo-isomerism** (Greek *stereos*, solid), and the two active varieties are said to be **enantiomorphous** (Greek *enantios*, opposite).

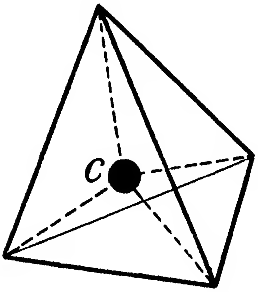


FIG. 85.—Showing Tetrahedral Arrangement of Valencies of Carbon Atom.

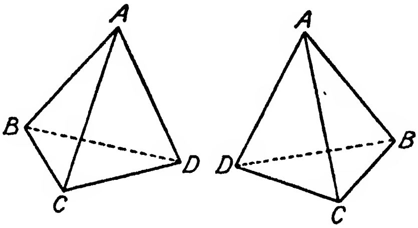
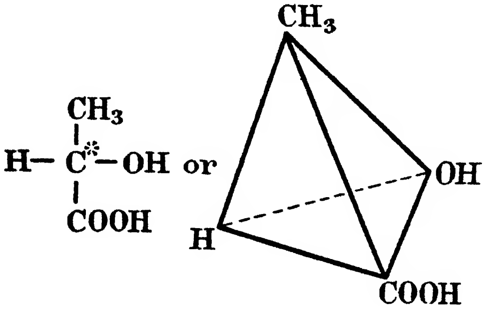


FIG. 86.—Configurations of Enantiomorphous Carbon Compounds.

According to the theory of Le Bel and van't Hoff, therefore, the difference between the dextro- (*d*-) and lævo- (*l*-) lactic acids is merely one of configuration, since, as shown in fig. 87, they possess an asymmetric structure, the one form affecting polarised light to the same extent in one direction as the other form does in the opposite direction.

But what about the natural inactive acid, the product of fermentation? This is a "mixture" of the dextro- and lævo-varieties in equal quantities, the effects of which cancel each other out. Such a mixture is designated as *dl-* and is said to be **externally compensated.** It is sometimes called a **racemic mixture** (p. 201).

Since the two forms are chemically identical, they are produced in equal quantities in ordinary synthetic reactions in the laboratory, and in many natural processes as well, so that an inactive product is produced.



$$\begin{array}{c} CH_3 \\ | \\ H-\overset{*}{C}-OH \\ | \\ COOH \end{array}$$

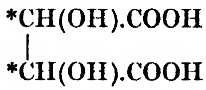
Fig. 87.—Asymmetric Structure of Lactic Acids.

We cannot separate the two forms by such processes as fractional crystallisation (p. 401) or distillation (p. 417), since their solubilities are identical, as also their boiling points. Their ordinary metallic salts also possess identical solubilities, for they, too, are optical isomers, and therefore cannot be separated by fractional crystallisation. If, however, we neutralise a *dl*-mixture of lactic acid with an optically active base, such as strychnine, which is lævo-rotatory, two different kinds of molecules are produced, namely :

d-lactic acid, *l*-strychnine,
l-lactic acid, *l*-strychnine.

These two derivatives are no longer optical isomers, and may therefore be expected to differ in their solubilities. By fractionation (see p. 401) pure specimens of both compounds can be obtained, and from these the free dextro- and lævo-acids can easily be liberated (Purdie and Walker, 1892).

A somewhat more involved example of optical isomerism is afforded by tartaric acid, which has, as its formula shows, two asymmetric carbon atoms, distinguished below by asterisks :



$$\begin{array}{l} {}^*CH(OH).COOH \\ \;| \\ {}^*CH(OH).COOH \end{array}$$

Each of the asymmetric carbon atoms has the same four groups attached to it, and each may therefore be expected to affect the rotation of light to the same quantitative extent. Four varieties of tartaric acid are therefore possible, and four are known, namely :

(i) *Ordinary* or *dextro-tartaric acid.* This form yields large monoclinic crystals melting at 168° to 170° C. It was first recognised by Scheele in 1769 and occurs as the acid potassium salt in the juice of grapes. Biot in 1838 was the first to show that its solution is dextro-rotatory. Since both of the asymmetric carbon atoms are equally active, both must be dextro-rotatory.

(ii) *Lævo-tartaric acid* is identical chemically with the dextro-acid, and has the same melting point, but its solutions are lævo-rotatory to exactly the same quantitative extent as those of the previous acid are dextro-rotatory. Both of the asymmetric carbon atoms are equally active and both must therefore be lævo-rotatory.

The salts of the two foregoing acids are usually isomorphous. Examination of the disodium diammonium salts, $Na_2(NH_4)_2(C_4H_4O_6)_2.2H_2O$, shows that they are not quite identical, however, although nearly so. The crystals of the corresponding acids and salts are related to one another as an object is to its image in a plane mirror—its *mirror image* (fig. 88). This was first noted by Pasteur in 1848.

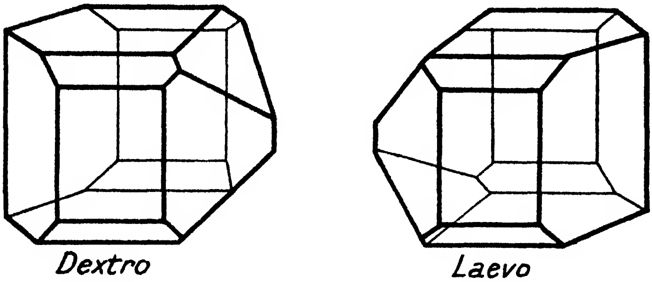
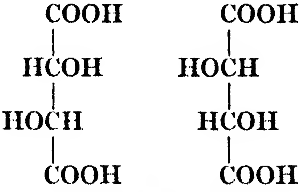


FIG. 88.

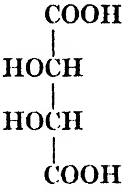
(iii) *Meso-tartaric acid* (Greek *mesos*, middle) is optically inactive and results when the dextro-acid is refluxed for several hours with a solution of sodium hydroxide. It melts at 143° C. The reason this acid is inactive is that its molecule contains one dextro-rotatory asymmetric carbon atom, and one lævo-rotatory carbon atom, so that these atoms neutralise each other. The acid is therefore said to be **internally compensated.**

The three foregoing varieties of tartaric acid may therefore be represented as follows :



$$\begin{array}{c}COOH\\|\\HCOH\\|\\HOCH\\|\\COOH\end{array}\qquad\begin{array}{c}COOH\\|\\HOCH\\|\\HCOH\\|\\COOH\end{array}$$

The two active acids.



$$\begin{array}{c}COOH\\|\\HOCH\\|\\HOCH\\|\\COOH\end{array}$$

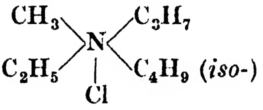
Meso-tartaric acid.

(iv) *Racemic* or *Para-tartaric acid* is the form which results by synthesis in the laboratory. It melts at 204° C., and is optically inactive. It differs fundamentally from meso-tartaric acid in that it is a " mixture " of equal quantities of the dextro- and lævo-acids ; it is not, therefore, internally compensated ; like inactive lactic acid it is externally compensated. It can be resolved into its dextro- and lævo-components by converting into the sodium ammonium salt, crystallising and separating the crystals by hand. More usually it is resolved by combining with an optically active base and fractionally crystallising, as explained in the case of lactic acid (p. 200). Cinchonine may be used, in which case the lævo-tartrate is the first to separate, being less soluble.

Resolution may also be effected by **biological methods** based on the observation of Pasteur in 1860 that a solution of ammonium racemate or para-tartrate containing a little alkali phosphate becomes lævo-rotatory if a green mould, *penicillium glaucum*, is allowed to grow in it. The organism exhibits **selective assimilation** and destroys the dextro-acid in preference to the lævo-acid. Many other organisms have been studied in this way, and the method has been applied to a considerable variety of substances including acids, alcohols and sugars. It is particularly useful for determining whether or not an inactive substance is capable of resolution. Only one of the isomers, however, can be obtained in this way with any one mould, so that theoretically half of the material is lost. In practice the loss is even greater. Furthermore, the products of fermentation may be numerous and render the subsequent purification of the material a matter of some difficulty.

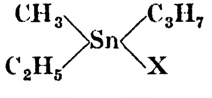
The carbon atom is not the only one that can exhibit optical activity. According to the theory of Le Bel and van't Hoff all molecules containing an asymmetric atom of any polyvalent element should be capable of existing in two chemically identical forms, both of which are active, one possessing dextro-rotatory power and the other lævo-rotatory power of the same extent. Experiment bears this out.

In 1891 Le Bel succeeded in resolving methyl ethyl propyl *iso*butyl ammonium chloride into its active isomers. In this case the asymmetric arrangement occurs around the nitrogen atom. Thus

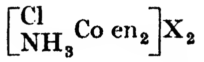


The nitrogen is pentavalent. No compounds of trivalent nitrogen of the type $NR_1R_2R_3$ have as yet been resolved.

The central atom need not be a non-metal. In 1900 Pope and Peachey succeeded in resolving compounds of metallic tin of the type

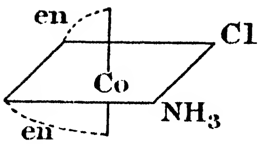


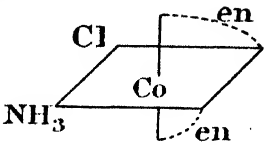
where X represents a halide; whilst Werner and his co-workers isolated many series of active derivatives containing chromium, iron, cobalt, etc., as the central atom. Consider, for example, the complex salt



$$\left[\begin{matrix}Cl\\ NH_3\end{matrix}\,Co\,en_2\right]X_2$$

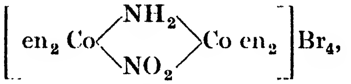
"en" here represents ethylenediamine, $\begin{array}{l}CH_2.NH_2\\ |\\ CH_2.NH_2\end{array}$. The portion within the square brackets constitutes the undissociable zone, and may be grouped spatially round the cobalt atom as follows :





These clearly are related as mirror images, and experiment shows that the two optically active varieties exist.

In many of the polynuclear compounds optical activity exists also. For example tetraethylenediamino-μ-amino-nitro-dicobaltic bromide,



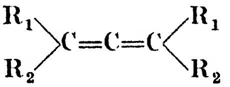
$$\left[\mathrm{en}_2\,\mathrm{Co}\begin{matrix}\diagup\mathrm{NH}_2\diagdown\\ \diagdown\mathrm{NO}_2\diagup\end{matrix}\mathrm{Co\,en}_2\right]\mathrm{Br}_4,$$

has been obtained in four varieties, namely the dextro-rotatory and lævo-rotatory forms with equal and opposite rotation, the racemic form made up of equal quantities of *d*- and *l*-forms, and a modification which could not be resolved, namely the meso-form, which is inactive through internal compensation. These varieties may be regarded as the cobalt analogues of the tartaric acids.

In the following list are given the elements of which optically active derivatives have been prepared, arranged in the order of the vertical groups of the Periodic Table (Frontispiece):

Group	I.	Cu.
,,	II.	Be, Zn.
,,	III.	B.
,,	IV.	C, Si, Sn.
,,	V.	N, P, As.
,,	VI.	S, Se, Cr.
,,	VII.	None.
,,	VIII.	Fe, Co, Ru, Rh, Ir, Pt.

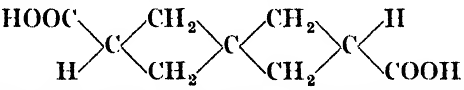
Optically active compounds are known containing no asymmetric atoms. van't Hoff predicted this for certain possible derivatives of allene, such as



$$\begin{matrix}\mathrm{R}_1\diagdown\\ \mathrm{R}_2\diagup\end{matrix}\mathrm{C{=}C{=}C}\begin{matrix}\diagup\mathrm{R}_1\\ \diagdown\mathrm{R}_2\end{matrix}$$

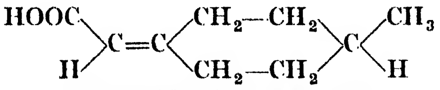
which can yield isomers related as object to mirror image, as shown in fig. 89.

Compounds corresponding to the above formula have not been prepared, but derivatives related in structure have been resolved into optical isomers. Examples are afforded by



*cyclo*Butane-*spiro*-cyclobutane-1 : 1′-dicarboxylic acid
(Backer and Schurink, 1928)

and



Methyl*cyclo*hexylidene-acetic acid
(Perkin and Pope, 1906).

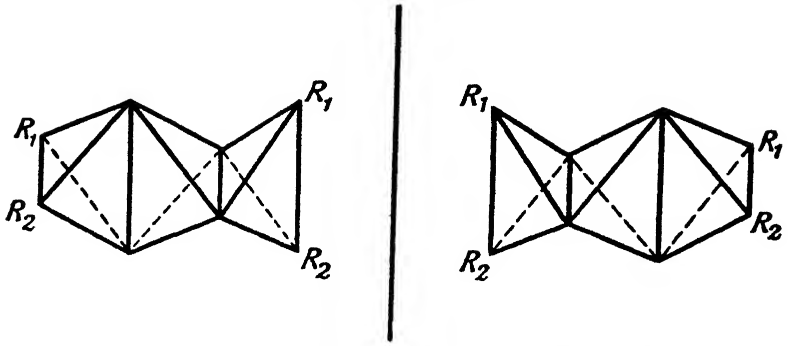
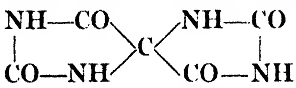


FIG. 89.—Showing Optical Activity of Allene Derivatives.

Another example of a somewhat different type is

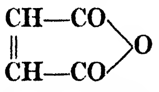


Spiro-5 : 5′-Dihydantoin
(Pope and Whitworth, 1930).

Thus, in order that a molecule shall be asymmetric and, consequently, show optical activity towards polarised light, *it is necessary and sufficient that the spatial configuration shall not be superimposable on its mirror image.*

Geometrical Isomerism is a second type of spatial or stereoisomerism. It occurs in certain cases where double bonds are present in the molecule, but cannot be explained as due to lack of symmetry. It can also occur in certain types of cyclic compounds.

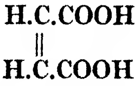
The earliest examples were afforded by maleic and fumaric acids, which have the general formula $(CH.COOH)_2$. These two acids are interconvertible. The former melts at 130° C., and, when heated above its melting point, yields the anhydride



Maleic anhydride.

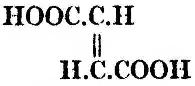
When heated to 200° C. in a sealed tube maleic acid is converted to fumaric acid, which sublimes, without melting. Both acids yield succinic acid upon reduction. Fumaric acid occurs in the common fumitory *fumaria officinalis*, whence its name.

The fact that maleic acid gives the anhydride on heating is taken as indicating that the two carboxyl groups are near together in the molecule. Fumaric acid yields the same anhydride, but less readily. For this and for other reasons the two carboxyl groups in the fumaric acid molecule are regarded as being separated as widely as possible. The two acids are represented therefore as follows :



$$\begin{array}{c}H.C.COOH\\ \|\\ H.C.COOH\end{array}$$

Maleic acid.

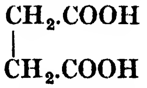


$$\begin{array}{c}HOOC.C.H\\ \|\\ H.C.COOH\end{array}$$

Fumaric acid.

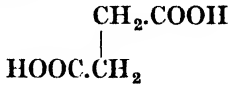
Maleic acid is said to possess the *cis* or *malenoid* structure ; fumaric acid the *trans* or *fumaroid* structure.

The fact that only one form of succinic acid is known, namely



$$\begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array}$$

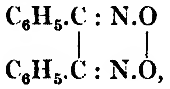
is explained on the assumption that the two middle carbon atoms joined by one bond only are able to rotate freely, so that if at one moment the molecule has the configuration



$$\begin{array}{r} CH_2.COOH \\ | \quad\quad\quad \\ HOOC.CH_2 \quad\quad \end{array}$$

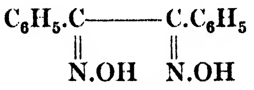
at the next moment the carboxyl groups may have swung round to juxtaposition, and so on. The double bond of the unsaturated acids, however, prevents this free rotation and "freezes" the molecules into their *cis* and *trans* positions respectively.

Geometrical isomerism is shown also by substances containing the C=N group, such as the oximes. Goldschmidt in 1883 discovered the first example of this when he found a second or β-benzil dioxime, structurally identical with the one already known, which then became designated as the α-compound. In 1889 Victor Meyer and Auwers discovered yet a third form, namely the γ-dioxime. All three have the same molecular weight. On reduction they yield dibenzyl, on oxidation a dioxide,



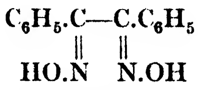
$$\begin{array}{l} C_6H_5.C : N.O \\ \quad\quad\quad | \quad\quad | \\ C_6H_5.C : N.O, \end{array}$$

whilst hydrochloric acid decomposes them into the original benzil and hydroxylamine. They are supposed to have the following configurations :



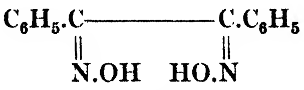
$$\begin{array}{ccc} C_6H_5.C & \text{———} & C.C_6H_5 \\ \| & & \| \\ N.OH & & N.OH \end{array}$$

α- or *amphi*-Form,
M.pt. 237° C.



$$\begin{array}{ccc} C_6H_5.C & — & C.C_6H_5 \\ \| & & \| \\ HO.N & & N.OH \end{array}$$

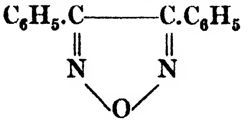
β- or *anti*-Form,
M.pt. 206° to 207° C.



$$\begin{array}{ccc} C_6H_5.C & \text{—————} & C.C_6H_5 \\ \| & & \| \\ N.OH & & HO.N \end{array}$$

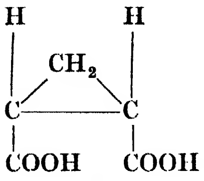
γ- or *syn*-Form,
M.pt. 164° to 166° C.

These configurations have been arrived at as follows. The γ-isomer can be converted readily into the anhydride, phenyl furazan,

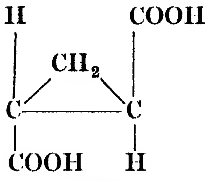


It is therefore presumed that the two hydroxyl groups lie in close proximity, as indicated. The β-isomer appears to be the most stable of the three, and may be obtained by heating the α-isomer with alcohol in a sealed tube to 170° C. It is therefore given the *anti*-configuration. This leaves the *amphi*-arrangement for the α-isomer.

As an example of cyclic compounds not containing a double bond but showing geometrical isomerism, 1 : 2-*cyclo*propanedicarboxylic acid may be mentioned, the *cis-* and *trans*-forms of which are known, and may be represented as follows :



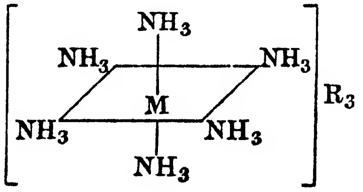
cis-



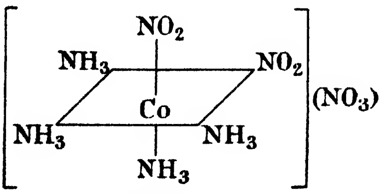
trans-

Geometrical Isomerism of Complex Inorganic Derivatives.—Reference has already been made to Werner's method of representing the constitution of complex salts (p. 196), and in a subsequent chapter (see Vol. II) Werner's general theory of valency is discussed in greater detail. It will suffice at this stage to mention that in very many cases the number of ammonia, water and monovalent acid radicals within the inner, undissociable zone, or constituting what is called the "Co-ordination Complex," is six. The *co-ordination number* is thus said to be six.

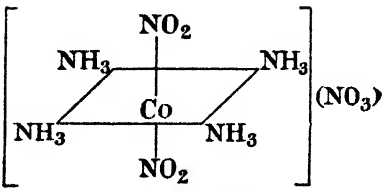
Werner assumed such compounds to possess a spatial configuration, the six co-ordination groups being arranged around the central metallic atom in such a manner that they occupy the corners of an imaginary octahedron. That is, to the compounds of general formula $[M(NH_3)_6]R_3$ is given the configuration



Such a configuration should on replacement of one ammonia molecule by an acidic or other monovalent radical yield only one compound, and this proves to be the case. On the other hand, if two acidic or other groups replace two ammonia groups in the complex, isomerism should be possible, yielding two isomers of the formula $[M(NH_3)_4R_2]R$. In the case of dinitro-tetrammino-cobaltic nitrate, $[Co(NH_3)_4(NO_2)_2]NO_3$, two isomeric forms are known to exist, one brown in colour, the other yellow. The two substances may be represented by the following formulæ :

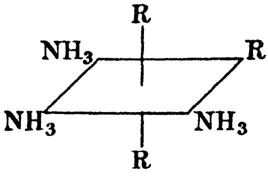


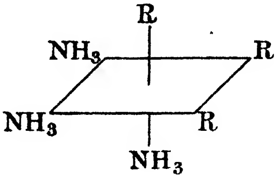
1 : 2-Dinitro-, or *cis*-salt
(Brown variety).



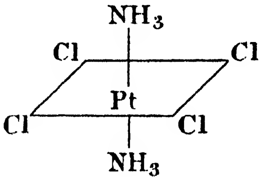
1 : 6-Dinitro-, or *trans*-salt
(Yellow variety).

When three ammonia groups are substituted by acidic groups triacido-triammino-metallic salts are obtained, for which two isomers are theoretically possible, and this is again proved by experimental evidence. The configurations of the complexes are represented thus :

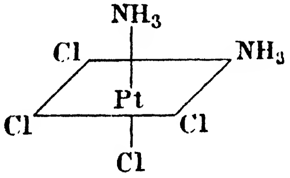




The two isomeric tetrachloro-diammino-platinum salts also belong to this class of isomerism, the configurations being



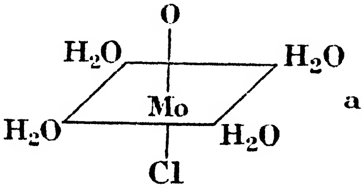
Tetrachloro-*trans*-diammino-platinum.



Tetrachloro-*cis*-diammino-platinum.

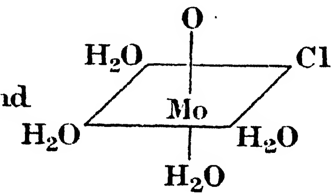
The *trans*-salt crystallises as lemon-yellow octahedra, the *cis*-salt as small orange-yellow plates. These are not electrolytes, all the acidic groups being within the complex.

Molybdenum oxychloride, MoOCl, affords an interesting example of isomerism (Wardlaw and Wormell, 1924). Electrolysis of a solution of molybdenum trioxide in diluted hydrochloric acid yields, under suitable conditions, two hydrated oxychlorides of empirical formula $MoOCl.4H_2O$, neither of which is ionised in solution. One of the isomers is brown, the other green. Two isomers are theoretically possible, namely



trans-Salt
(Green)

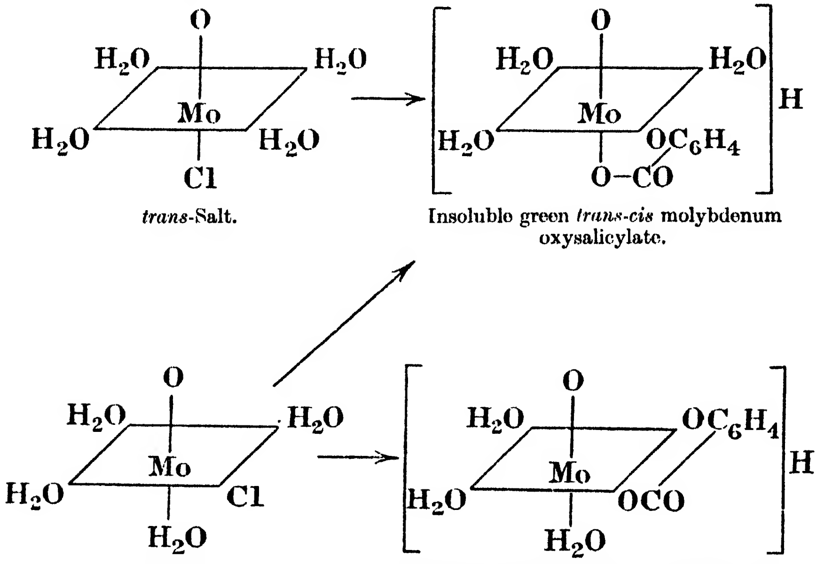
and



cis-Salt
(Brown)

and these structures have been assigned to the salts as indicated.

The student may wonder how it is ascertained which isomer corresponds to any particular configuration. One illustration will suffice. Let us take the two molybdenum oxychlorides as our example. They react with sodium salicylate as follows : the green isomer gives one derivative only, the brown isomer gives the same derivative and another in addition. Consideration of the two possible isomerides of the oxychloride shows that the *trans*-salt can yield only one derivative, whereas the *cis*-salt can yield two ; thus



trans-Salt.

Insoluble green *trans-cis* molybdenum oxysalicylate.

cis-Salt.

Soluble *cis-cis* molybdenum oxysalicylate.

Dynamic Isomerism.—Just as two allotropic modifications of an element in the liquid form can be in equilibrium at various temperatures, as witness S_λ and S_μ (p. 181), so two modifications of a compound can often exist together. This is known as dynamic isomerism or **tautomerism** (Greek *tauto* same, *meros* part), this latter name being due to Laar. Various other names have been applied, such as *pseudomerism*, *desmotropism* (Greek *desmos* a bond, *trepein* to change), *mesotropism* and *tropomerism* ; these are only mentioned here since the student may come across them in reading earlier literature.

One of the best-known examples is ethyl acetoacetate, which gives many reactions suggesting that it contains a ketonic group, thus

$$CH_3.CO.CH_2.COOC_2H_5$$

(Frankland's formula).

Thus, like a ketone, it unites with hydroxylamine and with phenylhydrazine, and it yields a secondary alcoholic group on reduction, being converted into

$$CH_3.CHOH.CH_2.COOC_2H_5$$

β-Hydroxybutyric ester.

On the other hand, it seems equally clear for many reasons that the sodium derivative is represented by

$$CH_3.C(ONa) : CH.COOC_2H_5$$

which suggests that ethyl acetoacetate itself possesses the structure of an unsaturated hydroxy compound, namely β-hydroxycrotonic ester ;

$$CH_3.C(OH^*) : CH.COOC_2H_5$$

(Geuther's formula).

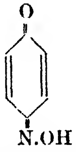
This is explained on the assumption that the hydrogen atom marked with an asterisk is *labile*, that is, it can pass from the oxygen in the unsaturated or *enolic* form to the adjacent carbon atom, converting the hydroxyl group into ketonic oxygen and thus removing unsaturation. When occasion serves, it can pass back again. Ordinarily, the liquid consists of a mixture of these two isomerides in dynamic equilibrium, which means that the rate of formation of the enolic form from the ketonic form equals the rate of the reverse change. By cooling ethyl acetoacetate to −80° C. the substance has been obtained in almost pure solid crystalline ketonic form, however.

Many other examples are known, such as succino-succinic ester, acetyl acetone, phloroglucinol and dihydroresorcinol, all of which function as ketones and also as enolic derivatives.

Another variety of dynamic isomerism is afforded by the compound obtained both by the action of nitrous acid on phenol and by hydroxylamine on quinone. The product may be represented as

Nitrosophenol

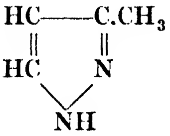
or



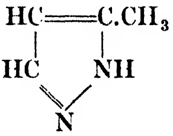
Quinone oxime

and behaves as though it could possess both structures. Nitromethane (p. 226) is closely similar.

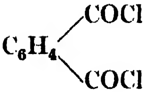
Neither oxygen nor hydrogen is essential to the occurrence of dynamic isomerism. Methyl pyrazole contains no oxygen, but must be represented by two formulæ, namely :



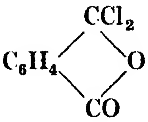
and



Phthalyl chloride (see p. 277) contains no labile hydrogen, but is tautomeric :

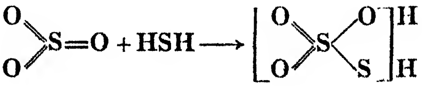


and

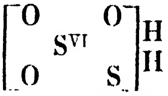


The foregoing examples will suffice.

Valency Isomerism.—An interesting example is afforded by thiosulphuric acid, $H_2S_2O_3$. By allowing sulphur trioxide and hydrogen sulphide to react in carbon dioxide solution at very low temperatures, Piccard and Thomas in 1923 obtained a product which they regard as true thiosulphuric acid. Thus :

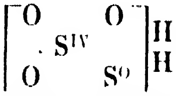


The central sulphur atom thus has a valency of six, and the molecule represents a mixed anhydride of sulphuric acid and hydrogen sulphide. Ordinary thiosulphuric acid is regarded as a valency isomer of this, the central atom being tetravalent, the second sulphur being neutral, and constituting part of the co-ordination complex in a similar manner to the NH_3 groups in the metal-ammines (p. 206). The full significance of this difference will be appreciated at a later stage, when modern views on the nature of valency have been studied (Vol. II). It is sufficient for present purposes to note that the two sulphur atoms are attached in a different manner to each other in the different molecules. This is represented as follows :



$$\left[\begin{array}{ccc} O & & O \\ & S^{VI} & \\ O & & S \end{array}\right]\begin{array}{c} H \\ H \end{array}$$

" True " thiosulphuric acid.



$$\left[\begin{array}{ccc} O & & O \\ & S^{IV} & \\ O & & S^{0} \end{array}\right]\begin{array}{c} H \\ H \end{array}$$

Ordinary thiosulphuric acid.

CHAPTER XII.

SPECIFIC HEATS OF ELEMENTS AND COMPOUNDS.

Units.—The amount of heat required to raise the temperature of a substance through one degree on some fixed scale, usually the centigrade scale, is termed the **heat capacity** of that substance. If the absorption of Q units of heat raises the temperature from $t_1°$ to $t_2°$, the mean heat capacity is given by the expression

$$\frac{Q}{t_2 - t_1}.$$

The **specific heat,** c, of a substance is the heat capacity of unit mass, that is, the amount of heat required to raise the temperature of one gramme of the substance through one degree centigrade. When the "true" specific heat of a substance at $t°$ is referred to, it is understood to mean the heat absorbed by one gramme between $(t - 0{\cdot}5)°$ and $(t + 0{\cdot}5)°$. This is an important point, since the specific heat of a substance usually changes with the temperature.

If Q is the heat absorbed by m grammes of a substance for a finite rise in temperature from t_1 to t_2, it is clear that

$$Q = m\int_{t_1}^{t_2} c\,dt \quad . \quad . \quad . \quad . \quad (1)$$

We cannot integrate this unless we know in what manner c varies with t, but we can put

$$Q = mc_m(t_2 - t_1)$$

where c_m is the mean specific heat between the two temperatures chosen. This expression serves to define the term "mean specific heat" over the specified range, since

$$c_m = \frac{Q}{m(t_2 - t_1)}$$
$$= \frac{1}{t_2 - t_1}\int_{t_1}^{t_2} c\,dt \quad . \quad . \quad . \quad . \quad (2)$$

We may represent this diagrammatically as shown in fig. 90. Curve AB shows how the value of c changes with t. The heat absorbed, namely Q, is represented by the area t_1ABt_2. If, now, we project t_1A to C and draw CD parallel to t_1t_2, the height of C being such that

$$\text{area } t_1ABt_2 = \text{area } t_1CDt_2,$$

then the ordinate $t_1C = t_2D = c_m$, the mean specific heat.

The **atomic heat** of an element is the product of its atomic weight and specific heat. Similarly the **molecular heat** of a substance, elementary or compound, is the product of its molecular weight and specific heat.

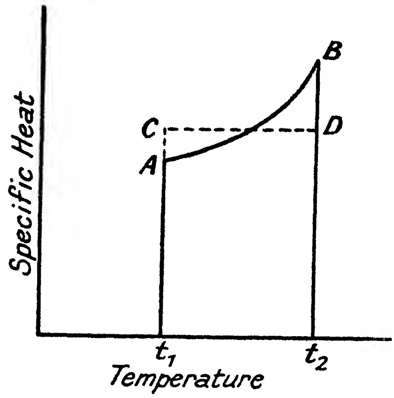


FIG. 90 (see p. 211).

The c.g.s. **unit of heat,** in terms of which specific heats are expressed, is the **gramme-calorie,** usually referred to simply as the **calorie,** which is the quantity of heat required to raise the temperature of one gramme of water through one degree centigrade. Sometimes the calorie at 15° C. is chosen; sometimes that at some other convenient temperature, as, for example, 20° C. in the table on p. 214, whilst at other times the mean value between 0° C. and 100° C. is adopted. These units are not identical, but the variation is small.

What happens to the absorbed heat?

The heat imparted to a substance may be utilised in three ways:

1. In increasing the kinetic energy of translation of the molecules, *i.e.*, in raising the temperature (c_t).
2. In performing work against external pressure consequent upon expansion (c_e).
3. In overcoming the mutual attraction of the molecules (c_i).

Hence

$$c = c_t + c_e + c_i \quad . \quad . \quad . \quad . \quad (3)$$

The quantity c_i depends upon several factors—such as dissociation, the breaking down of associated molecules, the overcoming of cohesive forces during change of state, etc.—the thermal effects of which, being closely connected, are conveniently grouped together.

It is clear that c will remain constant with rise of temperature only when c_e and c_i are very small. In such event

$$c = c_t \text{ (approximately).}$$

For solids and liquids c_e is negligible owing to their comparatively small coefficients of expansion, and

$$c = c_t + c_i.$$

c_i is generally regarded as negligible for elements the molecules of which are monatomic, to wit, most metals and the inert gases of Group 0 of the Periodic Table (Sohncke, 1898). For complex molecules it may be a very varying quantity, and the gradual fall of the specific heat of water until 40° C. is reached, and the subsequent rise in the same as that temperature is exceeded, is probably explained in this way.

Calculation of True Specific Heats.—The manner in which the specific heat varies with the temperature can be determined as follows:

Experiment shows that c varies but slowly with the temperature, and the relation can be expressed with considerable accuracy in the form of a power series :

$$c = \text{constant} + at + \beta t^2 + \gamma t^3, \text{ etc.} \qquad . \qquad . \qquad . \qquad (4)$$

where a, β and γ are constants. For most purposes we may neglect terms of higher orders than squares, so that, writing the initial constant as c_0, our equation becomes

$$c = c_0 + at + \beta t^2.$$

If, therefore, we integrate between the limits $t_1 = 0°$ and $t_2 = t°$:

$$\begin{aligned} \int_0^t c dt &= \int_0^t (c_0 + at + \beta t^2) dt \\ &= c_0 t + \tfrac{1}{2} at^2 + \tfrac{1}{3} \beta t^3 \\ &= c_m t \quad \text{(from equation (3)).} \end{aligned}$$

Whence :

$$c = \frac{d(c_m t)}{dt}. \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

or, in words, the true specific heat over the range 0° to $t°$ may be obtained by multiplying the mean specific heat by t and differentiating with respect to t.

An example will make this clear. For carbon dioxide the mean specific heat at constant pressure is given by the expression

$$c_{mp} = 0{\cdot}2028 + 0{\cdot}0000692t - 0{\cdot}0000000167t^2.$$

Let us determine the true specific heat at 100° C.

Multiplying both sides by t :

$$c_{mp}t = 0{\cdot}2028t + 0{\cdot}0000692t^2 - 0{\cdot}0000000167t^3.$$

Differentiation gives

$$\begin{aligned} c_p &= 0{\cdot}2028 + 0{\cdot}0000692 \times 2t - 0{\cdot}0000000167 \times 3t^2 \\ &= 0{\cdot}2161. \end{aligned}$$

Conversely, if the true specific heat is known, the mean specific heat is obtained by integration over the given temperature range and finally dividing by that range.

SPECIFIC HEATS OF SOLIDS AND LIQUIDS.

Specific Heat of Water.—As water, partly owing to its abundance, and partly also to the ease with which it can be prepared in a pure condition, is the standard substance for the measurement of heat quantities, it is important to determine with the utmost accuracy the variation of its specific heat with temperature. Numerous investigations have been carried out with this object in view, and the results given in the table on p. 214 are very reliable. It will be observed that the specific heats of water at 20° C. and 60° C. are identical. A minimum value occurs at 40° C.

As the gramme-calorie is inconveniently small for some purposes,

Specific Heat of Water.

(Callendar and Barnes, 1902.)

Temperature, °C.	Specific Heat.	Temperature, °C.	Specific Heat.
0	1·0094	40	0·9982
5	1·0054	50	0·9987
10	1·0027	*60*	*1·0000*
15	1·0011	70	1·0016
20	*1·0000*	80	1·0033
25	0·9992	90	1·0053
30	0·9987	100	1·0074

a larger unit, the **Calorie,** is sometimes used ; it is the quantity of heat required to raise one kilogram of water through one degree centigrade, and is thus equal to 1000 " small " or gramme-calories at the same temperature. Occasionally the quantity of heat required to raise one gramme of water from 0° to 100° C. is chosen as the unit. It is equivalent to 100·16 gramme-calories at 20° C. and is referred to as a **Kalorie,** K or Kal. This value divided by 100 is the **mean calorie.** The **zero calorie** (0° to 1° C.) is 1·005 times the 15° calorie.

Several empirical formulæ have been suggested whereby the true specific heat of water at any temperature can be calculated. Callendar suggested

$$\text{Specific heat} = 0{\cdot}98536 + \frac{0{\cdot}504}{t+20} + 0{\cdot}000084t + 0{\cdot}0000009t^2,$$

which satisfactorily represents the true specific heat of water in terms of the gramme-calorie at 20° C. at all temperatures between 0° C. and 100° C. and yields results in close agreement with those in the foregoing table.

The reason why the specific heat of water shows such unusual variation is discussed later (p. 227).

Determination of Specific Heat.—The " method of mixtures," as it is called, is the most usual method of determining the specific heats of solids and liquids. In the case of a solid, a given mass, m, at t° C., is plunged into a calorimeter containing M grammes of water at t_1° C., raising the temperature of the water to t_2° C. The mean specific heat, c_m, of the solid over the range t_2° to t° C. is then given approximately by the expression :

$$c_m = \frac{M(t_2 - t_1)}{m(t - t_2)}.$$

Some heat, however, is absorbed by the calorimeter, the stirrer and the thermometer. If the masses and specific heats of these are known, it is easy to calculate their combined **water value** or **water equivalent,** by which we mean the mass of water that would absorb the same number of calories as these pieces of apparatus do when raised through the same temperature interval. If this is denoted by w grammes, then

$$c_m = \frac{(M + w)(t_2 - t_1)}{m(t - t_2)}.$$

For accurate work great care must be taken to ensure that there shall be no loss of heat during transference of the hot body to the calorimeter, or, in other words, that the whole of the heat evolved by the hot body is received by the calorimeter and its contents.

In the case of liquids which boil at very low temperatures, such as liquid oxygen, the mean specific heat of the liquid between a given temperature and the boiling point is determined by dropping mercury or pieces of metal at the ordinary temperature into a known mass of the liquid contained in a Dewar flask until ebullition takes place. If the temperatures, masses, specific heat of the metal and, in the case of mercury, the latent heat of fusion, are known, all the data are to hand for calculating the specific heat of the liquid. Very high accuracy is not, of course, attainable. An apparatus similar to that shown in fig. 22 (p. 84) was used by Dewar for this purpose.

For solids at low temperatures a copper calorimeter of special design may be used. It consists of a block of copper in which a hole has been bored and which is in intimate contact with a thermocouple. After suitable cooling in liquid air the block is placed in a Dewar flask to prevent absorption of heat from surrounding objects. A known mass of the substance whose specific heat is required is now dropped into the block and the rise in temperature noted. If the original temperature of the substance is known, together with the mean specific heat of the copper over the range concerned, all the data are to hand for calculating the mean specific heat of the substance.

Sometimes a vacuum calorimeter is employed. This may consist of a block of the substance itself; but sometimes a small silver vessel is used in which the substance is placed. The block (or silver vessel) is furnished with an electric heating coil which serves the double purpose of thermometer and supplier of heat, suspended by fine wires inside a glass vessel, and cooled to a low temperature, say, in liquid air. The whole is now evacuated as completely as possible to prevent loss of heat by conduction and convection and the temperature noted by determining the resistance of the coil. An electric current is now passed until the desired temperature is attained. The heat is supplied given by the expression:

$$Q = \frac{A^2 R\theta}{4{\cdot}19}$$

(see p. 83), and the mean specific heat is readily calculable. This method is particularly suitable also for determining true specific heats, since the temperatures may be raised by successive small amounts without dismantling the apparatus.

Specific Heats of Elements.—For the majority of the elements the specific heat rises with the temperature, and over short ranges may be represented with fair accuracy by an empirical formula of the type

$$c = c_0 + at + \beta t^2 \quad . \quad . \quad . \quad . \quad (4)$$

where c_0, a and β are constants for a particular element.

In general, a is small and β very small, as the following data indicate:

Element.	Temperature Range, °C.	$c_0 \times 10^2$.	$a \times 10^5$.	$\beta \times 10^8$.
Platinum	0 to 300	3·05	2·99	5·6
Silver	0 to 907	5·76	0·88	. .
Aluminium	−100 to 650	20·89	16·2	29·4
Mercury	0 to 50	3·33	−0·92	. .
Iron (pure)	0 to 100	10·45	152·0	−617·0

Over those ranges of temperature for which the effect of β is negligibly small, the specific heat

$$c = c_0 + at$$

is a linear function of the temperature.

Between 0° C. and 100° C. the specific heat of most metals is almost constant.

It will be observed that β is negative for mercury, the specific heat falling to a minimum at 140° C. This is unusual. The specific heat of iron shows an abrupt change in the neighbourhood of 700° C., β changing its sign from positive to negative. This is undoubtedly connected with some internal change, such as due to allotropy, in the metal, as other physical properties show variation at about the same temperature (see p. 185). Calcium shows a break in its specific heat at about 400° C., and this is taken to indicate an allotropic change (Eastman, 1924) from Ca_α to Ca_β.

In the accompanying table (p. 217) will be found the mean specific heats and atomic heats of the solid elements (over the temperature intervals given in the second column).

Dulong and Petit's Law.—In 1819 Dulong and Petit drew attention to the fact that the **product of the atomic weight and specific heat** for the majority of the solid elements then known was **constant**—in other words, that the atoms had the same capacity for heat. From the data in the penultimate column of the table opposite the general applicability of Dulong and Petit's Law will be apparent.

Leaving out of consideration those elements which are gaseous at ordinary temperatures, it will be observed that the atomic heats of the elements do not vary greatly from the mean value 6·4. There are, however, a few notable exceptions, namely, boron, carbon, beryllium and silicon. In 1872 Weber showed that the specific heats of carbon (diamond and graphite) and silicon possess abnormally large temperature coefficients, and that at high temperatures the atomic heats of these elements approximate to the mean value found for the other elements, although a sufficiently high temperature was never attained at which the atomic heats actually became 6·4. He also gave data for "boron," but his material was really a boride of aluminium. A few of his results are given in the table at the top of p. 218.

Weber therefore suggested that for the purpose of applying Dulong and Petit's Law the values for the specific heats of the elements should be taken at those temperatures at which they increase most slowly.

Table of Specific and Atomic Heats of the Solid Elements.

Element.	Temperature Interval, °C.	Mean Specific Heat.	Approx. Atomic Weight (1931).	Mean Atomic Heat.	Mean Atomic Heat at 50° Abs. (Dewar, 1913).
Aluminium	16 to 100	0·2122	27·0	5·73	1·12
Antimony	0 to 100	0·0495	121·8	6·03	2·89
Arsenic (cryst.)	21 to 68	0·0830	74·9	6·22	1·94
Barium	−185 to 20	0·0680	137·4	9·34	4·80
Beryllium	0 to 100	0·4246	9·0	3·82	0·125
Bismuth	9 to 102	0·0298	209·0	6·24	4·54
Boron (amorph.)	0 to 100	0·3066	10·8	3·31	0·24
Bromine (solid)	−78 to −20	0·0843	79·9	6·73	3·62
Cadmium	0 to 100	0·0548	112·4	6·16	3·46
Cæsium	0	0·0522	132·8	6·93	6·82
Calcium	0 to 100	0·1490	40·1	5·98	2·86
Carbon (diamond)	11	0·1130	12·0	1·36	0·03
Cerium	0 to 100	0·0450	140·1	6·31	4·64
Chromium	22 to 51	0·1000	52·0	5·20	0·70
Cobalt	15 to 100	0·1030	58·9	6·07	1·22
Copper	15 to 238	0·0951	63·6	6·05	1·56
Gallium (solid)	12 to 23	0·0790	69·7	5·50	. .
Germanium	0 to 100	0·0737	72·6	5·35	. .
Gold	0 to 100	0·0316	197·2	6·23	3·16
Indium	0 to 100	0·0570	114·8	6·54	. .
Iodine (solid)	9 to 98	0·0541	126·9	6·86	4·59
Iridium	0 to 100	0·0323	193·1	6·24	1·92
Iron	20 to 100	0·1190	55·8	6·64	0·98
Lanthanum	0 to 100	0·0449	138·9	6·24	4·60
Lead	18 to 100	0·0310	207·2	6·42	4·96
Lithium	27 to 100	0·9410	6·94	6·53	1·35
Magnesium	18 to 99	0·2460	24·3	5·98	1·74
Manganese	14 to 97	0·1217	54·9	6·68	1·26
Mercury (solid)	−78 to −40	0·0319	200·6	6·40	4·65
Molybdenum	15 to 91	0·0723	96·0	6·94	1·36
Nickel	18 to 100	0·1090	58·7	6·40	1·22
Osmium	18 to 98	0·0311	190·8	5·94	1·49
Palladium	18 to 100	0·0590	106·7	6·30	2·03
Phosphorus (yellow)	13 to 36	0·2020	31·0	6·26	2·40
,, (red)	15 to 98	0·1698	31·0	5·26	1·34
Platinum	0 to 100	0·0323	195·2	6·31	2·63
Potassium	0	0·1728	39·1	6·75	5·01
Rhodium	10 to 97	0·0580	102·9	5·97	1·38
Rubidium	0	0·0802	85·4	6·85	6·05
Ruthenium	0 to 100	0·0611	101·7	6·21	1·11
Selenium (cryst.)	22 to 62	0·0840	79·2	6·65	2·86
Silicon (cryst.)	22	0·1697	28·1	4·77	0·77
Silver	17 to 507	0·0590	107·9	6·46	2·62
Sodium	0	0·2829	23·0	6·51	3·50
Strontium	. .	0·0742	87·63	6·50	. .
Sulphur (rhombic)	17 to 45	0·1630	32·1	5·23	1·75
Tantalum	−185 to 20	0·0326	181·4	5·91	. .
Tellurium (cryst.)	15 to 100	0·0483	127·5	6·16	3·68
Thallium	20 to 100	0·0326	204·4	6·65	4·80
Thorium	0 to 100	0·0276	232·1	6·41	4·58
Tin (tetragonal)	0 to 20	0·0540	118·7	6·41	3·41
Titanium	0 to 100	0·1125	47·9	5·39	0·99
Tungsten	15 to 93	0·0340	184·0	6·26	1·75
Uranium	0 to 98	0·0280	238·1	6·67	3·30
Vanadium	0 to 100	0·1153	51·0	5·88	. .
Zinc	20 to 100	0·0931	65·4	6·08	2·52
Zirconium	0 to 100	0·0660	91·2	6·02	2·38

The Atomic Heats of Carbon and Silicon at Different Temperatures.

(Weber, 1872.)

Diamond.			Graphite.			Silicon.		
Temp., °C.	Specific Heat.	Atomic Heat.	Temp., °C.	Specific Heat.	Atomic Heat.	Temp., °C.	Specific Heat.	Atomic Heat.
− 50·5	0·064	0·76	− 50·3	0·114	1·36	− 39·8	0·136	3·81
+ 10·7	0·113	1·35	+ 10·8	0·160	1·92	+ 21·6	0·170	4·75
85·5	0·177	2·11	138·5	0·254	3·05	86·0	0·190	5·32
206	0·273	3·28	249	0·325	3·90	129	0·196	5·50
615	0·444	5·33	640	0·450	5·41	184	0·201	5·63
987	0·462	5·55	982	0·469	5·62	232	0·203	5·68

Thirteen years later, Humpidge determined the specific heat of beryllium at various temperatures and showed that at 500° C. the value remained nearly constant. His results are embodied in the following table:

The Atomic Heats of Beryllium at Different Temperatures.

(Humpidge, 1885.)

Temperatures, °C.	Specific Heat.	Atomic Heat.
0	0·3756	3·39
100	0·4702	4·24
200	0·5420	4·87
300	0·5910	5·33
400	0·6172	5·57
500	0·6206	5·59

It accordingly appears that if the temperature at which the specific heats of these elements are taken is sufficiently high, carbon, silicon and beryllium may fall into line with the other elements and conform to the Law of Dulong and Petit, although as yet the value 6·4 has not been attained for the atomic heats of any of them.

It may well be urged, however, that it is not fair to take the specific heats of these four elements at the highest attainable temperatures and compare them with those of the other elements at lower temperatures in order to make them fall into line with an empirical law such as the one now under discussion, especially since the results of the numerous researches show that the atomic heats of certain metals rise considerably above the mean value of 6·4 when the temperature is raised. This latter is well illustrated by the following table:

The Specific and Atomic Heats of Different Metals at Varying Temperatures.

(Tilden, 1905.)

Absolute Temperature, °T.	Aluminium.		Nickel.		Platinum.	
	Specific Heat.	Atomic Heat.	Specific Heat.	Atomic Heat.	Specific Heat.	Atomic Heat.
300	0·2053	5·54	0·1054	6·19	0·0311	6·07
500	0·2384	6·44	0·1233	7·24	0·0344	6·71
700	0·2531	6·83	0·1301	7·64	0·0372	7·25
900	..	..	0·1338	7·85	0·0397	7·74
1500	..	..	..	..	0·0461	8·99

It is evident, therefore, that the law is merely an approximation to the truth, and whether or not any particular element falls into line depends largely upon the temperature at which the specific heat is determined.

Specific Heats at Low Temperatures.—In general the differences noticed between the atomic heats become accentuated at temperatures below 0° C. As the temperature is lowered, the specific heats of the elements fall, rapidly at first, particularly for the elements of low atomic weight (Behn, 1898), but afterwards more slowly, tending towards the limit zero at the absolute zero of temperature. The accompanying table contains some of the results that have been obtained:

Silver.		Lead.		Copper.		Zinc.		Aluminium.		Diamond.	
T° Abs.	Atomic Heat.	T° Abs.	Atomic Heat.	T° Abs.	Atomic Heat.	T° Abs.	Atomic Heat.	T° Abs.	Atomic Heat.	T° Abs.	Atomic Heat.
173	5·46	202	6·23	173	4·98	173	5·32	173	4·54	262	1·14
123	4·97	123	5·89	123	4·29	123	4·84	123	3·71	232	0·86
77	4·07	63	5·65	88	3·38	94	4·55	88·3	2·62	220	0·72
53·8	2·90	36·8	4·40	33·4	0·538	75	3·95	86·0	2·52	205	0·62
39·1	1·90	28·3	3·92	27·7	0·324	43·7	2·17	35·1	0·33	88	0·03
35·0	1·58	23·0	2·96	23·5	0·223	33·1	1·25	32·4	0·25	30	0·00

If the preceding values are represented graphically, it will be seen (fig. 91) that not only do they indicate that the specific heat of an element vanishes when the absolute zero is reached, but also that its rate of variation with the temperature, viz. dc/dT, vanishes also.

Reason for Deviations from Dulong and Petit's Law.—As has already been explained, for solids and liquids (p. 212),

$$c = c_t + c_i$$

since the change in volume with rise of temperature is negligible.

Boltzmann (1871) showed that when a solid absorbs heat, approximately half that heat is used up in performing internal work, the remaining half being utilised in increasing the kinetic energy of the atoms, that is, in raising their temperature. Our equation, therefore, becomes

$$c = c_t + c_i = 2c_t.$$

Now when a monatomic gas absorbs heat at constant volume, c_e (p. 212) is, of course, nil, and c_i is negligibly small, for the distance between the atoms is very great and, in consequence, their cohesive force is small. Practically all the heat, therefore, is utilised in raising the temperature, so that

$$c = c_t.$$

Experiment shows that the atomic heat of a monatomic gas is approximately 3 calories, so that the atomic heat of solid and liquid metallic elements which are believed to have monatomic molecules will be twice this, or 6 calories. This figure is not far removed from the mean value of 6·4 obtained empirically (see Table, p. 217).

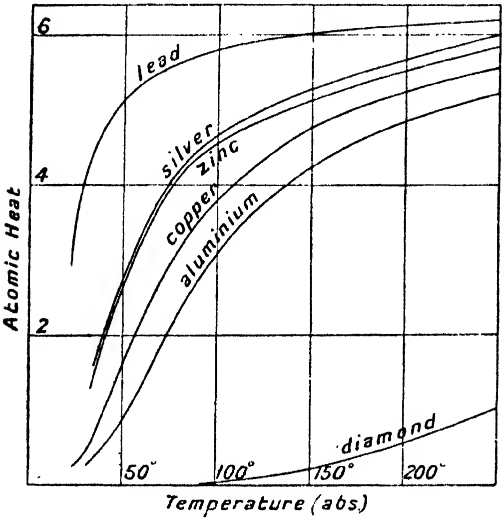


FIG. 91.—Variation of Atomic Heat with Temperature (see p. 219).

The atomic heat will not be normal unless the distance between contiguous atoms is considerable compared with the displacement of each atom, otherwise the atoms tend to interfere with each other's motion. The deviation will be greatest with those elements which have a small atomic volume coupled with a low atomic weight, for two reasons (Richarz, 1899):

(i) A small atomic volume means that the space between the atoms is small, so that a given displacement caused by rise of temperature may be relatively large.

(ii) A given amount of heat will cause more displacement with light atoms than with heavy atoms, since the kinetic energy given to the atoms is the same.

Consideration of the results in the table on p. 221 shows that when both the atomic weight and atomic volume are small, as in the case of boron, carbon (diamond), beryllium and crystalline silicon, the atomic heat is low. With lithium, however, a normal atomic heat is obtained, for, although its atomic weight is small, its atomic volume is relatively large, as indicated in the final column.

It is worthy of note that the atomic heats of the solid elements at **constant volume** (A_v) show more regularity than do the atomic heats at constant pressure (A_p). The former may be calculated by utilising the relationship

$$A_p - A_v = \frac{T\beta^2 V}{a} \quad . \quad . \quad . \quad . \quad (6)$$

Element.	Temperature Interval, °C.	Mean Specific Heat.	Atomic Weight.	Atomic Heat.	Atomic Volume.	At. Vol. / At. Wt.
Boron (Amorph.) .	0–100	0·307	10·82	3·32	4·01	0·37
Diamond . .	11	0·113	12·00	1·36	3·41	0·28
Beryllium . .	0–100	0·425	9·02	3·83	4·92	0·55
Silicon (Cryst.) .	22	0·170	28·06	4·77	11·4	0·41
Lithium . .	27–100	0·941	6·94	6·53	13·0	1·87

in which *T*, *V*, *a* and *β* denote the absolute temperature, atomic volume and coefficients of compressibility and expansion respectively. For fifteen elements, the compressibilities of which have been measured (Richards, 1907), the mean value for the atomic heat at constant volume is 5·9 at 20° C., and the average deviation only 0·09.

The preceding equation may be simplified to

$$A_v = A_p - kTc_e^2 \quad . \quad . \quad . \quad . \quad (7)$$

where *k* is constant for the particular element (Grüneisen, 1908). At very low temperatures A_v and A_p are almost equal.

Specific Heat and Allotropy.—From the foregoing it is clear that in those cases where elements exhibit allotropy, the allotropes of least density, and hence of greatest atomic volume, will have the higher atomic heats and will thus, in general, deviate least from Dulong and Petit's law. That such is the case is evident from the data in the following table:

Element.	Allotropic Form.	Temperature Interval, °C.	Specific Heat.	Atomic Heat.	Density.
Carbon .	Diamond . .	11	0·113	1·36	3·52
	Graphite . .	11	0·160	1·92	2·25
Phosphorus .	Red . . .	0–50	0·183	5·67	2·20
	White . .	13–36	0·202	6·26	1·83
Sulphur .	Rhombic . .	0–50	0·173	5·55	2·07
	Monoclinic . .	0–50	0·181	5·81	1·96
Tin . .	White (tetragonal)	0–20	0·054	6·41	7·28
	Grey (cubic) .	0–20	0·059	7·00	5·8

With rise of temperature the differences between the atomic heats of the allotropic forms of an element gradually diminish. This is well illustrated by Weber's data for diamond and graphite given in the table on p. 218.

The data in the above table serve also to illustrate van't Hoff's

Stability Rule, according to which, *when two modifications of a system exist the one with the higher specific heat becomes stable at higher temperatures.* Thus monoclinic sulphur is the stable form above 95·5° C. whilst rhombic sulphur is stable below this temperature. If the data for tin are correct, however, this metal does not obey the rule.

Determination of Atomic Weights.—For practical purposes it is best to assume that Dulong and Petit's Law represents a rough, empirical rule, valid when the mean specific heats are determined between 0° C. and 100° C., with three or four well-marked exceptions. In several cases the law has proved very useful as a means of fixing the atomic weights of several elements when their equivalent or combining weights have been known.

Uranium is a case in point. This element has a combining weight of 39·7 ; consequently its atomic weight is given by the expression

$$A = 39{\cdot}7 \times V$$

where A is the atomic weight and V the valency. On account of the supposed resemblance of uranium to iron, the valency of uranium was taken as 3, and hence its atomic weight as $39{\cdot}7 \times 3 = 119$ (approx.). Mendeléeff, however, placed the element in the sixth group of the Periodic Table along with chromium and sulphur. Hence an oxide of the formula UO_3 was to be expected, and therefore a valency of six. This meant doubling the atomic weight, which thereby became 238. The question was settled in 1882 by Zimmermann, who found the specific heat of the element to be 0·027, from which, according to Dulong and Petit's Law, the approximate value of the atomic weight is given by the expression

$$\text{Atomic weight} = \frac{\text{Atomic heat}}{\text{Specific heat}} = \frac{6{\cdot}4}{0{\cdot}027} = 237.$$

Mendeléeff's views thus received confirmation.

A second example is afforded by *indium*, which, for some time after its discovery in 1863 (Reich and Richter), was regarded as divalent and analogous to zinc. This view was based upon the facts that indium occurs naturally in association with zinc, notably in the blendes, and the two metals are very similar in their analytical reactions. Furthermore, all efforts to prepare indium alums, which would have indicated the trivalent character of the metal, and its analogy with aluminium, at first proved abortive. With a combining weight of approximately 38, divalent indium would have an atomic weight of 76. But this was not acceptable to Mendeléeff, who had no room for such an element in Group II of his Periodic Table. There was, however, a vacant space in Group III for an element of atomic weight intermediate between that of cadmium (at. wt. 112) and tin (at. wt. 119), and assuming indium to be trivalent, with an atomic weight of 38×3 or 114, the metal would fit into the table remarkably well. In 1870 Bunsen found the specific heat of metallic indium to be 0·057, whence

$$\text{Atomic weight} = 6{\cdot}4/0{\cdot}057 = 112 \text{ (approx.)}.$$

Mendeléeff's view of the trivalent character of indium was thus confirmed, and subsequent work fully substantiated the assumption.

Another element that gave considerable trouble was *zirconium*, which was regarded as trivalent until a determination of the vapour density of its chloride in 1857 indicated tetravalency. This was confirmed in 1873 when the specific heat of zirconium between 0° C. and 100° C. was found to be 0·066. The atomic weight was thus 6·4÷0·066 or 97, which is approximately four times the combining weight.

Dulong and Petit's Law has also been usefully applied in determining the valency of the *rare earth metals*. No compounds of these are known that volatilise without decomposition at temperatures suitable for vapour density determinations, so that no indication of the magnitude of the atomic weights of the metals is obtainable in this way. Also the Periodic Table is of little assistance beyond indicating that yttrium and lanthanum are trivalent and cerium tetravalent. Prior to 1870, the rare earths then known to chemists—ceria excepted—were represented as oxides of divalent metals, of general formula MO. This brought them into line with the alkaline earth oxides, which they were believed to resemble. The formula Ce_2O_3 was at one time given to ceria, that is, ceric oxide, but in later years the oxide came to be regarded as a compound $2CeO.CeO_2$ or Ce_3O_4. In 1870 Mendeléeff suggested that cerous oxide should be written as Ce_2O_3 (instead of CeO), and ceric oxide as CeO_2. This was confirmed in 1876 when Hillebrand determined the specific heats of cerium, lanthanum and "didymium" (essentially a mixture of prascodymium and neodymium, but at that time believed to be a simple element). The results were as follows:

Element.	Specific Heat, c, 0° to 100° C.	Approximate Atomic Weight, $=6{\cdot}4/c$.	Equivalent Weight Determined Experimentally.	Valency, $=\frac{\text{At. Wt.}}{\text{Equiv. Wt.}}$
Cerium . .	0·0448	143	46·7 (cerous)	3·1
			35·0 (ceric)	4·1
"Didymium" .	0·0456	140	47 (approx.)	3·0
Lanthanum .	0·0449	142	46·3	3·1

Further evidence of the trivalent nature of the rare earth elements was obtained later from a study of the molecular heats of some of their compounds (see p. 224).

Specific Heats of Compounds.—In 1831 Neumann extended Dulong and Petit's Law to certain groups of closely related compounds, as, for example, the carbonates of the alkaline earths, by drawing attention to the fact that these bodies exhibit the same molecular heats. This is well illustrated by the following table, in which the modern values for the specific heats and molecular weights of a number of sulphates are given:

Substance.	Formula.	Temperature, °C.	Specific Heat.	Molecular Weight.	Molecular Heat.
Calcium sulphate	$CaSO_4$	13–98	0·197	136·1	26·8
Barium sulphate .	$BaSO_4$	10–98	0·113	233·4	26·4
Strontium sulphate	$SrSO_4$	21–99	0·143	183·7	26·3
Lead sulphate .	$PbSO_4$	20–99	0·087	303·3	26·4

Regnault (1841) extended Neumann's observations, and confirmed the law by more accurate determinations of the specific heats of metallic oxides, halides, sulphides, carbonates, sulphates and nitrates.

Neumann's Law may therefore be formulated as follows :

Compounds of similar chemical composition and structure have the same molecular heat.

This law has been advantageously applied to the study of the oxides and sulphates of the rare earth metals. The similarity of their molecular heats to those of the corresponding compounds of aluminium, indium, etc., which are known to be trivalent metals, is an argument in favour of the trivalency of the rare earth metals themselves. The following data illustrate this point :

Molecular Heats of the Oxides and Sulphates of Certain Rare Earth Metals.

(Nilson and Pettersson, 1880.)

Metal.	Oxide.	Mean Specific Heat, 0° to 100° C.	Molecular Heat.	Sulphate.	Mean Specific Heat, 0° to 100° C.	Molecular Heat.
Aluminium .	Al_2O_3	0·1879	19·3	$Al_2(SO_4)_3$	0·1855	63·6
Indium .	In_2O_3	0·0807	22·2	$In_2(SO_4)_3$	0·1290	66·4
Iron . .	Fe_2O_3	0·1600	25·5	$Fe_2(SO_4)_3$	0·1656	66·2
Cerium .	. .	. .	. .	$Ce_2(SO_4)_3$	0·1168	66·2
Erbium .	Er_2O_3	0·0650	24·7	$Er_2(SO_4)_3$	0·1040	64·5
Lanthanum .	La_2O_3	0·0749	24·4	$La_2(SO_4)_3$	0·1182	66·9
Yttrium .	Y_2O_3	0·1026	23·3	$Y_2(SO_4)_3$	0·1319	61·6

Neumann's Law, however, is only of limited application, inasmuch as it applies merely to chemically related substances. Joule (1844) and Woestyn (1848) soon pointed out, however, that

the molecular heat of a compound is the sum of the atomic heats of its constituent atoms.

This most important generalisation enables us to connect together all types of compounds ; it is thus as universally applicable as Dulong and Petit's Law for the various elements. Since Kopp (1864) did much to establish its approximate truth, this generalisation is usually termed **Kopp's Law**, although it cannot be claimed that he was its originator.

It will be clear that Kopp's Law is tantamount to postulating that the atomic heats of the elements remain approximately the same whether the latter are free or combined, and that such is actually true in many cases is evident from the table at top of p. 225. As enunciated above, the law is assumed to be additive, and for most inorganic substances this appears to be the case. It will be seen later, however, that the molecular heat of a substance is partly constitutive also, since the specific and hence the molecular heats of isomerides of different structure are by no means identical.

Substance.	Formula.	Specific Heat.	Molecular Heat.
Silver chloride . .	AgCl	0·091	13·1 = 2 × 6·6
Cuprous chloride .	CuCl	0·138	13·6 = 2 × 6·8
Potassium chloride .	KCl	0·173	12·9 = 2 × 6·5
Barium chloride .	$BaCl_2$	0·090	18·8 = 3 × 6·3
Mercuric iodide . .	HgI_2	0·042	19·1 = 3 × 6·4
Lead iodide . .	PbI_2	0·043	19·7 = 3 × 6·6

Kopp's Law is further supported by the following observations :

1. Bodies containing equal proportions of those elements which do not conform to Dulong and Petit's Law have approximately equal molecular heats. This is evident from a consideration of the different compounds of oxygen and sulphur shown in the table below, both oxygen and sulphur possessing abnormal atomic heats. The regularity here noticed is, of course, merely a special case of Neumann's Law.

Substance.	Formula.	Molecular Weight (O = 16).	Specific Heat.	Molecular Heat.
Cupric oxide . .	CuO	79·6	0·142	11·3
Mercuric oxide . .	HgO	216·6	0·052	11·3
Nickelous oxide . .	NiO	74·7	0·159	11·9
Ferrous sulphide .	FeS	87·9	0·136	12·0
Lead sulphide . .	PbS	239·3	0·051	12·2
Mercuric sulphide .	HgS	232·7	0·051	11·9

2. The values obtained for the atomic heats of abnormal elements are the same (approximately) whether deduced from the molecular heats of their compounds or calculated directly from the observed specific heats of the elements. Thus, in the table above, copper oxide (CuO) has a molecular heat of 11·3. Now, the specific heat of copper is 0·094 at temperatures ranging from 20° to 100° C., so that the atomic heat is 0·094 × 63·6 = 6·0 (approx.), and the atomic heat of oxygen is in consequence 11·3 − 6·0 = **5·3**. The observed specific heat of liquid oxygen at −190° C. is 0·347, whence its atomic heat is 0·347 × 16 = **5·55**. This is a rather favourable example of the nature of the agreement observed.

For combined water, that is so-called water of crystallisation, the molecular heat is found to be 8. This value is almost the same as that obtained for ice, namely 8·3.

Kopp's Law may be used to **determine the atomic weight of an element** the equivalent of which is known, irrespective of whether or not the pure element itself has been isolated. Thus, for example, suppose the atomic weight of mercury is required. Analysis of mercuric chloride shows the equivalent of the metal to be 100·3, and, by applying one of the methods detailed in Chapter VIII, it is found that the molecular weight of mercuric chloride is approximately 271·5. Evidently, therefore, the formula of the salt is Hg_nCl_2, and the problem is to find the value of n. A determination of the specific heat of mercuric chloride yields the value 0·069, and the molecular heat is therefore $0·069 \times 271·5 = 18·7$. From Kopp's Law, then, the number of atoms present in the molecule is $18·7/6·4 = 3$ (approximately); whence $n = 1$, the formula for mercuric chloride is $HgCl_2$, and the atomic weight of the metal $100·3 \times 2 = 200·6$.

Although Kopp's Law was originally formulated from data obtained in the neighbourhood of the ordinary temperature, it has been found to apply with considerable exactness even at low temperatures such as 100° Abs. (Tilden, 1904).

Organic Liquids.—As in the case of most metals, over short ranges of temperature the specific heat of an organic liquid is a linear function of the temperature, so that

$$c = c_0 + at.$$

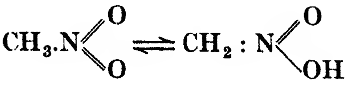
For substances of analogous chemical composition β shows remarkable constancy, although a may vary considerably (Schiff, 1886). Thus, for example:

Substance.	$c_0 + at.$
Allyl oxalate	$0·4122 + 0·00066t$,
*Iso*Butyl oxalate . . .	$0·2274 + 0·00066t$.
Methyl benzoate . . .	$0·363 + 0·00075t$,
Ethyl benzoate. . . .	$0·374 + 0·00075t$.

Isomers of similar chemical constitution have almost identical specific heats, whilst those of different structure have different specific heats (von Reis, 1881). These facts show that whilst the specific heat is partly additive, as Kopp's Law demands, it is also partly constitutive. Thus, for the temperature interval 20° to 100° C.:

Substance.	$c.$
Methyl valerate, $CH_3(CH_2)_3COOCH_3$. .	0·5028
Ethyl butyrate, $CH_3(CH_2)_2COOC_2H_5$. .	0·5044
Allyl alcohol, $CH_2{:}CH.CH_2OH$ . .	0·6441
Propaldehyde, $CH_3.CH_2.CHO$ . . .	0·5794

An interesting case is that of *nitromethane*, which is capable of existing in two tautomeric forms (p. 208), viz.



$$CH_3.N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O} \rightleftharpoons CH_2 : N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown OH}$$

These isomerides are in dynamic equilibrium. Near 20° C. the specific heat of the dried liquid begins to fall rapidly to a minimum at about 30° C. (fig. 92). A maximum occurs below 20° C. When this maximum has been passed most of the molecules stable at lower temperatures have been converted to the other kind, so that as the temperature rises, the heat, c_i, absorbed in this transformation becomes increasingly less, and the falling off more than neutralises the normal rise of the true specific heat, c_t, with temperature. Above 30° C., c_i is negligibly small, so that c_t becomes virtually equal to c, and steadily rises with the temperature (Williams, 1925). The presence of moisture raises the temperature of minimum specific heat, as shown in the figure. Vapour pressure and vapour density curves do not show this interesting feature.

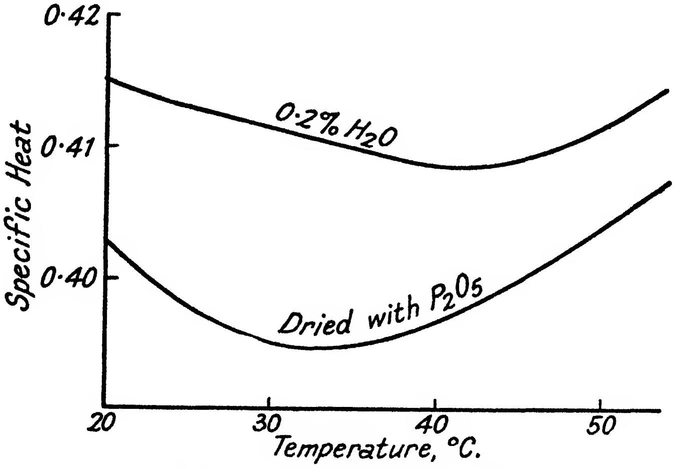


FIG. 92.—Specific Heat of Nitromethane (Williams, 1925).

Specific Heat and Molecular Complexity.—When, upon raising the temperature of a substance composed of associated molecules, a breaking down into simpler molecular aggregates occurs, a great deal of heat may be absorbed in the process. The fact that many solid substances possess abnormally high specific heats in the neighbourhood of their melting points may receive explanation in this way.

The so-called " latent heat of fusion " may be regarded as a special example of exceptional specific heat at the melting point, and the high value found in the case of ice is attributable to the relatively large amount of heat absorbed in converting the " ice " molecules, $(H_2O)_3$, into " water " molecules, $(H_2O)_2$. Water at 0° C. still contains appreciable quantities of " ice " molecules, and the fluctuations in the specific heat of water at various temperatures between 0° and 100° C., to which reference has already been made (p. 214), is attributable to successive depolymerisation of " ice " and " water " to " steam " (H_2O) molecules as the temperature is raised, liquid water at 100° C. containing appreciable quantities of " steam " molecules. Thus :

$$\underset{\substack{\text{“ Ice ”}\\ \text{molecules}\\ \text{(Trihydrol).}}}{(H_2O)_3} \rightleftharpoons \underset{\substack{\text{“ Water ”}\\ \text{molecules}\\ \text{(Dihydrol).}}}{(H_2O)_2} \rightleftharpoons \underset{\substack{\text{“ Steam ”}\\ \text{molecules}\\ \text{(Monohydrol).}}}{H_2O}$$

Mixtures of Non-Electrolytes.—In view of the general applicability of Kopp's Law, it seems reasonable to suppose that a substance will retain its normal specific and molecular heats when mixed with one or more substances with which it does not combine chemically. If so, we may write

$$cM = c_1m_1 + c_2m_2 + c_3m_3 + \ldots \qquad (8)$$

where c is the specific heat of the mixture, c_1, c_2, c_3, etc. are the specific heats of the constituents of masses m_1, m_2, m_3, etc. respectively, and M the total mass of the constituents.

Experiment shows that many alloys obey this rule at temperatures well below their melting points, although near the melting point discrepancies are observed, the specific heat being greater than theory demands. This may be due to the formation of unstable compounds which break down, as the temperature rises, with absorption of heat (c_i).

Mixtures of organic liquids that are either entirely free from association or only very feebly associated are found to conform to equation (8). Such are, for example,

Chloroform and benzene,
Benzene and carbon disulphide.

A few mixtures, such as benzene and acetic acid, have a smaller specific heat than either constituent. Probably, therefore, upon admixture, the constituents undergo a certain amount of depolymerisation, so that the heat absorbed in doing internal work, namely c_i, is less in the mixture than in the separate constituents. In many cases, however, the specific heat of the mixture is greater than that calculated from equation (8). This suggests a tendency to association or the formation of molecular compounds. A mixture of ethyl alcohol and water is a case in point (fig. 93). A maximum difference between the observed and calculated specific heats occurs at about 30 per cent. alcohol concentration, corresponding to $C_2H_5OH.6H_2O$.

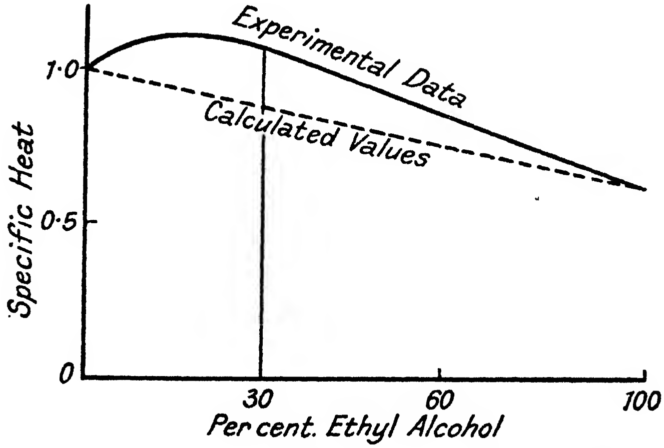


FIG. 93.—Specific Heats of Mixtures of Ethyl Alcohol and Water at 0·5° to 1·25° C. (Bose, 1906).

SPECIFIC HEATS OF GASES.

Hitherto we have been concerned mainly with the specific heats of solids and liquids, and in general it has not been necessary to consider the effect of c_e in the equation (p. 212)

$$c = c_t + c_e + c_i \quad . \quad . \quad . \quad . \quad (8)$$

because, in these cases, c_e is negligibly small. With gaseous bodies c_e may or may not be negligible, according as the specific heat of the gas is determined at **constant volume**, c_v, or **constant pressure**, c_p. Of these two specific heats that at constant pressure is the greater, and exceeds that measured at constant volume by the thermal equivalent of the work required to overcome the resistance offered by the atmosphere to the expansion of the gas.

It is often convenient to take as our unit of mass of a gas its gramme-molecular weight. We thus obtain the **molecular heats**, which are denoted by C_p and C_v. If M is the molecular weight of the gas, $C_p = Mc_p$, and $C_v = Mc_v$. We may therefore write equation (3) as follows:

$$Mc = Mc_t + Mc_e + Mc_i$$

or

$$C = C_t + C_e + C_i.$$

Suppose, now, that we raise the temperature of a truly monatomic gas, keeping the volume constant. Both C_e and C_i may be neglected, and hence

$$C = C_t.$$

The whole of the added heat is thus utilised in raising the temperature, that is, in increasing the kinetic energy of the molecules.

Since the average kinetic energy, E, of a gramme-molecule of gas is $\frac{1}{2}Nmu^2$ (p. 55), it follows (p. 55) that

$$RT = PV = \tfrac{1}{3}Nmu^2 = \tfrac{2}{3}E,$$

whence

$$E = \tfrac{3}{2}RT \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If, therefore, a gramme-molecule of monatomic gas is warmed at constant volume from T to $T+1$ degrees, the increase in kinetic energy, δE, or, in other words, the molecular heat at constant volume, C_v, is given by the expression

$$\begin{aligned} C_v = \delta E &= \tfrac{3}{2}R(T+1) - \tfrac{3}{2}RT \\ &= \tfrac{3}{2}R \\ &= 3 \text{ gramme-calories.} \end{aligned}$$

since R is approximately 2 (p. 40).

The values obtained for the molecular heats of helium and argon at constant volume are given in the table on p. 230, and closely approximate to 3. These gases therefore are monatomic.

If, now, instead of keeping the volume constant, we allow the gas to expand at constant pressure as the temperature rises through one degree from T to $T+1$, more heat is absorbed, because the gas has to make room for itself by pushing the atmosphere away. Denoting the molecular heat at constant pressure by C_p, ordinary atmospheric pressure being understood, and writing the initial and final molecular volumes of the gas as V_0 and V respectively, it is clear that the difference between the two specific heats equals the external work done:

$$\begin{aligned} \textit{i.e.}\quad C_p - C_v &= C_e \\ &= P(V - V_0) \\ &= R(T+1) - RT \\ &= R \quad . \quad . \quad . \quad . \quad . \quad (10) \\ &= 2 \text{ gramme-calories} \end{aligned}$$

on the assumption that we are dealing with an ideal or perfect gas which obeys the gas laws absolutely. From this it follows that

$$\begin{aligned} C_p &= 2 + C_v \\ &= 2 + 3 \\ &= 5 \text{ gramme-calories} \end{aligned}$$

and the ratio

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1{\cdot}666.$$

This, of course, only applies to ideal monatomic gases, for which C_i is negligibly small. Reference to the table below will show that both helium and argon conform very closely to the foregoing, C_p being approximately 5 calories and γ very nearly 1·67 in both cases. In addition to the inert gases, the vapours of many metals, such as potassium, sodium, mercury, zinc, etc., are found to be monatomic, the ratio of their specific heats being approximately 1·67.

For polyatomic molecules C_i is not negligible, and

$$\begin{aligned} \gamma = \frac{C_p}{C_v} &= \frac{C_t + C_e + C_i}{C_t + C_i} \\ &= \frac{5 + C_i}{3 + C_i} \quad . \quad . \quad . \quad . \quad . \quad (11) \end{aligned}$$

As C_i increases, the ratio steadily falls, always tending towards unity. For diatomic gases, such as H_2, N_2, O_2, etc., the value of γ approximates to 1·4; for triatomic gases, such as CO_2, γ falls to about 1·3; and so on, indicating that, as the molecular complexity increases, more and more of the absorbed heat is utilised in doing internal work within the molecule.

Molecular Heats of Gases.

(Scheel and Heuse, 1912 to 1919.)

Gas.	Formula.	Temp., °C.	C_p.	C_v.	$R = C_p - C_v$.	$\gamma = C_p/C_v$.
Argon . .	A	+ 15	5·07	3·07	2·00	1·65
		− 180	5·31	3·01	2·30	1·76
Helium . .	He	+ 18	4·99	3·01	1·98	1·66
		− 180	4·93	2·95	1·98	1·67
Hydrogen . .	H_2	+ 16	6·86	4·88	1·98	1·41
		− 181	5·33	3·34	1·99	1·60
Oxygen . .	O_2	+ 20	6·98	4·99	1·99	1·40
		− 181	7·30	5·04	2·26	1·45
Nitrogen . .	N_2	+ 20	6·98	4·99	1·99	1·40
Air . . .	. .	+ 20	6·97	4·97	2·00	1·40
Carbon monoxide	CO	+ 18	7·01	5·01	2·00	1·40
Nitrous oxide .	N_2O	+ 20	9·24	7·20	2·04	1·28
Carbon dioxide .	CO_2	+ 20	8·88	6·85	2·03	1·30
Methane . .	CH_4	+ 15	8·50	6·50	2·00	1·31
Ethane . .	C_2H_6	+ 15	12·40	10·33	2·07	1·20
		− 82	10·44	8·15	2·29	1·28

γ is not only affected by the number of atoms in the molecule, but also by their nature. Thus, for example, by the substitution of chlorine for hydrogen in methane, the value of γ progressively falls, although the actual number of atoms in the molecules is constant (Capstick, 1895). The values obtained were

	γ
Methane, CH_4	1·313
Methyl chloride, CH_3Cl	1·279
Methylene chloride, CH_2Cl_2	1·219
Chloroform, $CHCl_3$	1·154
Carbon tetrachloride, CCl_4	1·130

Effect of Temperature on C_p and C_v.—Reference to the preceding table shows that the effect of temperature on the molecular heat of helium is very slight. For polyatomic gases the molecular heat usually rises with the temperature, and over a considerable range the rise is linear. Thus

Variation of C_v with Temperature.

(Dixon, 1921.)

Gas.	Temperature Range, °C.	C_v.
Nitrogen	0 to 1000	$4{\cdot}775 + 0{\cdot}00042T$
Air	0 to 700	$4{\cdot}8 + 0{\cdot}0004T$
Carbon dioxide . . .	0 to 600	$6{\cdot}3 + 0{\cdot}00205T$ $+ 0{\cdot}0000007T^2$
Methane	0 to 600	$6{\cdot}6 + 0{\cdot}019t$

T = °Abs., t = °C.

If marked dissociation occurs, C_v usually falls with rise of temperature as the amount of dissociation taking place becomes less, since C_i becomes proportionately less, until C_i becomes too small to counterbalance the normal rise in the true specific heat with temperature.

Effect of Temperature on γ.—The value for γ in the case of the permanent and stable gases falls only very slightly with rise of temperature. Thus, for nitrogen the following values have been obtained (Dixon, 1921):

Temperature, °C.	0	100	200	500	1000
γ (Nitrogen)	1·408	1·404	1·400	1·389	1·374

Methods of Determining c_p.—Since very considerable volumes of gases are required for the accurate determination of their specific heats at constant pressure, it is usual to pass a known mass of the gas at constant temperature through a calorimeter at a slightly different temperature and measure the heat liberated or absorbed.

As an example the apparatus used by McCollum (1927) for the determination of the specific heat of nitrogen tetroxide may be instanced. The essential features are shown in fig. 94. The pure, dry gas was made to circulate through a coil in a large calorimeter A, kept at constant temperature t_1. Each cubic centimetre of gas took about 45 minutes to pass through the coil, before it entered into the slightly warmer calorimeter B, which was oil-filled and fitted with an electrical heating coil by which it was maintained at t_2°. Each cubic centimetre of the gas remained in B for 4 minutes and escaped at t_2°. The heat, *H*, absorbed by the gas in rising from t_1° to t_2° was, of course, equivalent to the electrical energy supplied through the heating coil, and could be calculated from Joule's Law (1841) embodied in the expression

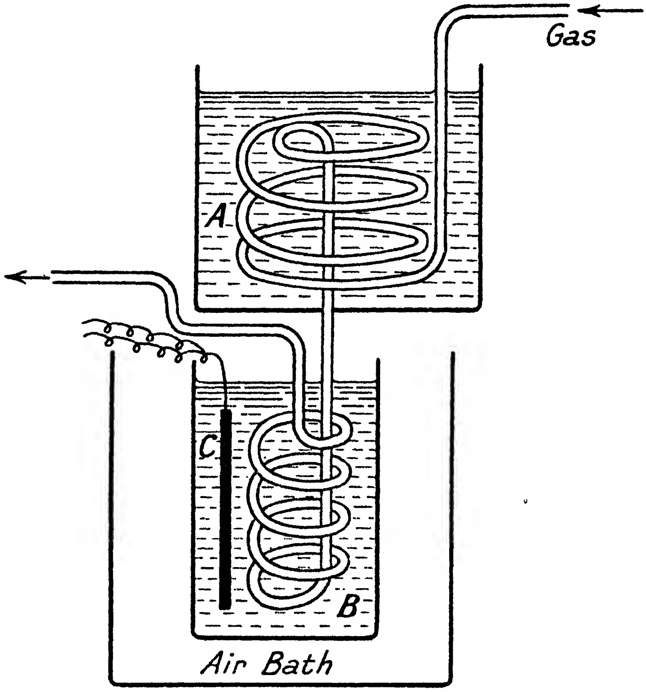


FIG. 94.—McCollum's Apparatus for Specific Heat of N_2O_4 at Constant Pressure.

$$H = \frac{A^2R\theta}{4{\cdot}19} \text{ gramme-calories} \qquad . \quad . \quad . \quad (12)$$

where *A* is the current in ampères, *R* the resistance of the coil in ohms and θ the duration of the passage of the current in seconds; whence, if *m* is the mass of gas passing through the calorimeters, the mean specific heat c_{mp} is given by

$$c_{mp} = \frac{H}{m(t_2 - t_1)}$$
$$= A^2R\theta/4{\cdot}19m(t_2 - t_1) \qquad . \quad . \quad . \quad (13)$$

By making the temperature interval $(t_2 - t_1)$ sufficiently small, the true specific heat at constant pressure may be obtained directly.

Methods of Determining c_v.—Of these, one of the best known is that introduced by Joly (1892), the principle of which is to determine the amount of steam that must be condensed in order to raise the temperature of a given mass of gas from that of the room to 100° C.

Two copper spheres A and B (fig. 95), fitted with catch pans C, are exhausted and suspended by wire in a box at room temperature, t, each hanging from one arm of a balance. Steam at 100° C. is admitted to the box; some condenses on the cold spheres and collects in the catch pans. If the heat capacities of the two spheres are the same, equal quantities of water collect and equilibrium is maintained. If the balance is deflected, equilibrium is restored by adding the necessary weights to P_1 or P_2. Wires W_1 and W_2 are electrically heated and prevent condensation of moisture on the suspension wires. The spheres are now removed, dried, and A is filled with gas under pressure, say 40 atmospheres, B remaining exhausted. On replacing in the box the balance is readjusted on account of the gas content in A. On admitting steam, more water collects on A than before, because heat is absorbed in raising the temperature of the enclosed gas. The mass w that must be added to P_2 to restore equilibrium is equal to the mass of that extra water. The heat absorbed by the gas, therefore, is wl, l being the latent heat of steam, whence the mean specific heat of the gas is given by

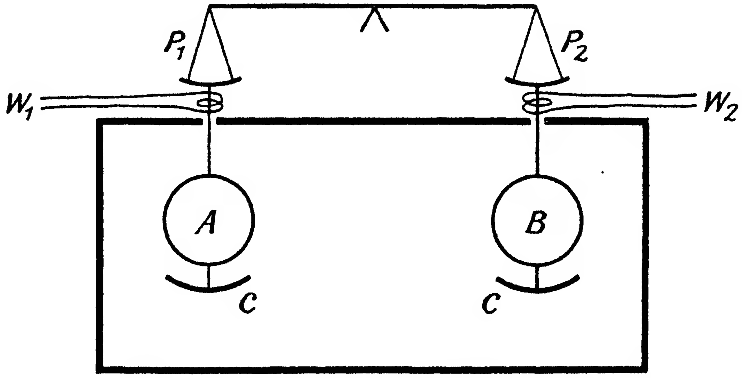


FIG. 95.—Joly's Calorimeter for Determining the Specific Heat of a Gas at Constant Volume.

$$c_{mv} = wl/m(100 - t) \quad . \quad . \quad . \quad . \quad (14)$$

where m is the mass of the gas in A. The water equivalent of A does not enter into the calculation, as this is compensated by B.

An explosion method has been developed mainly by Berthelot, Le Chatelier, Pier (1908 to 1910) and Bjerrum (1912). A known amount of electrolytic gas, for example, diluted with an inert gas, such as hydrogen, oxygen or argon, is exploded in a steel bomb by the passage of an electric spark, the whole being kept cool in a bath of water. If t_1 is the final temperature of the bath, and t_2 the maximum temperature of the explosion, it follows that:

$$Q = (t_2 - t_1)(m_1 c_{m1} + m_2 c_{m2})$$

where Q is the heat liberated by the explosion of the electrolytic gas, m_1 and c_{m1} the mass and mean specific heat of the steam, presumed known, m_2 and c_{m2} the known mass and unknown mean specific heat of the inert gas.

The value of t_2 is determined indirectly by noting the maximum pressure, p_2, attained in the explosion, and applying the equation

$$\frac{p_2}{p_1}=\frac{(t_2+273)}{(t_1+273)}$$

where p_1 is the initial pressure. A correction must, of course, be applied to allow for the change in volume owing to the formation of water. The main difficulty is to ascertain the maximum pressure. Pistons working against steel springs do not respond sufficiently rapidly. Pier covered a hole in the bomb with a steel membrane which carried a mirror, so that a beam of light could be reflected on to a rotating drum and its movement photographically recorded.

Determination of the Ratio $c_p/c_v=\gamma$.—(1) One of the most convenient methods for determining this quantity depends upon the relationship between the specific heats and the velocity of sound in the gas. The velocity, v, of the propagation of sound waves in an elastic medium, according to Newton's formula, is given by

$$v=\sqrt{\frac{E_\phi}{d}} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where d is the density of the medium and E_ϕ the coefficient of elasticity of the gas under adiabatic compression. E_ϕ is greater than the coefficient of elasticity, E, under isothermal compression, E being equal numerically to the pressure, p. The ratio between these two elasticities is the same as that between the two specific heats, namely

$$\frac{E_\phi}{E}=\gamma=\frac{c_p}{c_v} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

If, therefore, in the gas under investigation, λ is the wave-length of a sound of frequency n, and if the isothermal elasticity is p and the density d, we have

$$v=n\lambda=\sqrt{\frac{p\gamma}{d}}=\sqrt{\frac{\gamma}{D}} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where D is the density of the gas under unit pressure. Writing λ_1 and D_1 for the corresponding quantities in another gas for which the value of γ_1 is known, the wave-length λ_1 of a note of the same frequency n will be given by

$$n\lambda_1=\sqrt{\frac{\gamma_1}{D_1}},$$

whence

$$\frac{\gamma}{\gamma_1}=\frac{\lambda^2 D}{\lambda_1^2 D_1} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

As the ratio p/d is independent of the pressure, we do not require to know the actual pressures and densities of the gases in the two cases, and any variation of temperature can be allowed for in the values of D and D_1, though it is usual, for the sake of simplicity, to adopt the same temperature in each case.

Air, for which $\gamma = 1{\cdot}403$ (Partington, 1913), is used as the standard gas, and the determination of γ for any other gas thus resolves itself into a comparison of the wave-lengths of the same sound in air and in the gas. This is usually accomplished by a method due to Kundt (1866), and the foregoing equation becomes

$$\gamma_{\text{gas}} = 1{\cdot}403\lambda^2_{\text{gas}}D_{\text{gas}}/\lambda^2_{\text{air}} \quad . \quad . \quad . \quad . \quad (19)$$

where the density of the gas is expressed relative to that of air.

The particular form of Kundt's tube used by Ramsay and his co-workers (1895) in determining the value of γ for the inert gases is shown in fig. 96. A long tube T, which may be of narrow bore (2 mm.), is closed at one end, and through this end is sealed a glass rod R, half of which is inside and half outside the tube. Some lycopodium powder is distributed along the tube, dry air is introduced, and the rod R is set into longitudinal vibration by rubbing it with a rag wet with alcohol. By moving the clip C on the thick-walled rubber tubing fitted to the open end of T, the length can be adjusted till the tube resounds to the note. The stationary waves thus set up in the tube by interference between the waves incident upon and reflected from the ends of the tube are made evident by the disposition of the lycopodium, which is swept away from the points of greatest movement and heaped up at the nodes. The distance between adjacent nodes—the half wave-length—is determined by direct measurement. The tube is next evacuated, filled with the gas under examination and the measurement of wave-length repeated.

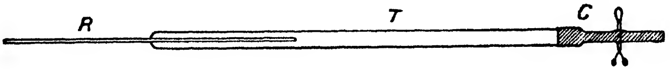


FIG. 96.—Kundt's Dust Tube.

Owing to the lightness of helium it is difficult to get good dust figures with this gas. The following values for γ have been obtained by this method :

Helium	1·652	Krypton	1·689
Neon	1·642	Xenon	1·666 .
Argon	1·65		

(2) Dixon and his co-workers in 1921 made a direct determination of the velocity of sound in various gases over a wide range of temperatures, *e.g.* in the case of nitrogen, over 0° to 1000° C. Having ascertained that the velocity of sound, like the velocity of an explosion wave (Vol. II.), is the same in coiled as in straight tubes, these investigators sent sound waves through coiled tubes of lead, silica or steel, containing various gases, and noted the time taken for transmission. Each end of the coiled tube was fitted with an apparatus similar to that shown in fig. 97, which is self-explanatory. As the sound wave generated by the electromagnetic hammer striking the steel tympanum passed the platinum disc P, a mark was made by a self-recording chronometric apparatus, and a similar mark was produced when the wave reached the other end of the coiled tube and moved the corresponding piston. The coil measured from 15 to 20 metres in length and from 25 to 30 mm. in diameter.

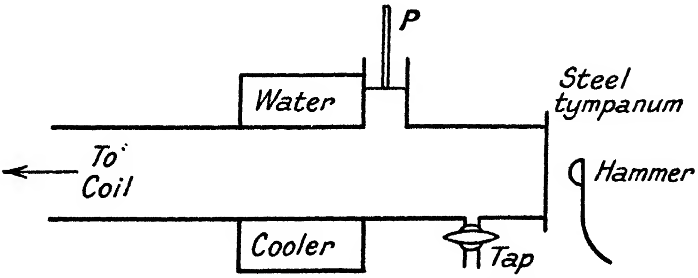


FIG. 97.—Dixon's Apparatus for Determining Velocity of Sound in Gases.

Since the velocity of sound conveyed through a tube is not quite the same as when the gas is "free," special corrections had to be applied.

The following results were obtained :

Gas.	Velocity of Sound (metres per second).			$\gamma = C_p/C_v$ at 0° C.
	0° C.	100° C.	500° C.	
Nitrogen . .	337·5	394	564·5	1·408
Carbon dioxide .	258	300	426	1·296
Methane . .	429	487	671	1·301

The value for γ was calculated with the aid of the Berthelot-Warburg equation :

$$\gamma = C_p/C_v = \frac{v^2 M}{RT}\left[1 - \frac{9\pi}{128}2\tau(1 - 6\tau^2)\right] \quad . \quad . \quad (20)$$

where v is the velocity of sound in the gas of molecular weight M, R the gas constant, T the absolute temperature of measurement, π the ratio of the pressure to the critical pressure, i.e. p/p_c, and τ is similarly T/T_c.

It will be noted that the velocity of sound in a gas rises very appreciably with the temperature.

(3) The cooling observed during the adiabatic expansion of a gas from a high pressure to a low one has been utilised in calculating γ. This method was used by Clement and Desormes in 1812 although the results were not published until 1819. The essential features of the apparatus used by Partington, who adopted an improved form of this method in 1921, are shown in fig. 98. Air from a steel cylinder under 100 atmospheres pressure was passed into a large globe of hammered copper, S, of 120 to 130 litres capacity, immersed in a water bath. A bolometer, B, enabled the temperature to be read to 0·01° C., and when the whole had attained a steady temperature, T, the expansion valve was opened, when the air in S fell to atmospheric pressure, P, and to a temperature T_1.

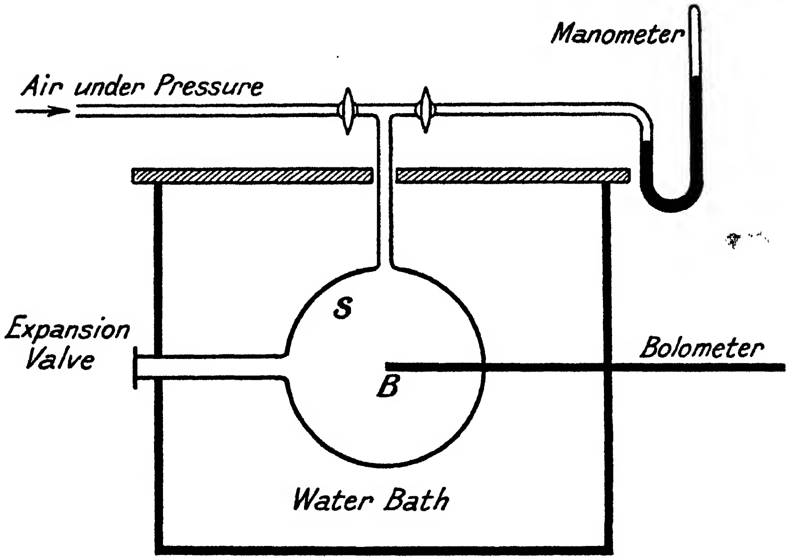


FIG. 98.—Partington's Apparatus for Determining γ.

Assuming the initial pressure of the air to be P_1, the value for γ can be calculated from the equation (see p. 239):

$$\frac{T}{T_1} = \left(\frac{P}{P_1}\right)^{\frac{\gamma - 1}{\gamma}}$$

or

$$\gamma = \frac{\log P_1 - \log P}{(\log P_1 - \log P) - (\log T - \log T_1)} \quad . \quad . \quad . \quad (21)$$

A correction must be applied for heat interchange, for radiation and for the fact that gases under high pressures deviate somewhat from the gas laws. The value of γ obtained for air at 17° C. was 1·403.

Molecular Heat and Dissociation.—An interesting example of the influence of dissociation upon the molecular heat at constant pressure is afforded by nitrogen tetroxide, which, at the ordinary temperature, consists of N_2O_4 and NO_2 molecules in dynamic equilibrium. The molecular heat of the gas at various temperatures was determined by McCollum (1927) using the apparatus shown in fig. 94, a steady flow of the pure gas being obtained by allowing the liquid substance to evaporate at the requisite speed. The heat of dissociation of gaseous nitrogen tetroxide is approximately 13,000 gramme-calories, a value that is very large compared with the molecular heat, so that c_i (equation (8), p. 228) at first exerts an enormous influence on the value obtained for c.

The equation representing the apparent molecular heat at constant pressure may be written as follows:

$$C_p = (1 - \alpha)C_{N_2O_4} + 2\alpha C_{NO_2} + \delta Q\frac{d\alpha}{dt} \quad . \quad . \quad . \quad (22)$$

where α, as usual, represents the extent of dissociation, δQ the heat of dissociation of one gramme-molecule of N_2O_4, and $C_{N_2O_4}$ and C_{NO_2} the molecular heats of N_2O_4 and NO_2, all at constant pressure.

In this equation the value for $\delta Q\frac{da}{dt}$ cannot be obtained at present with great accuracy. The results obtained for C_p are shown in fig. 99. A maximum is obtained at about 63° C. at which temperature about 50 per cent. of the molecules are NO_2. The molecular heat then falls as the number of N_2O_4 molecules decreases, which means that the value for $\delta Q\frac{da}{dt}$ likewise progressively falls.

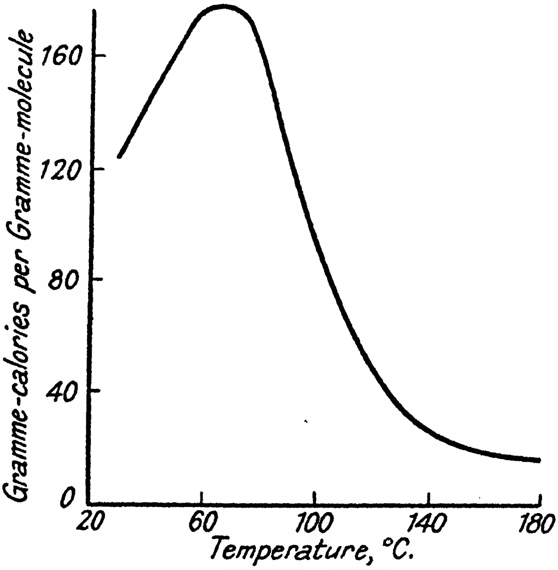


FIG. 99.—Molecular Heats at Constant Pressure of N_2O_4 (McCollum, 1927).

Adiabatic Gas Equation.—The numerical relationship between the pressure of a gas and its volume as given by Boyle's Law applies only when the temperature is kept constant. When a gas is suddenly compressed, its temperature rises, and its observed new volume only agrees with that calculated with the aid of Boyle's Law when its temperature has fallen to the original value. Similarly, when a gas suddenly expands, its temperature falls, and it is only when its original temperature has been restored by the absorption of heat from surrounding objects that the observed and calculated volumes become identical. In other words, Boyle's equation is an **isothermal gas equation.**

Let us now seek a mathematical connection between the pressure and volume of a gas subjected to adiabatic changes, that is, to changes under such conditions that no heat is lost or absorbed by the system (p. 38). Suppose, for example, a gramme-molecule of gas is allowed to expand adiabatically against a constant pressure P. Any external work, PdV, is done at the expense of the energy of the gas itself, and this is indicated by a fall in temperature, dT. We may therefore write d passing in unit time is given by

Since $PV = RT$, it

$$\text{...stant} \times \frac{pr^4}{l\theta} = \frac{Kpr^4}{l} \quad . \quad . \quad . \quad (1)$$

...tion ... xperiment in seconds.

or ... nt mathem ... analysis of the problem by Wiedemann ... Hagenbach (1860) led to the enunciation of the formula

For ... in t...

$$V = \frac{\pi pr^4}{8\eta l} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

... onstan... acteristic of the liquid. Wiedemann pro... d to ... this constant the "coefficient of viscosity."

Sin... ...ing

and

$$K = \frac{\pi}{8\eta}$$

...hat equations (1) and (2) are identical, and the purely

eq... ormula given by Poiseuille thus receives theoretical support.

This formula assumes the following conditions:

...at there is no slip at the surface of the capillary. This may ...ed.

2. That the layers of liquid move, without turbulence and eddies, ...ant velocity parallel to the axis of the tube. In other ...e formula refers to a purely **laminar flow**.

or

... e rate of flow is increased, a **critical rate** is ultimately reached, ...lue of which depends both upon the tube and the liquid, at which ...ence arises, the liquid particles no longer moving in regular paths.

Si...

...ritical rate of flow, other things being equal, is proportional ... viscosity divided by the density—the so-called **kinematic** ...sity.

a...

That there is no kinetic energy of efflux. This, however, cannot

it ...y well be arranged, for obviously the moving liquid as it leaves ...e capillary carries away a certain amount of kinetic energy with it, ...which has been obtained at the expense of the pressure p. This can ...e allowed for by applying what is known as the **Couette correction**, which consists in subtracting from the viscosity coefficient the quantity

$$\frac{Vd}{8\pi l}$$

where d is the density of the liquid. With narrow capillaries and small pressures this correction may become very small, especially with liquids of high viscosity, so much so that in many cases it may be neglected.

The pressure, p, is frequently obtained by arranging a head of the liquid. If h is the effective head,

$$p = hgd.$$

Inserting this value into equation (2), and applying the Couette correction, we obtain

$$\eta = \frac{\pi hgdr^4\theta}{8Vl} - \frac{Vd}{8\pi l\theta} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where θ is the duration of the experiment in seconds.

This equation may be simplified to :

$$\eta = Ad\theta - \frac{Bd}{\theta} \quad . \quad . \quad . \quad . \quad (4)$$

where A and B are constants for each apparatus, and the liquid volumes are the same.

Measurement of Absolute Viscosity.—The direct experimental measurement of the absolute viscosity of a liquid requires considerable manipulative skill. The apparatus used by Koch (1881) is shown diagrammatically in fig. 100. Tubes A, B and C have the same radius r_1. The liquid in A is allowed to fall from A_1 to A_2, that in C rising from C_1 to C_2, the time occupied being θ seconds. Clearly h_1 and h_2 are the initial and final "heads."

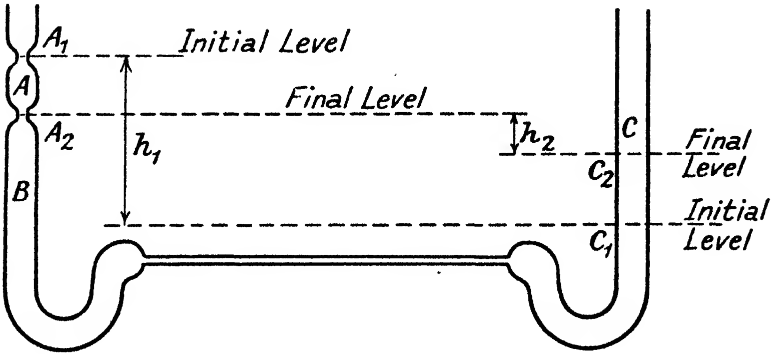


FIG. 100.—Koch's Apparatus for Absolute Viscosity of Liquid.

If we assume that, in the course of an experiment, the small volume dV of liquid is passed through the capillary tube in $d\theta$ seconds, equation (2) may be written

$$dV = \frac{\pi hgdr^4}{8\eta l}d\theta \quad . \quad . \quad . \quad . \quad (5)$$

where h is the variable head of liquid at the moment.

Now the connection between V and h is given by the expression

$$V = \pi r_1{}^2 \frac{h_1 - h_2}{2} \quad . \quad . \quad . \quad . \quad (6)$$

Inserting this value into equation (5) and integrating, we obtain

$$\eta = \frac{\pi(h_1 - h_2)gdr^4\theta}{8Vl \log_e \frac{h_1}{h_2}}$$

The temperature must, of course, be rigidly controlled during each experiment.

The viscosity coefficients of a few typical substances at 20° C. are given in the following table :

Viscosity Coefficients at 20° C.

Substance.	$\eta \times 10^3$.	Substance.	$\eta \times 10^3$.
Hexane	3·20	Benzene	6·49
Heptane	4·16	Toluene	5·90
Octane	5·42		
		Methyl alcohol	5·91
Chloroform	5·64	Ethyl alcohol	11·9
Carbon tetrachloride	9·69	Propyl alcohol	22·5
Carbon disulphide	3·67		
		Formic acid	17·8
Mercury	15·6	Acetic acid	12·2
Bromine	9·93	Propionic acid	11·0

Relative Viscosity.—For many purposes a knowledge of relative viscosities is all that is required. For this purpose the **Ostwald viscometer** is widely used. A usual form is shown in fig. 101. A definite quantity of water is added to the wide left limb and drawn up the right limb to C, slightly above the graduation mark A. The quantity of liquid should be sufficient to fill the viscometer between C and C′ approximately. The liquid is now allowed to flow back and the time taken for the meniscus to travel from A to B is noted. Denoting this time by θ, it is clear that

$$\begin{aligned}\theta &\propto \eta \\ &\propto \frac{1}{d}\end{aligned}$$

whence

$$\eta = kd\theta$$

where d is the density. Since η (see table, p. 246) and d for water are known it is easy to calculate k, which is the constant for the instrument.

For a second liquid

$$\eta_1 = \eta \frac{d_1\theta_1}{d\theta} = kd_1\theta_1.$$

The viscosity of this second liquid is thus obtained relative to water, and may be expressed either relatively, by taking the viscosity of water under the experimental conditions as unity, or, if desired, the actual value of η for water may be introduced into the equation.

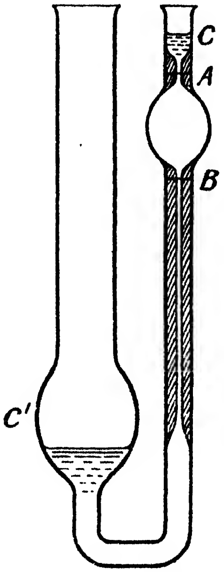


Fig. 101.—The Ostwald Viscometer.

It is important to ensure that the mean head of liquid shall remain constant in all the tests; this is effected for all ordinary purposes by employing a constant volume of liquid throughout.

The Falling Sphere Viscometer.—A sphere falling through a viscous liquid soon attains a constant velocity, u, the magnitude of which is given by Stokes's formula

$$u=\frac{2r^2g(d-d_l)}{9\eta}$$

where g is the acceleration due to gravity, r the radius of the sphere, and d and d_l the densities of the sphere and liquid respectively. This expression is valid provided

1. There is no slip between the surface of the sphere and the liquid. This may be conceded.
2. The velocity of the falling sphere is small. This can be arranged experimentally.
3. The size of the containing vessel is infinite, so that no disturbing effect shall be introduced by the walls. This condition cannot, of course, be realised experimentally, but it can be shown that the velocity of a sphere, falling axially through a liquid contained in a long cylinder of radius R, is given with considerable accuracy by the expression

$$u=\frac{2r^2g(d-d_l)}{9\eta(1+2{\cdot}4r/R)}.$$

As the correction term $(1+2{\cdot}4r/R)$ is independent of η, the relative viscosities of two liquids of densities d_1 and d_2 can readily be determined by inserting the times of fall for them, θ_1 and θ_2, into the following equation :

$$\frac{\eta_1}{\eta_2}=\frac{d-d_1}{d-d_2}\cdot\frac{\theta_1}{\theta_2}$$

where d is the density of the sphere.

A simple form of the falling sphere viscometer is shown in fig. 102. Small steel balls generally are used, the diameters of which range from about 1·6 to 3·2 mm. for liquids of viscosity ranging from 10 to 250 poises. The ball is dropped into the tube containing the liquid being tested at A and the time required for it to fall from B to C is noted. The large cylinder is a water bath, fitted with thermometer, T, and stirrer.

In 1890 Couette devised an apparatus for determining the viscosity of liquids by means of concentric cylinders, and a modified form of the apparatus, due to Hatschek (1913), has been used extensively in studying the viscosities of emulsoids (p. 448). The essential features of **Hatschek's viscometer** are shown in fig. 103. A cylinder C, provided with fixed guards A and B to prevent irregular action at the ends, is suspended in a cylindrical vessel, D, on a rotating stand. As D rotates, the liquid drags C with it, until the twist on the suspension wire neutralises the effect. The deflection, δ, is noted with the aid of the mirror M.

The instrument is graduated first with water. It is clear that

$$\begin{aligned}\delta &\propto \eta\\ &\propto u\text{ (velocity)}\end{aligned}$$

or

$$\delta=k\eta u.$$

Once k, the viscometer constant, has been determined, the instrument may be used to determine the viscosity of other liquids.

For the determination of the relative viscosities of liquids under pressure, up to 12,000 kgrm. per sq. cm., Bridgman (1925) used the apparatus shown in fig. 104. A hollow steel cylinder C, with spherical ends, fits into a steel tube, leaving a small annular space through which the liquid can flow. Pressure is applied and the time taken for the cylinder to fall through the liquid is noted, the moment it reaches the bottom of the steel tube being registered electrically. By turning the tube through 180° round a horizontal axis whilst its contents are still under pressure, the experiment can be repeated as often as desired.

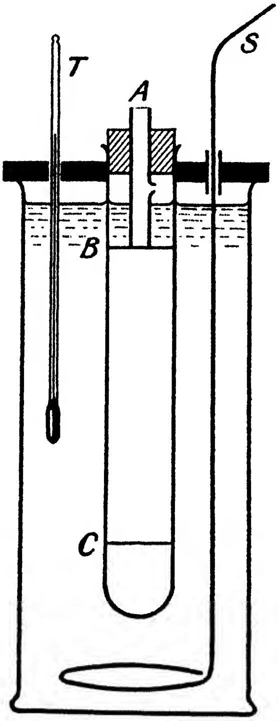


Fig. 102.—Simple Falling Sphere Viscometer.

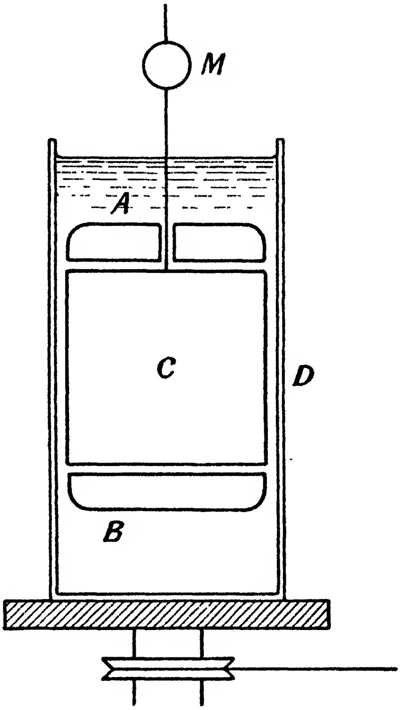


Fig. 103.—Hatschek's Viscometer.

Experiments with various liquids of known viscosities showed that the times of fall were proportional to the viscosities.

Since the rate of flow of a liquid is, other things being equal, inversely proportional to the viscosity, it is frequently convenient to express viscosities in terms of the times required for constant volumes of the liquids in question to flow through an orifice under standard conditions. This method is largely used in the technical testing of oils. **Redwood's viscometer,** which is recommended for this purpose by the British Standards Institution, consists of a copper cylinder which contains the oil to be tested, surrounded by a water bath fitted with a heating apparatus and stirrer to maintain a constant temperature. At the bottom of the cylinder is an agate jet or orifice through which the oil is allowed to flow. The viscosity of the oil is expressed as the time in seconds required for the outflow of 50 c.c. of the oil. The tests are carried out in duplicate and should agree to within 2·0 per cent.

In the following table are given the viscosities of water at various temperatures :

Viscosity of Supercooled Water :

t° C.	0	−4·7	−7·23	−9·30
η (poises)	0·0180	0·0212	0·0234	0·0255

Viscosity of Water :

t° C.	0	10	20	30	50	100
η (poises)	0·0180	0·0130	0·01006	0·0080	0·0055	0·0028

If a liquid is appreciably more viscous than water, it may be more convenient to determine its viscosity relative to a more viscous liquid than pure water. For this purpose the British Standards Institution recommend solutions of cane sugar. The viscosities of such solutions at 25° C. can be calculated with great accuracy from the equation

$$\log \eta = \bar{1}\cdot95134 + 2\cdot9728x + 3\cdot2212x^2 + 24\cdot254x^3$$

where η is the viscosity at 25° C. in centipoises, and x is given by the density of the sugar solution, d, less the density of pure water, that is, $d - 0\cdot99709$, both at 25° C. Thus, for example, the viscosity of a sugar solution of density 1·17439 at 25° C. is 5·187 centipoises.

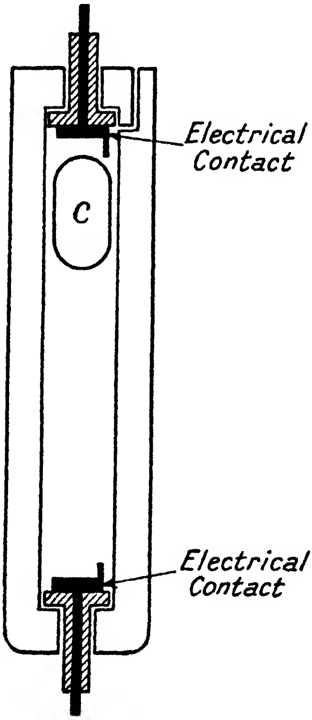


FIG. 104.—Bridgman's Apparatus for Relative Viscosities of Liquids under Pressure.

Rate of Shear.—It is usually assumed that the coefficient of viscosity of a liquid is independent of the velocity gradient. The subject has not received a great deal of experimental study, but for water, at any rate, it has been found that the viscosity is the same for very low rates of shear as for higher ones, provided, of course, the critical velocity (p. 241) is not attained. Its viscosity coefficient at any particular temperature may therefore be regarded as a real physical constant. Presumably the same is true for other pure liquids.

Temperature.—The effect of rise in temperature is, in general, to reduce the viscosity of liquids. For water Poiseuille found that

$$\eta_t = \frac{\eta_0}{1 + \alpha t + \beta t^2}$$

where α and β are constants, η_0 and η_t the viscosities of water at 0° C. and t° C. respectively. An equation which has been found to give results of considerable accuracy with a large number of pure liquids is :

$$\log \eta = \frac{\alpha}{T} + \beta$$

where α and β are constants (Sheppard, 1930). This is similar in form to the vapour pressure equation (17) on p. 90. Very good results are also obtained with an equation similar to Kirchhoff's vapour pressure equation, in which three constants occur. The equation may be written as

$$\log \eta = \frac{a}{T} + \beta \log T + \gamma$$

where a, β and γ are constants (Friend, 1932). Liquid carbon dioxide is exceptional for, at low temperatures, its viscosity rises with the temperature.

Pressure.—For all liquids that have hitherto been investigated, with the single exception of water, the viscosity has been found to become higher at a rapidly increasing rate with the pressure, so that on plotting the viscosity (ordinate) against the pressure (abscissa), curves with very steep slopes are obtained. This is exceptional, for most pressure effects become progressively less as the pressure increases.

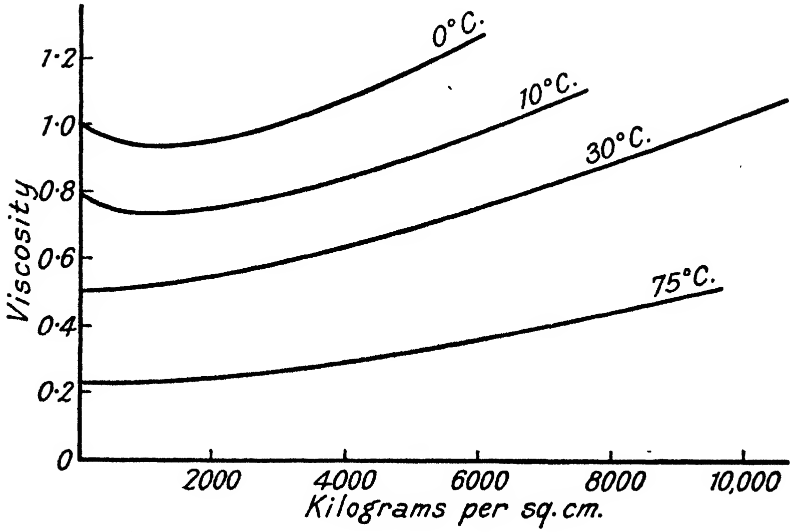


Fig. 105.—Viscosity of Water.

Water is anomalous ; its viscosity at 10° C. and below at first falls with increase of pressure (fig. 105), a minimum being attained at approximately 1000 kgrm. per sq. cm., after which the viscosity rises. At higher temperatures the viscosity rises as with other liquids (fig. 105). The fall at low temperatures is undoubtedly connected with the association of water molecules to bulky trihydrol or " ice " molecules of high viscosity, which tend to break down under the pressure, thus reducing the viscosity at first to a greater extent than corresponds to the normal increase caused by pressure directly.

Nature of Liquid Viscosity.—The viscosity of a pure liquid differs from that of a gas in several important ways. Thus, gaseous viscosity rises with the temperature, whereas in almost all instances liquid viscosity falls with rise of temperature. Again, within limits, gaseous viscosity is independent of the pressure, whereas, in general, liquid viscosity increases with the pressure. In gases, viscosity is due to the passage of gas molecules from one layer to the next, a process that impedes the flow of the layers. In liquids, however, viscosity is believed (Andrade, 1930) to be due to an interchange of momentum between adjacent layers, effected by a temporary union of molecules, which, however, does not persist for longer than the brief time required for the molecules to acquire a common velocity of translation—a temporary " holding of hands between individuals of two parallel rows moving past one another " rather than a " stepping bodily," as in gases, from one row to the other. The liquid thus orients itself or crystallises in minute patches temporarily. At the temperature of solidification crystallisation becomes general and permanent ; at the boiling point crystallisation must be very small.

Solutions of Non-Electrolytes.—The effect of adding cane sugar, which may be taken to represent a typical non-electrolyte, to water is to increase the viscosity, and an equation was given on p. 246 whereby the viscosity at 25° C. of sugar solution of known density can be calculated. The viscosity rapidly falls with rise of temperature, much more rapidly, indeed, than does that of the pure solvent, so that the ratio of the solution viscosity η to that of water η_w at the same temperature steadily falls with rise of temperature. Thus, for a 60 per cent. cane sugar solution :

Temp., °C. . . .	0	20	50	100
η/η_w	133·0	56·2	25·4	11·8

In general the reverse has been found to hold for **solutions of electrolytes** in water. Most electrolytes increase the viscosity of water ; rise of temperature reduces the viscosity, but to a less extent than that of pure water, so that the ratio η/η_w increases with the temperature. A few alkali metal and ammonium salts at first reduce the viscosity, producing what is called a **negative viscosity** ; a minimum viscosity is reached, after which further increase in salt concentration raises the viscosity, which may ultimately exceed that of the water itself, as shown in fig. 106.

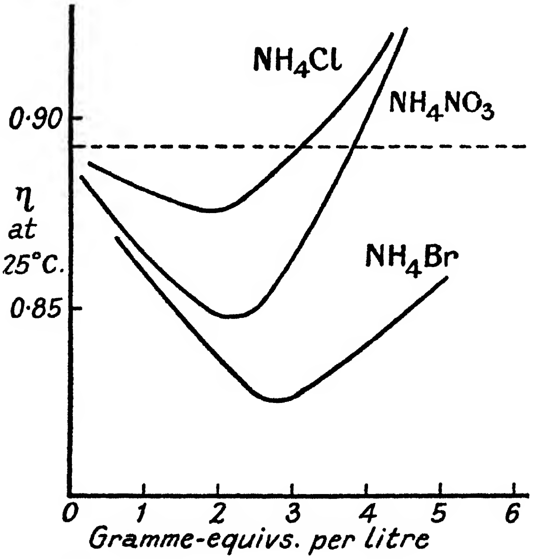


FIG. 106.—η for Aqueous Solutions of Ammonium Salts (Getman, 1908).

Chemical Constitution.—That a connection should exist between viscosity and chemical constitution is to be anticipated, and a few general rules have been found. For example, in a homologous series the increase in viscosity in successive members bears a rough proportionality to the number of CH_2-groups. Alcohols are in general more viscous than the corresponding ketones, and normal esters than the *iso*-compounds. Halogens, hydroxyl and the NO_2-group, when they replace a hydrogen atom, increase the viscosity. As illustrating the effect of hydroxyl, mention may be made of ethyl acetoacetate. On standing after being freshly distilled, its viscosity steadily increases in consequence of gradual change from the ketonic to the enolic form, namely $CH_3CO.CH_2.COOC_2H_5$ to $CH_3C(OH) : CHCOOC_2H_5$.

An empirical relationship between viscosity and molecular volume is as follows :

$$\frac{\eta \times 10^6}{Mv} = 40 \text{ to } 60$$

for non-associated liquids, but greatly exceeds this amount for associated liquids (Dunstan, 1909). From the data given below it will be noted that substances containing the hydroxyl group show considerable association.

Substance.	Formula.	$\frac{\eta \times 10^6}{Mv}$.
Benzene	C_6H_6	65
Toluene	$C_6H_5CH_3$	53
Chloroform	$CHCl_3$	67
Acetone	CH_3COCH_3	43
Water	HOH	493
Glycol	$CH_2OH.CH_2OH$	2750
Lactic acid	$CH_3.CHOH.COOH$	5410

Since Mv represents the molecular volume, $(Mv)^{2/3}$ represents the area over which an equal number of absolute molecules is distributed ; it is therefore called the **molecular surface.** The product of this into the viscosity, namely $\eta(Mv)^{2/3}$, thus represents the force in dynes required to maintain a molecular surface in motion with unit velocity relative to a second surface unit distance from it. This is termed the **molecular viscosity,** and was found by Thorpe and Rodger (1894) to be additive at the boiling point. Atomic and structural constants could thus be evaluated and the molecular viscosities of normal substances of known constitution could be calculated. The following atomic and structural constants were determined :

H	80	S	155
C	−98	Cl	284
O (hydroxylic) . .	196	Double bond . .	113
O (ethereal) . .	35	*Iso*-union . . .	15
O (ketonic) . .	248	Ring formation . .	610

A good example of the calculation is given by propionic acid, C_2H_5COOH. Thus :

6H	480
O (hydroxylic)	196
O (ketonic)	248
	924
3C	−294
Molecular viscosity at boiling point	630

The observed value was 630.

A more important observation is that the logarithm of the viscosity coefficient possesses an additive character, like molecular volume, for example. It is thus often possible to calculate with fair accuracy the viscosity of a compound from values for the atomic and group constants that have been evaluated from existing data (Dunstan and Thole, 1909). The following values for log $\eta \times 10^5$ hold for 20° C. :

	log $\eta \times 10^5$.
CH_2	+0·107
H	+0·934
OH	+2·102
CO	+0·407
O (ethereal)	+0·098
$COOC_2H_5$	+1·573
C	−1·761
Double bond	+1·847
Iso-union	−0·030

A very good example of the calculation is afforded by *iso*butyl ethyl ether, $(CH_3)_2CHCH_2OC_2H_5$. Thus :

	log $\eta \times 10^5$.
$6CH_2$	0·642
O	0·098
2H	1·868
	2·608
Iso-union	−0·030
	2·578
	= log 0·00378 × 10^5.

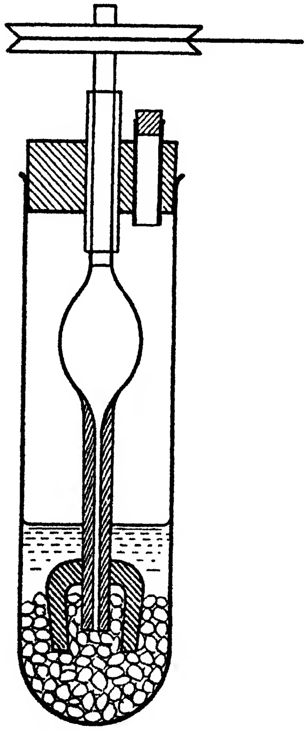


FIG. 107.—Apparatus for Determining Transition Points of Soluble, Hydrated Salts (Hartshorne, 1924).

The calculated viscosity coefficient is thus 0·00378 poise, the observed value at 20° C. being 0·00376 poise.

Transitional Points may be determined viscometrically. A convenient apparatus for determining the transition points of soluble, hydrated salts, by the use of a combined stirrer and viscometer, is shown in fig. 107. The solution and crystals are vigorously stirred at successive temperatures and either their relative viscosities or times of flow, θ, are noted. On plotting η or θ against the temperature, breaks are obtained in the curves at the transition points. The following salts have been found to work well:

$$Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$$
$$Na_2HPO_4.12H_2O \rightleftharpoons Na_2HPO_4.7H_2O + 5H_2O$$
$$NiSO_4.7H_2O \rightleftharpoons NiSO_4.6H_2O + H_2O$$

Emulsoids possess many exceptional features, and their viscosities are discussed in a later chapter.

CHAPTER XIV.

SURFACE TENSION AND THE PARACHOR.

It has long been observed that liquids behave as if their surfaces are covered with a thin, elastic skin, which tends to contract and reduce the surface area to a minimum. This is due to the mutual attraction of the molecules of a liquid, for the surface molecules are attracted towards the interior of the liquid without experiencing a compensating pull in the opposite direction. Once they leave the surface, the molecules are attracted equally in all directions, so that the effects due to attractions in different directions neutralise each other or mutually cancel each other out. The pull on the surface molecules is known as **surface tension**, and manifests itself in a number of curious phenomena, such as the formation of spherical drops, the flotation of dense solids on liquids of lower density, and capillarity. It was not until 1751, however, that the conception of surface tension was introduced, namely, by von Segner.

Some simple experiments illustrating surface tension are as follows: If we take an ordinary camel-hair brush and hold it in a beaker of water, the hairs spread out in much the same way as they do when dry in dry air. But if we withdraw the brush from the water the hairs appear to be glued together.

If a copper wire, bent into circular form and having a piece of silk thread tied loosely to two opposite points, be dipped into soap solution so that a thin soap film stretches across the disc upon withdrawal, the silk thread will swim easily in the film, because it is acted upon by the surface tension of the film in every direction. But if the film is punctured, say, in its upper half A (fig. 108), the silk is now subjected to pull only on its B side, where the soap film is intact. The result is that the thread assumes the shape shown in the figure, the area of the film B being reduced to a minimum. Similarly, if the thread contains a loop, and the film within the loop is punctured, the loop assumes a circular form C, as a circle has a maximum area for a given circumference. The soap film outside the loop has thus reduced its area to a minimum.

The surface tension of water is reduced by the addition of ethyl alcohol. If a little coloured water is poured into a flat-bottomed dish in just sufficient amount to form a shallow layer, upon touching the water at some point with a glass tube that has been dipped in alcohol, the liquid will rush away from the part touched and show the bottom of the dish. This is because the water has a greater surface tension than the solution formed where the glass rod touches it, so the water surface contracts, causing the surface of the solution to expand.

The difference in the surface tensions of water and of aqueous solutions of alcohol is the cause of the peculiar movements up the sides of a wine glass containing strong wine. The liquid creeps up the sides of the glass above the general level of the wine, gathers into drops and runs down again. The reason is, that the wine on the side of the glass loses alcohol by evaporation more rapidly than elsewhere; its surface tension therefore increases and it pulls up more wine from below. This process continues until so much liquid has been drawn up that a drop forms, which trickles back into the wine again. This movement in strong wines has long been known; indeed, it is referred to in Holy Writ, where we read (Prov. xxiii, 31): "Look not thou upon the wine when it is red, when it giveth his colour in the cup, when it moveth itself aright."

A solution of grease in benzene has a higher surface tension than pure benzene. If a spot of grease has fallen on to one's coat, the natural thing to do is to add benzene and rub with a cloth, then add more benzene and rub again. But this is not a good policy, because the greasy benzene has a higher surface tension than the pure solvent and, on adding the second lot of benzene the greasy solution pulls it out in all directions and the grease spot spreads. If, however, a ring of pure benzene is first made round the grease spot, on applying benzene to the grease the greasy solution pulls the benzene from the ring inwards into a heap, and its removal with a fresh rag is thus facilitated.

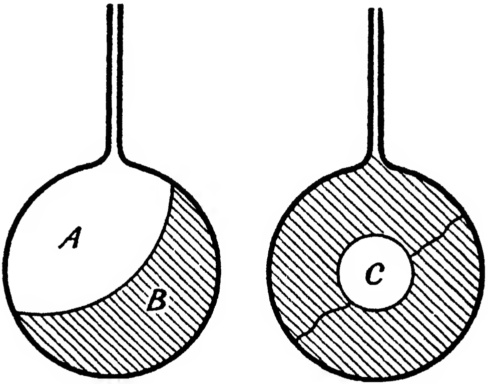


FIG. 108.

The *dancing* of camphor on water is due to a similar cause. The piece of camphor is continuously dissolving in the water, yielding a solution of lower surface tension than the water. If, therefore, the camphor is irregular in shape, or if dissolution at any point proceeds irregularly, the side of least solution concentration will possess the greatest surface tension and the camphor will be dragged in that direction. A very thin layer of oil is sufficient to prevent the movement of camphor on water by reducing the surface tension. A 2 $\mu\mu$ layer will effect this. Many substances besides camphor show this movement. Chief among these are thymol, menthol and *p*-toluidine, the last-named showing the most vigorous action of all.

Definition of Surface Tension.—If we allow a soap film to form in the more or less triangular area between the straight wire AB and the curved wire CDE (fig. 109) and then suspend the whole vertically from the point D, the loose wire AB will slide down under the influence of gravity towards CE, but ultimately will come to rest at some place as shown on the figure when the upward pull of the soap film balances the downward pull due to gravity.

Let m be the mass of the sliding wire AB, σ the surface tension exerted across unit length of the film and l the length of AB in actual contact with the film; then, the film having two surfaces, one in front and one behind, the total upward pull on AB is $2l\sigma$. This is balanced by mg; so that

$$\sigma = \frac{mg}{2l} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

σ is usually measured in dynes per centimetre. It is clearly a derived unit, and its dimensions are

$$\begin{aligned}[\sigma] &= [F][L^{-1}] \\ &= [MT^{-2}].\end{aligned}$$

The surface tensions of a few liquids are given in the table on p. 263.

Drop Formation.—Since a sphere possesses the minimum surface for a given volume, there is always a tendency for small isolated portions of liquid to assume a spherical shape. If, therefore, water is allowed to escape very slowly from a burette a drop gradually forms, as shown in fig. 110. As the volume of the water increases, the effect of gravity becomes more pronounced; the water sags more and more in the middle, ultimately forms a neck at B and breaks away in almost perfectly spherical form.

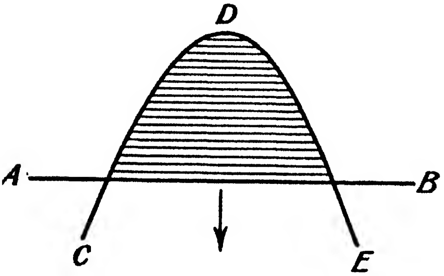


FIG. 109.

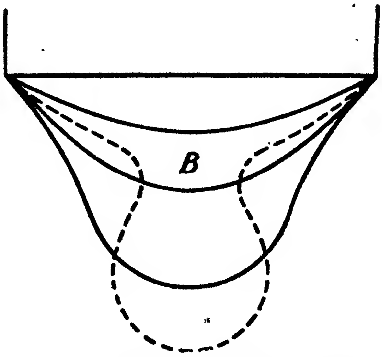


FIG. 110.—Illustrating Drop Formation.

If, now, the water in the burette is replaced by oil, and the end of the burette is made to dip into an aqueous solution of alcohol of similar density to the oil, the effect of gravity is neutralised, and the oil, on flowing in, forms a perfect sphere.

If two burettes are taken, one containing water and one alcohol, and these liquids are allowed to flow out slowly into the air, it will be observed that the drops of water are appreciably larger than those of the alcohol. Since the alcohol is less dense than water this cannot be a gravitational effect; it is due to the fact that the alcohol has a smaller surface tension than the water, so that the force holding each drop to the burette is smaller, and the drop more easily breaks away (see table, p. 263). In dealing with drop formation, therefore, we have two forces to consider, namely surface tension and gravity.

When water flows out of a jet, it is at first cylindrical in form, but as it travels farther from the orifice, necks begin to appear and ultimately the jet breaks up into a series of drops. The gradual breaking-up of a jet is shown in fig. 111, taken from an instantaneous photograph. Cylinders of water are unstable when their length is greater than their bottle it always tends to take up a central position, unless the diameter of the bottle exceeds some 4 or 5 cm. This is due to the fact that the centre is slightly lower than the sides, the curvature due to surface tension not being completely eliminated. With a bottle or tube of diameter 2·54 cm. the level at the centre is 0·11 mm. lower than in a tube 3·8 cm. in diameter. The difference in level becomes inappreciable with greater diameters. This means that the surface tensions, as measured by Ramsay and Shields, were all slightly too high.

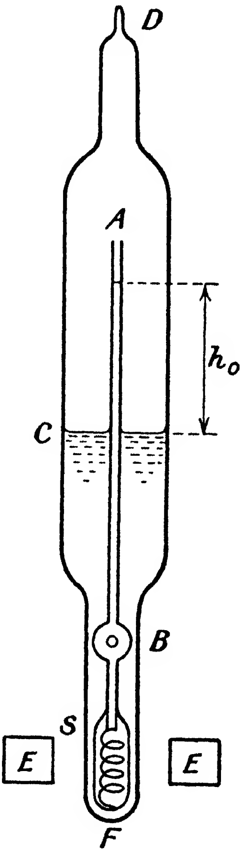


FIG. 114.—Ramsay and Shields' Apparatus.

To avoid this error Richards and Coombs used the apparatus shown in fig. 115. The glass plunger P served to reduce the quantity of liquid required. The apparatus was thoroughly exhausted prior to sealing, and after determining h_0 it was turned through 180° and the difference in levels observed again. By taking the mean of several readings a very accurate result is obtainable.

Sugden's Differential Method (1921).—This consists in comparing the relative heights of the liquid columns in several capillary tubes of different radii, r_1, r_2, r_3, etc., placed in the same apparatus and under identical conditions. Assuming two capillary tubes are employed, the equation

$$\sigma = \frac{r_1 r_2 g(3\delta h + r_2 - r_1)(D - d)}{6(r_1 - r_2)} \quad . \quad (8)$$

enables the surface tension of the liquid to be calculated. One advantage of this method lies in the fact that the value of δh only is required ; the actual height of the meniscus above the general level need not be ascertained, so that no error is caused by concavity in the general level.

The Drop Method.—A drop will cling to the end of a tube until its mass is so great that, under the influence of gravity, it overcomes the surface tension effect and falls. If m is the maximum mass of liquid that can hang from a tube of radius r, since the upper portion of the drop is cylindrical we should expect that

$$mg = 2\pi r\sigma \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This, however, is not the case ; for even if the tension at the circumference of the tube acted vertically and the whole of the liquid below this level passed into the drop, equation (9) makes no provision for the fact that the pressure inside the drop is above atmospheric, owing to curvature. This excess pressure equals $\pi r\sigma$, and if the surface of the liquid could be regarded as a cylindrical prolongation of the tube, the theoretical formula for the maximum mass of the drop would be

$$mg + \pi r\sigma = 2\pi r\sigma$$

or

$$mg = \pi r\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

If the detachment of the drop could be regarded as following immediately, it would then follow that

$$mg \propto r.$$

This is **Tate's Law**, and was discovered by Tate experimentally in 1864. The law, however, is only approximately true. For tubes of moderate diameter π in equation (10) must be replaced by 3·8, thus

$$mg = 3{\cdot}8r\sigma \quad . \quad . \quad . \quad (11)$$

If the diameter is either very large or very small, the numerical factor rises above 4. Indeed, it is never strictly constant. This is due to the fact that the actual detachment of the drop is a complex dynamical process, and an adequate theoretical formula has not as yet been devised to meet the situation. For purely comparative purposes, however, when absolute values of great accuracy are not required, the drop method has proved very useful.

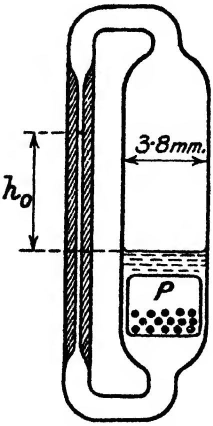


Fig. 115.—Richards and Coombs' Apparatus.

Wilhelmy's Method consists in measuring the downward pull exerted on a thin sheet of glass or metal partly immersed in the liquid, which wets it. This is effected by suspending the plate from one arm of a balance and then adding additional weights, δW, to counteract the pull on the plate when it is partially immersed, a correction being applied for the small amount of liquid displaced (fig. 116).

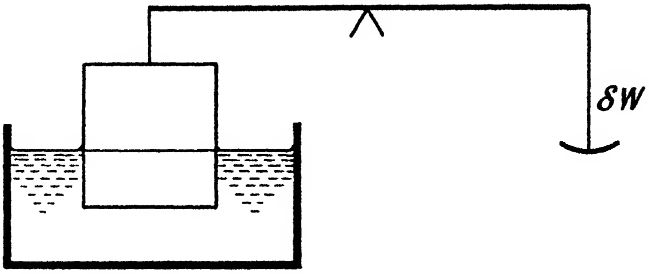


Fig. 116.—Wilhelmy's Apparatus.

If l is the length of the liquid line, it will be clear that

$$\delta W = l\sigma \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Jaeger's Method, which is useful when relative values only are required, consists in measuring the minimum pressure required to force a bubble of air from a capillary tube dipping into the liquid. A bubble of air in a liquid is spherical and is acted upon by two pressures, namely

(i) External pressure, due to the surface tension of the liquid, which may be regarded as acting on the circumference of any great circle dividing the bubble into two hemispheres. This is balanced by

(ii) Internal pressure, P, tending to force the two hemispheres apart.

Equating these two, it is clear that, if r is the radius of the bubble

$$2\pi r\sigma = P\pi r^2$$

or

$$P = 2\sigma/r \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Hence the pressure required to detach a bubble of air from the end of the capillary tube exceeds the hydrostatic pressure at that end by an amount that is directly proportional to the surface tension of the liquid. A comparison of the observed minimum pressures, therefore, indicates the relative surface tensions.

This method appears capable of yielding very accurate comparative results. With the apparatus shown in fig. 117, Mills and Robinson (1931) state that results with a relative accuracy of ±0·006 dyne per cm. were realised. Mercury, under the control of tap F, ran into G, thus causing air, filtered through cotton wool, to be drawn through the liquid in A, the manometer, M, registering the difference in pressure. Measurements of the height of liquid in the manometer were made with a cathetometer with an accuracy of ±0·02 mm. The apparatus is first standardised by using with, say, water of known surface tension, σ_w, at the desired temperature. Measurements are then made with the liquid to be studied, the surface tension of which, σ_l, is given by

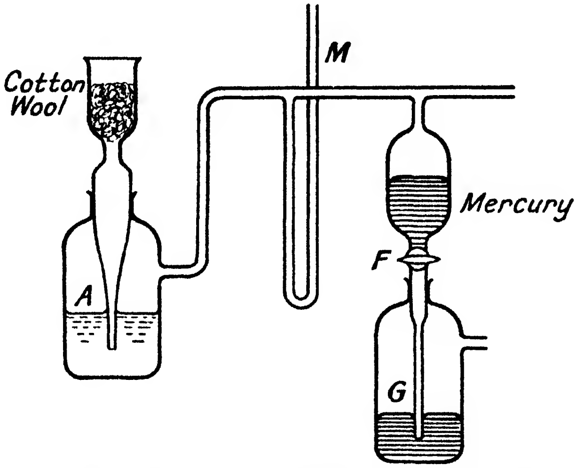


FIG. 117.—Apparatus for Jaeger's Method (Mills and Robinson).

$$\sigma_l = \sigma_w \times \frac{\text{Jet pressure with liquid}}{\text{Jet pressure with water}}.$$

Quincke's Method.—The surface tension of mercury has recently been determined by Cook (1929) with great accuracy using a method involving the measurement of a drop of mercury, as originally suggested by Quincke in 1871. The essential features of the apparatus employed by Cook are shown in fig. 118. Mercury was distilled from A into the cup B and the necessary measurements were made with a cathetometer through the window C. Fig. 118 (a), which represents an enlarged drop, indicates the measurements required.

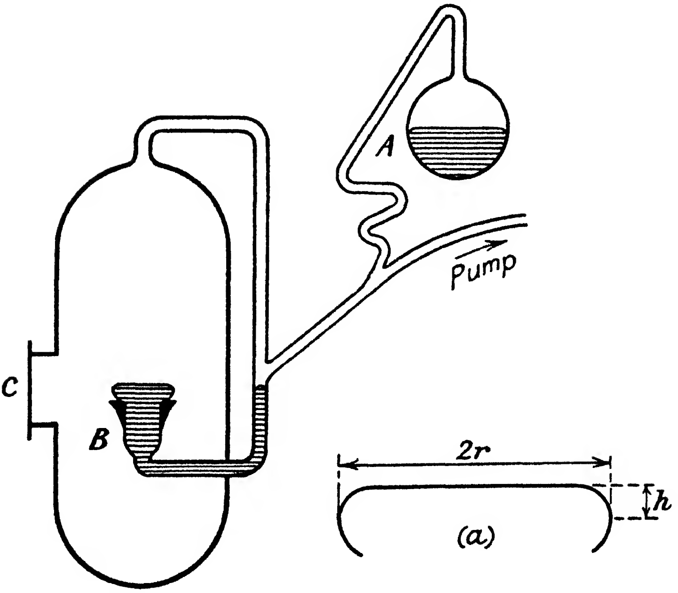


FIG. 118.—Cook's Apparatus.

Quincke's general formula, as modified by Worthington (1885), is

$$\frac{\sigma}{d}=\frac{h^2g}{2}+\frac{2h\sigma}{d}\left(\frac{1}{b}-\frac{1}{3{\cdot}282r}\right) \quad . \quad . \quad . \quad . \quad (14)$$

where d is the density of the liquid and b the radius of curvature at the top of the drop. For mercury drops of suitable size, b is very large and $\frac{1}{b}$ may be neglected, equation (14) simplifying to

$$\sigma=\frac{h^2dg}{2\left(1+\frac{2h}{3{\cdot}282r}\right)} \quad . \quad . \quad . \quad . \quad (15)$$

A few data obtained, unless otherwise stated, in the presence of vapour of the liquid only, are given in the table on p. 263. It will be noted that, for a non-metallic substance, water has a high surface tension. Reference is made to this again later (p. 269). Molten metals usually have very high surface tensions also.

Effect of Temperature.—Rise of temperature invariably reduces the surface tension of a pure liquid, provided, of course, no abrupt chemical or physical change takes place, until at the critical temperature the tension becomes negligibly small, but does not vanish altogether.

The general equation connecting the two phenomena may be written as

$$\sigma_t=\sigma_0(1-at+\beta t^2) \quad . \quad . \quad . \quad . \quad (16)$$

where a and β are constants, and σ_0 is the tension at 0° C. Usually β

Surface Tension.

Substance.	Temp., °C.	Surface Tension, dynes/cm.	Change in Surface Tension per degree C. $-d\sigma/dT$.
Water	20	72·90	0·15
Methyl alcohol (in air)	20	22·61	0·09
Ethyl alcohol	20	22·05	0·09
Glycerol (in air)	18	63·4	0·07
Acetic acid	20	27·8	0·10
Carbon tetrachloride	20	26·95	0·12
Chloroform	20	27·14	0·14
Carbon disulphide	19·4	32·33	0·15
Benzene	20	29·02	0·13
Toluene	20	28·58	0·11
Mercury (*in vacuo*)	15	515	0·23
Lead (molten, in CO_2)	335	473	..

is very small, so that over a small range of temperature we may write

$$\sigma_t = \sigma_0(1 - at) \quad . \quad . \quad . \quad . \quad . \quad (17)$$

that is, the surface tension is a linear function of the temperature. This applies to temperatures at least 40° C. below the critical temperature.

If, now, we plot the surface tension (ordinate) against the temperature (abscissa), as shown in fig. 119, and extrapolate to zero tension, the line cuts the abscissa a few degrees, δ, below the critical temperature. For many substances the numerical value of δ is approximately 6.

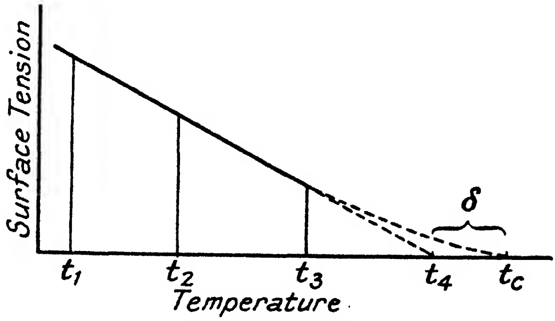


FIG. 119.—Surface Tension/Temperature.

It is clear that the surface tension at any temperature, say t_1, is proportional to $t_4 - t_1$, or, generally

$$\sigma_t \propto (t_c - \delta) - t$$
$$= b(t_c - t - \delta) \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where b is a constant.

Application of the theorem of Le Chatelier (p. 23) tells us that if we stretch a liquid film adiabatically its temperature will fall, because its total surface energy is increased and the film offers a greater resistance to further extension. If the film is stretched isothermally, as is usually the case, heat flows in to maintain a constant temperature. In other words, the total increase in the surface energy is the sum of two items, namely the work done against the surface tension and the amount of heat absorbed isothermally during the extension.

Denoting the total surface energy by E, and the variation of surface tension with temperature by $\frac{d\sigma}{dt}$, Kelvin's equation connecting the surface tension and the total surface energy at any temperature t may be written as

$$\sigma = E + t\frac{d\sigma}{dt} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Since, as already shown, the relation between σ and t is linear over considerable ranges of temperature, it follows that $\frac{d\sigma}{dt}$ is constant and negative.

Numerous attempts have been made to find a formula of wider applicability than equation (17). Sugden (1924) found that, for many non-associated liquids, the following relationship holds with great accuracy:

$$\sigma = \gamma(1 - \theta)^{1\cdot 20} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where θ is the reduced temperature and γ a constant, proportional to $T_c^{1/3}P_c^{2/3}$.

Calculation of the Critical Temperature.—Using equation (18) it should be possible to calculate, by extrapolation, the critical temperature of a liquid when its surface tension at not fewer than two different temperatures is known, the correction δ, which is approximately 6, being applied. The following critical temperatures have been calculated in this manner:

Critical Temperatures as Calculated from Surface Tension Measurements.

(Ramsay and Shields, 1893.)

Substance.	Calculated Critical Temperature, °C.	Observed Critical Temperature, °C.
Carbon disulphide	280	273
Carbon tetrachloride . . .	282	283
Methyl formate	214	214
Ethyl acetate	250·5	251
Benzene	288	288·5
Chlorobenzene	360	360
Aniline	405	425

In some cases the calculated data are extraordinarily close to those observed experimentally; in most other cases they are somewhat lower. The calculated data are based on the original surface tension measurements made by Ramsay and Shields. These, as we have seen, are slightly too high, but the principle is the same.

The Theory of Laplace (1806).—This is based on the hypothesis that any two molecules in a pure liquid attract one another very strongly when the distance between them is small. If, however, the distance is increased beyond what is termed the **range of molecular attraction,** which is of the order of $5\mu\mu$, the forces between the two molecules rapidly diminish. This may be illustrated by bringing two plane and highly polished surfaces of glass together; they are then very difficult to separate; but if the glass surfaces are not perfectly clean and plane, they do not adhere, as the molecules do not approach sufficiently close. Now, as we have mentioned already (p. 252), in the mass of a liquid the molecules are attracted on all sides by other molecules, so that the individual effects neutralise each other, or "cancel out," to use a mathematical expression. At the surface, however, the molecules are drawn inwards and experience no compensating pull outwards. Hence liquids, like gases (p. 63), possess **intrinsic pressure** and offer resistance to enlargement of volume (see p. 101). This intrinsic pressure in the case of gases enters into Hirn's equation (p. 63) as P_i, and into van der Waals' equation (p. 63) as a/V^2. Assuming these equations apply to liquids, it is easy to calculate the value of P_i. For water this is approximately 11,000 atmospheres.

We have already seen (p. 84) that the latent heat of vaporisation, l, of a liquid is made up of two items, namely, the heat required to separate the molecules, l_i, and that required to overcome the pressure of the atmosphere, l_e. So that

$$l = l_i + l_e$$

or

$$\begin{aligned} l_i &= l - l_e \\ &= 498 \text{ gramme-calories per gramme in the case of water} \\ &\simeq 498 \times 4{\cdot}18 \times 10^7 \text{ dynes/cm.}^2 \\ &\simeq 21{,}000 \text{ atm. (approx.).} \end{aligned}$$

Laplace assumed that half the work of removing a molecule of a liquid is done when the molecule is brought to the surface. Thus, in fig. 120 AB represents the surface of the liquid, whilst the circles represent the spheres of molecular attraction of the enclosed molecules. Molecule 1 is free to move in any direction. Molecule 2 is drawn into the liquid with a resultant force represented by the segment CD. Molecule 3 is drawn inwards with a maximum force represented by the

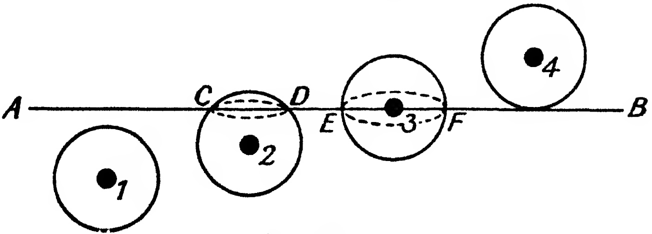


FIG. 120.

hemisphere EF. As the molecule rises still further the force of attraction falls off, until in the position assumed by molecule 4 it is negligible and the molecule is free to escape. The work required to lift molecule 3 to the position occupied by molecule 4 is thus, according to Laplace, one-half of l_i, or 10,500 atm. in the case of water. This value agrees very satisfactorily with that calculated from Hirn's equation and from van der Waals' equation.

Surface Tension and Compressibility.—The force required to diminish the volume of a given mass of liquid by a given small amount is the same as that required to increase it by the same amount. We should therefore expect to find a general relationship between the compressibility β (p. 163) and the surface tension, since the greater the surface tension the less the compressibility will be, as the liquid offers a proportionately greater resistance to change in volume. A few data are given in the following table:

Substance.	σ at 20° C.	$\beta \times 10^5$ per megabar.	$\sigma\beta \times 10^5$.
Water	72·9	4·59	335
Glycerol	65·0	2·48	161
Acetic acid	27·8	4·02	112
Mercury	515	0·388	200
Carbon disulphide	32·33	8·59	278
Carbon tetrachloride	26·95	8·96	242
Chloroform	27·14	9·3	252
Benzene	29·02	9·08	264
Toluene	28·58	7·8	223

It will be observed that, in general, high surface tension accompanies low compressibility. But the product $\sigma\beta$ is not constant, although, if we except liquids such as water, glycerol and acetic acid, which are known to be associated, there is a slight improvement in that direction.

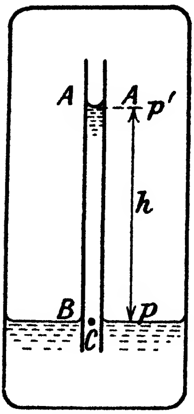


FIG. 121.

Surface Tension and Vapour Pressure.—The vapour pressure in equilibrium with a curved liquid surface is different from that over a plane surface of the same liquid. We can find the connection between the difference in vapour pressure and the radius of curvature as follows: Consider a capillary tube AB, of radius r, suspended vertically with its lower end dipping into a liquid and contained in an evacuated vessel (fig. 121). The vapour pressure of the liquid at the general level or plane surface B is p; let that at the level of the meniscus A at a height h cm. be p'.

Assuming the curved surface inside the capillary tube to be hemispherical, the pressure just above the curved surface is greater than that just below it by the amount $2\sigma/r$, for, as we have already seen (p. 261), this is the difference in pressure between a spherical air bubble and the surrounding liquid. Hence the pressure just below the meniscus at A is $p' - 2\sigma/r$. The pressure at C is thus the pressure due to column h of liquid + the pressure below the meniscus

$$= hdg + p' - 2\sigma/r$$

where d is the density of the liquid. But the pressure at C is also equal to that at B, namely p. We may therefore write

$$p = hdg + p' - 2\sigma/r$$

or

$$p - p' = hdg - 2\sigma/r \quad . \quad . \quad . \quad . \quad (21)$$

Now the difference between the pressures at A and B is due to the column, h, of vapour, of density d', so that

$$p - p' = hd'g \quad . \quad . \quad . \quad . \quad (22)$$

Combining these two equations, we have

$$\begin{aligned} 2\sigma/r &= hg(d - d') \\ &= hgd' \, . \, \frac{d - d'}{d'} \\ &= (p - p') \, . \, \frac{d - d'}{d'} \end{aligned}$$

or

$$p - p' = \frac{2\sigma}{r} \, . \, \frac{d'}{d - d'} \quad . \quad . \quad . \quad . \quad (23)$$

This equation is only approximately true. More rigid mathematical analysis gives

$$RT \log_e p/p' = \frac{2\sigma}{rd} \quad . \quad . \quad . \quad . \quad (24)$$

Supersaturated Vapour.—Both equations (23) and (24) show clearly that by reducing r the difference between p and p' increases. These equations will still hold for small drops, but the radius, r, will then be of opposite sign and p', the vapour pressure at the curved surface, will now be greater than p. If the radius of a spherical drop of water at 0° C. is 1 $\mu\mu$, the equilibrium vapour pressure of the curved surface is more than twice as great as that at the plane surface. This explains the ease with which a supersaturated vapour can be obtained in the absence of the liquid phase. On cooling a vapour saturated at a particular temperature to a lower temperature in the entire absence of dust particles or other bodies that can serve as condensation nuclei, there is little tendency at first for drops to form, as these would be small and, if momentarily produced, would tend to evaporate owing to their high vapour pressure. It is possible to cool air, free from dust, to such an extent that the water vapour present is no less than eight times that required to saturate it at the lower temperature, without any fog formation.

If a saturated vapour contains drops of different size, the smaller ones will evaporate and the larger ones will grow.

Liquids that do not wet Capillary Tubes.—It has hitherto been assumed that the liquids considered wet the capillary tube and thus stand at a higher level within than without. Such is not always the case. Mercury, for example, does not wet glass, and its meniscus in a capillary tube is reversed, the surface of the mercury being convex instead of concave and standing at a lower level in the capillary than without. The foregoing equations ((23) and (24)) still apply, the radius being regarded as negative.

Surface Tension of Solids.—There is no reason to suppose that surface tension abruptly ceases when a liquid solidifies. Certainly an abrupt change appears to take place, but all available evidence points to the view that solids possess relatively high surface energies, the values of which admit of calculation with the aid of a modified form of equation (23).

It is well known that large crystals in a saturated solution tend to grow, so to speak, at the expense of the small ones, just as large drops of liquid grow at the expense of smaller ones, for small crystals, as we shall see later (p. 370), have a greater solubility or solution pressure than larger ones. In solution we have to deal, not with gaseous pressure, but with osmotic pressure. If, therefore, we write π for the osmotic pressure of a saturated solution in equilibrium with a solid substance of large area, and π' for the pressure when in equilibrium with a crystal of radius r, d being the density of the solid, equation (24) becomes

$$RT \log_e \frac{\pi'}{\pi} = \frac{2\sigma}{rd} \quad . \quad . \quad . \quad . \quad (25)$$

Since the osmotic pressures are proportional to the numbers of dissolved molecules per unit volume, that is, to the solubilities, S and S', of the large and small crystals respectively, it follows that

$$RT \log_e \frac{S'}{S} = \frac{2\sigma}{rd} \quad . \quad . \quad . \quad . \quad (26)$$

This is a particularly useful equation, as it gives us a method of calculating the surface tension of a soluble solid.

Using the data given on p. 370 for the solubilities of different-sized particles of barium and calcium sulphates, their surface tensions work out at 4000 and 1100 dynes per cm. respectively.

Surface Tension of Gases.—Although at the critical point the surface tension of a liquid becomes very small, it does not altogether vanish. Vapours and gases have surface energies also. This is recognised in van der Waals' equation by the term a/V^2. A practical illustration is afforded by smoke rings, which may be formed in a variety of ways.

Surface Tension and Molecular Weight.—In the ordinary gas equation the product PV may be termed the **volume energy** of the gas. An analogous equation to the gas equation can be written in which the volume energy is replaced by **surface energy.** This was first pointed out by the Hungarian physicist Eötvös in 1886, and confirmed experimentally by Ramsay and Shields in 1893.

If M is the molecular weight of a liquid of specific volume v, then Mv is proportional to the volume of its molecule, $(Mv)^{1/3}$ to its linear molecular dimension, and $(Mv)^{2/3}$ to its molecular surface area. Its molecular surface energy is thus proportional to $\sigma(Mv)^{2/3}$.

We have already seen (p. 263) that the prolongation of the linear σ/t relationship to the critical point, t_c, cuts the abscissa $\delta°$ below the observed critical temperature. We will therefore measure the temperature, τ, downwards from t_c and subtract δ. As σ falls with rise of temperature, it will clearly rise as the value of τ increases, and by equating

$$\sigma(Mv)^{2/3} = k(\tau - \delta) \quad . \quad . \quad . \quad . \quad (27)$$

we arrive at an equation analogous to the gas equation.

In order to eliminate δ and arrive at the value for the constant k, measurements are made of the specific volume and surface tension at two different temperatures. Denoting simultaneous values by the same suffix, the equations

$$\sigma_1(Mv_1)^{2/3} = k(\tau_1 - \delta)$$
$$\sigma_2(Mv_2)^{2/3} = k(\tau_2 - \delta)$$

lead to the following equation for k:

$$k = \frac{\sigma_1(Mv_1)^{2/3} - \sigma_2(Mv_2)^{2/3}}{\tau_1 - \tau_2} \quad . \quad . \quad . \quad . \quad (28)$$

Now it is found that if k be determined from this equation, using for M the molecular weight of the substance in the gaseous state, the value is 2·12 (using c.g.s. units) for quite a number of substances. It is therefore concluded that these substances undergo no change in molecular weight on their passage from the gaseous to the liquid state. Among such *normal liquids* are benzene, chlorobenzene and ether. When, therefore, it is observed that the value of k for a liquid is less than 2·12, it is concluded that association takes place when the vapour condenses to liquid (since to obtain the normal value of k a greater value for M is necessary than the one that has been assumed). From the observed value of k for any particular substance, it is thus possible to derive an approximate measure of the **degree of association.** Thus, if association has taken place, k is less than 2·12, simply because the mass of the molecule is not truly represented by M, but by xM, where x is greater than unity and represents the degree of association. Hence, by substituting xM for M, equation (27) becomes

$$\sigma(xMv)^{2/3} = 2{\cdot}12(\tau - \delta)$$

whence

$$x = \left(\frac{2{\cdot}12}{k}\right)^{3/2} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

approximately.

The values obtained for x in the case of water at temperatures ranging from 0° to 100° C. as given by Ramsay and Shields are detailed in the table below.

Degree of Association of Water.

Temperature, °C. . .	0	20	40	60	80	100
x (Ramsay and Shields) .	3·81	3·55	3·18	3·00	2·83	2·66
x_1 (Dutoit and Mojoiu) .	2·52	2·41	2·30	2·18	2·07	1·96

In the following table are given data indicating the extent to which a few typical substances are believed, from surface tension measurements, to be associated in the liquid state.

Substance.	Temperature Interval, °C.	Degree of Association.
Methyl alcohol	16 to 78	3·43 to 3·24
Ethyl alcohol	16 to 78	2·74 to 2·43
Acetic acid	16 to 132	3·62 to 2·77
Acetone	17 to 78	1·26
Formamide	20 to 75	6·18 to 3·34
Acetamide	85 to 120	2·47 to 2·11
Phenol	46 to 184	1·42 to 1·18
Benzamide	130 to 170	2·70 to 1·81
Phosphorus	78 to 132	3·76
Sulphur	115 to 160	6·00
Nitrogen dioxide	2 to 20	2·02
Sodium nitrate	300 to 400	10·68
Potassium nitrate	341 to 407	8·73
Silver chloride	446 to 580	3·29
Lead chloride	480 to 600	3·60

Several cogent criticisms have been urged against the foregoing method of measuring the degree of association of a liquid. These may be summarised as follows :

(i) The equation itself (28) is only an approximation.

(ii) The value 2·12 ascribed to k was originally believed to be fairly universal, but it has since been shown that many substances believed to be non-associated yield much higher values for k. Thus, whilst k may be constant for one type of substance, different types of substances may yield different values for k. For example :

Substance.	Temperature, °C.	k.
Amyl stearate	55 to 150	3·34 to 3·33
Benzylamine	20 to 75	2·08 to 2·23
Tristearin	58 to 135	6·21 to 5·35

(iii) Attention has been very usefully directed by Dutoit and Mojoiu to the fact that molecular weights, as determined by surface tension phenomena, are most probably, in the case of associated liquids, only the particular molecular weights of the surface layers of the liquids. If the liquid is not associated, there will, of course, be no difference between the bulk and the surface, and the molecular weights calculated from the foregoing formulæ may be expected to be correct. But where association takes place, it is highly improbable that the surface layers will possess the same state of aggregation as the interior. The probability is that the association will be accentuated in the surface, so that the calculated molecular weights will be too high.

The only conclusion that can safely be drawn from the foregoing data for water is that water at all temperatures between 0° and 100° C. manifests an appreciable degree of association.

Equation of Dutoit and Mojoiu.—Another method of calculating the molecular complexity from the surface tension is that given by Dutoit and Mojoiu (1909), who employ the empirical formula

$$M = 0{\cdot}6T(4{\cdot}8 - \log p)/a^2,$$

where a^2 is the **specific cohesion,** defined by

$$a^2 = 2\sigma/d,$$

where d is the density of the liquid and p the vapour pressure, which, however, must not exceed 2 atmospheres. This latter restriction places an upper limit upon the temperature and prevents the formula from being used to determine the molecular aggregation of water at the critical point. The degrees of association, x_1, as calculated by this formula at various temperatures, are given in the table on p. 269. They are appreciably lower than those calculated by Ramsay and Shields.

Walden's Equations.—Several interesting relationships between the specific cohesion, as defined above, and certain other physical constants of liquids have been noted by Walden (1909). A few of these may be mentioned.

1. The latent heat of evaporation, l, of a liquid is proportional to its specific cohesion, as measured at the boiling point, provided no association occurs. That is

$$l/a^2 = \text{constant} = 17{\cdot}9 \text{ (mean value)} \quad . \quad . \quad (30)$$

Dutoit and Mojoiu also came independently to the same conclusion.

A few illustrations are as follows :

Non-associated Substances.	l/a^2.	Substances Suspected of Association.	l/a^2.
Stannic chloride .	17·35	Water . . .	44·1
Silicon tetrachloride .	17·03	Methyl alcohol . .	51·3
Methyl iodide . .	18·13	Ethyl alcohol . .	45·3
Ethyl iodide . .	17·90	Acetone . . .	24·2
Carbon disulphide .	17·89	Phenol . . .	27·5

For associated substances the ratio l/a^2 greatly exceeds the normal value, and is thus an excellent qualitative test of association.

We have already seen that, by Trouton's Rule (p. 88)

$$\frac{Ml}{T} = 21 \text{ (approx.)}.$$

By substituting in this equation the value

$$l = 17{\cdot}9a^2$$

the expression becomes

$$M = \frac{1{\cdot}17T}{a^2} \quad . \quad . \quad . \quad . \quad (31)$$

from which the molecular weight of the liquid can be calculated. Ma^2 is termed the **molecular cohesion.**

2. Substances at their boiling points are at approximately comparable temperatures, for, very roughly, the boiling point temperature is two-thirds of the critical value, both measured on the absolute scale. If the melting points of substances could similarly be regarded as comparable temperatures, then the expressions $\frac{l_m}{a^2}$ and $\frac{Ml_m}{T_m}$ would also be constant at the melting point. Therefore, in turn, the expression

$$M = \frac{\text{constant} \times T_m}{a^2} \quad . \quad . \quad . \quad . \quad (32)$$

would be applicable at the melting point. Walden tested this expression for measurements made at the melting point and found, for a large number of non-associated liquids, that equation (32) does hold, and that the constant is equal to 3·65. Hence the molecular weight of a liquid at its freezing point is obtainable from the equation

$$M = \frac{3{\cdot}65T_m}{a^2} \quad . \quad . \quad . \quad . \quad (33)$$

The results all indicate that fused salts have very complex molecules, the degree of complexity of sodium chloride being 10, sodium bromide 8, sodium iodide 6·2. In all the cases investigated the chloride is most and the iodide least associated.

3. A third relationship, namely

$$P_i = 75{\cdot}3\sigma_b \quad . \quad . \quad . \quad . \quad (34)$$

where P_i is the intrinsic pressure and σ_b the surface tension at the boiling point is very interesting, but of little practical value owing to the difficulty of determining the intrinsic pressure.

Presence of Foreign Substances.—In the preceding sections on surface tension we have been dealing with pure liquids in the presence of their own vapour only. We must now inquire into the effects produced on the introduction of a second substance into the system.

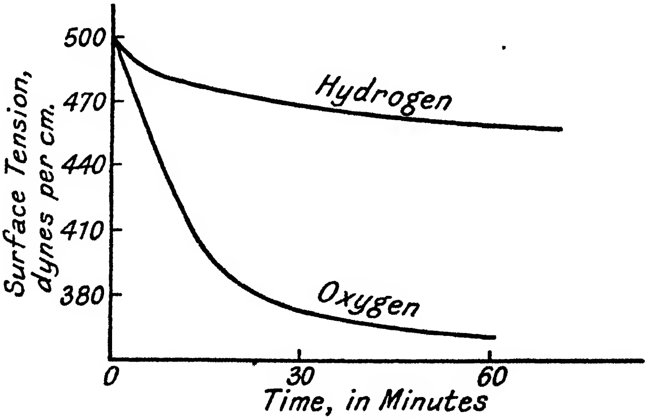


FIG. 122.—Surface Tension of Mercury (Cook, 1929).

Let us first consider the case of mercury. According to the latest measurements *in vacuo* its surface tension is 515 dynes per cm. at 15° C. (p. 263). If small quantities of a gas are introduced, the surface tension rapidly falls to an asymptotic value (fig. 122), reaching about 460 dynes per cm. in hydrogen and 360 dynes per cm. in oxygen after an hour's exposure at atmospheric pressure (Cook, 1929). The effect is, no doubt, due to adsorption (Chap. XXI) of the gases on the surface of the mercury.

With many liquids the presence of air has an almost or entirely inappreciable effect on the surface tension. Thus :

	$\sigma_{20°}$ C. (air).	$\sigma_{20°}$ C. (own vapour).
Phosphoryl chloride . .	32·2	32·2
Carbon tetrachloride . .	26·77	26·95
Chloroform . . .	27·14	27·24
Carbon disulphide . .	32·33	32·33
Benzene	28·88	29·02
Water	72·75	72·90
Acetic acid . . .	27·63	27·8

The surface tension of liquids is often greatly affected by the presence of dissolved substances. Thus, small quantities of water raise the surface tension of ethyl alcohol, and the values for σ usually quoted for this substance are high for this reason (Mills and Robinson, 1927).

The effect of dissolved salts is generally to raise the surface tension of pure water. This effect may be expressed mathematically (Dorsey, 1897) by the equation

$$\sigma_n = \sigma + An \quad . \quad . \quad . \quad . \quad (35)$$

where σ_n is the surface tension of the solution containing n gramme-equivalents of dissolved salt per litre, σ is the surface tension of pure water at the same temperature, and A is a constant for each salt. The following values of A are illustrative :

	A.		*A.*
NaCl . . .	1·53	$\frac{1}{2}(Na_2CO_3)$ . .	2·00
KCl . . .	1·71	$\frac{1}{2}(ZnSO_4)$ . .	1·86

On the other hand organic substances frequently reduce the surface tension of water. If C is the molar concentration of the solute, the ratio $d\sigma/dC$ is fairly constant for dilute solutions. For solutions generally, Szyszkowski's empirical formula (1908)

$$\frac{\sigma_l - \sigma_s}{\sigma_s} = b \log\left(\frac{C}{c} + 1\right)$$

connecting surface tension and concentration is fairly satisfactory. σ_l and σ_s are the surface tensions of the pure solvent and solution respectively ; b is a constant for each specific solute, its value varying slightly with different solutes ; c is also a constant for each solute, but differs greatly with different solutes, and its reciprocal, $1/c$, is termed the **specific capillary activity** of the solute. The **molar capillary activity** of a solute is defined on p. 278.

THE PARACHOR.

In an earlier chapter (p. 161) mention was made of Macleod's equation (1923):

$$\sigma = k(D - d)^4 \qquad . \quad . \quad . \quad . \quad (36)$$

$$= kD^4 \qquad . \quad . \quad . \quad . \quad . \quad (37)$$

where d is small. For non-associated bodies k is a constant, independent of the temperature.

If M is the molecular weight of the liquid, equation (37) may be written

$$\sigma M^4 = kM^4D^4$$

or

$$\frac{M\sigma^{\frac{1}{4}}}{D} = k^{\frac{1}{4}}M.$$

The expression $\frac{M\sigma^{\frac{1}{4}}}{D}$ is of special interest because it is the product of the molecular volume and the fourth root of the surface tension. If, therefore, two liquids are examined at such temperatures that their surface tensions are equal, the values of the foregoing expression will be proportional to their molecular volumes. The expression $\frac{M\sigma^{\frac{1}{4}}}{D}$ has therefore been christened the **parachor** (Greek *para*, alongside of; *khora*, space) and is denoted by $[P]$ (Sugden, 1924). In comparing the molecular volumes of substances at their boiling points in accordance with Kopp's Law (p. 159) many irregularities were observed. This was due in part to the fact that the molecular volumes were compared at the boiling points of the liquids under atmospheric pressure. This was a convenient but somewhat arbitrary temperature to choose, for the Guldberg-Guye Rule (p. 105) is not universal and the boiling points of substances are not exactly corresponding temperatures. The molecular volumes were not, therefore, compared under strictly comparable conditions.

We have already seen that a close connection exists between surface tension and intrinsic pressure; by comparing molecular volumes at constant surface tension, an attempt is made to level up the effects due to intrinsic pressure and thus to compare molecular volumes under conditions of greater uniformity. This receives support from the fact that the ratio of the parachor to the critical volume for different substances shows great constancy (see following table). The mean of a considerable number of values for the ratio $[P]/V_c$ is 0·77.

The Parachor an Additive Property.—The parachor of a given molecule is the sum of its atomic and structural parachors, and thus admits of calculation. The atomic parachors of hydrogen and carbon are of fundamental importance in organic chemistry and have been deduced from the molecular parachors of series of hydrocarbons and other homologous series as determined experimentally. The procedure

Substance.	Parachor $[P]$.	Critical Volume, V_c (c.c. per gramme-molecule).	$[P]/V_c$.
Carbon tetrachloride	219·9	276	0·80
Benzene	206·3	256	0·81
Chlorobenzene	244·5	308	0·79
Methyl acetate	177·0	228	0·78
Ethyl acetate	217·1	286	0·76
Propyl acetate	256·1	345	0·74

is as follows: Subtraction of the parachors of two successive members in a homologous series gives the parachor for the methylene group, CH_2, the mean value for which is found to be 39. The atomic parachors of hydrogen and carbon are then calculated by combining the mean difference for CH_2 with the data for the saturated hydrocarbons. Thus:

Observed molecular parachor of $C_{10}H_{22}$	424·2
Mean value for 10 CH_2-groups	390·0
∴ Molecular parachor for H_2	34·2

This value for hydrogen agrees very satisfactorily with that observed for liquid hydrogen, namely 35·1, when one remembers the great difficulty of working with a liquid at such low temperatures. Subtraction of the value for molecular hydrogen from that of the methylene group gives the atomic parachor of carbon, namely 39·0 - 34·2 or 4·8.

In a similar manner the parachors of other atoms, and the parachors corresponding to structural and valency arrangements, admit of deduction. In the following table are given the values for various parachors as published by Sugden:

Atomic and Structural Parachors.

H	17·1	Single bond	0·0
C	4·8	Double bonds:	
Si	12·0	Non-polar	23·2
N	12·5	Semipolar	−1·6
P	37·7	Triple bond	46·6
O	20·0	3-Membered ring	17·0
S	48·2	4- ,, ,,	11·6
F	25·0	5- ,, ,,	8·5
Cl	54·3	6- ,, ,,	6·1
Br	68·0		
I	91·0		

The significance of the difference between the different types of valency termed electronic, non-polar and semipolar, is discussed in a later chapter (see Vol. II). For present purposes it suffices to state that the increment for the non-polar double bond, namely 23·2, applies to the following groups :

C=C, C=O, C=N, C=S, N=O.

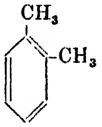
Esters are found to give a slightly low value for the combined parachors of their two oxygen atoms, namely 60·0, whereas we should expect 20 × 2 + 23·2 or 63·2. This suggests some interaction between the two atoms, and there is other evidence supporting this idea. Ethers and ketones behave in accordance with the foregoing table.

By way of illustration let us consider benzene, C_6H_6, assuming Kekulé's formula, which contains 3 double bonds :

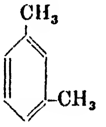
Parachors of 6 C	28·8
,, ,, 6 H	102·6
,, ,, 3 double bonds	69·6
,, ,, 6-membered ring	6·1
Total	207·1

The observed value was 206·2, which may be regarded as very good agreement, and as supporting Kekulé's formula.

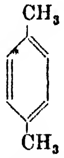
Parachors of Isomerides.—Since the parachor is additive, it cannot distinguish between isomerides which differ merely by the position of a group or valency bond. Thus, for example, the three xylenes yield the same value for the parachor. Thus :



ortho-Xylene
Obs. [*P*] = 283·3.

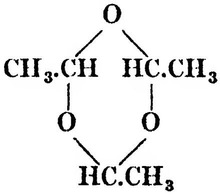


meta-Xylene
Obs. [*P*] = 283·8.



para-Xylene
Obs. [*P*] = 283·8.

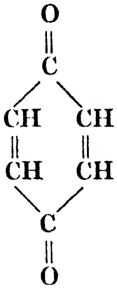
When, however, unsaturated isomerides differ in structure, as when a double bond is replaced by a ring, or when the size of a ring is varied, the change is evidenced by a different value for the parachor. For example, *paraldehyde*, formed by the condensation of three molecules of acetaldehyde, of parachor 121·2, has a parachor of 298·7, which is appreciably less than 3 × 121·2 or 363·6. It is presumed, therefore, that paraldehyde has the following cyclic formula :



for which the calculated value of the parachor is 300·1.

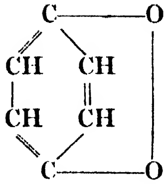
Another interesting example is afforded by *p-benzo-quinone*, most of the reactions of which appear to agree most satisfactorily with formula I:

I.



Calc. [P]=236·1.

II.

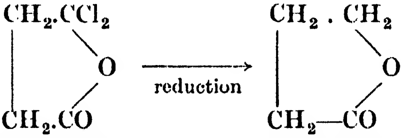


Calc. [P]=219·0.

But the second formula agrees also with certain chemical reactions (Graebe, 1868), with the absorption spectrum (Hartley and Leonard, 1909), and with the heat of combustion (Binder, 1921). The observed value for the parachor is 236·8, which strongly supports formula I (Sugden, 1927).

Succinyl chloride is usually given the unsymmetrical formula I, as this explains its reduction with hydrogen to γ-butyrolactone. Thus:

I.



Succinyl chloride.
Calc. [P]=267·9.

γ-Butyrolactone.

The formation of succinyl chloride by the action of phosphorus pentachloride on succinic acid, however, might equally well result in a symmetrical molecule, thus:

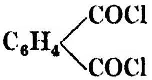
$$\begin{matrix} CH_2.COOH \\ | \\ CH_2.COOH \end{matrix} \longrightarrow \begin{matrix} CH_2.COCl \\ | \\ CH_2.COCl \end{matrix} \quad \text{II.}$$

Succinic acid.

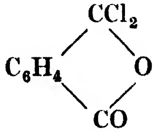
Succinyl chloride.
Calc. [P]=282·6.

Determination of the molecular volume suggested that the ordinary substance was an equilibrium mixture of I and II. The observed value for the parachor is 282·6 (Sugden, 1927). It appears, therefore, that the liquid has the symmetrical structure and cannot contain any appreciable amount of the unsymmetrical form.

As a final example *phthalyl chloride* may be chosen. Two forms are known, melting at 15° and 88·5° C., the latter form being the less stable. But which is which? Determination of the parachors of both forms (Sugden, 1927) indicates that the stable form is symmetrical, thus:



Stable phthalyl chloride.
M.pt. 15° C.
Calc. [P]=377·5.
Obs. [P]=373·9.



Unstable phthalyl chloride.
M.pt. 88·5° C.
Calc. [P]=362·8.
Obs. [P]=367·8.

The application of the parachor to **valency** problems is dealt with later (see Vol. II).

Molar Capillary Activity, Δ.—This is a term due to Mills and Robinson (1931), and by it is understood the depression of the surface tension of a solvent by the dissolution of a solute at a concentration of one gramme-molecule per 1000 grammes of solvent. This value is usually obtained by extrapolation. For aqueous solutions of a considerable number of organic substances, including acids, alcohols, esters, ketones and amines, it is found that

$$\Delta = k[P]^4,$$

$[P]$ being the parachor of the solute and k a constant, approximately $7{\cdot}9 \times 10^{-8}$. From this it appears that Δ is a function directly connected with constitution.

CHAPTER XV.

OPTICAL PROPERTIES.

THE SPECTRUM.

Historical.—The beautiful play of colours shown by various gem stones such as the diamond and opal must have attracted the attention of man at a very early date, but the systematic study of the composition of ordinary daylight may be said to date from 1666, when Sir Isaac Newton carried out his world-famous experiment of passing a beam of sunlight through a wedge-shaped piece of glass, termed a prism (Greek *prismatos*, thing sawn), thereby obtaining a **continuous spectrum.** This spectrum was not pure, for the beam of light was admitted through a circular hole, and the colours overlapped. When Wollaston (1766 to 1828), more than a century later, repeated the experiment, he allowed a thin ribbon of light to pass through the prism, thus reducing the overlapping of the colours and obtaining a fairly pure spectrum. It was then observed that the spectrum was not perfectly continuous, but was crossed by series of fine dark lines. Fraunhofer (1787 to 1826), the famous Munich optician, examined the spectrum through a telescope and measured the relative positions of several hundred of these lines, designating the more prominent ones, beginning at the red end of the spectrum, by letters, namely A, B, C. . . . Although Fraunhofer died before the explanation of the occurrence of these dark lines in the solar spectrum was known, the lines are known as **Fraunhofer Lines.**

It was soon observed that incandescent vapours and gases yield spectra consisting of bright lines. Some of these are simple, such as those of sodium and thallium vapours. Others are complex, many being extremely so; thus uranium and iron are known to yield some 5000 lines each, although a large proportion of these lies in the ultra-violet.

It was at first thought that the dark Fraunhofer lines, or **lacunæ** (Latin *lacus*, lake), as they are called, in the solar spectrum, were due to the lack of those particular colours in the light as it left the sun; it was observed, for example, that one of the dark lines coincided exactly with the position of the yellow line given by sodium vapour. Believing that this indicated the absence of sodium in the sun, Foucault, in 1849, passed sunlight through a flame containing sodium vapour and which, therefore, gave the yellow sodium line. He expected in this way to reinforce the sunlight and fill up the dark sodium lacuna. To his surprise, however, the lacuna was rendered even more intense than before. He then passed light that would yield a truly continuous spectrum, such as that from an incandescent solid, through the flame, and found the sodium lacuna was developed in it. The conclusion was inevitable that the same kind of light evolved by an incandescent vapour is also absorbed by that vapour. The dark lines, therefore, are not absolutely dark, only relatively so.

In this way it came to be realised (Kirchhoff, 1859) that the dark lines in the solar spectrum are not due to the absence of certain elements in the sun; on the contrary, they are generally due to the presence of these elements in the vapours around the sun, the vapours absorbing their own characteristic spectra from the solar light passing through them. An exception is afforded by the Fraunhofer lines A and B, which are due to absorption by the oxygen in the earth's atmosphere.

The dark lines were termed by Kirchhoff the **reversed spectra** of the elements concerned. They are a special type of **absorption spectra**, the bright lines constituting what are known as **emission spectra.**

As a result of extensive researches on the emission spectra of different elements, Bunsen and Kirchhoff enunciated the following fundamental principles:

(i) Every element when sufficiently excited in the gaseous state yields its own characteristic spectrum; and, conversely,

(ii) The presence of the vapour of an element can be inferred with certainty by spectrum analysis when its characteristic lines are present.

Indeed the spectrum of an element is so definite that in 1900 an International Congress, meeting in Paris, accepted the suggestion of de Gramont that no new substance should be recognised as an element until its spark spectrum had been measured and found to be different from that of every other known form of matter.

Hitherto we have been discussing the visible spectrum. In 1800 Herschel discovered the **infra-red** or heat rays, which are chemically inactive. The following year Ritter discovered the **ultra-violet rays.** These are chemically reactive and are absorbed largely by ordinary glass, but to a much less extent by quartz.

In the succeeding sections, therefore, we have two types of spectra to consider, namely, emission spectra and absorption spectra.

The Nature of Light.—Two important theories as to the nature of light have been held from time to time, namely, the **emission theory** and the **wave** or **undulatory theory** (Huyghens, 1678). The former was adopted by Newton. According to it a luminous body was regarded as emitting a continuous stream of innumerable minute light particles which travelled in all directions in rectilinear paths with the same velocity in the same medium. If, by any chance, these light particles entered the eye, the sensation of light was produced by their impact on the retina. The undulatory theory presupposes the existence of a perfectly elastic, imponderable fluid which possesses inertia and is termed the **ether** of space. It pervades all matter and all space. A luminous body is believed to set up disturbances in this fluid, which disturbances are periodic both as regards space and time, and are termed **waves.** The waves travel through the ether with an enormous velocity, namely 3×10^{10} cm. per second, and when they enter the eye they excite the sense of vision. In a similar manner the transmission of electricity was believed to take place through the agency of an

" ether." At this time the sciences of light and electricity were regarded as separate and entirely distinct studies. As both light and electricity required an " ether " for their propagation, Maxwell (1831 to 1879) was led in 1873 to suggest his famous electromagnetic theory, according to which only one " ether " exists and light is regarded as an electromagnetic disturbance of this " ether." Light waves consist of a periodic alteration in the electrical and magnetic condition of the ether, not movements of particles of " ether " after the fashion of sound waves in air.

General Remarks on Emission Spectra.—As already mentioned, every element in the gaseous state, when sufficiently excited, emits a characteristic spectrum, which may consist of **bands** and/or **lines.** Under a low dispersion the " lines " appear narrow compared with the adjacent unillumined spaces ; but under high dispersion these " lines " frequently are found to be complex, being resolved into **components** the breadth of which is comparable with the distance between them. Thus, for example, the red hydrogen line H_a is a **doublet.** Other lines may have faint narrow lines associated with them. These subsidiary lines are termed **satellites.** The green line of mercury is a case in point. If the degree of dispersion is still further increased, a stage is reached at which no further resolution occurs ; the " lines " merely broaden out. This shows that they have a finite width, which is attributable to two causes, namely, the Döppler Effect and Collision Effects. If the atoms were perfectly still, and infinitely distant from each other, so that collisions were impossible, we should expect the spectral lines to be perfectly sharp and homogeneous. By reducing the pressure we can reduce the collision effect, and the width of the " lines " is then attributable to the Döppler Effect, according to which the spectrum of a receding atom would be displaced slightly towards the red end of the spectrum and that of an approaching atom displaced towards the blue end, exactly as has been observed for the spectral lines of receding and approaching stars. If a source of light approaches an observer with velocity v, the change in wavelength, $d\lambda$, is given by

$$\frac{d\lambda}{\lambda}=\frac{v}{u}$$

where u is the velocity of light, the wavelength being diminished. If the source of light recedes, the numerical value of $d\lambda$ is the same, but the wavelength of the light is increased.

Since in a given mass of gas some atoms will be moving in every direction, the components of their velocities will thus have all possible values in the line of sight from zero to a maximum approaching or receding velocity, and light of every wavelength will be emitted from the mass within the range of the extreme displacements, thus producing a spectral " line " of finite width. By measuring the width of these " lines " it is not difficult to calculate the rate of movement of the atoms, just as the rate of stellar movement has been calculated. Lord Rayleigh found that at 0° C. mercury atoms in mercury vapour moved at about 200 metres per second, a value that agrees very closely with that calculated with the aid of the kinetic theory (p. 56).

Collisions among the atoms cause vibrations, and as the number of collisions increases with the pressure, so will the width of the spectral " lines " ; under considerable pressure the " lines " will broaden into bands, and under high pressures the bands will broaden so much as to unite and yield a continuous spectrum. That such widening is due to the pressure and not to the temperature is clear from the following: If an electric current is passed through rarefied hydrogen, the characteristic line spectrum is obtained. On increasing the pressure of the gas the " lines " broaden, and ultimately, after a continuous spectrum has been obtained, the resistance of the gas becomes so great that the electric current cannot pass. If, on the other hand, the pressure of the rarefied hydrogen is continuously reduced, the resistance to the passage of electricity falls to a minimum and then increases again; the spectrum still consists of lines and remains a line spectrum until finally the resistance becomes so great that again the current will not pass. The resistance of the gas when the current just ceases is evidently the same in both cases, and in the former case, where a continuous spectrum is obtained, the temperature is not as high as in the latter case. Hence the observed broadening of the lines cannot be attributed to increase of temperature; it is a pressure effect.

The effect of temperature is important, however. As the temperature of a gas rises, new lines may appear, and old ones, observed at lower temperatures, may fade away altogether. Lithium, for example, in the electric arc yields a blue line not detectable in the Bunsen flame. It frequently happens, also, that with rise of temperature existing lines become more complex. Thus the sodium D line is found to be double at the temperature of the Bunsen flame, but at very high temperatures three other pairs of lines appear elsewhere in the spectrum.

In addition to line spectra, some elements also show band or fluted spectra. Compounds and elementary polyatomic molecules yield band spectra unless the temperature is sufficiently high to decompose them into atoms, when the characteristic lines of the elements may appear. Thus, in the ordinary flame tests as used in qualitative analysis, the chlorides of the metals are inserted into the Bunsen flame on the end of a platinum wire. The chlorides volatilise and dissociate, so that the spectra of the metal atoms are obtained, the chlorine spectrum being invisible. The reason that undissociated molecules have spectra of their own and do not give the line spectra of their constituent atoms, lies in the fact that the outermost electrons of the atoms (see Vol. II), which are concerned in the production of atomic spectra, are also concerned in causing chemical combination. They are the so-called " valency electrons," and in the undissociated compound they are not free to act optically in the same way as in the element. Incandescent solids and liquids yield continuous spectra.

The wavelength, λ, of light varies with the refractive index, μ, of the medium through which the light passes. For our standard in theoretical work we use the wavelength in a vacuum, since the refractive index, μ, of a vacuum is unity. For dry air at N.T.P. $\mu = 1{\cdot}0003$, and usually, in practical work, wavelengths are expressed with reference to air as unity. The value of λ for light waves may be determined by interference methods with astonishing accuracy, namely of the order of 1 in 10 millions, an accuracy far transcending that at present attainable for the wavelengths of X-rays.

If u is the velocity of light in centimetres per second, and n the **frequency** of the light, that is the number of waves passing a point per second, clearly

$$u = n\lambda.$$

But u is known only approximately, whereas, as we have seen, λ is known with great accuracy. So instead of using n, we frequently find it convenient to consider the number of waves of light per centimetre. This is termed the **wave number,** ν. Obviously

$$\nu = \frac{1}{\lambda} = \frac{n}{u}$$

or

$$n = u\nu.$$

Waves only of a comparatively small range in length are visible to the human eye. The vast majority of waves in the ether are invisible to us. Heat waves can be detected by our sense of touch, but the waves of wireless telegraphy and X-rays, to mention two of the best known of the remaining types, cannot be detected by us with our unaided senses.

In the following table are given the wavelength ranges of the more important types of waves:

Typical Wavelength Ranges.

	λ (cm.).
Wireless telegraphy	57 to 5×10^6
Infra-red spectrum	4×10^{-2} to $7{\cdot}7 \times 10^{-5}$
Visible red spectrum	$7{\cdot}7 \times 10^{-5}$
Visible violet spectrum . . .	$3{\cdot}8 \times 10^{-5}$
Ultra-violet rays	4×10^{-5} to $1{\cdot}85 \times 10^{-5}$
Extreme ultra-violet and soft X-rays .	$1{\cdot}85 \times 10^{-5}$ to 3×10^{-8}
Röntgen or X-rays	10^{-8} to 10^{-9}

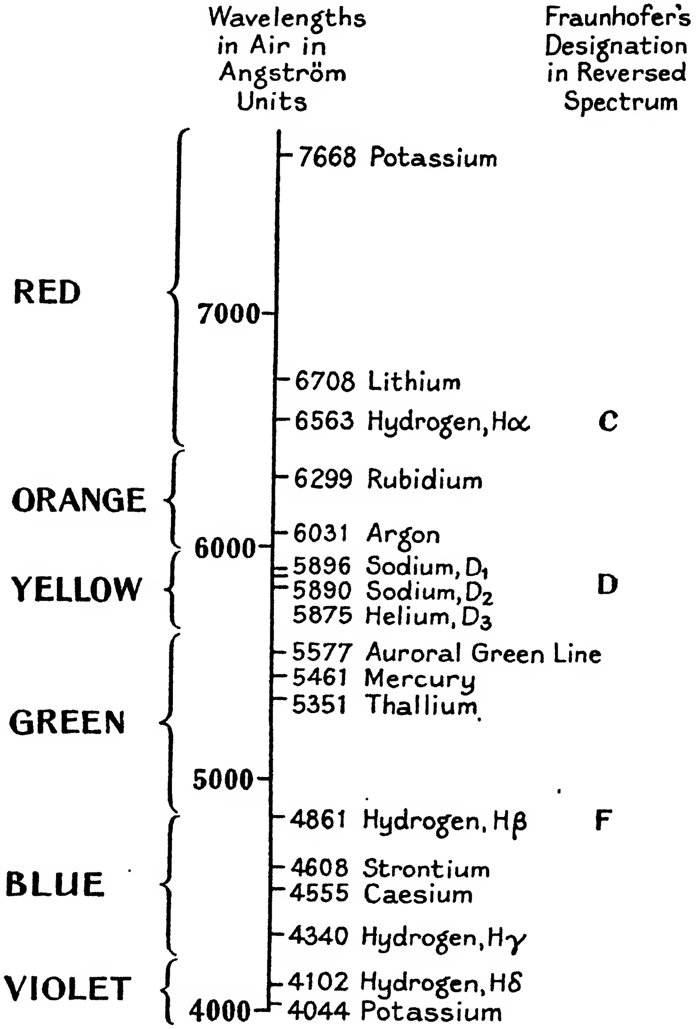
The ordinary range of the visible spectrum is roughly from $3{\cdot}8 \times 10^{-5}$ to $7{\cdot}7 \times 10^{-5}$ cm. These wavelengths, however, are usually expressed in Ångström units, each unit corresponding to 10^{-8} cm., so that the above range may be written as 3800 to 7700 Å (p. 8). Some people can perhaps see over a slightly wider range, whilst others can see only over a smaller range. With colour-blind people the range may be severely limited and the eyes or brain may exert a rigidly selective action, certain colours only being appreciated.

In the table (p. 284) are given a few typical wavelengths, expressed in Ångström units, from the line spectra of well-known elements.

Excitation of Emission Spectra.—The spectra of elements may be excited in many ways. A favourite method consists in feeding the element or some volatile compound of it into a Bunsen flame. This gives the **flame spectrum.** Passage through an electric arc gives the **arc spectrum**; the **spark spectrum** results with an electric spark discharge; the **fluorescent emission spectrum** is obtained under the action of incident light of suitable frequency. Sparking is very violent treatment and the temperature is high, so that the spectrum obtained in this way frequently is very different from the arc and ordinary flame spectra. Certain lines may appear only in the spark spectrum or, if they appear in the flame spectrum, their intensity is enhanced in the spark spectrum; such lines are termed **enhanced lines** (Lockyer). These new lines and enhanced lines constitute the spark spectrum.

A convenient method of obtaining the spectrum of a gas consists in introducing the gas into a Plücker tube, that is, a vacuum tube consisting of two bulbs fitted with electrodes and joined by a capillary tube. The pressure of the gas is reduced to 2–3 mm. and the electrodes are connected to the terminals of an induction coil. As the discharge passes, the capillary portion becomes intensely luminous. If this is placed in front of the slit of a spectroscope, the spectrum is easily seen. Photographs of the spectra of the inert gases obtained in this way are shown in Plate I.

The Visible Spectrum.



Phosphorescent spectra of the rare earths are excited by bombardment with cathode rays (p. 289).

Series Spectra.—The spectral lines of many elements have been resolved into series connected by comparatively simple numerical relationships. In 1885 Balmer made the remarkable observation that the wave numbers of the successive lines in the ordinary hydrogen spectrum, beginning at the red end, could be represented with great accuracy by an equation of the type

$$\nu = \text{constant}\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

where n is given the value of successive integers beginning with 3 for the line known as H_α. For H_β n is given the value 4; for H_γ n is 5; and so on. The constant, now known as **Rydberg's constant,** has in the case of hydrogen the numerical value of 109677·7, and is denoted by R_H.

The remarkable accuracy of Balmer's formula is clearly shown in the following table, in which are compared the calculated and observed values for the wave numbers of the first four lines of the hydrogen spectrum. In calculating these data an earlier value of R, namely 109678·8, was used:

	H_α.	H_β.	H_γ.	H_δ.
Observed .	15233·22	20564·79	23032·54	24373·06
Calculated .	15233·17	20564·77	23032·54	24373·06

As n increases, the values for ν gradually approach each other, and at the violet end of the spectrum the lines become crowded together, continuously decrease in intensity and become increasingly difficult to resolve. More than 30 hydrogen lines are known, however. The **limiting wave number** is obtained by putting $n = \infty$, when

$$\begin{aligned}\nu &= R\left(\frac{1}{4} - \frac{1}{\infty}\right)\\ &= \frac{R}{4}\\ &= 27419{\cdot}70.\end{aligned}$$

Balmer's formula was derived empirically, but it is now possible, by making certain assumptions as to the structure of the atom, to derive this formula from theoretical considerations. In a later chapter (see Vol. II) this aspect of the subject is considered.

It was soon found that Balmer's formula is a special case of a more general formula, namely

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right).$$

This is termed the **Balmer-Ritz formula.** Putting $n_1 = 1$, we obtain the wave numbers of lines in the ultraviolet region. Thus

$$\nu = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right).$$

These lines constitute the **Lyman Series** (1914).

When $n_1 = 2$, the lines lie in the visible region and form the **Balmer Series.**

When $n_1 = 3$ and 4 respectively, the lines lie in the infra-red range and constitute the **Paschen** (1908) and **Brackett** (1922) **Series.** Of the last-named series, two hydrogen lines only are known, of wavelengths 40,500 and 26,300 Å respectively.

Other elements yield spectra which are less simple than the hydrogen spectrum; but several of them contain similar series which can be represented with fair approximation by **Rydberg's formula**:

$$\nu = R\left(\frac{1}{(n_1 + \mu_1)^2} - \frac{1}{(n + \mu)^2}\right)$$

where R has the same value as for hydrogen, μ_1 and μ being constants, special to each series and usually fractional. When μ_1 and μ are both equal to zero, Rydberg's formula reduces to that of Balmer for hydrogen.

In general, most of the lines in either the arc or the spark spectrum may be allocated to four associated series, referred to as the **Principal, Diffuse** or **First Subordinate, Sharp** or **Second Subordinate,** and **Fundamental Series,** respectively. In Rydberg's formula, the first line of a Principal Series is given when $n = 1$, with the two Subordinate Series when $n = 2$, and with the Fundamental Series when $n = 3$.

Fowler's method of showing the different series is indicated in fig. 123 for lithium. At the top of the diagram the mixed spectral lines are shown, in the order of their wave numbers, expressed as $\nu \times 10^{-4}$, and in the four succeeding spaces these lines are sorted out into the various series. Below these the values of ν are plotted against n. As n increases, the curves approach the broken lines, which give the limit values for $n = \infty$. It will be noted that the diffuse and sharp series have a common limit.

In general, the spectral series are not quite so simple as those indicated for lithium, in which each line may be regarded as a single line of one component only—a so-called **singlet**—although in reality they are doublets, but so close that they could not be differentiated in the diagram (fig. 123). It frequently happens that lines consist of two or more components. If there are two components, as in the case of the well-known sodium D_1 and D_2 lines, which constitute the first pair of the sodium principal series, they are termed **doublets.** The shorter wavelength components of each doublet are then taken together as one series and the longer wavelength components as a second series, so that two series are now to be considered in place of each singlet series in the lithium spectrum. If the lines contain three components they are termed **triplets** and the series are then triplicated. Lines even more complicated than these may occur, and are known generally as **multiplets.** They are all characterised by the same value of n. It is important to note that the difference between the wave numbers of the components of doublets in a principal series decreases with increasing values of n, so that the two series have the same limit. This difference is termed the **doublet interval.** In the diffuse and sharp series the doublets do not close up but have a constant interval, which is the same for the diffuse as for the sharp series and is also equal to the interval of the first principal doublet.

The data given in the table on p. 288, referring to some of the doublets in the principal, diffuse and sharp series of rubidium, will serve to illustrate the preceding statements.

Doublets may often be recognised by the eye, but frequently the doublet intervals are so large that other spectral lines come between the components of the doublet, which are thus difficult to find. It

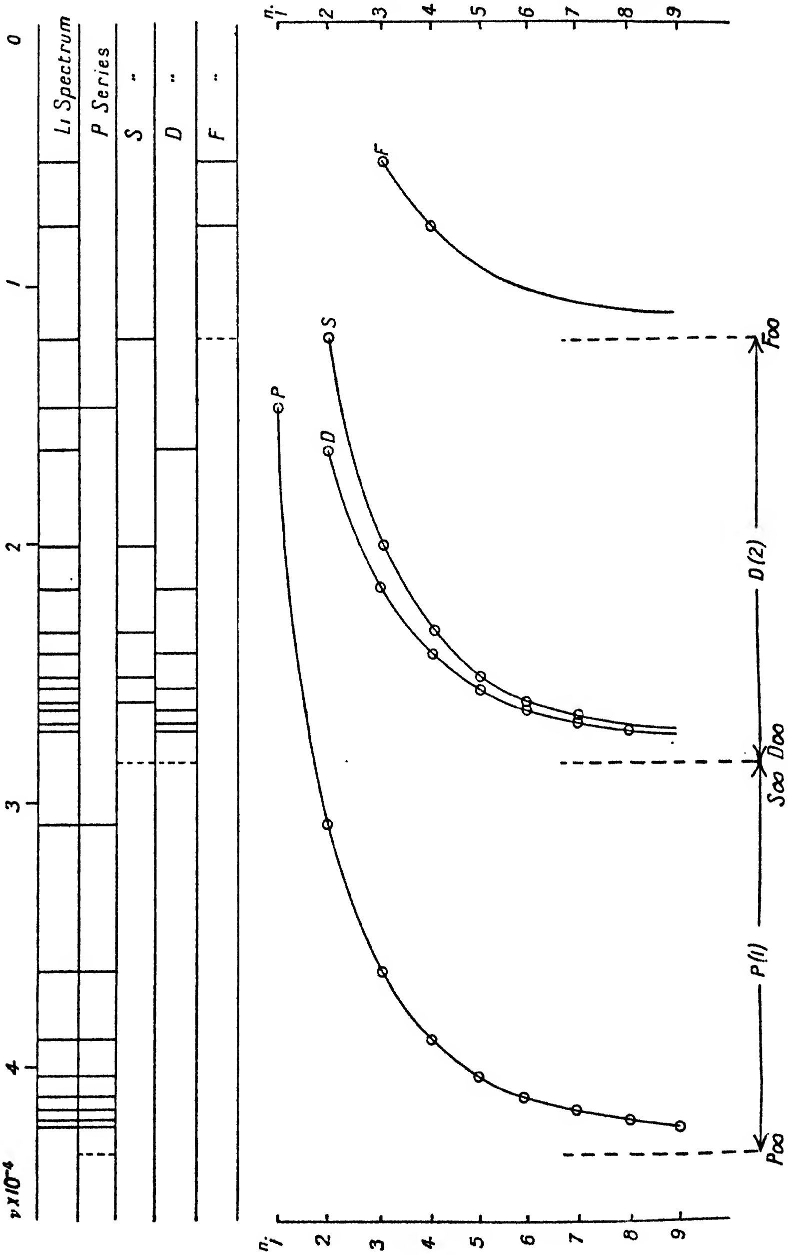


FIG. 123.—Series in the Lithium Spectrum.

In this diagram the letters P, D, S and F are used to indicate the Principal, Diffuse, Sharp and Fundamental Series respectively.

will be noticed that the diffuse and sharp series for rubidium overlap in this manner.

Rubidium Series Lines.

Principal Series, ν.	Diff.	Diffuse Series, ν.	Diff.	Sharp Series, ν.	Diff.
12,579	238	12,887	234	13,494	238
12,817		13,121		13,732	
23,715	77	15,872	235	16,229	238
23,792		16,107		16,467	
27,834	35	17,463	236	17,681	237
27,869		17,699		17,918	
29,834	19	18,405	236	18,546	235
29,853		18,641		18,781	
30,958	10	19,005	236	19,101	232
30,968		19,241		19,333	

The lines belonging to one and the same series are similar in character. Lines in different spectra (*i.e.* the spectra of different elements) that are similar in character and correspond to the same value of n in series of the same type were at one time called **homologous lines.**

It has been mentioned that one series of lines, the Balmer series, has been found in the hydrogen spectrum; other series are also known in the same spectrum, and the same is true for the spectra of helium and neon. The spectra of the alkali metals lithium, sodium, potassium, rubidium and cæsium contain principal, diffuse and sharp doublet series. Aluminium, gallium, indium, thallium, and probably scandium, yttrium, lanthanum, gadolinium and ytterbium, show doublet series in their spectra. The spectra of magnesium, calcium, strontium, barium, radium, zinc, cadmium, mercury and europium contain triplet series, although all the principal series are not yet known. Generally speaking elements of odd atomic number have even multiplicity, those of even atomic number having odd multiplicity.

One of the most valuable methods for detecting homologous lines and series is to examine the influence of the magnetic field on the spectra. When a source of light which gives rise to a line spectrum is placed in a powerful magnetic field, many of the spectral lines are found to be resolved into two, three, or even more, components, lying close together. This was discovered by Zeeman in 1896, and is called the **Zeeman Effect.** It is readily accounted for on the hypothesis that an atom consists of a central core surrounded by negative electrons, to the motions of which the spectral lines of the element are due, for the motions of the electrons, which are electrically charged, would be affected by the magnetic field.

It was discovered by Preston (1899) that, for the same magnetic field, all lines belonging to the same series exhibit exactly the same magnetic resolution when the results are expressed in wave numbers (**Preston's Law**), and Runge and Paschen (1902) found that this law could be extended to corresponding series for different elements. From the point of view of the Zeeman effect, it is necessary to consider a doublet (or triplet) series as being made up of two (or three) separate series, since the components of a doublet (or triplet) usually exhibit different types of resolution ; in the case of helium, however, the types are all the same and of the simplest variety.

Line Spectra and the Periodic Table.—It was noted in the early days of spectroscopy that a rough spectroscopic relationship exists between the various members of a sub-group in a vertical column of the Periodic Table ; further, on comparing analogous lines in the spectra of the allied elements there is a shifting of the whole spectrum towards the red or violet end with increasing atomic weight. Boisbaudran (1869), who discovered this relationship, used it, with surprising success, to calculate the approximate atomic weight of gallium, which element he discovered in 1875, obtaining the value 69·86. The accepted value at the present time (1931) is 69·72.

A more accurate relationship was discovered by Runge and Precht, and is dealt with on p. 291.

Cathodic Phosphorescence Spectra.—In 1881 Crookes discovered that, after exposure to the bombardment of cathode rays, many substances emit a phosphorescent light. If this light is analysed spectroscopically, in general a faint continuous spectrum is obtained together with a more or less decided concentration in the region corresponding with the colour of the emitted light. Less commonly the spectrum is discontinuous. A curious feature of the results is that pure substances are not sensibly phosphorescent when exposed to cathode rays. The phosphorescence is due to the presence of traces of foreign substances, termed **phosphorogens,** intimately associated with the original substance or **diluent,** A, more intimately, for example, than could be attained by mere mechanical mixing.

Experiment shows that, as the amount of the second substance, B, is increased from a very small percentage, the intensity of the phosphorescence increases to a maximum and then steadily diminishes, it being assumed, of course, that the mode of excitation is the same throughout. The optimum percentage of B depends upon the nature of both A and B, but is of the order of 0·5 to 1·0 per cent., and mixtures containing 20 per cent. or more of B often are not sensibly phosphorescent. It is of interest to notice the analogy between this result and that connecting the percentage of ceria added to thoria in the gas mantle industry to yield a maximum illumination with coal gas. The optimum amount of ceria is 0·9 per cent. Increase or reduction of this amount diminishes the lighting efficiency very markedly.

When B is a rare earth compound the phosphorescence spectrum is sharply discontinuous, often exhibiting a large number of narrow bands. As the percentage of B alters, so does the colour of the phosphorescent light. The colour changes are due to the fact that for mixtures of A and B each band in the spectrum has its own optimum concentration of B, in general the most refrangible bands being at their maxima with smaller amounts of B than the least refrangible bands. Hence, as the percentage of B increases, the colour of the phosphorescent light changes in the direction from blue to red along the spectrum.

The phosphorescence spectra of a phosphorogen in different diluents exhibit a marked similarity, but are not identical; whilst bands occur in the same region of the spectrum, their absolute positions do not coincide. There is very little difference in passing from one diluent to another if the metallic constituents of the diluent are the same, as, for example, when samarium compounds, such as the oxide, sulphate and fluoride, are diluted with the corresponding salts of calcium. But a change in diluent from, say, lime to yttria, produces a decided, if small, change in the positions of the bands. The physical state of the diluent also plays a small part.

In general it may be stated that diluents are colourless compounds, practically incapable of conducting the electric current; phosphorogens, on the other hand, are coloured substances, namely compounds of metals which are coloured and exhibit absorption spectra in solution.

These remarks apply to systems which are visually phosphorescent; it is possible, however, for a colourless substance, like gadolinia, to act as a phosphorogen in the ultraviolet region. It is significant that gadolinium salts exhibit well-defined ultraviolet absorption spectra.

Various ternary systems have been studied in which two phosphorogens share a common diluent. The spectrum of such a system is composed of the spectra of the two phosphorogens, but each phosphorogen appears to diminish the intensity of the spectrum of the other.

So far as visible phosphorescence is concerned, alumina, beryllia, lanthana, gadolinia, yttria, calcium oxide, etc. act as diluents, whilst compounds of iron and chromium, praseodymia, neodymia, samaria, terbia and europia may be cited as typical phosphorogens.

The form of vacuum tube best suited to the observation of cathodic phosphorescence spectra is shown in fig. 124. The electrodes A and C are made of aluminium. The substance under examination is placed in the lower part of the apparatus, with its surface slightly inclined. The upper part of the apparatus is sealed on to a mercury pump, not shown in the figure. If it is desired to include the ultraviolet region, a special form of tube with a quartz window B is used.

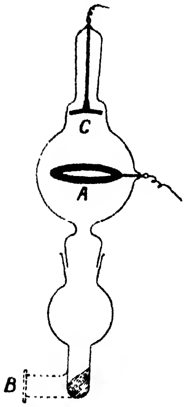


FIG. 124.—Apparatus for Producing Cathodic Phosphorescence Spectra.

Traces of manganese in lime produce an orange phosphorescence; traces of chromium in alumina give red. Praseodymia diluted in lime gives a red phosphorescence; samarium, orange; europium, generally orange-red or carmine-red; terbium, blue to green, according to the amount of terbium present.

Binary rare earth mixtures may be prepared by precipitating the oxalates together from a mixed solution and calcining to oxide. Rare earth-lime mixtures are obtained by precipitating the mixed carbonates and igniting to oxide. Finally, rare earth-alumina (or beryllia) mixtures are obtained by ignition of the mixed hydroxides.

Applications of the Emission Spectrum.

The spectrometer has been of very great use to the physical chemist, and a few important illustrations of its application to chemical problems may be cited conveniently at this stage.

1. To Characterise an Element.—De Gramont's suggestion has already been mentioned (p. 280).

2. To Determine the Approximate Atomic Weight of an Element.—According to **Runge and Precht's Law,** the logarithms of the doublet intervals of corresponding series in the spectra of families of elements are proportional to the logarithms of the atomic weights. This is well illustrated by the aluminium sub-group of Group III of the Periodic Table, as shown in fig. 125.

Runge and Precht in 1903 applied their method to deduce the atomic weight of *radium* by comparing its spectrum with the spectra of magnesium, calcium, strontium and barium, and deduced the result Ra = 257·8. Ordinary chemical methods, however, show that the correct value for the atomic weight is 226. The method of Runge and Precht is therefore inexact. The relationship between the logarithms of the atomic weights and of the frequency intervals is, in fact, not strictly linear.

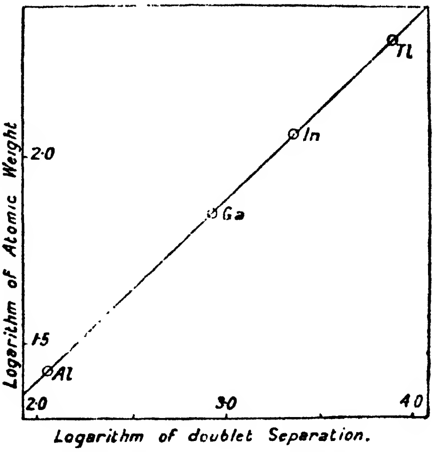


FIG. 125.—Relationship between Spectra and Atomic Weights of Al, Ga, In, Tl.

Another relationship between the wave numbers of certain homologous lines of analogous elements was observed by Ramage (1902), namely, that the differences between the wave numbers of the lines are proportional to the differences between the squares of the atomic weights of the elements. For example, the following are homologous lines :

	Ca.	(diff.).	Sr.	(diff.).	Ba.
ν =	23657·9		21703·7		18064·6
		(1954·2)		(3639·1)	

If, then, the atomic weights of calcium and barium are taken to be 40·1 and 137·4 respectively, and the value for strontium is denoted by x,

$$\{x^2 - (40\cdot1)^2\}/\{(137\cdot4)^2 - x^2\} = 1954\cdot2/3639\cdot1,$$

whence $x = 87\cdot4$, in good agreement with the experimental value. The relationship thus illustrated is, however, only of limited application, *e.g.* in general it is not possible to choose the analogous elements so that some are in Mendeléeff's short periods and the others in the long periods (see Chapter XVI).

3. To Detect the Presence of Traces of Elements.—Spectroscopy affords one of the most delicate means of detecting traces of elements. Under suitable conditions it is possible to detect the presence of the following elements in the quantities stated :

Sodium	0·0000003 mgrm.
Lithium	0·00001 ,,
Strontium	0·00006 ,,

When the spark spectra of solutions of metallic salts are observed, it is found that, upon dilution, the lines weaken, then shorten and finally disappear. All the lines, however, do not disappear at the same dilution, although under given conditions the same lines disappear at the same dilutions. Those lines which persist the longest on increasing dilution are known as **residual or ultimate rays.**

With the aid of photography permanent records of any particular spectrum may readily be obtained, and, further, the spectrum is not confined to the visible portion, but can extend down into the ultraviolet region for very considerable distances. This is particularly valuable, as the most characteristic lines of certain elements occur only in the ultraviolet and thus are not detectable by the unaided human eye.

In the preparation of exceptionally pure substances, as, for example, those required for accurate atomic or combining weight determinations, the spectroscope has repeatedly proved itself of enormous value to the chemist. The purified substance is not usually regarded as sufficiently free from contamination until a pure spectrum is obtained with it.

The detection of mercury in explosives is carried out spectroscopically, a solution being electrolysed, the cathode consisting of a platinum wire. After electrolysis the cathode is put into a vacuum tube and heated. If mercury is present it is easily detected by its spectrum, notably by its green line λ 5461, and two yellow lines λ 5790 and λ 5770 respectively. The same platinum wire must not be used twice, however, owing to the extraordinary difficulty of removing every trace of mercury from it.

Spectroscopic analysis has proved very useful in determining the qualitative composition of dust in the air (see p. 481), and of solids dissolved in tap water and in mineral waters. It has been used to detect the presence of traces of nickel, which is used as a catalyst in the hydrogenation or hardening of oils to fats. It has enabled the presence of zinc to be detected in the ash of cobra venom. Indeed, the list of its applications might be very greatly extended.

4. The Discovery of New Elements.—The presence of two new blue lines in the spectrum of residues from the waters of a spring at Dürkheim led Bunsen and Kirchhoff in 1860 to conclude that a new metal was present. This metal ultimately was separated as an amalgam with mercury and named **cæsium** (Latin *cæsius*, sky-blue). A second element was discovered the following year (1861) by the same investigators also in the Dürkheim waters with the aid of the spectroscope and named **rubidium** (Latin *rubidus*, dark red) in recognition of the two dark red lines in its spectrum. **Thallium** was discovered in 1861 independently by Crookes in England and Lamy in France. Each of these scientists observed a new green line in the spectrum of some material under examination, attributed it to a new element and succeeded in isolating the element. Crookes, who in March 1861 was the first to make the discovery, was engaged in extracting selenium from a deposit obtained at a sulphuric acid factory at Tilkerorde in the Hartz. He called the new element thallium in allusion to the green colour of its spectrum (Latin *thallus*, a budding twig).

During the solar eclipse visible in India on the 18th August 1868, a spectroscope was for the first time turned upon the solar chromosphere—the luminous atmosphere of gas which surrounds the sun. Many observers noticed in the chromospheric spectrum a yellow line, supposed by them to be a D line of sodium. Janssen pointed out, however, that this line did not exactly coincide with the sodium lines D_1 and D_2, and he proposed to call it D_3. Later in the same year Frankland and Lockyer came to the conclusion that this line could not be attributed to any known terrestrial substance, but must be due to a new element existing in the sun. To this hypothetical element they gave the name **helium** (Greek *helios*, the sun), a name which was generally accepted by astronomers to denote the substance giving rise to the line D_3. The actual discovery of terrestrial helium was also made spectroscopically by Sir William Ramsay in the later part of 1894 when searching for new sources of argon, then recently discovered. While engaged in this investigation he received a letter from Miers, the eminent mineralogist at that time connected with the British Museum, in which it was suggested that it might be worth while to examine certain uraninites (varieties of pitch-blende) from which Hillebrand had in 1889 obtained a gas which he had supposed to be nitrogen. Ramsay considered it improbable that nitrogen could have been obtained from its compounds by the methods Hillebrand had used, and therefore proceeded to re-examine clèveite, one of the minerals from which the supposed " nitrogen " had been obtained.

It was really a most unfortunate chapter of accidents that prevented Hillebrand from making the discovery of helium. He had confirmed the presence of nitrogen in the clèveite gas in various ways : (*a*) the gas when sparked with oxygen gave nitrous fumes ; (*b*) sparked with hydrogen in the presence of hydrochloric acid it gave ammonium chloride, the identity of which was proved by conversion into ammonium platinichloride and estimation of the platinum in that salt ; (*c*) when subjected to an electrical discharge in a vacuum tube the gas gave a strong nitrogen spectrum. Ramsay was able to confirm the accuracy of these results, as he found about 12 per cent. of nitrogen in the helium from clèveite.

Hillebrand, writing to Ramsay after the discovery of helium had been announced, explained that he had noticed that in his experiments the formation of nitrous fumes and ammonia proceeded very slowly, and that the spectrum contained many lines not attributable to nitrogen. To the first phenomenon he attached but little significance as he was using only a small current. He was aware that the spectra of gases are profoundly influenced by changes of pressure, and therefore, though he and his assistant jocularly suggested that they might be dealing with a new element, the matter was allowed to drop, and helium remained undiscovered for another five years. Truly a great discovery narrowly missed !

Ramsay heated powdered clèveite with dilute sulphuric acid, sparked the resulting gas with oxygen over soda, removed excess of oxygen with alkaline pyrogallate, washed with water, dried and transferred to a vacuum tube. The light given by the passage of electricity through this tube was examined visually in a spectroscope alongside that from a Plücker tube containing argon, as a comparison. It so happened that this second tube, owing to impurities contained in the magnesium electrodes, gave the spectra of hydrogen and nitrogen as well as the argon spectrum. It was at once evident that the clèveite gas contained some argon and hydrogen, but it gave also a brilliant line in the yellow, nearly, but not quite, coincident with the yellow sodium lines.

The wavelength of this line was measured by Crookes and proved to be exactly that of the solar D_3 line. It thus became known that helium could thenceforward be reckoned among the number of terrestrial elements.

The spectroscope was of the greatest use in confirming the existence of argon, neon, krypton and xenon. The spectra of helium and these other inert gases as produced in ordinary vacuum tubes are shown on Plate I.

The presence of two new indigo lines in the spark spectrum of a specimen of Freiberg zinc blende led Reich and Richter in 1863 to suspect the presence of a new element. Their suspicions were confirmed and they succeeded in isolating a new metal, which they appropriately called **indium.**

In 1875 Lecoq de Boisbaudran observed a new violet line, λ 4170, in the spark spectrum of some material he had separated from the zinc blende of Pierrefitte; further work led to the discovery of another new line, λ 4031, and established the fact that both lines belonged to the spectrum of a new element, to which the discoverer gave the name **gallium,** in honour of his native country.

5. The Composition of Celestial Bodies.—As we have already seen, with the aid of the Fraunhofer lines and by examination of the sun's chromosphere, the qualitative composition of the sun has in part been elucidated. Altogether the presence of some forty of our elements has been detected in the sun. The presence of some terrestrial elements in certain stars has also been ascertained spectroscopically.

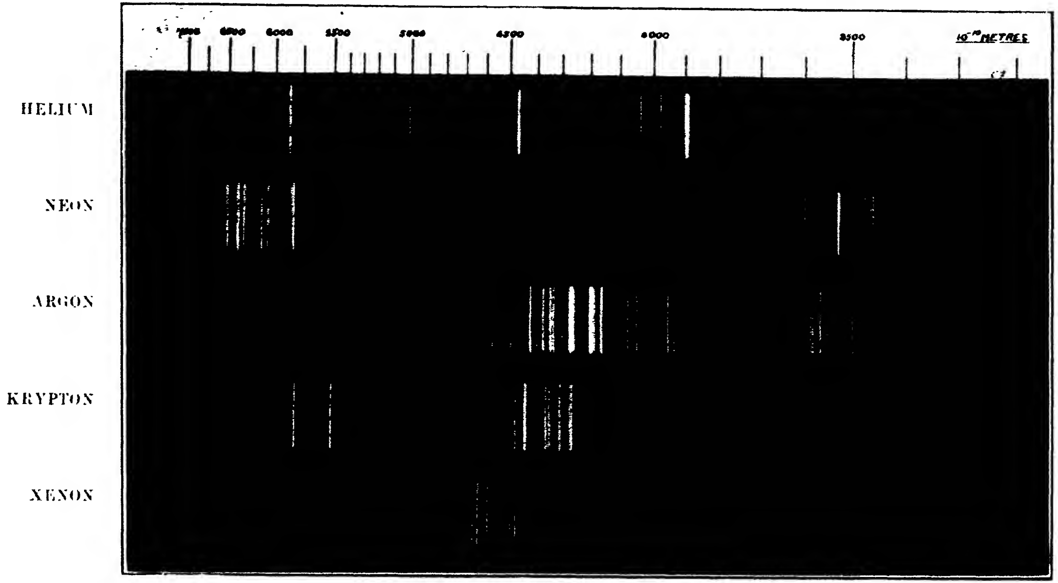
That curious phenomenon known as the **aurora borealis** (Latin *Aurora*, the Roman goddess of dawn; *Boreas*, (God of) north wind) has attracted man's attention from very early times. Several references to it were made in the sixteenth century, and it was regarded as a portent of disaster. When krypton was discovered by Ramsay and Travers in 1898, its spectrum was observed to contain two important lines, namely a green line λ 5570 and a yellow line λ 5871. Sir William Huggins directed attention to the similarity of the green krypton line with a very pronounced green line in the auroral spectrum, and these were regarded as identical, although we now know that they are not quite the same. It was therefore suggested that the aurora might be due to an electric discharge through rarefied krypton at great heights. But the yellow krypton line does not occur in the aurora, and alterations in the conditions of the electric discharge through krypton do not give any variation in the intensities of the green and yellow lines of the gas. It seems improbable, therefore, that the auroral phenomena can be connected with krypton. The clue was obtained eventually by McLennan, who produced the auroral line by passing heavy electric discharges through mixtures of argon and oxygen or of helium and oxygen—the oxygen being essential. It thus appears that the auroral green line is due to oxygen. A red line occurring also in the aurora is presumed to be due to nitrogen.

The spectroscope has also been used in proving the **identity of α-particles with helium nuclei** (see Vol. II), and in the calculation of **atomic speeds** from the width of the spectral lines (p. 281).

The Absorption Spectrum.

When a solution of, say, neodymium chloride is examined in ordinary daylight, it is found to have a clear rose colour by transmitted

SPECTRA OF THE INERT GASES.



Spectra Produced in Ordinary Vacuum Tubes by the Uncondensed Discharge from an Induction Coil.

light. The explanation is, that as the white daylight passes through the solution, many of its constituent rays are absorbed. The cumulative effect of the rays that are not absorbed is to impart to the human eye the sense of a rose colour. If the transmitted light is analysed spectroscopically, it is found to consist of bands of light of various wavelengths, whilst the remainder of the field, that otherwise would have been occupied by the various light waves of the continuous spectrum, is now dark, giving the appearance of dark bands, the so-called **absorption bands.** The whole constitutes the **absorption spectrum** of the given solution.

The absorption spectra of solids may be examined in the ordinary manner applicable to liquids if thin, transparent crystal slices are available; otherwise it is necessary to examine the light they reflect for absorption bands. The latter spectra are termed **reflection spectra.** The two kinds of spectra for the same substance usually are not identical.

Absorption spectra are not confined to the narrow range of wavelengths visible to the human eye; they extend into the infra-red and the ultra-violet; except in the remote infra-red region they can be recorded by photographic methods. In the infra-red region the bolometer (Greek *bole*, ray) or more frequently the thermopile is used.

What happens to the absorbed light waves? Usually they cause a rise in temperature of the absorbing medium; sometimes fluorescence is produced (p. 311), and sometimes they promote chemical changes by supplying the necessary energy. In this latter capacity absorbed light plays a most important part in biological processes, being largely instrumental in the production of alkaloids, oils, and numerous other complex organic derivatives in plants (see Vol. II).

In order to observe an absorption spectrum, a suitable source of light is focussed on to the slit of the spectroscope and the absorbing medium interposed between the light source and the slit, close up to the latter. For observations in the visual region, the solution may conveniently be contained in an absorption cell with a pair of plane, parallel ends; diffused daylight serves as a suitable source of light. With the aid of photography permanent records are obtainable. If observations are to be made for a considerable distance into the ultra-violet region, all glass parts between the slit and light source must be replaced by quartz, and the source of illumination may be the arc spectrum of a metal such as iron. A useful form of cell is shown in fig. 126. Tubes A and B are joined by a broad rubber band C, and the absorbing solution is admitted at D; the plates E and F, which close the ends of the tubes, are made of quartz if necessary. The changes in the absorption spectrum as the thickness of the absorbing medium is varied can easily be followed by sliding the inner tube in and out of the outer one. Tube A may be graduated so that the thickness of the liquid column EF can be read directly or logarithmically. Photographs of the absorption spectra of praseodymium and neodymium nitrates are shown on Plate II for various thicknesses of the absorbing layers. The results may be shown graphically by plotting either the wavelengths or the frequencies against the concentration. When, however, a wide range of concentrations is used, the procedure is cumbersome.

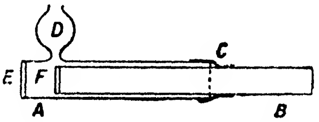


Fig. 126.—Absorption Cell (Baly).

It is usual, therefore, to express the concentration logarithmically as shown in fig. 127, which shows the absorption spectrum of an aqueous

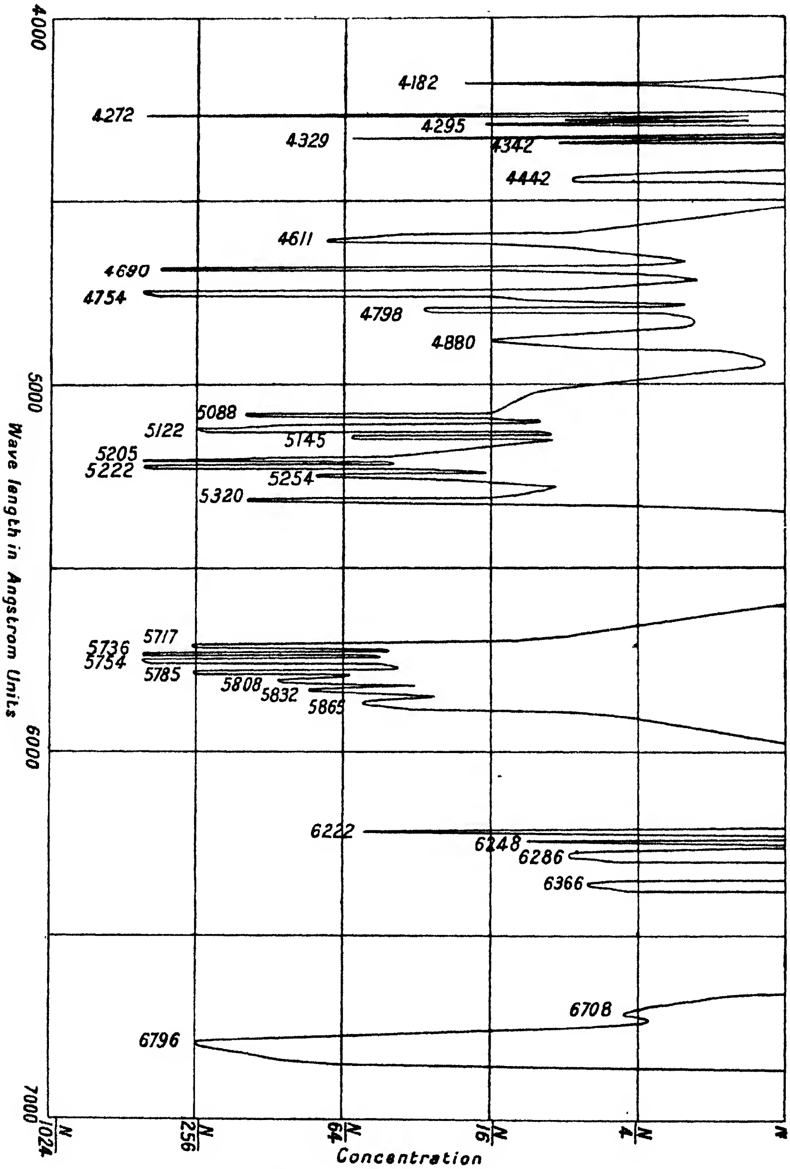
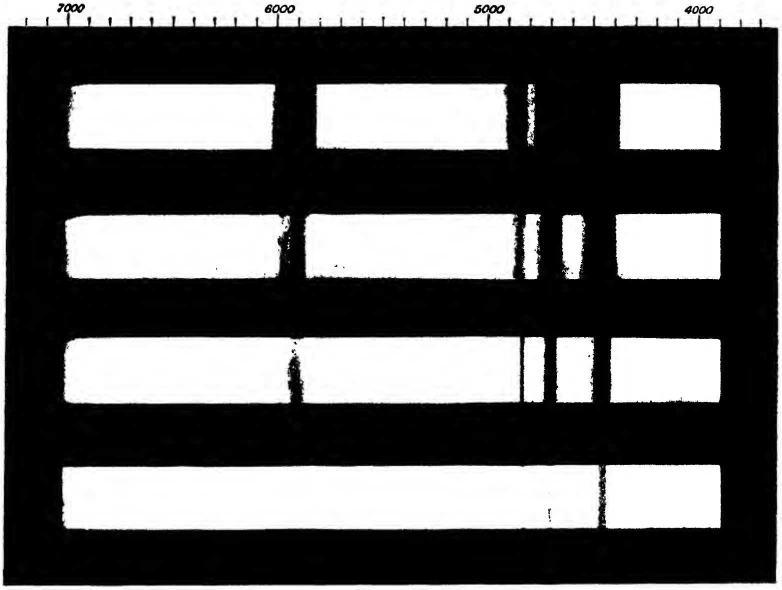


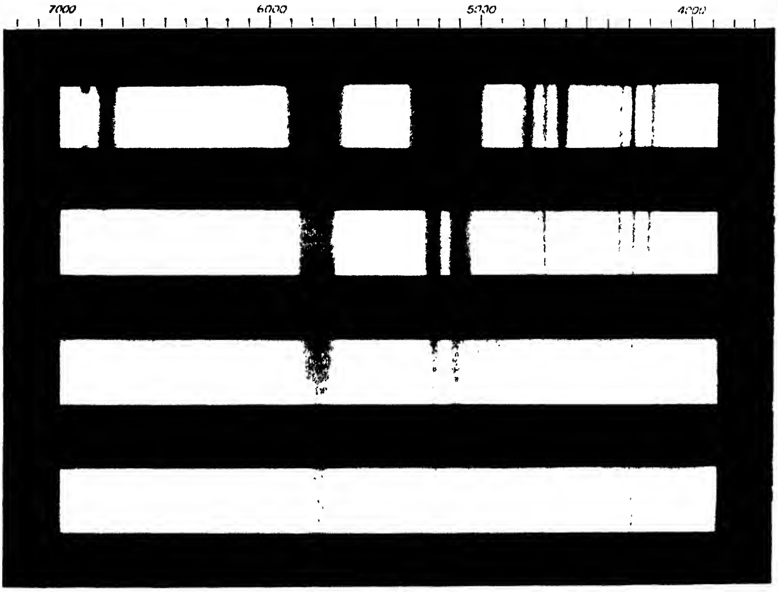
Fig. 127.—Absorption Spectrum of Aqueous Neodymium Chloride (Rech). (Thickness of absorbing layer = 20 cm.)

solution of neodymium chloride. Examination of this spectrum shows that certain broad bands seen in the normal solution become resolved into a number of narrower bands as the dilution is continued.



PRASEODYMIUM.

Absorption Spectrum of a Normal Solution of Praseodymium Nitrate. Thickness of absorbing layer 10·0, 3·3, 1·1 and 0·4 cm. respectively.



NEODYMIUM.

Absorption Spectrum of a Normal Solution of Neodymium Nitrate. Thickness of absorbing layer = 10·0, 3·3, 1·1 and 0·4 cm. respectively.

Eventually, as dilution proceeds, the bands disappear, but the dilution at which any one band disappears is not necessarily the same as that at which any other band ceases to be visible. Some bands can be observed only in moderately concentrated solution, while others are still visible in extremely dilute solution. It should therefore be borne in mind, when consulting complete lists of absorption bands, that all the bands enumerated cannot be seen at one and the same time, for in solutions sufficiently concentrated to exhibit the weak bands, others will have coalesced, producing a smaller number of broader bands.

It is frequently convenient to describe an absorption spectrum by stating for each band the wavelength corresponding to the position of maximum absorption—the so-called **peak** of the band. This is not necessarily at the middle of the band ; moreover, a broad band may show two or more peaks. The positions of these peaks are, in general, practically independent of the concentration of the solution.

The foregoing illustrates the principle of **selective absorption.** In some cases the transmitted light consists of a definite and continuous fraction of the spectrum and is not obviously split up into separate bands. Thus, for example, absorption may begin in the yellow region, the waves of greater wavelength being transmitted and those of smaller wavelength absorbed. This is termed **general absorption,** and is illustrated by succinic acid. There is no real, hard and fast distinction between these two types of absorption, however. Thus, for example, quartz begins to absorb in the infra-red at about 40,000 Å. The absorption increases slowly with the wavelength, ultimately reaching complete opacity in a way that would entitle it to be termed general absorption ; but further still in the infra-red the quartz becomes increasingly transparent again, and at 1,080,000 Å a plate 2 mm. thick will transmit more than 80 per cent. of the radiation (Rubens and Wood, 1911).

From the photographs it is evident that the edges of the bands are often hazy and difficult to define, so that whilst direct comparison of two such photographs can yield results of very great interest and importance, their value is limited by the fact that they are of little more than qualitative significance. It was not until early in this century, upon the introduction of the spectrophotometer, that truly quantitative measurements became possible in the ultra-violet, although in the visible region important work had been done even before 1880, as, for example, Vogel's spectroscopic determination of carbon monoxide in the blood.

Laws of Absorption.—Before explaining the principle of the spectrophotometer it is desirable to enunciate the two principal laws of absorption.

(1) **Lambert's Law** states that—

the proportion of light absorbed by a substance is independent of the intensity of the incident light.

This law appears to be rigidly true, and upon it is based the conception of what is termed the Bunsen-Roscoe **extinction coefficient,** usually denoted by ϵ. It is easy to visualise some method of determining the thickness, l, of the medium under examination that is required to absorb exactly nine-tenths of the incident light, thus reducing the intensity of the transmitted light to one-tenth. For some substances, such as quartz or glass, which are termed "transparent," l, measured in centimetres, may be great; for an optically dense medium like glue it may be small. The reciprocal of l is taken as the "extinction coefficient," so that, for a given wavelength

$$\epsilon = \frac{1}{l}.$$

If I_0 is the intensity of the incident light entering a medium, and I that remaining after passage through a path of length d cm., then

$$I = I_0 10^{-d\epsilon}$$

or

$$\log_{10}\frac{I_0}{I} = d\epsilon.$$

Another useful term is the **optical density,** which has the following specialised meaning (Hurter and Driffield, 1890). Giving I_0 and I the same significance as before, the density, D, is defined by the expression

$$D = \log_{10}\frac{I_0}{I}.$$

The total density of a number of media is equal to the sum of their separate densities.

(2) According to **Beer's Law,** the intensity of absorption is directly proportional to the concentration of the solution. More correctly stated—

the increase in intensity of absorption at any point in the spectrum, due to increase of concentration of the absorbing substance, may be exactly nullified by a diminution in thickness of the absorbing solution in the same ratio.

This law is obeyed with considerable accuracy when variation in the concentration of the solution is not accompanied by disturbing factors such as hydration, association, dissociation, etc.

If c is the concentration of the solution and d the thickness through which the light passes, Beer's Law states that

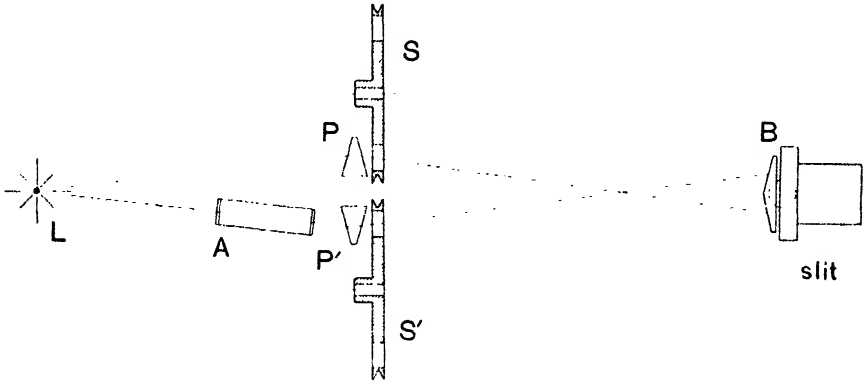
$$I = I_0 a^{-dc}$$

where a is a constant for the liquid under investigation, and represents the ratio of the transmitted to the incident light for unit thickness and concentration. Looking at this in another way, we can write

$$I = I_0 10^{-d\epsilon c}$$

where ϵ is the "extinction coefficient" of the solution of unit thickness and concentration; that is to say, Beer's Law states that the extinction coefficient, for a given wavelength, of a solution of concentration c, is c times that of the same solution of unit concentration.

The Spectrophotometer.—The principle of the Hilger Sector Photometer, designed by Twyman in 1910, is shown diagrammatically in fig. 128. The source of light L is usually a spark discharge between electrodes of steel alloyed with tungsten and other metals which yield an enormous number of lines in the spectrum and make it easy to determine points of equal intensity in two spectrum photographs when placed close together. Immediately in front of the slit of the spectrograph is a bi-prism B, which receives the light from the source in the following manner. The light emanates from the source L, and may reach the slit by two alternative paths. An upper beam passes through the wedge prism P, and then through a rotating sector S, the aperture of which can be varied. The beam falling on the bi-prism, B, is deviated by the lower half of that prism to pass axially along the collimator of the spectrograph. The second beam traverses first the absorbing liquid under examination, contained in a suitable cell A, then a wedge prism P′, similar to P but so arranged as to divert the light upwards instead of downwards, and finally through a rotating sector S′, of fixed aperture. The beam is then diverted by the upper half of the bi-prism B, and passes axially along the collimator of the spectrograph like the first. We thus have the spectrograph fed by two beams, the one capable of being varied in intensity at will by varying the aperture of the rotating sector, the other subject to the absorption of a known thickness of the liquid under examination. A series of photographs is taken on a single photographic plate with the sector S set to different apertures. Each of these photographs consists of a pair of spectrum photographs in close juxtaposition, one of which is of reduced density throughout its whole length, the other—that corresponding to passage through the material under test—being more dense than the first in certain parts and less so in others, there being certain wavelengths where the densities of the two are equal. The places of equal density being spotted, everything necessary is known for the plotting of the absorption curve.



ADAM HILGER L^TD LONDON

FIG. 128.—Principle of Hilger Sector Photometer.

The kind of result obtained is beautifully illustrated in Plate III, where points of equal intensity are shown by white dots. These photographs were actually obtained with a later form of instrument than that described above, namely the Spekker Photometer, designed by Twyman about 1930. Fig. 129 shows the absorption curve drawn from the photographs in Plate III.

Absorption Spectrum of Water.—The absorption of light by water has been studied by passing a beam of light through a column of water several metres in length. A faint and narrow band was observed in the orange at a wavelength of approximately 6000 Å. This band became slightly more distinct and a general absorption of the extreme red was noticed as the thickness of the water layer was increased from 3·3 to 4·5 metres.

In small quantities water appears colourless, but in deep layers it is possessed of a bluish tinge, which tends to become greenish as the temperature is raised. The cause of the coloured appearance of natural waters has been the subject of considerable discussion. The light blue hue of water that has been softened by Clark's process has frequently been commented upon, and points to the suggestion that the colour is due to the scattering of light by suspended particles. Threlfall (1899) found that the following solution, when viewed through a tube 18 cm. in length, matched with considerable precision the colour of a sample of water from the Mediterranean :

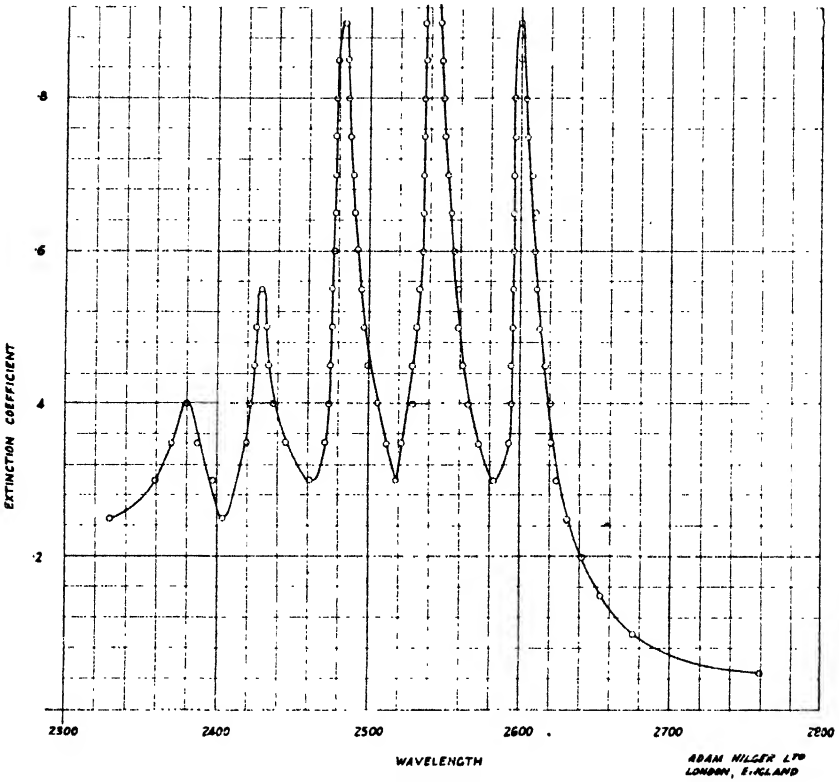
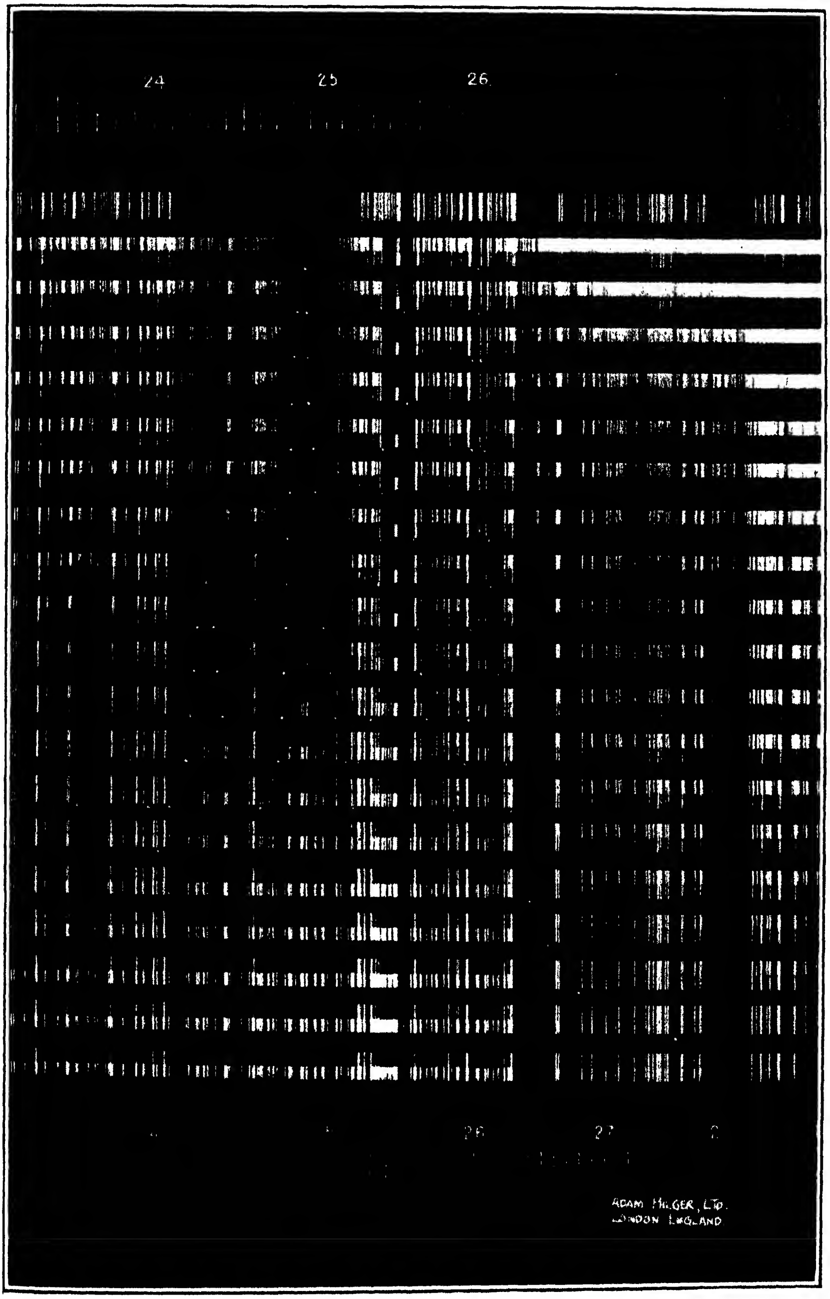


FIG. 129.—Absorption Curve drawn from Photograph on Plate III.

500 c.c. distilled water.
0·001 grm. soluble Prussian blue.
5 c.c. saturated lime water just precipitated by the smallest excess of sodium hydrogen carbonate.

According to Aitkin (1882) the Mediterranean Sea owes its colour to minute suspended particles which reflect rays of all colours, whilst



[Reproduced by kind permission of Messrs Hilger, Ltd.

ABSORPTION PHOTOGRAPH OF BENZENE (IN HEXANE).

the water, by virtue of selective absorption, allows only the blue rays to escape. The solid particles thus determine the brilliancy of the colour, whilst the selective absorption by the water determines the colour itself. The green colour, so frequently noticed in the sea, is attributed to the presence of yellowish particles in suspension. On the other hand, the green colours of such lakes as Constance and Neuchâtel are ascribed to the mixing of the natural blue of the waters with yellow produced by the presence of finely divided particles of suspended matter, which latter may themselves be quite colourless. Sometimes lakes, normally greenish in colour, become temporarily colourless. This is attributed to the presence of fine reddish mud, containing oxide of iron, which counteracts the green.

The greenish colour of the sea off the coast of Western Australia may be due to the presence of traces of organic colouring matter dissolved out of living or dead seaweed. The green colour of Antarctic waters has been attributed to diatoms and the excretions of minute animals, whilst the sea water at Mogador (Morocco) and off Valparaiso and San Francisco is believed to be coloured green by chlorophyll.

Perfectly pure water is almost a chemical impossibility, inasmuch as contact with any containing vessel must lead to contamination. Even optically pure water is difficult of attainment ; it cannot be prepared by mere filtration or distillation ; even water obtained by distillation from acid permanganate solution and subsequent redistillation from a copper vessel in a hydrogen atmosphere is not optically void. Tyndall obtained optically pure water by melting clear block ice in a vacuum. It showed a blue tinge when examined in a three-foot layer.

Now, if pure water is coloured slightly blue, as is generally conceded, the effect cannot be due to either of the foregoing causes, namely, the presence of suspended or dissolved materials, which are known to accentuate, if not to be the sole cause of, the colours of natural waters. It must be due to a pure absorption effect of the water itself. The relation between colour and constitution is by no means clear, but the suggestion has been made that the greenish tinge acquired on raising the temperature is a consequence of the depolymerisation of the water molecules, the polymerised molecules being bluish in colour, whilst the single monohydrols are green. This receives support from the fact that solutions of colourless salts, which may be expected to contain fewer polymerised molecules than solutions of coloured salts, are more green than pure water at the same temperature.

The brown colours of certain natural waters are sometimes due to ferruginous suspensions, but in many cases are attributable to colloidal organic matter. Typical waters of this class occur in the uplands of Lancashire and Yorkshire. The colloid is usually electronegative in character, exhibiting electrophoresis in the direction of the anode and being precipitable by positively charged ions and colloids and by electrical treatment (p. 461).

Absorption in the Infra-red.—Water molecules exert a powerful absorption in the infra-red region, both in the free state and when loosely combined as so-called "water of crystallisation." The strongest bands lie at 3μ and 6μ, other well-marked bands occurring at $1{\cdot}5\mu$, 2μ and $4{\cdot}75\mu$ (p. 8). On the other hand, when the water is more firmly attached to other atoms in a molecule, as, for example, in hydroxides, where it functions as "water of constitution," the foregoing bands do not appear (Coblentz, 1905). A few results are given in the following table :

Substances showing No Water Bands.	**Substances showing Water Bands.**
Anhydrite, $CaSO_4$.	Gypsum, $CaSO_4.2H_2O$.
Quartz, SiO_2.	Opal, $SiO_2.xH_2O$.
Brucite, $Mg(OH)_2$.	Alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$.
Manganite, $MnO.OH$.	Potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$.
Goethite, $FeO.OH$.	

Manganite is usually written as $Mn_2O_3.H_2O$, and goethite as $Fe_2O_3.H_2O$, but their infra-red absorption spectra suggest the hydroxylated formulæ are more correct. Anhydrite and quartz show weak bands in the neighbourhood of the water bands. Talc, when heated to redness, loses water ; it does not, however, show water bands, from which we infer that the expelled water was present as "water of constitution." Serpentine, on the other hand, shows the water band at 3μ and is therefore a hydrated mineral.

Absorption Spectra of Inorganic Salt Solutions.—Solutions of salts containing a common coloured radical united with a colourless radical frequently possess similar, if not identical, absorption spectra. Ostwald in 1889 showed that this was the case with soluble permanganates, such as those of the alkali metals. Chromates and dichromates behave similarly. The foregoing examples refer to coloured negative radicals attached to colourless metallic radicals. If a coloured metallic radical is attached to a series of colourless acid radicals, in general the absorption spectra are also very similar, although sometimes marked differences occur. It must be remembered, however, that in aqueous solution several disturbing factors may influence the spectrum, such as combination with the solvent, hydrolysis and ionisation. This last-named factor is exceedingly important, and is dealt with in detail in Vol. II.

Rare Earths.—The absorption spectra of the rare earths have proved very useful in rare earth analysis. These earths and their salts so closely resemble one another in their chemical and physical properties that the detection and separation of any particular member of the series in a complex mixture by ordinary chemical methods may be a matter of the utmost difficulty. Salts of the following rare earth metals when in aqueous solution yield characteristic visual absorption spectra : praseodymium (Plate II), neodymium (Plate II), samarium, europium, dysprosium, holmium, erbium, thulium, and probably also the exceedingly rare element illinium. Unfortunately, however, these absorption spectra overlap a great deal, and the presence of some of the elements may completely obliterate the evidence of the presence of others. Praseodymium, neodymium and erbium can readily be identified in mixtures. Samarium can usually be detected by the presence of an absorption band the centre (not the head) of which has a wavelength 4020 Å. It is an unfortunate circumstance that the strongest of the samarium bands lie very closely in the neighbourhood of prominent bands of neodymium and europium, for these are the two elements most difficult to remove from samarium. Dysprosium, which was originally characterised by its visible absorption spectrum, may also be identified by its ultraviolet absorption spectrum.

The wavelengths of the peaks of the chief bands of the visible absorption spectra of a few of the more important rare earth metals are given below, and the student is recommended to compare the data for praseodymium and neodymium with the photographs on Plate II.

Praseodymium . .	λλ 4815, 4690, 4435.
Neodymium . .	7324, 5800, 5780, 5740, 5200, 5120, 5090, 4274.
Samarium . . .	4760, 4630, 4170, 4020.
Europium . . .	5251, 5234, 4656, 4645.

Salts of Cobalt.—For many years chemists have been greatly attracted by the colour changes manifested by salts of cobalt, some of which have been used for invisible or "sympathetic" inks. Aqueous solutions of cobalt chloride may be obtained by dissolving the carbonate in diluted hydrochloric acid, and upon crystallisation at the ordinary temperature, *deep rose-red* monoclinic prisms of the *hexahydrate*, $CoCl_2.6H_2O$, are obtained. These lose four molecules of water when warmed to 50° C. over sulphuric acid, yielding the *rose-coloured dihydrate*, $CoCl_2.2H_2O$. At 100° C. one further molecule of water is expelled, a *violet monohydrate*, $CoCl_2.H_2O$, remaining. At 120° C. the *blue anhydrous* salt is obtained.

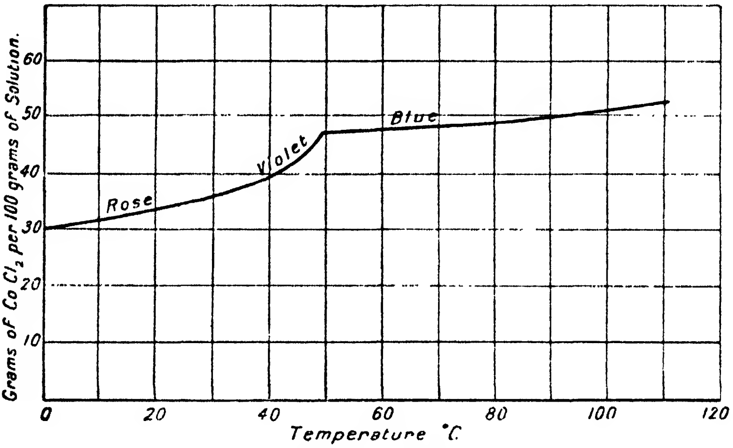


FIG. 130.—Solubility Curve of Cobalt Chloride.

The solubility curve of cobalt chloride in water is shown in fig. 130. In the cold the saturated solution is a deep rose-red colour, like the solid hexahydrate. On warming, it becomes violet between 25° and 50° C., above which latter temperature it is blue. This was at one time attributed to a change in hydration of the cobalt salt in solution from the hexahydrate through the violet monohydrate to the blue anhydrous salt (von Babo, 1857). This appeared to receive support from the fact that cobalt chloride dissolves in ordinary ethyl alcohol yielding a blue solution, which first becomes violet and then red on continued addition of water. The explanation, however, is not quite as simple as this; it does not, for example, explain why some substances, such as zinc chloride, when added to the solution, do not affect its colour, whereas others, such as hydrochloric acid and calcium chloride, tend to change the colour from red to blue.

Ostwald in 1893 suggested a simple ionic explanation, namely, that the red colour is that of the cobalt ion, the blue that of the undissociated salt. This is certainly not a complete explanation, for the solid crystalline hexahydrate is dark red in colour, not blue. Further, the theory demands a very marked decrease in ionisation in solution with rise of temperature, which experiment does not support.

An important clue was given by Donnan and Bassett in 1902 when they found by electrolytic experiments that the blue solutions contain a blue anion, in which the cobalt atom is present, whereas the rose solutions possess a rose-coloured cation, containing the cobalt.

The true explanation appears to lie in the tendency of cobalt in solution to yield complex ions. When associated with four monovalent groups or their equivalent, that is, when the co-ordination number (Vol. II) is four, the colour is blue. When the co-ordination number is six, the colour is red (Hill and Howell, 1924). Thus, for example, using Werner's notation (Vol. II), in cool solutions the rose colour is due to hexaquo-ions, thus

$$[\mathrm{Co(H_2O)_6}]^{++}.$$

The reason that zinc chloride and mercuric chloride do not change the colour of the solutions appreciably is due to the presence of complex ions of the type:

$$\left[\mathrm{Co}\begin{matrix}\mathrm{Cl_4}\\ (\mathrm{ZnCl_2})_2\end{matrix}\right]^{++}, \quad \left[\mathrm{Co}\begin{matrix}\mathrm{Cl_4}\\ (\mathrm{HgCl_2})_2\end{matrix}\right]^{++}, \text{ etc.}$$

The blue colour caused by the addition of hydrochloric acid to the solutions is attributed to the formation of blue negative ions containing the cobalt, namely

$$[\mathrm{CoCl_4}]^{--}.$$

Dilution breaks these ions down, and the rose-coloured hexaquo-ions are produced; for this reason dilute solutions of cobalt chloride, sulphate and nitrate yield identical absorption spectra.

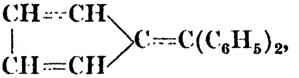
Chromophores.—In 1876 Witt suggested that the colours of organic substances are connected with the presence of certain unsaturated groups which he called chromophores. Of these the most important are

$$\mathrm{C{=}C},\quad \mathrm{C{=}O},\quad \mathrm{C{=}S},\quad \mathrm{C{=}N},\quad \mathrm{N{=}N},\quad \mathrm{N{=}O},\quad \text{and}\quad \mathrm{NO_2}.$$

Quinonoid structures are also associated with colour, and may be regarded as coming within the purview of the above in that they consist of compact assemblages of $\mathrm{C{=}C}$ groups (Nietzki, 1888). Molecules containing a chromophoric group are termed **chromogens.** These chromogens are not of necessity coloured bodies themselves. Thus benzophenone, $\mathrm{C_6H_5COC_6H_5}$, is a chromogen, as it contains the chromophoric group $\mathrm{C{=}O}$, although it is colourless. On introducing the amino-group into the molecule aminobenzophenone is obtained. This is a yellow compound, and the amino-group "developing" this colour is termed an **auxochrome** (Latin *augere*, to increase). Another well-known auxochrome is the hydroxyl group. When a chromogen is already coloured, introduction of an auxochrome serves to intensify the colour. Thus nitrobenzene is pale yellow, and the nitranilines have a deeper or more golden colour.

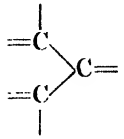
Colour depends not merely on the presence of a chromophore, but is influenced by the number and position of the chromophores within the molecule. Thus, for example, diphenylethylene, $C_6H_5CH : CHC_6H_5$, is colourless, but diphenylhexatrïene, $C_6H_5.CH : CH.CH : CH.CH : CH.C_6H_5$, is yellow.

Ring formation causes an increased compactness of chromophores and thus tends to promote colour phenomena. Thus diphenylfulvene,

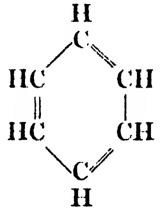


which may be regarded as the cyclic analogue of diphenylhexatrïene, is dark red in colour.

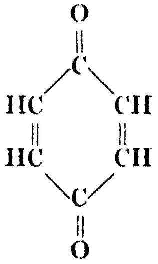
Although benzene is not visibly coloured, yet it possesses a definite absorption spectrum in the ultraviolet region. Pronounced colour is associated with the



group. Thus



Benzene
(Colourless).



Quinone
(Golden-yellow).

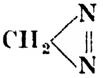
The C=O group produces no colour effect in the simple ketones and aldehydes, although these substances may show selective absorption in the ultraviolet region. Acetone is a good example. Reduction of this ketone to *iso*propyl alcohol, $CH_3CHOHCH_3$, removes the power of selective absorption, the alcohol showing only general absorption. The introduction of a second ketonic group into a molecule may or may not induce a colour effect, according to circumstances. Thus, acetyl acetone, $CH_3COCH_2COCH_3$, is colourless, but diacetyl, $CH_3CO.COCH_3$, in which the two chromophores are in juxtaposition, possesses a yellow colour. Introduction of a third and of a fourth C=O group into the molecule results in the production of orange and orange-red products respectively. Thus :

Acetone, CH_3COCH_3	Colourless.
Diacetyl, $CH_3CO.COCH_3$	Yellow.
$\beta\gamma\delta$-Triketopentane, $CH_3CO.CO.CO.CH_3$ . .	Orange.
$\beta\gamma\delta\epsilon$-Tetraketohexane, $CH_3CO.CO.CO.COCH_3$.	Orange-red.

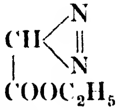
The C=S group appears to possess greater colour-producing power than C=O for, whilst acetophenone and benzophenone are colourless, their thio-derivatives are blue. Thus

$C_6H_5.CO.CH_3$ Acetophenone (Colourless).	$C_6H_5.CS.CH_3$ Thio-acetophenone (Blue).
$C_6H_5.CO.C_6H_5$ Benzophenone (Colourless).	$C_6H_5.CS.C_6H_5$ Thio-benzophenone (Blue).

The N=N group is powerfully chromophoric. Aliphatic substances containing this group are generally yellow. Thus

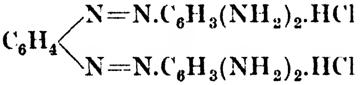


Diazomethane
(Yellow).



Diazoacetic ester
(Yellow).

Aromatic compounds containing the N=N group are often brilliantly coloured. Artificial dyestuffs, known as azo-dyes, contain this group, and are of world-wide reputation. Examples are afforded by

Azobenzene, $C_6H_5.N=N.C_6H_5$	Brilliant red.
Methyl orange, $SO_3Na.C_6H_4.N=N.C_6H_4.N(CH_3)_2$.	Orange.
Bismarck brown,  $C_6H_4\left<\begin{matrix}N=N.C_6H_3(NH_2)_2.HCl\\N=N.C_6H_3(NH_2)_2.HCl\end{matrix}\right.$.	Brown.

The NO_2 group acts as a weak chromophore, some derivatives, such as the nitroparaffins, being colourless; others are yellow or orange. A curious feature of the nitro-group lies in the fact that duplication in the molecule does not enhance the colour, but may reduce it. This is shown, for example, by nitrobenzene, which is pale yellow, whereas dinitrobenzene is colourless. On the other hand multiplication of the C=O group enhances the colour, as we have already seen.

Groups which, on introduction into an organic compound, shift the absorption band towards the red are termed **bathychrome groups** (Greek *bathus*, deep); **hypsochrome groups** have the reverse effect. Thus bromine and the methyl group are bathychromic, whilst the nitro-group is often hypsochromic. The following examples illustrate this:

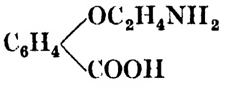
	Region of Maximum Absorption $\mu\mu$.		Region of Maximum Absorption $\mu\mu$.
Indigo . . .	604·8	Fluoresceïn . .	494
Methyl indigo . .	619·7	Tetrabromfluoresceïn	515·9
		Tetranitrofluoresceïn	489

The nitro-group may, however, exert a bathychromic influence, as in the nitranilines and nitrophenols, which are more highly coloured than aniline and phenol respectively.

An auxochrome usually exerts a bathychromic influence; for example anthraquinone is yellow, whereas α-amino-anthraquinone is red.

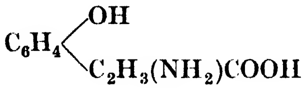
Chemical Constitution.—The nature of the absorption spectrum of an organic derivative may, in certain cases, afford a clue to the chemical constitution of that derivative, the assumption being made that *compounds of similar structure will give analogous absorption spectra.* This is **Hartley's Rule.**

One of the first examples of this rule was **tyrosine,** to which either of the following formulæ might apply :



$$C_6H_4{<}\begin{matrix}OC_2H_4NH_2\\COOH\end{matrix}$$

(I)

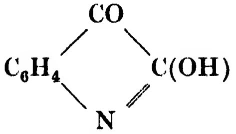


$$C_6H_4{<}\begin{matrix}OH\\C_2H_3(NH_2)COOH\end{matrix}$$

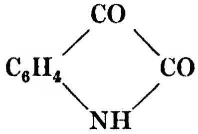
(II)

The first formula represents tyrosine as a derivative of oxybenzoic acid, the second as a phenol. The absorption spectrum bore no resemblance to that of *p*-oxybenzoic acid, but it did resemble that of phenol. So Hartley assumed the second formula to be correct.

A second example is afforded by **isatin,** for which the following formulæ have been suggested :

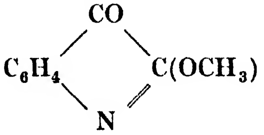


(I) (Lactim).



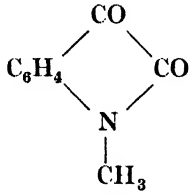
(II) (Lactam).

Hartley found that the introduction of a methyl or ethyl group into a molecule does not markedly affect its absorption spectrum. Thus benzoic acid, C_6H_5COOH, and methyl benzoate, $C_6H_5COOCH_3$, give practically identical absorption spectra. Two isomeric methyl derivatives of isatin are known, namely



(I)

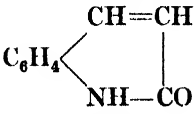
and



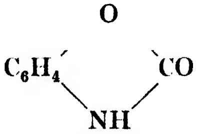
(II)

Examination of the absorption spectra of these derivatives showed very definitely that the second derivative resembled the parent substance in structure. Isatin is thus a lactam, and its constitution is represented by formula (II).

In a similar manner **carbostyril** and **o-oxycarbanil** have been shown to possess the lactam structure. Thus

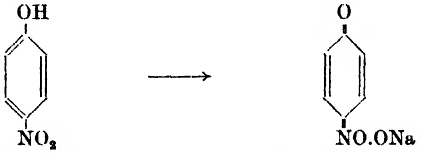


Carbostyril.



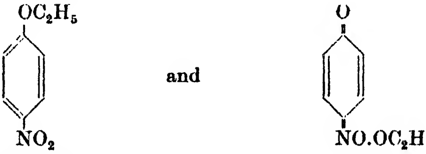
o-Oxycarbanil.

When converted to its sodium salt, colourless *p*-nitrophenol undergoes a marked change in colour, becoming deep yellow. This is generally regarded as indicating a change in constitution, a quinonoid structure being ascribed to the sodium salt; thus



p-Nitrophenol (Colourless). Sodium *p*-nitrophenate (Deep yellow).

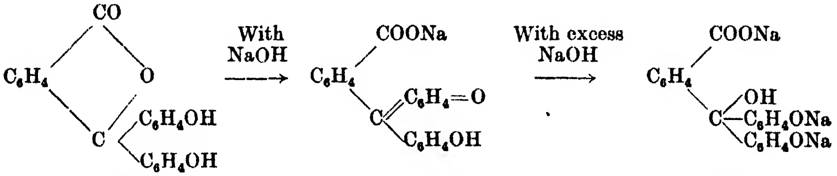
From *p*-nitrophenol two isomeric ethers are obtainable; the one is yellow, labile or unstable, and readily transforms into the colourless, stable isomer. To the former, therefore, the quinonoid structure is assigned, and the colourless isomer is presumed to have the same structure as the free *p*-nitrophenol. Thus



Colourless, stable isomer. Coloured, unstable isomer.

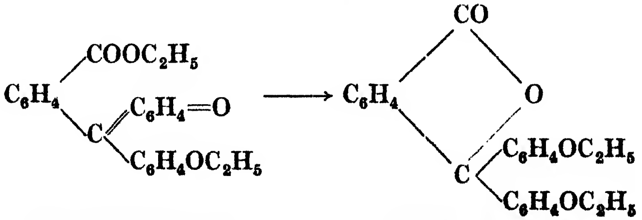
This is known as **chromo-isomerism.**

It is well known that, in acid solution, **phenolphthalein** is colourless, whereas in alkaline solution it possesses a beautiful red colour. It is extensively used as an *indicator* in volumetric analysis (see Vol. II). In the presence of excess of sodium hydroxide the colour vanishes. These colour changes indicate the following variations in the structure of phenolphthalein (Stieglitz, 1903):



Colourless phenolphthalein. Coloured sodium salt. Colourless trisodium salt.

It was discovered by Meyer and Marx (1907) that by treating the silver salt of phenolphthalein with ethyl iodide a deep yellow diethyl ester is at first produced, which is very unstable and readily yields a colourless, stable ester. Simple recrystallisation of the unstable form suffices to effect the change, which may be represented as follows:



Coloured, labile isomer. Colourless, stable ester.

ABSORPTION OF X-RAYS.

If X-rays are allowed to fall normally on to a slab of any material, the fraction of the rays absorbed by that slab gives a measure of the **opacity** of the material. In order to compare the opacities of different substances it is necessary to have some standard of reference. This is termed the **specific opacity,** and refers to the fraction of the X-rays absorbed when they fall normally on to the base of a right cylinder, 1 square centimetre in base area and of mass 10 grammes. The specific opacity of an element for X-rays of a definite quality is independent of its state of aggregation and of the temperature ; it is also independent of whether the element is free or in combination, so that the specific opacity of a compound may be calculated from the opacities of its constituent elements.

The **equivalent transparency** of a substance is the mass in decigrams of a right cylinder, the area of whose base is 1 square centimetre, which produces, when X-rays are passed through it parallel to its axis, the same absorption as a cylinder of paraffin wax, 75 millimetres high and 1 square centimetre in cross-section. If masses m_1, m_2, m_3, etc. of elements of equivalent transparencies e_1, e_2, e_3, etc. are present in a total mass M of a substance of equivalent transparency E, then

$$\frac{M}{E}=\frac{m_1}{e_1}+\frac{m_2}{e_2}+\frac{m_3}{e_3}+\ . \ . \ .$$

Benoist (1897 to 1901) observed that for X-rays of one definite quality the specific opacities of elements increase in a regular manner with the atomic weight. This is conveniently indicated by plotting the equivalent transparencies of the elements against their atomic weights. The points lie on a smooth curve, such as shown in fig. 131, Curve I, and the curve is somewhat similar to a hyperbola (Curve III), which is the graphical representation of the connection between specific heat and atomic weight.

Each quality of X-ray, however, yields its own particular curve. Thus in fig. 131, Curve I refers to rays of medium "hardness," or penetrating power, whereas Curve II refers to soft rays, that is rays possessing less penetrating power.

In seeking the atomic weight of an element by the X-ray method, each possible multiple of the combining weight is independently assumed, the elements which would immediately precede and follow it on the curve noted in each case, and the transparencies of each of these elements and of the element under investigation determined for a particular quality of X-rays, or, better, for two decidedly different qualities. The results are superior to those based upon specific heats, in that they are neither influenced by the temperature nor the physical condition of the element, and thus are applicable to gaseous elements. The method has been applied both to indium and cerium, which elements at the times of their discovery presented considerable difficulty to chemists. Both metallic indium and its acetylacetonate have been examined, and the results clearly indicate an atomic weight of approximately 115. The element is thus trivalent (see p. 222). Similarly cerium in its cerous salts has been shown to be trivalent, thorium tetravalent and beryllium divalent. For a further consideration of **X-rays the reader is referred to Volume II.**

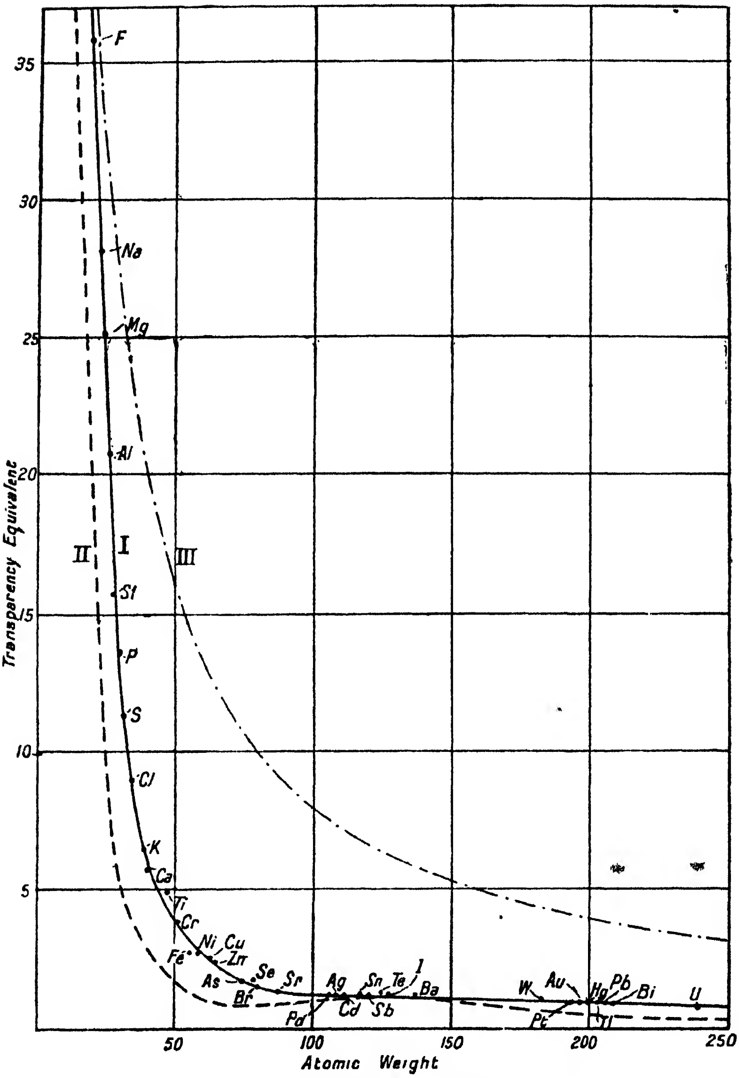


FIG. 131.—Benoist's X-ray Transparency Curves.

LUMINESCENCE.

When a substance emits light from one cause or another it is said to be luminous or to luminesce (Latin *lumen*, light; *escere*, of inceptive verbs). Several different kinds of luminescence are recognised. The term **phosphorescence** (Greek *phōs*, light; *phero*, I bear) is used widely to include the emission of light unaccompanied by any appreciable heat evolution. Sometimes phosphorescence is purely a physical phenomenon, as, for example, the phosphorescence shown when certain rare earths are subjected to the bombardment of cathode rays (p. 289). The effect persists after the removal of the exciting influence. On the other hand phosphorescence may be the result of chemical action, as, for example, the luminosity of phosphorus and of many other substances at temperatures near their ignition points. This type of phosphorescence is frequently termed **chemiluminescence** (p. 313). A particular type of luminescence which appears only whilst the exciting influence is acting is termed **fluorescence.** That produced by the mechanical breakdown of crystalline structures is known as **triboluminescence** (p. 313).

Fluorescence.—When examined by reflected light many substances show a peculiar surface colour which is distinct from that due to ordinary absorption of light. When gently warmed, the mineral fluorspar, CaF_2, popularly known as " Blue John," becomes luminous, an observation that gave rise to the term " fluorescent " [the mineral received its name from its use as a flux (Latin *fluere,* to flow), not from its optical properties].

As soon as the exciting influence is withdrawn fluorescence ceases, a property which enables it to be distinguished from phosphorescence. As in the case of absorption, fluorescence is not confined to the visible portion of the spectrum ; it has been observed in the ultra-violet region also.

Not every incident ray can produce fluorescence in a substance, for if a beam of sunlight is directed through two vessels containing the same fluorescent liquid, the second vessel does not fluoresce, the first one having absorbed the exciting rays from the beam. To produce fluorescence the incident light must fall on an absorption band ; that is, it must itself be absorbed and its energy emitted again in waves of different length.

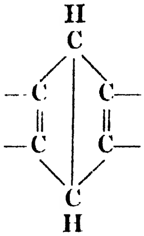
On allowing a beam of light to fall on to an acidified solution of quinine sulphate, a blue fluorescence is emitted at the point of incidence, and blue light is emitted from the path of the beam inside the solution, clearly visible in a darkened room. The intensity of the fluorescence decreases with the thickness of the solution traversed and, if the solution is sufficiently thick, the fluorescence fades away within it. The whole of the exciting rays in the original beam have then been absorbed and their energy emitted again as fluorescence.

Fluorspar fluoresces with a blue light like sulphate of quinine, chlorophyll with a red light, fluoresceïn and uranium glass with a green light, and so on.

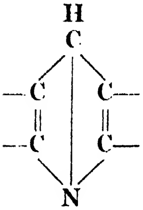
Some years ago it was thought that the wavelengths of fluorescent light were always greater than those of the exciting luminosity, and this was known as **Stokes' Rule** (1852). But this rule is not universal, eosin and fluoresceïn constituting exceptions.

The fluorescence of a solute may be greatly influenced by the nature of the solvent ; not only may the colour vary, but the fluorescence may disappear altogether in some solvents. Chemical combination of the solute with the solvent, ionisation, or some particular physical property of the solvent, such as selective absorption of the incident exciting light waves, may account for these differences.

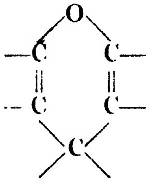
Fluorescence is closely connected with chemical constitution, and certain groups termed **fluorophores** (R. Meyer, 1897) are usually associated with it. A few such groups are :



Occurring in the *anthracene* series.

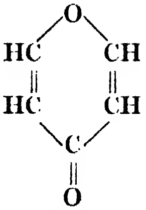


Occurring in the *acridine* series.

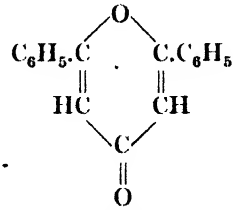


Occurring in derivatives of *fluoresceïn*.

Many other fluorophores are known, but these will suffice to illustrate their general nature. The presence of a fluorophore does not necessarily imply fluorescence any more than the presence of a chromophore necessitates colour. Thus γ-pyrone is not fluorescent, although fluorescence appears if the molecule is loaded with dense atomic groups such as benzene nuclei. For example :

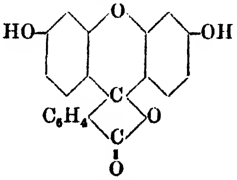


γ-Pyrone.
Non-fluorescent.



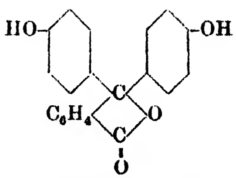
Diphenylpyrone.
Fluorescent in concentrated sulphuric acid.

In this connection it is interesting to compare :



Fluoresceïn.
Green fluorescence in alkaline solution.

and



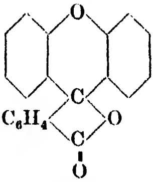
Phenolphthalein.
Non-fluorescent.

It will be noted that the phenolphthalein does not contain the fluorophore with the bridge oxygen.

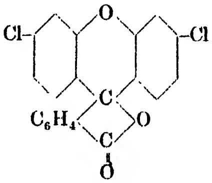
Substitution of hydrogen by various groups may remove fluorescence entirely. The most active group in this respect is the NO_2 group, which is particularly inimicable to fluorescence. Other groups, in the order of weakening inimicability, are :

$$NO_2 > I > Br > Cl > OH.$$

As an example we may take



Fluorane.
Strongly fluorescent.



Dichlorofluorane.
Non-fluorescent.

As might be expected, the position occupied by the substituted group within the molecule is very important also.

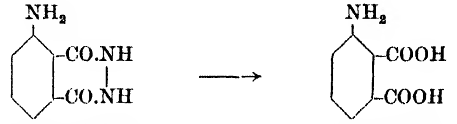
Triboluminescence.—When two pieces of sugar are rubbed together in the dark, light is emitted, in consequence of the breaking down of the crystals. This is termed triboluminescence (Greek *tribo*, I rub). When a trace of a radioactive substance is brought near to a screen of zinc sulphide, the latter appears, if examined through a lens, to be illumined with a large number of minute spots of light which come and disappear in flashes (see Vol. II). This is the principle of the **spinthariscope** (Greek *spinther*, a spark ; *skopein*, to see). The spots of light are caused by impacts of α-particles from the radioactive matter striking the crystals of zinc sulphide in the screen, causing them to break down and emit some of their energy as light waves. Crystals of uranyl nitrate emit flashes of light when mechanically shaken or crushed.

Chemiluminescence is the term applied to the luminosity produced at atmospheric temperature as the result of chemical action, the liberated energy of the reaction appearing as light, without appreciable heat. The luminosity of phosphorus, of many fungi, of the glow-worm, etc. are well-known examples.

The luminous organs of insects represent one of the most efficient sources of light in so far as the human eye is concerned, as almost all the energy is concentrated in a narrow band in that part of the spectrum towards which the eye is most sensitive. In the fire-fly the band covers 5230 to 6550 Å. For the glow-worm the band is only half as broad, namely 5290 to 5860 Å.

If to a solution of strontium chloride contained in a tall gas jar some dilute sulphuric acid is added, a white precipitate of strontium sulphate is immediately obtained. When the experiment is carried out in a dark room the precipitation is seen to be accompanied by very considerable luminosity. This was first observed by Davy, *c.* 1798.

A striking example of chemiluminescence is afforded by *o*-aminophthalic cyclic hydrazide, a yellow crystalline powder, when oxidised in alkaline solution (Albrecht, 1928). The maximum effect is obtained when a mixture of hydrogen peroxide and potassium ferricyanide (or hypochlorite) is used as oxidiser. To an alkaline solution of the hydrazide a little hydrogen peroxide is added and the mixture poured dropwise into an alkaline solution of the ferricyanide. Each drop produces a brilliant bluish-white luminous pearl. The chemical changes involved are complex, but the initial and final substances are



o-Aminophthalic cyclic hydrazide.

o-Aminophthalic acid.

Phosphorescence, which is the result of slow combustion in air, is dealt with later (see Vol. II).

The Dielectric Constant.

Let C be the capacity of a condenser formed by two conducting plates placed parallel to one another *in vacuo*, and C_1 the capacity when the plates are separated by an insulator such, for example, as paraffin wax. Then the specific inductive capacity or the dielectric constant, ϵ, of the paraffin wax is given by

$$\epsilon = \frac{C_1}{C}.$$

The dielectric constant of air is very nearly unity, and the dielectric constants of substances are frequently expressed relative to air taken as unity. The constants of a few typical substances using waves of low frequency are as follows :

Solids at Room Temperature.	ϵ.	Gases under Atmospheric Pressure, $\lambda = \infty$.	Temperature, °C.	ϵ.
Calcite . .	7·6	Air	0	1·000586
Fluorite . .	6·8	,, ...	20	1·000576
Gypsum . .	6·3	Hydrogen . .	20	1·000273
Ice (– 2° C.) .	93·9	Nitrogen . .	20	1·000581
Rock salt . .	5·6	Carbon dioxide .	0	1·000985
Selenium (16° C.)	6·1			
Sulphur . .	4·0	For Liquids see Table, p. 315.		

In general the dielectric constant falls with rise of temperature in accordance with the equation

$$\epsilon_t = \epsilon(1 - at)$$

a being the temperature coefficient, which usually is very small.

Maxwell's Law.—According to Maxwell's theory, if u is the velocity of electromagnetic waves in air,

$$u=\sqrt{\frac{1}{\epsilon\mu}}$$

where μ is the permeability. For any other medium

$$u_1=\sqrt{\frac{1}{\epsilon_1\mu_1}}$$

For substances transparent to light μ is almost unity, so that

$$\frac{u_1}{u}=\sqrt{\frac{\epsilon}{\epsilon_1}}$$

But the refractive index, n, of a transparent substance relative to air is given by the ratio u/u_1 and ϵ, as mentioned in the preceding section, is unity, so that

$$n=\sqrt{\epsilon_1} \quad \text{or} \quad \epsilon_1=n^2.$$

That is,

the dielectric constant of a transparent substance is equal to the square of the refractive index.

This is Maxwell's Law. It is not easy to test this law directly by experiment, for n changes with the wavelength, and it is obvious that the wavelength chosen should be that used in determining ϵ. But here comes a difficulty ; n can be determined only for comparatively short wavelengths, and ϵ for large ones, so that n for large wavelengths must be calculated by extrapolation, as, for example, with the aid of Cauchy's formula. For such data as are available, Maxwell's Law is found to hold fairly satisfactorily. For some substances the square of the refractive index, even for the sodium D line, closely approaches the numerical value for the dielectric constant, as shown in the following table. Water and the alcohols show marked discrepancies, but as the wavelength for which the dielectric constant of water is determined is reduced, the two values steadily approach each other, indicating that for identical wavelengths Maxwell's Law would hold.

Substance.	ϵ.	n (D line).	n^2.
Benzene	2·29	1·50	2·25
Carbon disulphide . . .	2·62	1·63	2·66
Carbon tetrachloride . .	2·25	1·46	2·13
Chloroform	5·2	1·45	2·10
Water		1·33	1·77
$\lambda=\infty$	81·0	..	..
$\lambda=1200$ cm. . . .	2·79	..	..
Methyl alcohol . . .	35·4	1·33	1·77
Ethyl alcohol	26·8	1·36	1·85

The connection between the density of a substance and its dielectric constant is given by the **Clausius-Mossotti Formula**:

$$\frac{\epsilon - 1}{d(\epsilon + 2)} = \text{constant}.$$

This formula has been tested (Tangl, 1908) up to 100 atmospheres with air, nitrogen and hydrogen, and has proved trustworthy.

As we shall see later, the dielectric properties of liquid solvents have an important bearing on the extent of association or dissociation (see Vol. II) of solutes dissolved in them.

REFRACTIVE POWER.

When light passes from one isotropic (Greek *isos*, equal; *tropos*, direction) medium to another, its velocity is altered and its rays are bent out of their course or refracted (Latin *frangere*, to break), as we say. If u_1 and u_2 are the velocities of a monochromatic light in two media, the ratio u_1/u_2 gives the **refractive index**, n, of the second medium with reference to the first. If i is the angle of incidence and r the angle of refraction, then

$$n = \frac{\sin i}{\sin r} = \frac{u_1}{u_2}.$$

This is **Snell's Law**, 1621.

Refractive indices are usually expressed relative to air as unity, and when accurate data are required, the wavelength of the light used should be stated, since the velocity of light in space occupied by matter varies with the wavelength. Thus n_D refers to the refractive index of a substance with reference to air, monochromatic sodium D light being used; a and γ lines of the hydrogen spectrum are also used largely.

Determination of the refractive index of a substance is frequently a convenient method of checking its composition or purity. The density of sea water, for example, may be calculated with a fair degree of accuracy from the refractive index which, at constant temperature, is directly proportional to the density at 0° C. In other words,

$$n_t' - n_t = k(d_0' - d_0)$$

where n_t' and n_t are the refractive indices of sea water and distilled water respectively at t° C., d_0' and d_0 the densities at 0° C., and k is a constant depending on the temperature (Vaurabourg, 1921). Refractive index measurements may also be applied to the analysis of liquid mixtures such as acetone-chloroform.

The rate of diffusion of a solute in a solvent can be followed by noting the change in refractive index at stated intervals (p. 381). The method is particularly valuable for this kind of experiment, as it does not involve any mechanical disturbance of the system under examination.

The refractive index affords a valuable indication of the purity of certain oils, notably linseed oil, for which n_D at 15° C. is approximately 1·480. This value is lowered by the presence of free organic acids and most animal and vegetable oils. Mineral oils and rosin oil raise the value, as do also polymerisation and oxidation. A determination of the refractive index constitutes one of the tests applied commercially to linseed oil.

The refractive indices of a few typical substances are given in the following table :

Refractive Indices.

With reference to air at 15° C. for the sodium D line.

Substance.	n.	Substance.	n (Mean Value).
Ice	1·31	Paraffin oil	1·44
Glass, Crown	1·51	Olive oil	1·46
Diamond	2·42	Rape seed oil	1·47
		Turpentine	1·47
Water	1·333	Cotton seed oil	1·48
Ethyl alcohol	1·362	Cod liver oil	1·48
Carbon disulphide	1·632	Linseed oil	1·48
Benzene	1·504	China wood oil	1·51
		Rosin oil	1·51
		Cedar oil	1·516

It will be observed that cedar oil has a high refractive index, closely similar to that of an average crown glass. For this reason it is used in microscopical work.

The refractive index varies with the physical condition of the substance, the most important factor being the density, d. In 1858 Gladstone and Dale established the following formula empirically :

$$\frac{n-1}{d} = \text{constant} = r$$

In 1880, however, a theoretical formula was deduced simultaneously and independently by Lorentz of Leyden and Lorenz of Copenhagen, namely :

$$\frac{n^2-1}{(n^2+2)d} = \text{constant}$$
$$= R$$

r and R are known as the **specific refractive power** or **refractivity,** as given by the n and n^2 expressions respectively. Both r and R are practically independent of the temperature. Thus, the value of R for water at 20° C. is 0·2061, and at 90° C. it is 0·2059. The product of these constants and the molecular weight gives the **molecular refractive powers** or **refractivities.**

The molecular refraction is partly additive and partly constitutive, so that isomerides may have closely similar, but not identical, values. This is shown by the following data for two pairs of isomers with reference to the H_α line :

	MR_α.
Ethylene dichloride, $CH_2Cl.CH_2Cl$	20·95
Ethylidene chloride, $CHCl_2.CH_3$	21·08
Aniline, $C_6H_5NH_2$	30·27
Methylpyridine, $C_5H_4N.CH_3$	28·66

When the molecular refractions of successive members of homologous series of hydrocarbons are examined, it is observed that the differences corresponding to successive additions of CH_2 groups in the molecules are nearly constant, the mean of a large number of values being 4·598 for the H_α line, using the n^2 formula. Subtracting the value for nCH_2 from the molecular refraction of the hydrocarbon C_nH_{2n+2} gives the value for two hydrogen atoms. The best mean value is 2·184, from which the **atomic refraction** of hydrogen is 1·092, and of carbon is 4·598 – 2·184 or 2·414. In a similar manner the atomic refractions, *AR*, of other elements can be deduced, as well as the effects due to double and triple bonds. The effect of ring formation is usually so small as to be negligible. The data in the accompanying table are illustrative:

Atomic and Structural Refractions for H_α and Na_D Lines (n^2 formula).

	AR_α.	AR_D.		AR_α.	AR_D.
CH_2	4·598	4·618	Cl	5·933	5·967
C	2·414	2·418	Br	8·803	8·865
H	1·092	1·100	I	13·757	13·900
O = (ketonic) . .	2·189	2·211	N = (in primary amines) .	2·309	2·322
O < (etheric) . . .	1·639	1·643	N - (in secondary amines)	2·475	2·499
O – (enolic) . . .	1·522	1·525	N (in tertiary amines) .	2·807	2·840
S (in mercaptans) . .	7·63	7·69	N (in nitriles) . .	3·054	3·070
S (in sulphides) . .	7·85	7·97	Double bond . .	1·686	1·733
S (in disulphides) . .	8·05	8·11	Triple bond	2·328	2·398
S (in thiocyanates) .	7·85	7·91			

By way of illustration let us take acetic acid, CH_3COOH.

2C	4·828
4H	4·368
O = ...	2·189
O –	1·522
MR_α =	12·907

The observed value is 12·93.

Ethyl acetoacetate can, as we have already seen (p. 208), exist in two isomeric forms, and it is of interest to compare the observed molecular refraction with the values calculated for these two forms, viz.:

$CH_3.CO.CH_2.CO.OC_2H_5$, Ketonic form.	
6C	14·484
10H	10·92
2O = ...	4·378
O <	1·639
MR_α =	31·421

$CH_3.C(OH):CH.CO.OC_2H_5$, Enolic form.	
6C	14·484
10H	10·92
O = ...	2·189
O –	1·522
O <	1·639
Double bond .	1·686
MR_α =	32·440

The observed value, 31·89, lies intermediate between these two calculated values, suggesting that at the ordinary temperature the liquid consists of a mixture of the two isomers. This conclusion is interesting in view of the results obtained for the magnetic rotation (p. 326).

In a similar manner it has been shown that pyruvic acid has the ketonic structure $CH_3CO.COOH$, and so has diacetyl, $CH_3CO.COCH_3$.

Optical Anomalies.—The introduction of a second unsaturated group into a molecule already containing one such group will cause one of three things to happen : It may cause the observed molecular refraction to rise above the calculated value, in which case it induces **optical exaltation** ; it may cause the refraction to fall, producing **optical depression** ; and, finally, it may produce no appreciable effect beyond that calculated. In the last-named case the unsaturated groups are regarded as **isolated** ; in the two former cases they are said to be **conjugated.**

Consider, for example, the two isomeric unsaturated hydrocarbons diallyl and *iso*diallyl, of empirical formula C_6H_{10}.

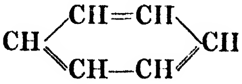
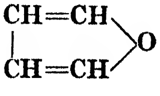
Diallyl, $CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2.$

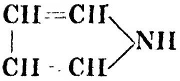
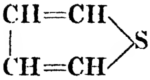
$$\begin{array}{rl} MR_\alpha \text{ observed} & = 28{\cdot}77 \\ MR_\alpha \text{ calculated} & = 28{\cdot}78 \\ \hline \Delta & = -0{\cdot}01 \end{array}$$

Iso*diallyl,* $CH_3{\cdot}CH{=}CH{-}CH{=}CH{-}CH_3.$

$$\begin{array}{rl} MR_\alpha \text{ observed} & = 29{\cdot}87 \\ MR_\alpha \text{ calculated} & = 28{\cdot}78 \\ \hline \Delta & = 1{\cdot}09 \end{array}$$

The molecular refraction of diallyl, in which the double bonds are some distance apart, is normal ; that of *iso*diallyl is a unit higher than theory demands. In this latter case the double bonds are conjugated, and optical exaltation is usual in such systems when the molecules are open chains. Some ring compounds containing conjugated groups, however, do not show this anomaly, notably benzene and toluene, and are optically normal ; others, such as furan and thiophen and, to a less extent, pyrrole, exhibit optical depression. Thus :

		MR_α Observed.	MR_α Calculated.
Benzene,		25·93	26·09
Toluene,	$C_6H_5CH_3$	30·79	30·69
Furan,		18·42	19·04

		MR_α Observed.	MR_α Calculated.
Pyrrole,		20·75	20·96
Thiophen,		24·14	25·25

Dispersive Power.

The refractive index of a substance varies, as we have seen, with the nature of the incident light. The difference in refractivity for two wavelengths, say, for example, for the H_α and H_γ lines, is termed the **dispersive power** or **dispersivity** over the range of wavelength examined (sometimes the range chosen is that between the sodium and lithium lines). Employing the n formula and denoting the specific refractivities for the H_α and H_γ lines by r_α and r_γ respectively, the specific dispersivity of a substance is given by :

$$r_\gamma - r_\alpha = \frac{n_\gamma - 1}{d} - \frac{n_\alpha - 1}{d} = \frac{n_\gamma - n_\alpha}{d}$$

Multiplication by the molecular weight gives the **molecular dispersivity** of the substance.

Similarly, employing the n^2 formula :

$$R_\gamma - R_\alpha = \frac{n_\gamma^2 - 1}{(n_\gamma^2 + 2)d} - \frac{n_\alpha^2 - 1}{(n_\alpha^2 + 2)d}.$$

Dispersivity is both additive and constitutive, but pre-eminently constitutive, being very sensitive to changes in structure. Since dispersivity is a differential effect, it is less influenced by the presence of impurities than refractivity, since the impurity affects the two refractive indices by closely similar amounts which tend to cancel each other out. Atomic and structural constants for dispersivity have been calculated by Brühl (1891) and Eisenlohr (1912) in an analogous manner to the refractivities already given.

The Raman Effect.

In 1928 Raman observed that on passing monochromatic light through a carefully purified substance such as benzene, and examining the beam, at right angles to its path, through a spectroscope, new lines appear on both sides of the main line of incident light. All transparent media behave similarly, whether solid, liquid or gaseous ; the diffused radiation is not monochromatic.

The new lines are due to a change in frequency imposed on some of the incident light scattered by the molecules on which it falls. The change is connected with the vibration and structure of the molecules, the difference between the frequency of a Raman line and of the exciting radiation being equal to the frequency of an infra-red absorption or the difference between the frequencies of two such absorptions. For a full explanation of this the reader is referred to Volume II.

The Raman effect differs in several ways from fluorescence. Thus, the frequencies of the fluorescent spectrum are independent of those of the exciting rays ; also the intensities of the Raman lines are of an entirely different order of magnitude, being much more faint ; further, many Raman lines are strongly polarised.

The explanation of the Raman effect has probably not yet been given in its final form. A close connection, however, has been observed between it and such factors as chemical constitution, ionisation, etc. For example, the introduction of a double bond into a molecule is accompanied by a change in the Raman lines. The subject is as yet in its infancy, but promises to throw new and valuable light on the modes of vibration and chemical constitution of the molecule.

OPTICAL ACTIVITY.

As has already been explained (p. 281), ordinary light is believed to consist of electromagnetic waves in the ether of space. Its vibrations are presumed to occur evenly distributed in all directions in a plane at right angles to the direction of transmission of the light. A variety of calcium carbonate found in Iceland, and hence called Iceland spar, possesses different physical properties in different directions. It is therefore termed **æolotropic** (Greek *aiolos*, changeful ; *tropos*, direction) or **anisotropic** (Greek *a*, not ; *isos*, equal). Iceland spar crystallises in various forms, but the crystals readily split along what are called *cleavage* planes, which are inclined to each other at fixed angles. By cleavage, therefore, crystals of the same kind can always be obtained. They are rhombohedra (fig. 78, p. 177), bounded by six parallelograms. Now if a beam of light falls normally on one of the faces of such a crystal, part of it will pass straight through, just as if it impinged on water or any other isotropic medium. This is termed the *ordinary* beam. But part of the light will travel in a slightly different direction. This is the *extra-ordinary* beam. The original beam has thus been split into two, as a result of the refractive indices for the ordinary and extra-ordinary rays being different, and an object viewed through Iceland spar thus appears to be doubled, hence the term **doubly refractive** as applied to this mineral.

This phenomenon of double refraction was first observed by Erasmus Bartholinus in 1669. It is not peculiar to Iceland spar, but occurs with all crystals, other than those belonging to the cubic system, to a greater or less extent ; but the phenomenon is more pronounced in Iceland spar than in other common minerals.

The two beams are not alike; each has been polarised ; that is, the vibrations are not evenly distributed around the axes of the rays composing the beam. The rays are plane-polarised, those in the one beam vibrating in one plane which, however, is at right angles to the plane in which the vibrations of the rays of light in the other beam are taking place.

It will be evident that a crystal of Iceland spar can be cut and treated artificially in such a manner that only one of the beams can pass through, the other beam being totally internally reflected. The arrangement thus obtained is known as a **Nicol prism**, after its inventor, William Nicol of Edinburgh (1758 to 1851), the extra-ordinary beam being the one transmitted.

If, now, the transmitted light is viewed through a second Nicol prism fixed in a precisely similar position to the first, the light will pass through this second prism unaltered. If, however, the second prism is rotated round its axis, the intensity of the emergent beam steadily falls until, when the angle of rotation is 90°, the field becomes dark. The plane of the second prism is now at right angles to that of the first, and the incident light is totally internally reflected.

The position is perhaps most easily appreciated by considering the mechanical illustration first suggested by Stewart. Let the Nicol prism be represented by a book lying flat on the table. We may resolve the light vibrations into two components at right angles to each other. Let these components be represented by two flat rules, one (A, fig. 132) parallel to the leaves of the book, the other (B) at right angles to them. Clearly A will pass through the book easily; B will not. The light, then, which passes through the Nicol prism represents the component vibrations in one plane; in other words, the light is plane-polarised. If, now, a second Nicol prism is placed in front of the first, the polarised light will pass through it if the position of the second prism resembles that of the second book in the figure. But if the prism is rotated through 90° it will exclude the polarised light, just as the first book excludes B.

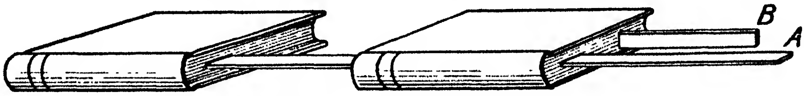


Fig. 132.—Stewart's Mechanical Illustration of Action of Nicol Prisms.

The second prism is called the **analyser**; the first, the **polariser.**

Leaving, now, our mechanical illustration, which has served its purpose, experiment shows that certain substances are capable of rotating the plane of polarisation of light. Such substances are said to be **optically active.** Some substances manifest optical activity only in the solid, crystalline state; when fused or dissolved in some solvent, the activity disappears. Other substances may display activity both in crystal and liquid form, and in solution.

If, now, an optically active solution is placed between "crossed" Nicols, the plane of polarisation of the light transmitted by the polariser is rotated to a certain extent, so that on entering the analyser it is not at right angles to it, and some of the light is transmitted. In order to cut off that light, the analyser must be rotated again, and this angle of rotation gives the angle through which the plane of polarisation of the light has been rotated by the active solution. If the analyser is turned to the right, that is, in a clockwise direction, the active substance is said to be **dextro-rotatory**; if to the left, **lævo-rotatory.**

An instrument comprising two Nicol prisms, together with facilities for measuring the optical activity of a substance, is called a **polarimeter.**

The angle of rotation, α, depends on a variety of factors, namely:

(i) The nature of the substance examined.
(ii) The thickness, l, of the layer through which the light is transmitted.
(iii) The density, d, of the substance, when examined in the pure condition, or the concentration, c, when examined in solution.
(iv) The temperature.
(v) The wavelength of the light employed.

Monochromatic light, such as the sodium D line, is frequently used.

In the case of a pure liquid the **specific rotatory power,** $[\alpha]_D$, at any temperature, $t°$ C., with respect to the D line, is given by the formula

$$[\alpha]_D^t = \frac{\alpha}{ld}$$

where α is the observed angle of rotation, l, the length of the liquid column, is measured in decimetres, and d is the density. The corresponding formula for a solution is

$$[\alpha]_D^t = \frac{\alpha}{lc}$$

c being expressed in grammes per cubic centimetre of solution. The **molecular rotation,** $[M]$, is given by

$$[M]_D^t = \frac{M[\alpha]}{100}.$$

In the case of cane sugar, $[\alpha]_D$ is almost independent of the temperature, and since the observed angle of rotation is directly proportional to the concentration of the sugar, polarimetric methods of determining the amounts of sugar in solution are used in commerce and in medicine. The method is known as **saccharimetry** (Greek *sakkharon*, sugar).

The connection between chemical constitution and the optical activity of organic compounds has already been dealt with in Chapter XI. It is a molecular property, which persists even when the compound is in a state of fusion or in solution. It arises from the presence within the molecule of one or more asymmetric atoms.

Another kind of optical activity, however, is known, which is a property of the crystal rather than of the molecule; it depends upon the way in which the molecules are built up in the crystal. Quartz affords an excellent example and has already been dealt with (p. 176).

MAGNETIC ROTATION.

In 1845 Faraday observed that when a beam of polarised light traverses a transparent substance placed between the poles of an electromagnet in such a manner that the light travels in the direction of the lines of force, the plane of polarisation of the light is rotated. The angle of rotation, ω, is proportional to the length, l, of the medium traversed and the strength, H, of the magnetic field. Whence:

$$\omega = \phi l H.$$

The constant ϕ is known as **Verdet's Constant,** and varies with the nature of the medium, the temperature, and the wavelength of the light employed. If l and H are each unity, Verdet's constant represents the rotation produced by unit length of the substance when placed in a magnetic field of unit strength. The effect of temperature is small, rise of temperature generally diminishing the rotation, and ϕ is approximately proportional to $1/\lambda^2$. Usually the sodium D line is employed. ϕ is positive if the plane of polarisation is rotated clockwise when the light is travelling in the direction of the lines of force, that is, from N to S.

In order to investigate the connection between magnetic rotation and chemical constitution it is not necessary to employ absolute units.

Perkin, whose classical researches on the subject were begun in 1882, used water as his standard. By employing the same apparatus throughout, under constant conditions, no correction is necessary for the length of tube used, or for the temperature or the wavelength of the light. In order to compare the effect of equal masses of different liquids, the observed rotation must be divided by the density. Thus, if with a given apparatus and magnetic field the angle of rotation observed with water is a_w, and that with a given liquid is a_l, the relative rotation, a, of the liquid, is given by

$$a = \frac{a_l}{a_w}.$$

Taking the density of water as unity and denoting that of the liquid by d, the **relative specific magnetic rotation,** r, is given by

$$r = \frac{a}{d}.$$

If M is the molecular weight, the **relative molecular magnetic rotation** is given by

$$r_M = \frac{Ma}{md} = \frac{Ma}{18d}$$

where m is the molecular weight of water.

If the **absolute molecular magnetic rotation,** R_M, of a substance is required, it is only necessary to multiply the preceding equation by the absolute value for water, namely 0·01312 at 20° C. Thus

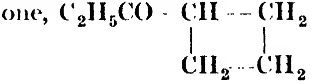
$$R_M = \frac{0{\cdot}01312Ma}{18d} \text{ minutes.}$$

Magnetic rotation is largely constitutive, but it is also in part additive. The constitutive properties are well shown by the study of isomers. Optical isomers yield practically identical results for their active and inactive forms. Structural isomers show differences that increase as the constitutions diverge. Geometrical isomers give high values for the fumaroid structure. These points are well illustrated in the following table :

Molecular Magnetic Rotations.

	r_M.
Ethyl *d*-tartrate, $(CHOH)_2(COOEt)_2$	8·766
Ethyl *dl*-tartrate, „	8·759
Pentane, $CH_3.CH_2.CH_2.CH_2.CH_3$	5·638
*Iso*pentane, $(CH_3)_2CH.CH_2.CH_3$	5·750
Acetaldehyde, CH_3CHO	2·385
Ethylene oxide, $(CH_2)_2O$	1·935
Ethyl fumarate,  $\begin{array}{l}EtOOC.CH\\ \qquad\quad\Vert\\ \qquad\quad HC.COOEt\end{array}$	10·112
Ethyl maleate,  $\begin{array}{l}HC.COOEt\\ \Vert\\ HC.COOEt\end{array}$	9·625

Unsaturated compounds show greater rotatory power than the corresponding saturated ones, and a decrease in rotatory power follows the conversion of a saturated open chain compound into a saturated ring by the removal of two hydrogen atoms. Thus :

	r_M.
Hexane, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$	6·670
Hexylene, $CH_3.CH_2.CH_2.CH{=}CH.CH_3$	7·473
Diallyl, $CH_2{=}CH.CH_2.CH_2.CH{=}CH_2$	8·420
Ethyl butyl ketone, $C_2H_5CO(CH_2)_3CH_3$	7·545
Ethyl *cyclo*butyl ketone,  $C_2H_5CO\cdot\begin{matrix}CH-CH_2\\ \vert\quad\ \ \vert\\ CH_2-CH_2\end{matrix}$	6·911

Replacement of hydrogen by a halogen or hydroxyl does not always affect the magnetic rotation to the same extent. With homologues the effect is practically constant, but differently constituted substances give various results, showing the constitutive nature of the rotatory power. The constancy in homologous series, however, is a very great advantage, as will presently appear.

Series Constant.—When the rotations of successive members of homologous series are compared, it is found that the addition of the methylene group, CH_2, causes practically a constant increase in the molecular rotation, the mean value being 1·023. If, therefore, we consider the molecular rotations of successive members of a homologous series of, say, paraffins, of general formula C_nH_{2n+2}, and subtract from each the value corresponding to each carbon atom present, a number is obtained, representing the rotation of the remainder of the molecule, which is practically constant for the series. This number is called the series constant, S. It will be evident that

$$S = r_M - 1{\cdot}023n$$

where n represents the number of carbon atoms. Thus, for example :

	r_M.	n.	S.
Pentane, C_5H_{12}	5·638	5	0·523
Hexane, C_6H_{14}	6·670	6	0·532
Heptane, C_7H_{16}	7·669	7	0·508
Octane, C_8H_{18}	8·772	8	0·588
Propionic acid, CH_3CH_2COOH	3·462	3	0·393
Butyric acid, $CH_3(CH_2)_2COOH$	4·472	4	0·380
Valeric acid, $CH_3(CH_2)_3COOH$	5·513	5	0·398

If the substance does not contain at least two atoms of hydrogen to each carbon atom, the series constant is calculated in the same way, by subtracting from r_M the value of $1{\cdot}023n$, where n is the total number of carbon atoms, but S clearly does not quite correspond to the rotatory effect of the remainder of the molecule. This, however, does not matter. For the fatty acids S is lower than for the hydrocarbons.

In the following table are given the series constants of several different classes of compounds :

Series Constants.

	S.
Paraffins (normal), C_nH_{2n+2}	0·508
Paraffins (*iso-*), ,,	0·631
Alcohols (primary), $C_nH_{2n+1}OH$	0·699
Alcohols (secondary), ,,	0·844
Aldehydes, $C_nH_{2n}O$	0·261
Ketones, $C_nH_{2n}O$	0·375
Ethyl esters, $C_nH_{2n}O_2$	0·337
Acetic esters, $C_nH_{2n}O_2$	0·370
Esters of higher acids	0·337

Using these data we can calculate the molecular rotations of a limited number of derivatives. Let us consider, for example, ethyl lactate, $CH_3.CHOH.COOC_2H_5$.

Series constant for sec. alcohols	0·844
,, ,, ethyl esters	0·337
Total	1·181
∴ Calculated series constant of ethyl lactate is 1·181÷2	0·591
Add 5 × 1·023	5·115
∴ Calculated molecular rotation of ethyl lactate	5·706

The observed value is 5·720.

It is interesting to study the magnetic rotations of tautomeric substances, such as ethyl acetoacetate, which can exist in two forms, namely, as a ketone and as a hydroxy-derivative (p. 208). The value for the ketonic form is readily calculated as follows :

$$CH_3.CO.CH_2.COOC_2H_5.$$

Series constant for acetic ester	0·370
Series constant for ketone	0·375
Total	0·745
Mean series constant	0·373
Add 6 × 1·023	6·138
Calculated molecular rotation	6·511

The value for the hydroxy or enolic form is obtained as follows :

$$CH_3.C(OH) : CH.COOC_2H_5.$$

Obs. molecular rotation of ethyl crotonate, $CH_3.CH{=}CH.COOC_2H_5$	7·589
Replacement of H by OH, add	0·194
Calculated molecular rotation	7·783

The observed value is 6·501, showing that the sample examined was the ketonic derivative. In a similar manner pyruvic acid is shown to have the ketonic structure $CH_3CO.COOH$.

Another interesting example is afforded by chloral, CCl_3CHO, which unites with water with considerable evolution of heat yielding a hydrated compound, the molecular magnetic rotation of which should be 7·591 if the product is merely a hydrate or molecular compound, namely $CCl_3CHO.H_2O$. But the experimental value is 7·037, from which it is concluded that the constitution has been modified, the water having combined to yield $CCl_3CH(OH)_2$. Similarly, in solution at the ordinary temperature, acetaldehyde appears to be present in part as $CH_3CH(OH)_2$. The constant boiling mixture of formic acid and water, on the other hand, is shown not to be a compound.

CHAPTER XVI.

CLASSIFICATION OF THE ELEMENTS.

Historical.—The educated mind always endeavours to classify and arrange isolated things or ideas. Hence it is not to be wondered at that, when once the Atomic Theory, as enunciated by John Dalton, had been accepted, numerous attempts were made by chemists to discover some method of grouping together those isolated portions of matter known as elements. Of these, the earliest was that of Prout, who, in 1815, suggested his famous hypothesis that the atomic weights of the elements were probably exact multiples of the atomic weight of hydrogen. In Prout's opinion hydrogen corresponded to the πρώτη ὕλη (protyle) of the ancients. This hypothesis was warmly welcomed by Thomas Thomson, who carried out a number of experiments with the direct object of proving the hypothesis to be true. The results, however, were viewed with the greatest suspicion, particularly by Berzelius, who, in 1825, published a revised table of atomic weights, the values for which differed very widely from those given by Thomson. The hypothesis was revived, however, by Dumas, who, in conjunction with his pupil Stas, showed that the ratio of the atomic weights of carbon and hydrogen was almost exactly 12 to 1. The atomic weight of chlorine (35·5) was a difficulty, however, and in addition copper, lead and a few other elements yielded fractions which conscientious chemists could not round off into whole numbers as Thomson had done. To overcome this, Marignac proposed to accept Prout's hypothesis as only approximately true—and in view of the atomic weight of chlorine being, according to his own researches, approximately 35·5—suggested that half the atomic weight of hydrogen might be taken as the unit, a suggestion warmly welcomed by Dumas, who, however, soon found it necessary to halve even this. Stas' further work on atomic weights, however, led him to discard Prout's hypothesis as an illusion.

Doebereiner's Triads.—In 1816 attention was directed by Doebereiner to the fact that certain triads of elements exist in which the elements exhibit both a peculiar regularity in their atomic weights and a close similarity in chemical properties. For several years, however, the subject was allowed to drop into abeyance, until Dumas, in 1851, again brought it to the fore, and both he and other chemists rapidly added to the list of regularities. Sulphur, selenium and tellurium were typical. At first it was hoped that all the elements might ultimately be grouped into triads, and that in this way a complete system of classifying them might be evolved, inasmuch as the Periodic Classification had not as yet been introduced. These hopes were, however, doomed to failure, and a severe blow was struck at the utility of the triads when Cooke showed that some of them actually broke into natural groups of elements. The halogens are a case in point, for chlorine, bromine and iodine are but three out of four closely similar elements, and no system of classification that deals with these to the exclusion of fluorine can be regarded as satisfactory. A similar objection applies to most of the other triads.

The triads may be divided into two groups. To the former belong those that exhibit an interesting relationship between the numerical values of the atomic weights of their constituent elements, the mean of the first and third being almost identical with the middle value. The best examples of these are given in the following table:

Elements.	Atomic Weights.	Differences.	Means of Extreme Atomic Weights.
Lithium	6·94	16·06	
Sodium	23·00	16·10	23·02
Potassium	39·10		
Calcium	40·07	47·56	
Strontium	87·63	49·73	88·72
Barium	137·36		
Phosphorus	31·02	43·91	
Arsenic	74·93	46·83	76·39
Antimony	121·76		
Sulphur	32·06	47·14	
Selenium	79·2	48·3	79·78
Tellurium	127·5		
Chlorine	35·46	44·46	
Bromine	79·92	47·01	81·20
Iodine	126·93		

The second group of triads, the atomic weights of the constituent elements of which are closely similar to one another, is listed in the following table:

Iron	55·84	Ruthenium	101·7	Osmium	190·8
Cobalt	58·94	Rhodium	102·9	Iridium	193·1
Nickel	58·69	Palladium	106·7	Platinum	195·2

In 1853 Gladstone arranged the elements in the order of increasing atomic weights, but, owing to the faulty values at that time accepted as correct, no generalisations of any particular importance were possible. A few years later, however, when the atomic weights had been revised by Cannizzaro, a number of independent investigators discovered that certain remarkable regularities were brought out by arranging the elements in the order of increasing atomic weights. Chancourtois appears to have been the first to observe this, and in 1862 he arranged the elements in a spiral round a vertical cylinder whose surface was divided into sixteen vertical sections. The elements situate in any vertical column were seen to possess analogous chemical and physical properties. This arrangement became known as the **Telluric Screw.**

About the same time Newlands was working along very similar lines, and in a series of classical papers (1864 to 1866) introduced his famous generalisation known as **The Law of Octaves.** At first Newlands' papers were made the subject of ridicule, but in 1869, and during succeeding years, Lothar Meyer and Mendeléeff both independently made similar observations. According to Newlands' Law of Octaves, *when the elements are arranged in the order of increasing atomic weights, the first and last of any eight consecutive elements possess similar properties;* in other words, the properties of the elements are periodic functions of their atomic weights—a generalisation which became known as the **Periodic Law.** At this time, however, not only was the number of known elements relatively small, but the values assigned to their atomic weights were still often faulty. As more elements were discovered, and their atomic weights were determined with greater accuracy, the value of the law became increasingly apparent. The periodic table drawn up by Mendeléeff in 1871 is shown on p. 331, and the modern table, which forms the usual basis of the classification of the elements accepted by chemists at the present time, is given as the Frontispiece. It will be observed that the two tables are substantially the same, save that an extra vertical group has been introduced into the modern table in order to enable the inclusion of the inert gases which, of course, were unknown in 1871. This new group was appropriately designated Group 0, for reasons that will be evident later.

The main features of **Mendeléeff's Periodic Table,** as given on p. 331, are as follows:

1. When the elements are arranged stepwise according to the magnitude of their atomic weights they show a stepwise change and periodic recurrence in properties.

It will be observed that there are two short horizontal series each containing seven elements, no two of which in either separate series resemble one another. But the first, second and succeeding members of the first series resemble very closely the corresponding members of the second series; in other words, there is a recurrence of properties with every eighth element as observed by Newlands.

In succeeding horizontal series it is the alternate elements in the vertical columns that resemble one another most closely. Thus, in Group I, copper and silver are more closely related to one another than are copper and rubidium or silver and cæsium; and so on. Hence it is customary (see Frontispiece) to group together the third and fourth horizontal series as one long series of odd and even members respectively and joined by what are termed the **transitional elements** of Group VIII. The successive horizontal series are arranged similarly.

2. Chemically analogous elements have atomic weights either similar to each other, as, for example, the three sets of triads in Group VIII, or increasing by regular amounts, as occurs with the other triads already referred to.

The table thus shows the connection between the various triads themselves, as also the relation between them and the other elements which exhibit no simple uniformity in the numerical values of the atomic weights assigned to them. So far from splitting up natural

MENDELÉEFF'S PERIODIC TABLE IN 1871.

Row.	Group I. — R_2O.	Group II. — RO.	Group III. — R_2O_3.	Group IV. RH_4. RO_2.	Group V. RH_3. R_2O_5.	Group VI. RH_2. RO_3.	Group VII. RH. R_2O_7.	Group VIII. — RO_4.
1	H=1							
2	Li=7	Be=9·4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27·3	Si=28	P=31	S=32	Cl=35·5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu′=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	? Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	? Di=138	? Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	? Er=178	? La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

groups of elements, as does the grouping into sets of triads, Mendeléeff's scheme collects together all the related elements and grades them.

3. The arrangement of the elements accords with their atom-fixing power or valency. Thus, considering the oxygen compounds only, the valencies increase from 1 in Group I to 8 in Group VIII. On the other hand, the most stable hydrides are yielded by the elements in Groups IV to VII, which now exhibit a valency falling from 4 in Group IV to 1 in Group VII.

4. The table illustrates the gradual passage from highly electropositive elements, such as the alkali metals, through the "amphoterics" of Group IV to the highly electronegative halogens.

5. It will be noted that the elements most widely distributed in Nature occur near the top of the table, and have the smallest atomic weights. Thus oxygen and silicon together constitute some 75·9 per cent. of terrestrial material (p. 4). As a general rule the metals possess the highest atomic weights.

Advantages of Mendeléeff's Table.—The main advantages accruing to this scheme were as follows :

1. It afforded the only known method of classifying the elements satisfactorily.

2. When the equivalent of an element was known, but its valency, and hence its atomic weight, were in doubt, the Periodic Table was frequently used as a guide in fixing the atomic weight.

Uranium affords an example of this. Its equivalent weight is approximately 40. On account of its resemblance to iron, the valency of uranium was taken as 3, and its atomic weight as 120. Mendeléeff, however, had no room in his table for a trivalent element between tin and antimony, but he had room in the oxygen group for an element with a valency of 6. So he placed uranium in this group, doubling its atomic weight, which thus became 240 (according to the data available in 1871). Its oxide was therefore written as UO_3, analogous to SO_3 and CrO_3, instead of U_2O_3, the analogue of Fe_2O_3. Mendeléeff's decision was justified in 1882 when the specific heat of uranium was determined and an atomic weight of 240 assigned to it on application of Dulong and Petit's Law (p. 216).

Indium was for several years regarded as divalent and analogous to zinc, with which it is frequently associated in Nature. With a combining weight of approximately 38, divalent indium would have an atomic weight of 76. But this was not acceptable to Mendeléeff, who had no room in his table for a divalent element between arsenic and selenium. There was, however, a vacant space for a trivalent element between cadmium (at. wt. 112) and tin (at. wt. 118), which a trivalent indium, of atomic weight 38×3 or 114, would neatly fill, and Mendeléeff accordingly placed it there. This accorded with Bunsen's simultaneous determination of the specific heat of indium as 0·057, yielding by Dulong and Petit's Law an atomic weight of approximately 112.

A third example is afforded by *beryllium*. The combining weight of this element was found to be approximately 4·7, and, owing to its resemblance to aluminium, Berzelius regarded it as trivalent, and its atomic weight was in consequence taken as $3 \times 4{\cdot}7$ or 14·1. There was no room for a trivalent element in Mendeléeff's table, however, between carbon and oxygen, as the only space was already occupied by nitrogen. If, however, beryllium was divalent, its atomic weight was reduced to

4·7 × 2 or 9·4, which brought it between lithium and boron, the position chosen by Mendeléeff. This was not in accordance with Dulong and Petit's Law, however, for the specific heat of beryllium between 0° and 100° C. was found by Nilson and Pettersson (1878) to be 0·42, which suggests an atomic weight of 6·4÷0·42, or 15·2, which supports the conclusion of Berzelius. But beryllium is an exception to the rule, as we have seen (p. 220), and the correctness of Mendeléeff's decision has since been abundantly confirmed (p. 222).

3. Mendeléeff's table has led to the correction of inaccurate values for certain atomic weights. As an example the case of osmium, iridium and platinum may be mentioned. In 1870 these elements were believed to have the following atomic weights :

Osmium	198·6
Iridium	196·7
Platinum	196·7

According to this, their positions in Group VIII should be reversed, platinum coming under the same vertical column as iron and ruthenium, the metal osmium being relegated to the third vertical column, under nickel and palladium. But such an arrangement is opposed to the general properties of these elements, platinum resembling nickel and palladium more closely than it does iron and ruthenium, the reverse being true for osmium, and subsequent research has shown that the atomic weights assigned to the above three elements in 1870 were inaccurate, the values now recognised being as follows :

Osmium	190·8
Iridium	193·1
Platinum	195·23

The discrepancy, therefore, no longer exists.

4. The numerous blanks in Mendeléeff's table were assumed to indicate the existence of undiscovered elements.

Previous to 1875 there were three gaps in the table, pointing to the existence of three elements at that time unknown, the atomic weights of which were less than 75. Two of these occurred in Group III immediately below aluminium, and one in Group IV below titanium. To these hypothetical elements Mendeléeff gave the names of eka-boron, eka-aluminium and eka-silicon, respectively, and by studying the known elements in the immediate neighbourhood of the gaps, he was able to give in considerable detail the properties which these elements would be found to possess. His predictions were verified in a remarkable manner fewer than twenty years afterwards by the discovery of these elements. The first to be discovered was eka-aluminium. In 1875 Lecoq de Boisbaudran (see p. 294) observed a new violet line, λ 4170, in the spark spectrum of some material he had separated from the zinc blende of Pierrefitte ; further work led to the discovery of another new line, λ 4031, and established the fact that both lines belonged to a new element, to which the discoverer gave the name of *gallium*, in honour of his native country. It was observed very shortly afterwards that this element closely resembled, both in its physical and chemical properties, the hypothetical eka-aluminium. The following tabular statement shows how closely Mendeléeff had succeeded in forecasting the properties of gallium :

Eka-aluminium.	Gallium.
Atomic weight *c.* 68.	Atomic weight 69·72.
Metal density 5·9.	Metal density 5·95.
Low melting point.	Melting point 29·8° C.
Unaffected by air.	Unaffected by air.
Oxide M_2O_3.	Oxide Ga_2O_3.
Hydroxide soluble in acids and alkalies.	Hydroxide soluble in acids and alkalies.
With halogens yields salts of the type MX_3.	With halogens yields salts of the type GaX_3.
Anhydrous chloride more volatile than $ZnCl_2$.	Anhydrous chloride more volatile than $ZnCl_2$.
Sulphate should form alums.	Alums known.
Tendency towards basic salt formation.	Salts readily hydrolyse and form basic salts.

The discovery of the coincidence of gallium and eka-aluminium was a striking confirmation of the general correctness of the Periodic Law, and from that time onwards chemists began to appreciate with ever-increasing sincerity the utility of this new method of classification of the elements.

In 1879 Nilson was preparing ytterbia from euxenite and gadolinite and discovered a new earth, present in very small quantity, but characterised by its feeble basicity, its low chemical equivalent (approximately 15), and its spark spectrum. Only 0·3 gramme of the earth was obtained, and that in an impure state. To the new metal present in the earth Nilson gave the name of *scandium.* It was soon found that scandium corresponded very closely with Mendeléeff's hypothetical eka-boron. The properties of scandium and those predicted by Mendeléeff for eka-boron are summarised in the following table :

Eka-boron.	Scandium.
Atomic weight *c.* 44.	Atomic weight 45·10.
Oxide M_2O_3.	Oxide Sc_2O_3.
Carbonate insoluble in water.	Carbonate insoluble in water.
Double sulphates with alkali sulphates probably will not be alums.	Double sulphates known, but they are not alums.
Anhydrous chloride, MCl_3, should hydrolyse more easily than $MgCl_2$.	Anhydrous $ScCl_3$ hydrolyses in aqueous solution.

Finally, in 1886, Winkler analysed argyrodite, a mineral to which the formula $4Ag_2S.GeS_2$ is now given. His first analytical figures added up only to 93–94 per cent. The deficiency was accounted for by the discovery of a new element to which Winkler gave the name *germanium*. Winkler at first thought that this new element would fill the supposed gap (p. 331) between antimony and bismuth in Mendeléeff's table, but he soon recognised its tetravalent nature and its identity with eka-silicon. The predicted properties of eka-silicon and the observed properties of germanium are summarised below :

Eka-silicon.	Germanium.
Atomic weight *c.* 72.	Atomic weight 72·60.
Density 5·5.	Density 5·35.
Oxide MO_2.	Oxide GeO_2.
Chloride MCl_4, boiling slightly below 100° C., density 1·9.	Chloride $GeCl_4$, boiling at 86·5° C., density 1·89.
Fluoride MF_4, not gaseous.	Fluoride GeF_4, solid.
Ethide $M(C_2H_5)_4$, liquid, boiling at *c.* 160° C., density 0·96.	Ethide $Ge(C_2H_5)_4$, liquid, boiling at 163·5° C., density 0·99.

Extension of Mendeléeff's Table to include the Inert Gases.—The discovery of the elements of Group 0 could hardly have been predicted from Mendeléeff's table, for this involved a whole vertical series and not, as in the cases just considered, isolated gaps in known vertical groups. Looking back from our present viewpoint upon the scheme, we can now see that, in order to complete it absolutely, a group of chemically inactive elements was necessary to form a buffer between the electronegative halogens and the electropositive alkali metals.

Argon (Greek *argos*, inactive) was the first of these gases to be isolated by Rayleigh and Ramsay in 1895. Its density was found to be 20 (H = 1), so that its molecular weight would be about 40 ; the ratio of its specific heats, γ, was 1·65, from which it was concluded that its molecule was monatomic (p. 230), and its atomic weight was therefore 40. At first it did not seem possible to assign a place in the Periodic Table to such an element, but, when other inert gases were discovered and isolated, chemists generally accepted the suggestion, first made by Ramsay, that argon should be placed in a new group in the Periodic Table between chlorine and potassium. It was true that argon apparently possessed a slightly higher atomic weight than potassium, but it was thought that further investigation might rectify matters, as it had done the apparent irregularity in the atomic weights of osmium, iridium and platinum (p. 333). When helium fell into line between hydrogen and lithium, neon between fluorine and sodium, and so on (see Frontispiece), all doubt as to the necessity of adding Group 0 to the table rapidly vanished.

Imperfections of Mendeléeff's System.—It is not surprising that a system of classification which aimed at embracing not only all the known but also the unknown elements of the universe should have its weak points. The most awkward of these are the well-established exceptions to the law, which are as follows :

1. *Argon and Potassium.*—With an atomic weight of 39·94, argon should lie between potassium and calcium in the Periodic Table. But

there is no room for it, and to interchange the positions of argon and potassium by placing the latter element in Group 0 and the former in Group I, would obviously destroy the symmetry of the whole.

2. *Tellurium and Iodine.*—From chemical considerations tellurium properly belongs to Group VI and iodine to Group VII; but the atomic weight of the former element is found to be higher than that of iodine, which implies that the positions of these elements in the table should be reversed.

3. *Nickel and Cobalt.*—The atomic weight of nickel, as determined in a variety of ways, is slightly less than that of cobalt, a result which places it between iron and cobalt in the eighth group. Nickel, however, resembles palladium and platinum more closely than it does rhodium and iridium, the reverse being true for cobalt. Furthermore, by placing cobalt between iron and nickel, a more gradual variation in the properties of the three elements becomes observable. Thus, for example, whilst iron forms two series of well-defined salts, namely, the ferric salts and the ferrous salts, cobalt forms cobaltic salts only with comparative difficulty, and nickel yields only nickelous salts. Evidently, therefore, the true position of cobalt should be between iron and nickel.

4. *Hydrogen.*—This element might equally well be placed at the head of Group VII, containing the halogens, as at the head of Group I, containing the alkali metals. This anomaly is discussed on p. 338.

5. *Rare Earth Metals.*—There was no place for these as a class in the original scheme. Positions were suggested for yttrium, cerium, "didymium," lanthanum and erbium, but these clearly were only tentative. Detailed reference to this is made on p. 339.

The foregoing are definite exceptions to Mendeléeff's system, and there is no prospect that subsequent work will change the order of the atomic weights.

The Modern Periodic System.—The existence of well-defined exceptions to Mendeléeff's system led chemists to the conclusion that the position of an element in the Table is not dependent upon the atomic weight, but rather upon some other property of the atom to which the atomic weight bears some connection.

We have reason to believe that an atom consists of a central **nucleus,** in which is concentrated its positive charge and which constitutes the bulk of the mass of the atom, for each positive charge of electricity has a mass approximately equal to the mass of the hydrogen atom. This nucleus is surrounded by groups of separate isolated negative charges of electricity, known as **electrons,** the mass of which is negligibly small. These electrons neutralise the positive charge on the nucleus and render the atom electrically neutral, or practically so. The nucleus, except in the case of hydrogen, may be a very complex structure consisting of charges of positive and negative electricity, the former always outnumbering the latter, so that the resultant charge on the nucleus is always positive. The chemical properties of an element are believed to depend upon this resultant charge (see Vol. II).

To fix our ideas, let us consider the case of bromine. Its nucleus possesses a resultant positive charge of 35 units, and hence is surrounded by 35 electrons, which render the complete atom electrically neutral. Suppose, now, the nucleus of our bromine atom contains 79 positive charges, partially neutralised by 44 negative charges very closely associated with it. Its mass will be approximately 79 times that of a hydrogen atom, but its chemical properties will depend upon its resultant positive charge of 35 units, which, in the neutral atom, will be neutralised by external groups of electrons. Suppose, on the other hand, the nucleus contains 81 positive charges, partially neutralised by 46 negative charges. The mass of the atom will be 81 times as great as that of the hydrogen atom, but the chemical properties of our new atom will, as before, depend upon its resultant charge of 35 units. Evidently, therefore, it is possible to conceive of two atoms of bromine, masses 79 and 81 respectively, yet possessing identical chemical properties, because the resultant electrical charges on their nuclei are identical. Such atoms will occupy the same place in the Periodic Table, despite their difference in mass. They are therefore termed **isotopes** (Greek *isos*, equal ; *topos*, place).

Experiment shows that isotopes of this character really do exist. Bromine has been shown, by a method that will be explained later, to consist of two such isotopes, usually written Br 79 and Br 81 respectively. These are present in nearly equal proportions in ordinary bromine, so that the mean atomic weight, as ascertained chemically, is 79·916. Had there been only one kind of bromine atom, say Br 79, then selenium, with a mean atomic weight of 79·2, would have appeared anomalous.

The large majority of the elements are composite mixtures of isotopes, chromium possessing four and tin at least eight. A list of the isotopes at present known is given in the table on pp. 35, 36.

Now it so happens, and very fortunately so, that the mean atomic weights of the elements in most cases are approximately proportional to their nuclear charges, and do therefore work out in accordance with Mendeléeff's rule. The exceptions mentioned on p. 336 are readily accounted for as follows :

1. *Argon and Potassium.*—Argon has two isotopes, 36 and 40. Potassium consists essentially of K 39, with a mere trace of K 41. Had argon but possessed a higher proportion of A 36, or potassium more of K 41, the two elements would have obeyed Mendeléeff's rule.

2. *Tellurium and Iodine.*—Iodine has, apparently, but one atom, namely I 127 ; but tellurium has four isotopes, namely 125, 126, 128 and 130. Had tellurium possessed more of the 126 isotope, the anomaly would not have occurred.

3. *Nickel and Cobalt.*—Similarly, cobalt has one atom only, Co 59, whilst nickel has two, namely Ni 58 and 60. Had nickel possessed more of the heavier isotope, it would have fallen into line.

The modern Periodic Law, therefore, may be expressed as follows :

When the elements are arranged in the serial order of successively increasing resultant nuclear charges, they show stepwise gradations in their properties and certain properties recur periodically at regular intervals.

If, when arranged in this order, the elements are numbered serially, beginning with hydrogen as 1, helium 2, lithium 3, and so on, the number of each element is known as its **atomic number**, and, as we shall see later, gives the number of electrons surrounding the nucleus, and hence the numerical value of the resultant positive charge on the nucleus.

This modern interpretation of the Periodic Classification is a great improvement on the old, its main advantages being as follows :

1. There are no exceptions, all the elements conforming to the rule.

2. By means of its X-ray spectrum we can determine directly the atomic number of any element and hence the position to be assigned to it in the scheme. It is not even necessary to determine the combining weight or the atomic weight by the usual chemical methods.

It is important to note that the different isotopes of any one element have the same atomic number, although their atomic weights may differ appreciably.

3. The atomic number of uranium is found, in the foregoing manner, to be 92. This definitely fixes the number of possible elements between hydrogen and uranium, although of course it cannot give us any indication of the possible existence of elements of higher atomic weight than uranium.

This limitation of the possible number of elements is a very great advantage. By the old arrangement it was possible, as we have seen, to predict the existence of elements when well-defined gaps occurred in well-established vertical or horizontal groups of elements. But it was not generally possible to assert that all the horizontal and vertical groups were known at any one time, as witness the addition of Group 0 to the table at a time when most chemists imagined the scheme was complete.

4. The scheme enables us to define an element as a simple substance that possesses a definite and characteristic atomic number, but only one such number. Thus, for example, the ammonium group might be regarded as an element analogous to any alkali metal in view of the close similarity of ammonium and alkali metal salts. But the X-ray spectrum of ammonium would indicate two atomic numbers, one characteristic of hydrogen and one characteristic of nitrogen. Similarly, radium, by virtue of its disintegration into helium and a whole series of other products, might be regarded as a compound. But it possesses an X-ray spectrum characteristic of an element of atomic number 88. It is definitely an element, therefore, and not a compound.

The Position of Hydrogen.—The position to be assigned to hydrogen in the Periodic Classification was for many years a source of dispute. It is generally agreed that the valency of hydrogen is unity, and this opens up two possible positions for the element in the table, namely, at the head of either the first or the seventh group. Mendeléeff in 1870 placed hydrogen at the head of the alkali metals, whereas Newlands in 1872 placed it at the head of the halogens. Let us consider the arguments in favour of this latter arrangement :

1. Hydrogen, like fluorine and chlorine, is diatomic in the gaseous state, whereas the alkali metals are monatomic. This argument, however, is hardly conclusive, for the alkali metals combine with hydrogen to form hydrides, such, for example, as NaH and KH, so that the H_2 molecule may be looked upon as hydrogen hydride, H-H.

2. Solid hydrogen, although belonging to the cubic system like the alkali metals, does not look like a metal. It is a snow-white substance which melts to a clear transparent liquid which does not conduct the electric current, whereas metals are opaque and are in general good conductors of electricity.

3. Metallic hydrides do not conduct the electric current like true metallic alloys. Further, upon electrolysis of calcium hydride dissolved in a fused mixture of lithium and potassium chlorides, Bardwell (1922)

found that, whilst the calcium was liberated at the cathode, some of the hydrogen was evolved at the anode, and thus appeared to function as a typical non-metallic element.

4. The mutual replaceability of hydrogen and chlorine in organic compounds was noted by Dumas in 1839, who was thus led to compare the properties of several pairs of derivatives such as chloral, CCl_3CHO, and acetaldehyde, CH_3CHO, and trichloracetic acid, CCl_3COOH, and ordinary acetic acid, CH_3COOH. Dumas noticed that the essential characteristics of many substances apparently were unaltered by chlorination ; thus chloral still functioned as an aldehyde, and trichloracetic acid as a typical organic acid, splitting off CO_2 when the sodium salt was heated with soda-lime, just as acetic acid does.

5. The melting and boiling points of the alkali metals fall as the atomic weight rises, so that hydrogen, if regarded as a forerunner of lithium, might be expected to melt and boil at higher temperatures than does this metal. On the other hand, the reverse is true for the halogens, and hydrogen, melting at −259° C., is a very suitable forerunner of fluorine, m.pt. −223° C.

On the other hand, it must be admitted that in its ordinary chemical properties hydrogen reacts as though it were metallic. Thus, its most stable compounds, like those of the metals generally, are formed by union with non-metallic elements. For example, although the halogens exhibit but little tendency to combine amongst themselves, save in the case of the two extreme elements, fluorine and iodine, yet they yield very stable compounds with hydrogen and the metals. The same truth applies with more or less completeness to the other non-metallic elements known. Consequently, it seems most natural to regard hydrogen as analogous to a metal, and as such it is a more fitting forerunner of the alkali metals than of the halogens.

When aqueous solutions of acids, such as sulphuric or hydrochloric acid, are electrolysed, hydrogen is liberated at the cathode, just as metallic copper and silver are deposited there when their solutions are electrolysed.

Finally, it may be mentioned that hydrogen is capable of replacing metals from their salts. If the temperature is raised and the hydrogen is under considerable pressure it is found that the reaction

$$CuSO_4 + H_2 \rightleftharpoons H_2SO_4 + Cu$$

is more or less reversible, for metallic copper is precipitated out (Ipatieff, 1909).

Hydrogen therefore must be regarded as an **amphoteric element,** capable of functioning as a metal or a non-metal, as occasion serves. We shall see how this can be when we consider, in a later chapter, the general principles of atomic structure. Nowadays, it is usual to place hydrogen at the head of the alkali metals, as shown in the Frontispiece.

The Rare Earth Elements.—These comprise fifteen elements, namely: lanthanum, cerium, praseodymium, neodymium, illinium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium. Their atomic weights lie between those of barium (137·36) and hafnium (178·6). These elements, and their compounds, show a striking similarity to one another, much more close than that shown, for example, between iron, cobalt and nickel.

Until the method of determining the atomic number of an element had been discovered, it was impossible to say how many of the rare earth metals might exist. We now know, however, that their number is limited to 15. Fourteen of them were fairly easily discovered, but if chemists had not known that the existence of the fifteenth, namely, element No. 61, was possible, it might never have been found, as apparently it exists only in extraordinarily minute quantities, so

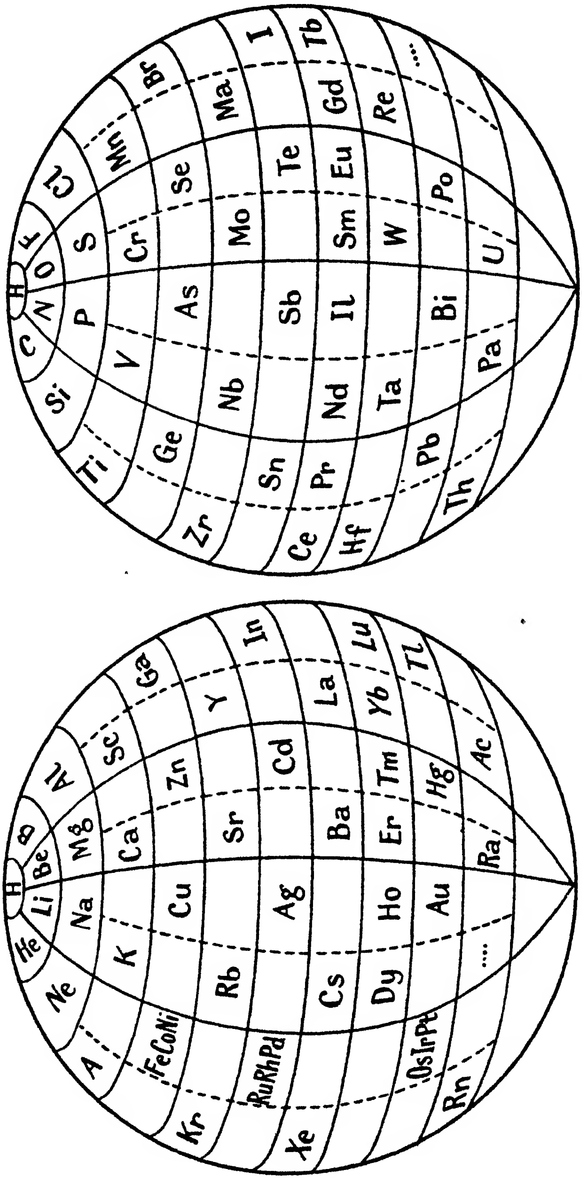


FIG. 133.—The Periodic Sphere (Friend, 1925).

minute indeed that it can be detected only after laborious concentration, and even now it has been obtained only in concentrations of the order of one part per thousand in rare earth mixtures. The element was first detected by Hopkins and his co-workers in 1926, and named illinium, to commemorate its discovery in the University of Illinois.

Now if we attempt to include these elements in the Periodic Table in the usual way, the result is far from satisfactory. Lanthanum falls naturally into Group III, and cerium, which in its ceric compounds is tetravalent, lies suitably in Group IV under zirconium; but praseodymium does not fit at all well into Group V, nor do the succeeding elements fall any more readily into their serial places. Sometimes, therefore, the rare earth elements are grouped all together into Group III and left there. This, however, destroys the symmetry of the whole, and various other suggestions have been made.

The Periodic Sphere.—By arranging the elements in the form of a spiral round the surface of a sphere, as shown in fig. 133, several interesting features become apparent. In the first coil the spaces or " cells " occupied by the elements are relatively small, but are steadily increasing, and in the second coil the " cells " are sufficiently large for the elements to show a distinct tendency to orient themselves excentrally. In the third and succeeding coils the orientation is very definite, giving rise to sub-groups in the vertical Groups I to VII, as indicated by the broken lines. When the equator is reached the cells are of maximum size, and may be presumed sufficiently large to contain two metals each. If, then, we insert cerium and praseodymium into Group IV and succeeding pairs of rare earth metals into successive cells, an equatorial belt of rare earth metals, closely packed together, is obtained. This arrangement is shown in the flat on the Frontispiece, and constitutes a sort of Mercator's Projection of the world of elements. The tendency of the rare earth metals to resemble each other in pairs is well brought out. Thus cerium and praseodymium resemble each other more closely than they do any other of the rare earth metals. Further, the similarity of sub-equatorial elements such as hafnium, tantalum and tungsten, to those in corresponding positions above the equator, namely zirconium, niobium and molybdenum, is indicated by their positions, which are approximately equidistant from the axis of the Periodic Sphere.

Although this arrangement is not ideal, there is much in its favour.

Missing Elements.—All but two of the possible 92 elements up to and including uranium have been detected and in most cases isolated. The latest elements to be discovered are:

Hafnium (72) by Coster and Hevesy (1923);
Masurium (43) and rhenium (75) by Noddack and Tacke (1925);
Illinium (61) by Hopkins and co-workers (1926).

Evidence has been obtained of the existence of eka-cæsium (No. 87) by Papish (1931). Numerous attempts have been made to trace eka-iodine (No. 85) and an element of higher atomic weight than uranium, but hitherto without success.

Radioactive Elements.—These are dealt with in Vol. II.

CHAPTER XVII.

SOLUBILITY AND DISSOLUTION.

A solution has already (p. 3) been defined as *a homogeneous mass, the composition of which may undergo continuous variation (between the limits of its existence), and which may be separated into two (or more) homogeneous substances by processes involving change of state.*

This definition does not restrict solutions to any particular state of matter, and several systems of solution are therefore possible. In so far as gases are concerned, experience shows that it is impossible for two or more different gases to remain in contact in separate layers, even though their densities differ to a very marked extent. Thus, if a few drops of liquid bromine are dropped on to the floor, the vapour rapidly diffuses into the air of the room, so that its odour becomes perceptible in every corner, despite the fact that its density is five and a half times as great as that of the air. In other words, gases are mutually soluble in each other to an unlimited extent. The same is true of certain liquids, as, for example, ordinary alcohol and water. But in the majority of cases in which two substances are mixed, the extent to which one can dissolve in the other is strictly limited.

Few pairs of substances, if any, refuse to dissolve in each other to some extent, however small. Carbon disulphide, for example, can absorb very small quantities of water, and water of carbon disulphide; again, water can take up small quantities of silica, as well as of many other substances, such as silver chloride, which, for most practical purposes, are regarded as insoluble.

If two substances which do not mix in every possible proportion are left in contact, and if at the end of a considerable time the added substance remains in excess, a **saturated solution** will have been formed. The rate at which this saturated state is reached depends on several factors, such as the state of subdivision of the solute, and the rate at which the solution formed diffuses away into the solvent. Agitation, which assists diffusion, causes solution to occur more quickly.

THE DISSOLUTION OF GASES IN GASES.

As gases are mutually soluble in all proportions, there is no question of determining the limits to which they mix.

When two or more gases are contained in the same vessel, the pressure of the mixture may be determined by a simple rule known as **Dalton's Law**, 1802, according to which

the pressure exerted by a gaseous mixture is equal to the sum of the pressures which the constituents would exert if each occupied separately the volume of the mixture.

The pressures which the constituents would exert separately are termed their **partial pressures** in the mixture. Denoting them by p_1, p_2, p_3, etc., and the total pressure of the gaseous mixture by P, then Dalton's Law may be stated simply thus :

$$P = p_1 + p_2 + p_3 + \text{etc.}$$

This is frequently termed the **Law of Additive Pressures.**

In common with the other gas laws, Dalton's Law is only approximate, and at high pressures it breaks down. At moderate pressures, however, it holds with reasonable accuracy for vapours as well as gases, provided that the corresponding liquids are not miscible, as was shown by Regnault. The law is commonly employed in deducing the volume, at any desired temperature and pressure, of a dry gas from observations of its pressure, volume and temperature when saturated with water or other vapour.

As this law involves the assumption that each gas retains its individuality irrespective of the other gases, it may be stated in another way, namely, that

the volume occupied by a mixture of gases is equal to the sum of the volumes occupied by its constituents under the same conditions of temperature and pressure.

This is termed the **Law of Additive Volumes.**

The law is only perfectly true, in either form, for ideal gases, and in certain other cases. In general, the former rendering appears to be more correct than the latter (Masson and Dolley, 1923).

THE DISSOLUTION OF GASES IN LIQUIDS.

The solution of a gas in a liquid never takes place to an unlimited extent, like that of one gas in another. Hence it is necessary to determine the limit of mixing or the **solubility** of the gas in the liquid or **solvent.**

The results of solubility determinations may generally be expressed in several ways, namely :

1. **Ostwald's Coefficient of Solubility.**—This is defined as the volume of the gas absorbed under the conditions of the experiment by unit volume of the liquid. It is usually denoted by l (German *löslich*, soluble), and is not reduced to 0° C. and 760 mm. pressure. This quantity may also be defined as the ratio of the concentration of the gas in the gaseous space in a closed vessel to that in the saturated liquid below, for, by Henry's Law (see later), the volume dissolved is independent of the pressure.

2. **Bunsen's Absorption Coefficient,** β, is the volume of gas at N.T.P. absorbed by unit volume of the liquid under a partial pressure of the gas itself of 760 mm. irrespective of the vapour pressure of the liquid. If measurement is made at atmospheric pressure it is clear that

$$l = \beta(1 + 0{\cdot}00367t).$$

3. By β' is meant the volume of gas reduced to 0° C. and 760 mm. which is absorbed by one volume of the liquid under a total pressure of

760 mm., which includes the vapour pressure, f, of the solvent. Hence

$$\beta' = \beta \cdot \frac{760 - f}{760}.$$

4. It is frequently convenient to express solubility results gravimetrically. By q is understood the number of grammes of gas dissolved in one litre of solvent under the experimental conditions.

Determination of Gaseous Solubility.—For this purpose volumetric methods are frequently employed, the volume of gas absorbed by a given volume of liquid being measured directly, or, conversely, the volume expelled from the saturated solution under suitable conditions.

For the former of these methods an **absorptiometer** is used, and a useful form, as employed by Ostwald, is shown in fig. 134. The gas is stored in the graduated tube A, closed at its upper end by a three-way tap T, and connected with B by a flexible tube sealed with mercury. The vessel C is completely full of the gas-free liquid, and is connected by pressure tubing to T. On opening taps T, C_1 and C_2 a definite quantity of liquid may be run out, its place being taken by an equal volume of gas from A. C_1 and C_2 are now closed, the vessel shaken and the absorption noted on connecting with A and readjusting the pressure.

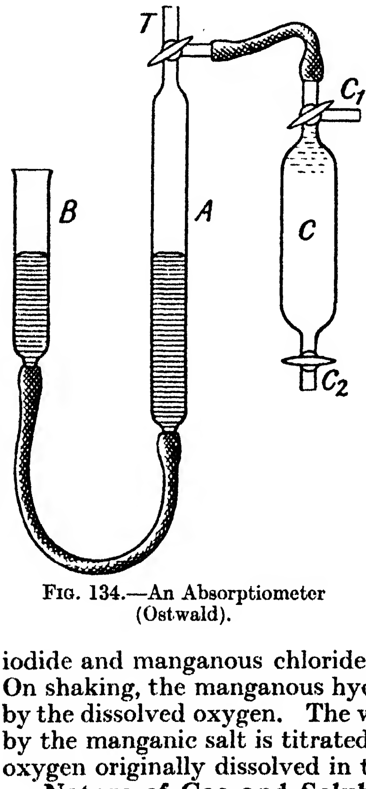


FIG. 134.—An Absorptiometer (Ostwald).

When the dissolved gases are chemically active they may be determined colorimetrically or titrimetrically. As an example may be mentioned the colorimetric method of estimating dissolved oxygen in water by the addition of a cuprous salt and ammonia, and comparing the depth of colour (blue) produced with that of standard coloured solutions. Winkler's method of estimating the same gas is titrimetric and consists in adding alkaline potassium iodide and manganous chloride solutions to a known volume of water. On shaking, the manganous hydroxide liberated by the alkali is oxidised by the dissolved oxygen. The whole is acidified and the iodine liberated by the manganic salt is titrated with thiosulphate. The amount of free oxygen originally dissolved in the water is then readily calculated.

Nature of Gas and Solubility.—In so far as their solubilities in water are concerned, gases may be divided broadly into two classes, namely, those that are chemically inert towards water, and those that combine with it, such as ammonia, hydrogen chloride, sulphur dioxide, and the like. The former group, which includes oxygen, nitrogen and many other "permanent" gases, frequently are so slightly soluble that for many chemical purposes they may be regarded as insoluble and may be collected and stored over water. The latter group usually possesses high absorption coefficients, and it is significant that as a rule these gases are more easy to liquefy. The inert gases xenon and radon (niton) lie between the two groups. In the following table are given the solubilities of a few typical gases in water at 0° C. in terms of Bunsen's absorption coefficient:

Boiling Points and Solubilities of Gases (β) in Water at 0° C.

Gas.	Boiling Point, °Abs.	β at 0° C.	Gas.	Boiling Point, °Abs.	β at 0° C.
Hydrogen . .	20·5	0·0214	Xenon	164	0·219
Nitrogen . .	77	0·0232	Radon	..	0·5
Carbon monoxide .	83	0·0354			
Oxygen . . .	90	0·0492	Carbon dioxide .	195	1·713
Methane . .	112	0·0556	Hydrogen sulphide .	213	4·62
Argon . . .	87	0·0561	Sulphur dioxide .	263	79·8
Nitric oxide . .	123	0·0738	Hydrogen chloride .	190	525
Krypton . .	121	0·120	Ammonia . .	240	1300

Effect of Pressure, Henry's Law.—The law connecting the effect of pressure with the solubility of a gas was discovered by Henry in 1803, and states that

the concentration of the solution is proportional to the pressure of the gas.

If the pressure of a gas above a liquid solvent be doubled, the mass of gas absorbed will be doubled; but by Boyle's Law the density of the gas is also doubled; hence the volume entering the solution remains constant. From this fact, as already stated, the volume of gas dissolved by a liquid is independent of the pressure. This may be indicated by the expression

$$S/P = \text{const.}$$

If a mixture of gases be shaken with a solvent, the amount of each absorbed depends on two factors, namely, the solubility and the partial pressure (see p. 343) which each exerts in the gaseous mixture. The partial pressures of oxygen and nitrogen in the air are in the ratio of their proportions by volume, but since the solubility of oxygen is greater than that of nitrogen, the gas expelled by boiling or by the aid of a vacuum pump from water which has been saturated with air will be proportionately richer in oxygen. If this gas is re-absorbed and again expelled, and the process repeated several times, fairly pure oxygen can be isolated. Mallet, in 1869, took out a patent for the commercial preparation of oxygen based on this principle. He found that after eight absorptions with water under pressure a gas containing 97·3 per cent. of oxygen could be obtained. His results for successive absorptions were as follows:

No. of absorptions	0	1	2	3	4	5	6	7	8
Percentage of oxygen . .	21	33·3	47·5	62·5	75·0	85·0	91·0	95·0	97·3
Percentage of nitrogen, etc. .	79	66·7	52·5	37·5	25·0	15·0	9·0	5·0	2·7

At the present time this method has no commercial importance. The relative solubilities of oxygen and nitrogen in various other solvents have been determined, but the results do not encourage the idea that oxygen can be obtained any more readily with these solvents than by the employment of water.

It is of historical interest to note that one of the methods used by Ramsay to demonstrate the existence of a new, heavy constituent of the atmosphere, now known as argon, was based on Henry's Law. Water, charged with air, was passed slowly into a heated vessel, which raised the water to the boiling point. The escaping gases were collected, the oxygen removed by passage over red-hot copper, and the density of the residual " nitrogen " determined. It was found consistently to be denser than atmospheric nitrogen, showing that the heavy gas, namely argon, was being concentrated in the nitrogen by this method. Reference to the preceding table shows that argon is more than twice as soluble as nitrogen in water.

Henry's Law is obeyed by the permanent gases with considerable exactness at pressures not widely removed from atmospheric. This is illustrated by the following data for the solubility of oxygen in water at 25° C. (Morgan and Richardson, 1930) :

Pressure, P (mm.) . .	175	202	300	414	610	760
Solubility, q (milligrammes per litre) . . .	9·5	10·7	16·0	22·0	32·5	40·8
$1000q/P \times 10^2$ . . .	5·43	5·29	5·33	5·32	5·31	5·37

Henry's Law is independent of the nature of the solvent, provided chemical action does not take place. Thus, for example, under pressures slightly less than atmospheric, the solubility of hydrogen sulphide in aniline at 22° C. conforms closely with the requirements of Henry's Law (Bancroft and Belden, 1930) :

Pressure (mm.) . .	102	199	390	579	874	1160
Solubility, q (grammes per litre)	2·74	5·32	10·6	15·8	24·0	31·6
$\frac{q}{P} \times 10^2$	2·68	2·67	2·72	2·73	2·75	2·72

To the very soluble gases, such as hydrogen chloride and ammonia, Henry's Law does not apply. The chief reason for their departure from the law lies in the fact that they combine with the water, whereas Henry's Law presupposes that merely physical solution takes place. The following data refer to ammonia :

P (mm.) . . .	20	80	200	500	1000
q (grammes per litre)	82	240	421	770	1126
q/P . . .	4·10	3·00	2·11	1·54	1·13

As the pressure is increased above atmospheric, the solubilities of even the permanent gases tend to deviate from Henry's Law. The following data refer to the solubility of oxygen in water at 23° C. (Cassuto, 1904):

Pressure (atmospheres)	1·26	2·74	5·59	6·76	9·61	10·71
Ostwald's coefficient $l \times 10^2$.	2·94	2·93	2·87	2·83	2·74	2·71

The solubility of oxygen in blood does not follow Henry's Law, relatively larger amounts of oxygen being absorbed at low pressures than the law demands. This is usually attributed to combination taking place between the gas and the hæmoglobin of the blood to form the characteristically bright red oxyhæmoglobin of the arterial blood. No doubt other factors are concerned, since the amount of both oxygen and carbon dioxide absorbed by blood are in accordance with the **adsorption law.** This point is adverted to later (see p. 439).

Effect of Temperature on Gaseous Solubility.—In general, the solubility of a gas decreases as the temperature rises. This is illustrated by the following table in which are given the solubilities of oxygen and argon-free nitrogen in water in terms of Bunsen's absorption coefficient, β:

Solubilities of Oxygen and Nitrogen in Water.

(Fox, 1909.)

Temperature, °C.	Oxygen. (β.)	Nitrogen. (β.)
0	0·04924	0·02319
10	0·03837	0·01863
20	0·03144	0·01572
30	0·02665	0·01375
40	0·02330	0·01233
50	0·02095	0·01160

It is frequently possible to represent the influence of temperature upon the solubility of a gas in a liquid by means of an expression of the type

$$\beta = a - bt + ct^2 - dt^3 \quad . \quad . \quad . \quad . \quad (1)$$

where a, b, c and d are constants. For example, in the case of oxygen this relationship is given approximately for a temperature interval of 0° to 30° C. by the expression

$$\beta = 0{\cdot}04924 - 0{\cdot}001344t + 0{\cdot}00002875t^2 - 0{\cdot}0000003t^3.$$

When a solution of a gas in a liquid is heated in a vessel open to the atmosphere, the gas is gradually expelled and, if its solubility is accurately expressed by Henry's Law (see p. 345), most of the gas should be expelled when the boiling point of the solvent is reached. In the case of aqueous solutions of the permanent gases, such as oxygen and nitrogen, the expulsion is almost complete; but it has long been known that the last traces of dissolved air are extremely difficult to expel (Scoresby, 1838), and Leduc (1906) calculated that at least 1 c.c. of gas remains behind in a litre of water even after thorough boiling.

Aqueous solutions of hydrogen chloride, bromide and iodide behave differently. When a cold, saturated solution of one of them is heated, gas is evolved, with some water vapour; but even when the solution boils it still contains much dissolved gas, and eventually it distils at a constant temperature unchanged in composition. This latter is known as a **constant boiling solution.**

Hydrogen and the inert gases, with the exception, perhaps, of helium, are unusual in that they show a minimum solubility under atmospheric pressure. The minimum for hydrogen lies at 90° C. (Bohr and Bock, 1891); for argon and xenon, at 40° C.; for krypton, between 30° and 40° C.; for helium, possibly at 10° C.; and for neon, probably near 0° C. (Antropoff, 1910). Under high pressures nitrogen shows a decided minimum solubility (Goodman and Krase, 1931); this occurs, for example, at 80° C. under a pressure of 300 atmospheres, as the following data indicate:

Temperature, °C. .	0	25	50	80	100	169
β (under 300 atm.) .	3·60	3·25	2·99	2·86	2·91	3·83

Rate of Dissolution of Gases in Water.—Comparatively little work has been carried out on the velocity with which partially or completely de-aerated water reabsorbs oxygen and nitrogen from the atmosphere. Two cases merit consideration, namely:

(1) When the water is subjected to agitation, so that fresh surface layers are continually formed, the rate of gaseous absorption is then at its maximum.

(2) When the water is quiescent. In this case the process is not purely one of absorption followed by diffusion into the body of the liquid from the surface layers, as has generally been supposed. It is considerably more rapid than this. Experiment shows that the gases do not remain concentrated in the surface layers, but tend to "stream" downwards under the influence of gravity, and thus promote comparatively rapid mixing. This is a point of very great biological and economic importance, for "**streaming**" has been shown to set up a process of mixing certainly to depths of 10 feet, and in all probability it proceeds to much greater depths.

Much of the research on the subject is due to Adeney and his co-workers (1918), whose initial work was concerned with the rate of absorption of air by water under gentle agitation. They began with the assumption that, during the process of solution, the rate of passage of gas into the liquid is proportional to the partial pressure of the gas, p, and the area, A, of the liquid exposed. Simultaneously with absorption, however, evaporation of the gas into the air takes place, and its rate of escape is proportional to the liquid area and the gaseous concentration in the upper layers of the liquid. On this basis the following formula was derived:

$$w = (100 - w_1)\left(1 - e^{\frac{-fA\theta}{v}}\right) \quad . \quad . \quad . \quad (2)$$

where w_1 = amount of gas in solution initially, expressed as a percentage of the total saturation.

w = amount of gas dissolved after a given time θ (expressed in minutes).

v = volume of water.

e = Naperian logarithmic base.

f = coefficient of escape of gas per unit area of liquid.

Now f varies both with the temperature and the humidity. For an atmosphere saturated with moisture the following values for f have been determined, the water being agitated gently to ensure thorough mixing:

For oxygen . . . $f = 0{\cdot}0096\ (T - 237)$
,, nitrogen . . . $f = 0{\cdot}0103\ (T - 240)$
,, air . . . . $f = 0{\cdot}0099\ (T - 239)$

T being the absolute temperature.

An example will make the value of the foregoing equation quite clear. Consider a cubic decimetre of water at 2·5° C. and containing 40 per cent. of its total saturation capacity for oxygen. If it exposes one side (100 sq. cm.) to oxygen, how much gas will be dissolved in one hour under gentle agitation? It is unnecessary to consider the pressure of the gas, since Henry's Law is obeyed, and the desired result is to be calculated in percentage of total saturation. Since $\theta = 60$, $w_1 = 40$, $f = 0{\cdot}0096\ (275{\cdot}5 - 237)$, it is easy to calculate that

$$w = 11{\cdot}8.$$

In other words, after an hour the oxygen content will have risen from 40 to approximately 52 per cent. of saturation.

The rate of solution of oxygen in water does not appear to be retarded appreciably by a thin layer of petroleum.

The foregoing values for f were determined experimentally for water under gentle agitation in an atmosphere saturated with moisture. Such conditions are largely artificial.

For quiescent bodies of water the following data have been obtained:

	Value of f at 15° C.
Air dried over calcium chloride	0·61
,, of average humidity	0·34
,, nearly saturated with moisture . .	0·23

These results are very striking, showing that dry air is much more rapidly absorbed than moist air. This is interpreted as meaning that the process by which the dissolved gas is carried down into the body of the liquid is influenced by the rate of evaporation of the liquid surface, this being at a maximum when the air is dry. In the case of pure water this is merely a temperature effect, the evaporation causing a cooling of the surface layers and, at temperatures above 4° C., a gravitational circulation.

The effect of the addition of soluble salts is interesting, for density changes, consequent upon variation in the superficial concentration of the solution, are superimposed upon the temperature effect, and with dilute solutions more rapid mixing is likely to occur. As the concentration of the salt is increased, however, the vapour pressure of the solution and, hence, the rate of cooling through evaporation, fall off, and this reduces the "streaming" effect. If, therefore, the rate of absorption of a gas through "streaming" be plotted against the concentration of dissolved salt, a curve of the type shown in fig. 135 is obtained. For sodium chloride solutions the optimum "streaming" effect is obtained at a concentration of about 1·5 per cent. of salt, with nitrogen as the gaseous phase.

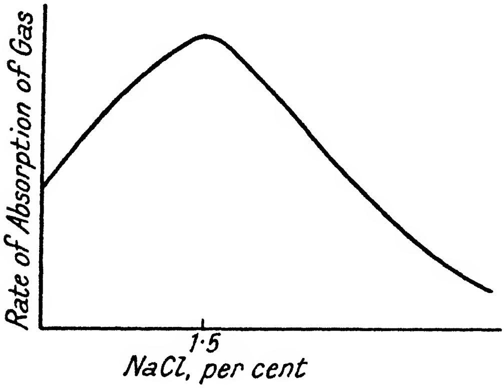


FIG. 135.—Rate of Absorption of Nitrogen by Aqueous Sodium Chloride Solutions.

"Streaming" proceeds more rapidly at temperatures of 10° C. and upwards than below this temperature.

Nature of the Solvent.—The influence of the nature of the solvent on the solubility of gases is very great. This is shown very well by the following values (Just, 1901) for the solubilities of nitrogen and carbon monoxide in various solvents at 25° C:

Solvent.	Solubilities (l) at 25° C.		$\frac{l_{CO}}{l_{N_2}}$.
	Nitrogen.	Carbon Monoxide.	
Water	0·0163	0·0240	1·47
Aniline	0·0307	0·0536	1·75
Carbon disulphide . . .	0·0586	0·0831	1·42
Nitrobenzene	0·0626	0·0937	1·50
Benzene	0·116	0·171	1·47
Glacial acetic acid . . .	0·119	0·171	1·44
Toluene	0·123	0·181	1·47

It will be observed that the order of increasing solvent power of the liquids is the same for both gases; further, the ratios of the solubilities of the gases in the different solvents are approximately constant.

Volume Changes on Dissolution.—When a gas dissolves in a liquid in a purely physical manner the latter expands slightly, the amount of expansion being proportional to the volume of gas absorbed. Ångström's (1882) **absorption dilatation coefficient**, δ, is defined by the expression

$$\delta = \frac{\text{Expansion of solvent}}{\text{Volume of gas absorbed}} = \frac{\Delta V}{v} \quad . \quad . \quad (3)$$

v being the volume of gas absorbed under a pressure of 760 mm. but at the temperature of the experiment, whilst

$$\Delta V = V - V_0$$

where V_0 and V are the initial and final volumes of the solvent.

δ is thus independent of the actual solvent volume. From equation (3) it follows that

$$\frac{\Delta V}{V} = \delta . \frac{v}{V} = \delta\beta$$

where β is Bunsen's absorption coefficient.

The following data refer to aqueous solutions at 0° C. (Ångström):

Gas.	Increase in Volume, ΔV, of Unit Volume of Water when Saturated at 0° C.	β at 0° C.	$\delta = \frac{\Delta V}{\beta}$.
Hydrogen	0·0000204	0·0214	0·00095
Nitrogen	0·0000294	0·0235	0·00125
Carbon monoxide . .	0·0000418	0·0354	0·00118
Oxygen	0·0000474	0·0489	0·00097

Influence of the Compressibility of the Solvent.—Since on solution of a gas in a solvent the latter tends to expand, it may be inferred that when the solution pressure of the gas is balanced by the resistance offered by the liquid to further expansion, no more gas will dissolve. The liquid will then be saturated with the gas.

Assuming the resistance offered by the liquid to expansion is inversely proportional to its compressibility, ϕ, we should expect the ratio l/ϕ to show an approach to constancy (Ritzel, 1907). Such is often the case, as is illustrated by the following data for carbon monoxide at 25° C. in various solvents:

Solvent.	Compressibility, $\phi \times 10^6$.	l_{25}.	l/ϕ.
Acetic acid . . .	87·5	0·171	1954
Acetone . . .	121·0	0·238	1967
Ethyl alcohol . .	104·7	0·192	1833
Benzene . . .	91·5	0·171	1870
Toluene . . .	90·8	0·181	1993

Influence of Dissolved Substances.—The presence of dissolved substances frequently affects very materially the absorption coefficients of neutral gases. Since solutions are less compressible than the pure solvents, a reduced solubility for gases is to be expected in view of the proportionality which has just been discussed. Several factors require consideration.

(i) The dissolved substance itself may not be responsible for more than an inappreciable fraction of the gaseous absorption. In that case, in the absence of other disturbing factors, we should expect the solubility coefficient to be proportional to the amount of pure solvent in the solution.

Chloral hydrate, $CCl_3CHO.H_2O$, affords an interesting illustration. For hydrogen gas the solubility coefficient β at 20° C. in water is 0·01883 c.c., or, what is very nearly the same thing, 1000 grammes of water are capable of absorbing 18·83 c.c. of hydrogen gas. For a 7·69 per cent. solution of chloral hydrate in water β at 20° C. is 0·01802 c.c., that is, 1000 c.c. of solution can absorb 18·02 c.c. of hydrogen gas. Such a solution, however, contains only 952·4 grammes of water, so that for every 1000 grammes of water in the solution, $18{\cdot}02 \times 1000 \div 952{\cdot}4$ or 18·92 c.c. of gas are absorbed. This is practically the same amount as found for pure water.

(ii) In the case of aqueous solutions, the dissolved substance may combine with the water to form a hydrate. Now if the dissolved substance itself, as before, has no appreciable effect upon the gaseous absorption, and if, moreover, the water "fixed" by hydration is likewise unable to absorb the gas, it is clear that the fall in the absorption coefficient for the neutral gas will be greater than in the first case considered.

Assuming that no other disturbing factors are involved it becomes possible to calculate the average degree of hydration of the dissolved substance. This has been done for aqueous solutions of cane sugar, and the results are given in the following table :

Hydration of Cane Sugar.

(Philip, 1907.)

Cane Sugar, per cent.	Volume of Hydrogen Absorbed at 15° C.		Molecules of Water to 1 Molecule of Sugar.
	By 1000 c.c. of Solution.	Calculating to 1000 Grammes of Water.	
0	. .	18·83	. .
16·67	15·61	17·55	6·5
30·08	12·84	16·27	6·0
47·65	8·92	13·95	5·4

It will be observed that the volume of hydrogen absorbed by 1000 grammes of the water steadily falls as the sugar concentration rises, as is to be expected, for we have independent evidence that the cane sugar molecule is hydrated in aqueous solution. The extent of hydration, as given in the fourth column, has been calculated as follows :

The solution containing 16·67 per cent. cane sugar can absorb hydrogen to the extent of 17·55 c.c. per 1000 grammes of water, which is 1·28 c.c. less than for 1000 grammes of "free" water. Hence $1{\cdot}28 \div 18{\cdot}83$ represents the fraction of the total quantity of water which is attached to sugar, so that the average number of water molecules attached to one sugar molecule (molecular weight 342) is

$$\frac{1{\cdot}28 \times 83{\cdot}33 \times 342}{18{\cdot}83 \times 16{\cdot}67 \times 18} = 6{\cdot}5.$$

As the sugar concentration rises, the average molecular hydration is seen to fall.

Solutions of inorganic salts behave in an analogous manner, as do also those of alkalis and acids, and in the following table a few data are given illustrating the magnitude of the effect on the solubility of oxygen at 25° C. of semi-molecular concentrations of salts:

Solubility of Oxygen in Half-molecular Aqueous Solutions of Inorganic Salts at 25° C.

(McArthur, 1916.)

Salt.	Grammes per litre.	Relative Density at 25° C.	Dissolved Oxygen, c.c. per litre.	Relative Solubility.
Water only . .	..	1·000	57·8	100
NaCl . . .	29·23	1·017	49·2	85·1
KCl . . .	37·28	1·020	49·8	86·2
KNO_3 . . .	50·55	1·029	51·1	88·4
Na_2SO_4 . . .	71·03	1·063	39·7	68·7
K_2SO_4 . . .	87·13	1·060	38·9	67·3
$MgCl_2$ . . .	47·61	1·044	43·7	75·6
$BaCl_2$ . . .	104·14	1·082	42·7	73·9

It is interesting to note that closely analogous salts in the foregoing table reduce the oxygen solubility by similar amounts.

The average hydration of these salts can be calculated from the foregoing data in an analogous manner to that employed for cane sugar solutions, but the results are not capable of quite so definite an interpretation, because, unlike cane sugar, the salts are converted partially into separate ions in solution, and it is not yet possible to differentiate between the water attached to the salt molecules and that attached to the ions.

(iii) A somewhat more complicated type than either of the preceding is afforded by solutions of oxygen, hydrogen and carbon monoxide in mixtures of ethyl alcohol and water. Results obtained with oxygen at 20° C. (Lubarsch, 1889) are indicated in fig. 136. In all three cases a decided minimum occurs at approximately 30 per cent. alcohol, which corresponds approximately to $C_2H_5OH.6H_2O$. Upon this slender basis alone, however, we could hardly postulate the existence of such a hydrate; nevertheless it is of interest to note that specific heat determinations also indicate the possible existence of a hexahydrate (p. 228).

(iv) The solubility of sulphur dioxide in aqueous sulphuric acid solutions is interesting. A minimum occurs with 85·8 per cent. H_2SO_4, and from that point, as shown in fig. 137, the curve inclines sharply upwards for both increase and decrease of the acid concentration. At the point of minimum solubility of the sulphur dioxide the composition of the solvent closely approximates to that required for the monohydrate $H_2SO_4.H_2O$ (namely, 84·5 per cent. acid), and it is significant that other physical properties of the acid pass through critical values at this concentration. On plotting the observed solubility against the percentage of acid up to 84·2 per cent. H_2SO_4 a straight line is obtained if the small deviations are regarded as due to experimental error. By extrapolation the solubility in pure water is approximately 10·0 grammes of sulphur dioxide per 100 grammes of water. The curve also gives a solubility of approximately 2·8 grammes of sulphur dioxide per 100 grammes of solution containing 84·5 per cent. of sulphuric acid, a composition corresponding to $H_2SO_4.H_2O$.

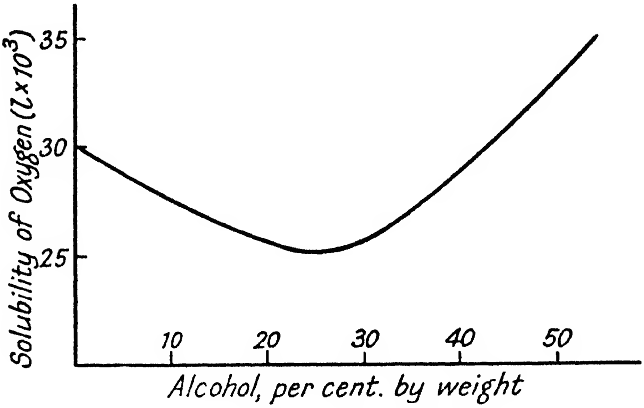


Fig. 136.—The Solubility of Oxygen in Aqueous Solutions of Ethyl Alcohol.

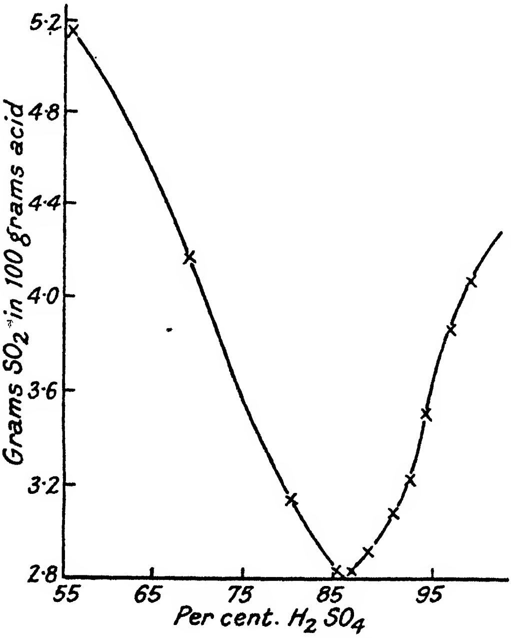


Fig. 137.—Solubility of Sulphur Dioxide in Sulphuric Acid at 20° C.

If, now, we assume that aqueous solutions of sulphuric acid of the high concentrations under discussion consist essentially of a mixture of water and $H_2SO_4.H_2O$, the solubility of sulphur dioxide in any particular concentration of acid may be regarded as made up of two quantities, namely, that in the free water and that in the monohydrate. From the foregoing extrapolated data we can then calculate the solubility. Thus, consider the solubility, S, in a solution containing 68·9 per cent. H_2SO_4, equivalent to 81·5 per cent. $H_2SO_4.H_2O$. The free water is then 100 − 81·5 or 18·5 grammes. Then

$$S = \frac{18{\cdot}5 \times 10{\cdot}0}{100} + \frac{81{\cdot}5 \times 2{\cdot}8}{100} = 4{\cdot}13 \text{ grammes.}$$

The observed value was 4·16 grammes.

The following results have been obtained in this way :

H_2SO_4 (per cent.) . .	55·1	59·6	61·6	68·9	74·1	78·3	80·2	82·5	84·2
S (calc.)	5·31	4·92	4·76	4·13	3·69	3·33	3·17	2·97	2·83
S (obs., Miles and Fenton)	5·13	4·90	4·82	4·16	3·63	3·23	3·12	2·99	2·88

The agreement is very close, and supports the assumption made.

Dissolution of Gases in Molten Metals.—Gases frequently are soluble in appreciable amounts in molten liquids ; indeed, in some cases their solubility is so great as to introduce irregularities into metallurgical processes. For example, molten silver absorbs some twenty times its own volume of oxygen ; the dissolved gas is largely expelled, though not completely, at the moment of solidification of the metal, and the phenomenon of " spitting " is thus produced. In this connection the following data are of interest:

Temperature, °C. . .	923	973	1024	1075	1125
c.c. Oxygen dissolved in 1 c.c. Silver . .	0·59 (Solid)	20·28 (Liquid)	19·53	18·42	17·56

Silver melts at 960° C., and oxygen is thus seen to be only slightly soluble comparatively in the solid metal.

THE DISSOLUTION OF GASES IN SOLIDS (OCCLUSION).

Gases have the power both of diffusing through, and of being retained by, solid substances, and some of the phenomena observed are to be interpreted as due to the formation of a true solution, analogous to that obtained when a gas dissolves in a liquid. The term **occlusion** (Latin *occludo,* I shut up) was used first by Graham in 1866 to signify the absorption of gases in solid substances. Metallic palladium possesses to a remarkable degree the power of occluding certain gases, the actual extent of the occlusion depending upon the physical condition of the metal. The occlusion of hydrogen by palladium foil is readily shown by passing an electric current through acidified water, using a platinum anode and a plate of palladium, just previously heated to redness, as cathode. Oxygen is evolved freely from the anode, but no bubbles of gas are liberated at the cathode until the palladium has become saturated with gas, after which hydrogen is freely evolved.

Graham observed that palladium which has been ignited *in vacuo* absorbs large quantities of hydrogen at ordinary temperatures and slowly yields it up again upon exposure to air. In a vacuum the gas is rapidly and almost completely evolved at 100° C. In experiments in which the foil was heated in hydrogen and allowed to cool in the gas, the metal absorbed 643 times its own volume of hydrogen, whilst in later experiments specimens of palladium wire were found to absorb over 900 times their volume of hydrogen. Under the impression that the hydrogen had condensed to a solid and was behaving as though it had formed an alloy with the palladium, Graham termed it "hydrogenium," to indicate its supposed metallic nature. Other chemists suggested that a definite chemical compound was formed by union of the hydrogen and palladium, to which the formulæ Pd_2H and PdH_2 were variously given. But the theory of physical solution was strongly supported by the work of Hoitsema in 1895. The variation in the amount of hydrogen absorbed with the pressure was studied at various temperatures.

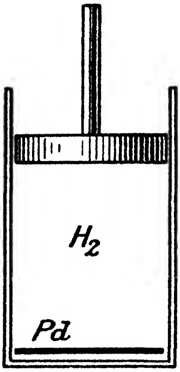


FIG. 138.

In order to appreciate the line of attack, let us assume the palladium to lie at the bottom of a cylinder filled with hydrogen gas and closed with a perfectly-fitting, frictionless piston (fig. 138). If at any one temperature a definite hydride is formed, then, by pressing the piston down and thus reducing the volume of hydrogen, no increase in pressure should be observed until the whole of the metal has been converted to hydride.

On plotting the hydrogen absorbed against the hydrogen pressure at different temperatures, the curves were found to consist of three portions, namely, (i) a preliminary rise in pressure with hydrogen content, followed (ii) by an almost stationary pressure with rise of absorbed hydrogen, and (iii) a further rise in pressure (see fig. 139). At first glance the horizontal portion of each curve appears to indicate the formation of a compound, but this is negatived by the fact that the length of the central horizontal portion not only diminishes with rise of temperature, but it does not end at the same concentration of hydrogen, marked A in the figure, as would otherwise be expected. The absorption of hydrogen, therefore, is physical and not chemical. This conclusion is supported by the results obtained by X-ray examination. The crystal structure of the palladium shows no abrupt change on saturation with hydrogen, and the data generally are inconsistent with the formation of a hydride (McKeehan, 1923).

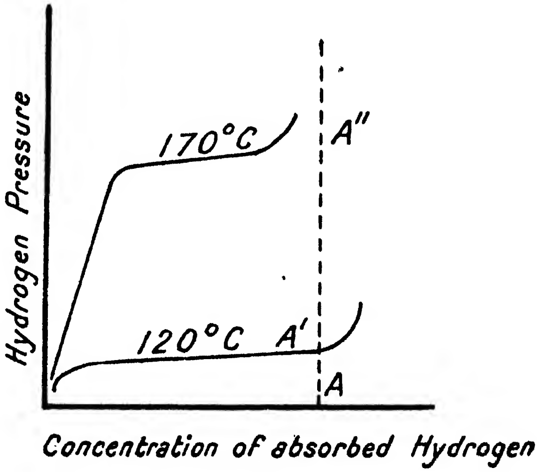


FIG. 139.

At low pressures the concentration of hydrogen dissolved in the metal is proportional to the square root of the pressure, that is

$$S/\sqrt{P}=\text{const.}$$

This is taken to mean that the dissolved hydrogen is mainly monatomic and in equilibrium with the gaseous diatomic molecules. Thus

$$\underset{\text{Gaseous.}}{H_2} \rightleftharpoons \underset{\text{Occluded.}}{2H}$$

In the case of a metal capable of forming more than one stable oxide there is some evidence that oxygen can dissolve in the lower oxide at a temperature above that at which the higher oxide decomposes (Le Blanc, 1926).

Porous substances, such as charcoal, have the power of absorbing gases. Certain features of this absorbent action resemble the solution of gases in liquids. Thus, with charcoal, the extent of absorption depends, like that of a gas in a liquid,

(1) On the nature of the gas, the most easily liquefied gases being absorbed to the greatest extent (see p. 345).
(2) On the temperature.

Both of these facts are illustrated by the following table of results obtained by Dewar (1904):

Gas.	Volume absorbed by 1 c.c. of Charcoal.		Boiling Point, °Abs.
	0° C. c.c.	−185° C. c.c.	
Helium	2	15	4·5
Hydrogen	4	135	20·5
Nitrogen	15	155	77
Carbon monoxide	21	190	83
Argon	12	175	87
Oxygen	18	230	90

As one might expect, the amount of gas absorbed increases with fall of temperature. But even at −185° C. helium is absorbed only to a relatively slight extent, and this fact is the basis of Dewar's method of isolating pure helium. The mixed gases are introduced into a suitable form of apparatus, such as that indicated in fig. 140, filled with coconut charcoal and immersed in liquid air in a Dewar flask. After half an hour the pure helium is pumped out, leaving all other gases occluded in the charcoal. An analogous method is also used for separating the rare gases of the air, and for producing high vacua.

The absorption of helium in charcoal follows Henry's Law. But this is exceptional for gases, and the question arises as to whether or not we are justified in regarding their absorption in solids as true solution.

In 1909 McBain was able to prove that the process occurring in, for example, the absorption of hydrogen by charcoal, is actually a combination of two processes—namely, a surface condensation termed **adsorption**, which takes place rapidly, followed by a slow diffusion into the interior of the solid, with the formation of a true solid solution. In view of this fact McBain proposed to employ the non-committal term **sorption** when referring to the absorption as a whole, to call the diffusion of gas into the interior **absorption**, and to restrict the word **adsorption** to the first stage of "sorption," namely, the surface condensation. The subject of adsorption is dealt with more fully later (Chap. XXI).

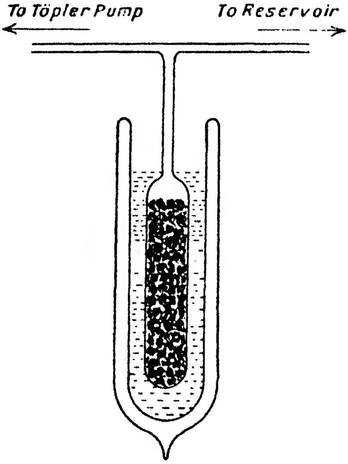


Fig. 140.

The Dissolution of Liquids in Liquids.

Considerable variation is possible in the limits of solubility of liquids. Some liquids are able to mix in all proportions over considerable ranges of temperature. Such is the case with methyl or ethyl alcohol and water, and it is easy to pass from what may be termed a solution of alcohol in water, by successive additions of alcohol, to a solution of water in alcohol, the latter liquid being so much in excess as to merit the term solvent, the water being the solute. The distinction between the two terms "solvent" and "solute" is, of course, purely conventional. Zinc and cadmium, zinc and tin, lead and tin, etc. provide examples of the same nature among fused metals.

The majority of liquids do not mix in all proportions with water at the ordinary temperature; in other words, they are only partially miscible with water. When phenol is added to water, two layers are produced, the upper one consisting of a solution of phenol in water, the lower of water in phenol. The two layers are spoken of as **conjugate solutions,** for the reason that, on sufficiently raising the temperature, if the solubility of each in the other increases as the temperature rises, or lowering it if the mutual solubility decreases with rise of temperature, a point is reached ultimately at which the

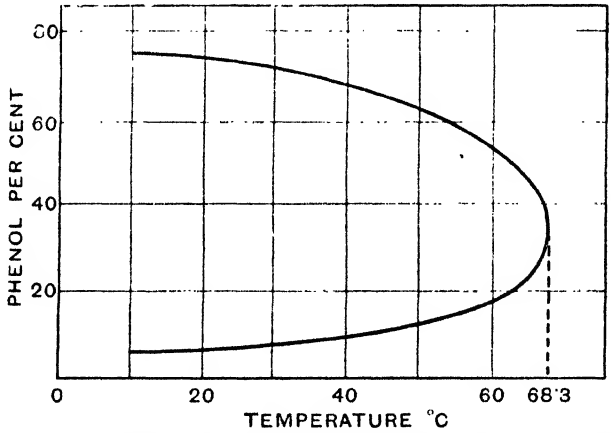


Fig. 141.—Solubility Curves for Water and Phenol (Rothmund, 1898).

composition of each layer is the same, and the two constituents then mix in all proportions. On gently warming and shaking, the phenol-water mixture becomes opalescent at about 68° C., and at 68·3° C.—termed the **critical solution temperature**, or less frequently the **consolute temperature**—the two liquids become entirely miscible. This is shown by fig. 141. For a given pressure this temperature is a well-defined point and is frequently termed the **upper** or **superior critical solution temperature**. Such phenomena are by no means confined to water and organic substances. Zinc and bismuth in the liquid state mix similarly in all proportions at and above 650° C., this being the upper critical solution temperature for the two metals, and below this point separation into two layers occurs.

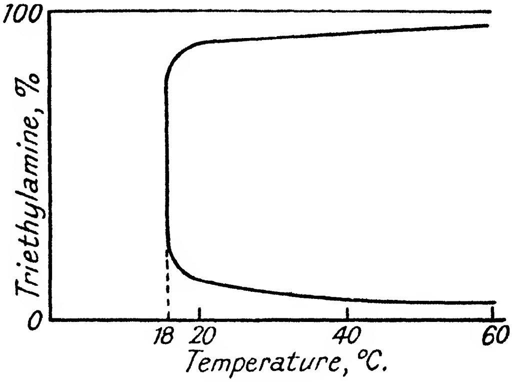


Fig. 142.—Solubility of Triethylamine in Water (Rothmund, 1898).

The solubility of triethylamine in water is represented in fig. 142. This is the reverse of the phenol-water curve, since below 18° C.—the **lower** or **inferior critical solution temperature**—the two liquids are miscible in all proportions, and only separate into conjugate layers at and above that temperature. If, therefore, a solution containing, say, 20 per cent. of triethylamine at temperatures below 18° C. be gently warmed to above that temperature, the liquid becomes turbid.

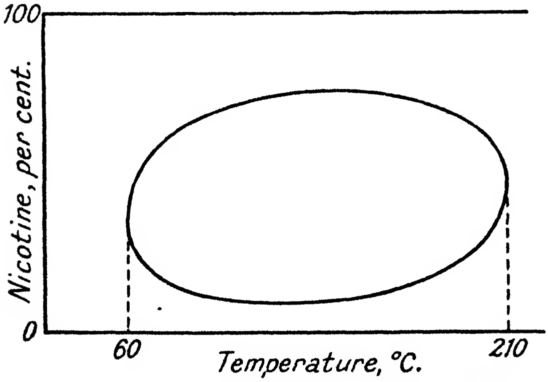


Fig. 143.—Nicotine-Water System (Hudson, 1904).

In the case of triethylamine and water an upper critical solution temperature has not been realised, but in several other similar systems it has. The first example to be discovered was that of nicotine and water (Hudson, 1904), the curve for which is shown in fig. 143. Below 60° C. and above 210° C. the two liquids mix in all proportions. The system thus possesses both an upper and a lower critical solution temperature.

From the foregoing it will be evident that many pairs of liquids, which we regard as miscible in all proportions simply because they are so at ordinary temperatures, may prove only partially miscible if the temperature is raised or lowered. An example is afforded by the system carbon disulphide-ethyl alcohol. These readily mix in all proportions under ordinary conditions, but below 14·4° C. they are only partially miscible (Guthrie, 1884). This temperature, therefore, is their upper critical solution temperature and corresponds to 68·3° C. on the phenol-water curve (fig. 141).

Influence of Pressure on Miscibility.—The critical solution temperatures are affected materially by pressure. Thus, between 1 atmosphere and 100 atmospheres an increase in pressure of 1 atmosphere raises the lower critical solution temperature of the system triethylamine-water (see fig. 142) by 0·021° C. Similarly, the upper critical solution temperature of the system propane-methyl alcohol is lowered 0·044° C. per atmosphere (Kuenen, 1903). If, now, pressure be applied to a closed ring system, such as that of nicotine and water, it will cause a rise of the lower and a fall of the upper critical points,* so that the area enclosed by the ring will steadily diminish until finally it disappears at what is termed the **critical solution end-point.** At this point, which has been completely determined with regard to pressure, temperature and concentration, since the upper and lower critical points have now coincided the two liquids are completely miscible. Further increase in pressure will not affect the miscibility, but reduction of the pressure will cause separation of the constituents again.

At the ordinary temperature γ-picoline is completely miscible with water, and resembles the nicotine-water system at a temperature very slightly above its upper critical solution temperature. If, therefore, the pressure be reduced, opalescence will be observed owing to separation of the system into two phases (Flaschner, 1909). In the majority of cases it may not be possible to reduce the pressure sufficiently to effect separation, but the same effect can be produced by the addition of a soluble substance.

Influence of Dissolved Substances on the Critical Solution Temperature.—The addition of a third substance to a pair of conjugate solutions may be accompanied by very appreciable changes in the critical solution temperatures. If the third substance is soluble in one of the liquids only, the mutual solubilities of the two original liquids are diminished, so that the upper critical solution temperature is raised, whilst the lower one is depressed. The effect is thus similar to that of decreased pressure, already described. If, on the other hand, the third substance is soluble to the same extent in both conjugate layers, the mutual solubility of the two original liquids is increased, with the result that the upper critical solution temperature is depressed, whilst the lower one is raised. In this case the effect is similar to that of increased pressure.

The critical points are very sensitive to the presence of dissolved substances. Thus, 0·6 per cent. of sodium chloride raises the critical point of the phenol-water system by 10° C. This forms the basis of a method of testing the purity of substances (Crismer, 1895), and has been found useful in detecting the adulteration of fats where ordinary chemical analysis may be difficult or even impossible.

Volume Changes on Dissolution.—When two mutually soluble liquids are mixed there is frequently a change in volume, and if

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* Systems *are* known in which pressure raises the upper critical solution point. The accompanying remarks do not apply to such systems.

chemical combination occurs the change may be very pronounced. When ethyl alcohol is mixed with water the solution occupies a smaller volume than the two unmixed constituents, a maximum contraction of 3·6 per cent. of the original volume occurring with 46·3 per cent. by weight of alcohol, corresponding approximately to the composition $C_2H_5OH.3H_2O$. It is frequently assumed, therefore, that ethyl alcohol combines with water to form a trihydrate. Similarly, a contraction occurs when sulphuric acid and water are mixed, maximum density occurring with a solution containing 97·5 per cent. of H_2SO_4. The change in volume is sometimes utilised in determining the percentage of H_2SO_4 in the concentrated acid. If in a 300 c.c. graduated flask 200 c.c. of the acid under investigation are added to 100 c.c. of water, then after restoring the temperature to 15° C. a contraction is evident; its amount can be measured by the addition of an inert liquid (for example, vaseline oil) from a burette to the mixture until the 300 c.c. mark of the flask is reached by the level of the liquid. The contraction with acid of various strengths is as follows:

Contraction, c.c. .	24·1	21·2	18·5	16·1	13·9
H_2SO_4, per cent. .	98	96	94	92	90

Purely physical admixture of two organic liquids is usually accompanied by very little, if any, change in total volume. Thus, equimolecular volumes of the following pairs of substances were mixed, and their final volumes expressed as percentages of the sum of their initial volumes (Young and Fortey, 1902 to 1903):

Mixture.	*Final Volume as per cent. of Original.*
Toluene + ethyl benzene	99·966
Hexane + octane	99·966
Carbon tetrachloride + benzene. . . .	99·849
Benzene + toluene	100·161
Chlorobenzene + bromobenzene. . . .	100·000

Methods of Determining the Mutual Solubilities of Liquids.—One of the most convenient of these is the **synthetic** method of Alexejeff (1886), in which known quantities of solvent and solute are introduced into a suitable vessel and the temperature at which complete mixing occurs is determined. For example, in determining the solubility of phenol in water, known quantities of the two are weighed into a tube which is suitably closed. If, upon shaking, a milky appearance is obtained, the tube is warmed in a bath until, on shaking, the opalescence just disappears. Upon slightly cooling, the opalescence re-appears, and the experiment may be repeated as often as desired; the mean temperature of disappearance of the opalescence is the point required. This is preferable to taking the mean of the disappearance and reappearance of the opalescence temperatures, as the latter may be retarded by supersaturation, and thus give a value for the temperature that is slightly too low.

This method possesses many obvious advantages: only small quantities of the materials need be taken; the composition of the mixture is known, so that analysis, which may be tedious, difficult, or even impossible, for the accuracy required, is unnecessary. Further, if the tube is efficiently sealed, there is no loss through volatilisation, and there need be no fear of oxidation by contact with air. It is true that in the case of sealed tubes the pressures vary with the temperature (see previously), but the influence of change of pressure is in general so small that in all ordinary cases it may be neglected.

THE DISSOLUTION OF SOLIDS IN LIQUIDS.

In no case will a solid dissolve to an unlimited extent in a liquid. The influence of various factors, such as rise of temperature, on the solubility, has therefore to be determined. The results are expressed numerically, as grammes (or gramme-molecules) of solid taken up by a fixed amount of solvent, or as grammes of solute in a fixed amount of solution.

The solubility of a solid in a liquid is influenced by many factors, such as the nature of both solute and solvent, the temperature, the pressure, and the size of the particles constituting the solid phase. Let us deal with each of these.

Nature of Solute and Solvent.—Although it is difficult to enunciate any universal rules connecting the solubility of a substance with the nature of the solvent, the following points clearly indicate the inter-dependence of solute and solvent on one another.

The majority of normal inorganic salts are soluble in water. This is the case for all nitrates and most of the chlorides and sulphates. The chlorides of silver and divalent lead, and of monovalent copper and mercury, are but sparingly soluble in water, but of these metals only silver is exerting its maximum valency. The chlorides of divalent copper and mercury are readily soluble in water. The sulphates of calcium, strontium, barium and radium are only sparingly soluble in water, their solubilities at 18° C. expressed as milli-equivalents per litre being :

Calcium sulphate	29·5
Strontium ,, ...	1·245
Barium ,, ...	0·019
Radium ,, ...	0·00013

The progressive decline in solubility with increase in atomic weight of the metal is very pronounced. The solubility of radium sulphate, although very small, is nevertheless very definite ; indeed it is doubtful if any substances are absolutely insoluble, so that the terms " soluble " and " insoluble " must be regarded as relative.

Increase in atomic weight of the metal does not always mean a fall in solubility of the salts. Thus, in general, the alkali halides show a progressive increase in solubility with rise in atomic weight, but the reverse is the case with the chloroplatinates and alums. Lithium chloride is exceptional, but the solid phase in equilibrium with the saturated solution at 20° C. is hydrated, namely $LiCl.H_2O$. Combination of solute and solvent naturally introduces disturbing factors, and usually enhances the solubility of the solute, as witness also sodium hexachloroplatinate (see following Table) and silver fluoride (see p. 363).

Similarly the solubilities may vary progressively with the weight

Solubilities of Alkali Salts.

(Grammes per 100 grammes of water.)

	Hexachloroplatinates, M_2PtCl_6. (18° C.)	Alums, $M_2SO_4.Al_2(SO_4)_3.24H_2O$. (20° C.)	Fluorides, MF. (18° C.)	Chlorides, MCl. (20° C.)
Lithium .	Very great	No alum	0·27	83·5
Sodium .	c. 40 *	121·4	4·5	35·9
Potassium	1·03	11·40	92·3	34·5
Rubidium	0·0283	2·59	130·6	91·1
Cæsium .	0·0086	0·65	366·5	186·5

* The sodium salt is hydrated, thus $Na_2PtCl_6.6H_2O$.

of the negative radical, as shown by the halides of silver, whose solubilities at 20° C. are given below in grammes per 1000 grammes of water :

Silver fluoride, $AgF.2H_2O$ . .	1720
„ chloride, AgCl . . .	0·00150
„ bromide, AgBr . . .	0·000084
„ iodide, AgI	0·0000028

Basic salts generally are insoluble in water; acid salts, on the other hand, usually are soluble.

Substances containing an hydroxyl group frequently are soluble in water. Many metallic and non-metallic hydroxides fall into this category. Amongst organic compounds it is a general rule that the introduction of hydroxyl increases the solubility. For example, the following derivatives are either completely miscible with water or readily soluble in it: methyl alcohol, CH_3OH, ethyl alcohol, C_2H_5OH, glycerol and the sugars; acids, such as formic acid, HCOOH, acetic acid, CH_3COOH; the phenols, such as ordinary phenol, C_6H_5OH, resorcinol, $C_6H_4(OH)_2$, and pyrogallol, $C_6H_3(OH)_3$. The hydrocarbons corresponding to these, namely, methane, CH_4, ethane, C_2H_6, etc. and benzene, C_6H_6, are practically insoluble in water. The CO and NH_2 groups likewise tend to impart solubility in water.

The metals are not appreciably soluble as such in water. The alkali and alkaline earth metals readily disappear in water, but that is due to chemical solution, their hydroxides being produced. Many metals, however, are soluble in mercury, **amalgams** being produced.

The solid non-metals likewise are practically insoluble in water. They do not, like the metals, undergo physical solution in mercury, but it is characteristic of them to dissolve in carbon disulphide and in many organic solvents. For example, sulphur is well known to be soluble in carbon disulphide, and one method of estimating the amount of sulphur in commercial samples consists in digesting with this solvent and from the density of the resulting solution calculating the percentage of sulphur present by the aid of empirical tables.

Hydrocarbons are insoluble in water, but readily dissolve in other hydrocarbons. Esters are soluble in alcohols and ethers, which solvents may be regarded as the organic counterparts of water.

From the foregoing generalisations it is evident that the composition of the solute alone does not determine its solubility in a liquid. No substance is equally soluble in different solvents, and the **nature of the solvent** must also be considered. This is strikingly illustrated by the data given in the accompanying table for the solubility of potassium iodide in various solvents:

Solubility of Potassium Iodide in Various Solvents.

(Walden, 1906.)

(Grammes KI per 100 grammes Solution at 25° C.)

Solvent.	Formula.	Dielectric Constant at 25° C.	Solubility.
Water	H_2O	77·95	59·54
Methyl alcohol . . .	CH_3OH	31·2	14·97
Acetonitrile	CH_3CN	36·4	2·00
Ethyl alcohol	C_2H_5OH	25·8	1·92
Acetone	CH_3COCH_3	25·0	1·30
Nitromethane	CH_3NO_2	40·4	0·31

It was considered possible that there was some connection between the dielectric constant, ϵ, of the solvent and the molecular solubility of the solute. The data at one time appeared to favour the view that

$$\frac{\epsilon}{\sqrt[3]{S}}=\text{constant}$$

where S is the molecular percentage solubility of the solute, defined by

$$S=\frac{100n}{n+N}\quad.$$

where n and N are the numbers of molecules of solute and solvent respectively in the solution (Walden, 1908). According to this equation liquids with the highest dielectric constants should be the best solvents. But further research has shown that this coincidence was largely fortuitous, and that no simple connection appears to exist between the two (Turner and Bissett, 1914).

Influence of Temperature upon Solubility.—This is well illustrated by the various solubility curves shown in fig. 144. A differentiation can be made by classifying the curves according as they are continuous or exhibit sharp changes of direction.

1. *Solubility Curve Continuous.*—Several different types exist :

(*a*) The solubility increases progressively with rise of temperature —rapidly, as with silver nitrate, or slowly, as with sodium chloride.

(*b*) The solubility decreases with rise of temperature, as with lithium sulphate and the sulphates of the rare earth metals, with calcium chromate, etc.

(*c*) The solubility increases to a maximum and then diminishes. For example, gypsum.

(*d*) The solubility decreases to a minimum and then rises, as exemplified by calcium acetate and calcium propionate, and also by anhydrous sodium sulphate, the minimum in this case occurring at about 120° C.

The solubility of a substance in water is closely connected with the heat evolved or absorbed when solution occurs. Many substances absorb heat on passing into solution, and in such cases the solubility increases with temperature. In general, the greater the heat absorption, the more rapid is the rise in solubility with the temperature. Salts capable of crystallising with water evolve heat when added to water in the anhydrous form, and it is found that the solubility of the anhydrous form usually decreases with rise of temperature; this is the case, for example, with anhydrous sodium sulphate, as mentioned above (see fig. 147).

Van 't Hoff gives two rules, which, although applying in theory only to the solution of a substance in a solution already practically saturated, usually hold for ordinary solution. The rules are as follows:

(i) If a substance on solution evolves heat, rise of temperature will tend to reduce its solubility.

(ii) If the substance absorbs heat on solution, rise of temperature will cause an increasing amount to pass into solution.

A moment's consideration will show that these rules are strictly in accord with the theorem of Le Chatelier (p. 23).

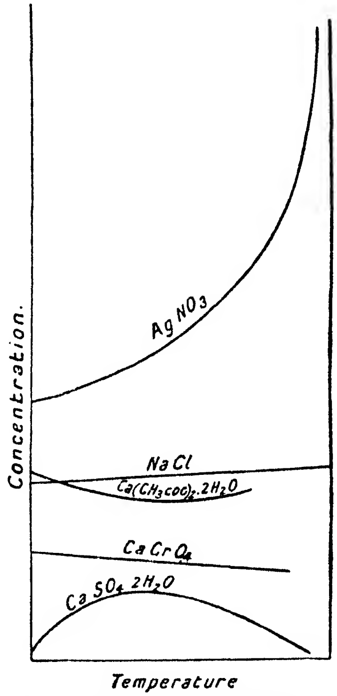


FIG. 144.—Solubility of Salts in Water.

Knowing the solubility of a substance at two different temperatures, it is possible to calculate its heat of solution in the solvent, as shown in Vol. II, provided no disturbing reactions are involved, such as ionisation or association. In the case of succinic acid, the ionisation in aqueous solutions is very slight, and the calculated value for the heat of solution agrees very satisfactorily with that found by direct measurement.

Certain substances, such as sodium hydroxide, do not appear to conform to these principles. Their heat of dilution is great and acts in opposition to the heat effects under consideration.

The solubility curve for calcium chloride hexahydrate (fig. 145) is of interest. On adding the anhydrous salt to ice, some of the latter melts, the salt dissolves and the temperature falls, the ice and the solution remaining in equilibrium. By proceeding in this manner we can travel along AB to the **cryohydric** or **eutectic point** B, at −55° C., where ice, calcium chloride hexahydrate and solution are in equilibrium, and where all three can therefore exist together permanently. AB is thus the fusion curve for ice in contact with the solution of calcium chloride. On addition of more of the salt and raising the temperature, ice disappears, the solution takes up more salt and the solid phase is now the pure hexahydrate. The curve BC is thus the ordinary solubility curve. At C the concentration is so high that the water of crystallisation is ample to effect complete solution of the salt. C, therefore, is the melting point of the hexahydrate, and since the liquid has the same composition as the solid, C is the **true** or **congruent melting point** (see p. 133) of the salt. If now we add anhydrous calcium chloride to the system, the solubility curve turns back in the direction CD. At t°, therefore, the salt appears to possess two solubilities represented by D and D′. This, however, is not the best way of looking at the problem. CD really represents the fusion curve of the hexahydrate,

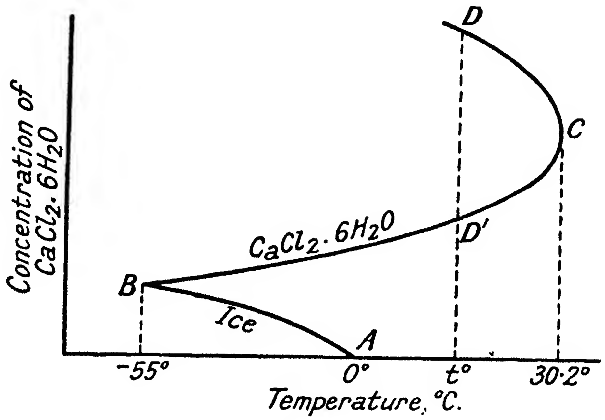


FIG. 145.—Solubility of $CaCl_2.6H_2O$ in Water.

and addition of one of the lower hydrates or the anhydrous chloride causes the hexahydrate to melt at a lower temperature, just as the successive additions of the salt to the ice in the first instance caused the melting point of the ice to fall from A to B.

2. *The Solubility Curve Exhibits Sharp Breaks.*—Two possible causes, namely, a change of polymorphic form or a change of hydration, will give rise to a sudden break in the curve. The former case is illustrated by ammonium nitrate, which is capable of existing in no fewer than five crystalline forms. Of these the β-rhombic passes into the γ-rhombic variety at about 32° C., and at this temperature a break occurs in the solubility curve (fig. 146).

The effect of change of degree of hydration in the case of those substances that can combine with water is shown by the solubility curve of sodium sulphate (fig. 147). Below 32·4° C. in air, or 32·6° C. under the pressure of its own vapour only, the stable form of this salt crystallises with 10 molecules of water, but above this temperature the anhydrous salt is stable. This transition point is sharply marked by a break in the curve. It is possible experimentally, however, to follow the curve CB into the metastable region, and by "seeding," that is, adding a crystal of a salt isomorphous with the particular form it is desired to obtain, to attain the metastable transition point D and to follow the solubility curve of the metastable heptahydrate. Owing to its great solubility, the tetrahydrate cannot be reached in this way even by most careful "seeding," but it can be obtained in solid solution with the corresponding chromate, $Na_2CrO_4.4H_2O$.

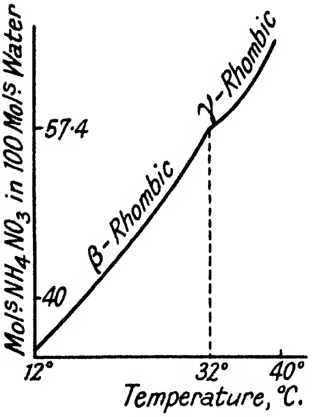


Fig. 146.—Solubility of Ammonium Nitrate in Water.

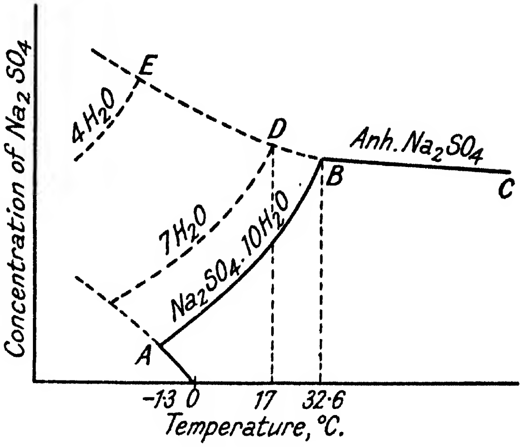


Fig. 147.—Solubility of Sodium Sulphate in Water.

The system ferric chloride–water is of considerable interest, in view of the large number of hydrates that exist. In fig. 148 AB represents

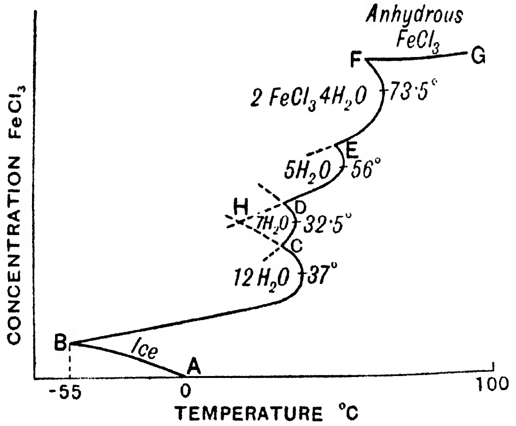


Fig. 148.—Solubility Curves of the Hydrates of Ferric Chloride (Roozeboom, 1892).

the various states of equilibrium between ice and ferric chloride solution, a minimum temperature being reached at the **cryohydric point** B. At this point ice, solution and the dodecahydrate of ferric chloride, $2FeCl_3.12H_2O$, are in equilibrium. If the mixture is now warmed, the ice will melt and the dodecahydrate will pass into solution, as indicated by the curve BCH. At 37° C. the dodecahydrate melts, and further addition of anhydrous ferric chloride lowers the temperature at which the dodecahydrate remains in equilibrium with the solution until C is reached at 27·4° C. At this point the dodecahydrate and heptahydrate, $2FeCl_3.7H_2O$, are able to exist together. The curve has been followed in the direction of the broken line CH to 8° C., the solution being supersaturated with respect to the dodecahydrate. Similarly the curve ED has been followed backwards until it intersects the previous curve at H (15° C.). At this point the dodecahydrate and pentahydrate, $2FeCl_3.5H_2O$, can exist together, although both are metastable in this area, because the heptahydrate is not immediately formed. From B to the maximum temperature of 37° C. the curve is the solubility curve of

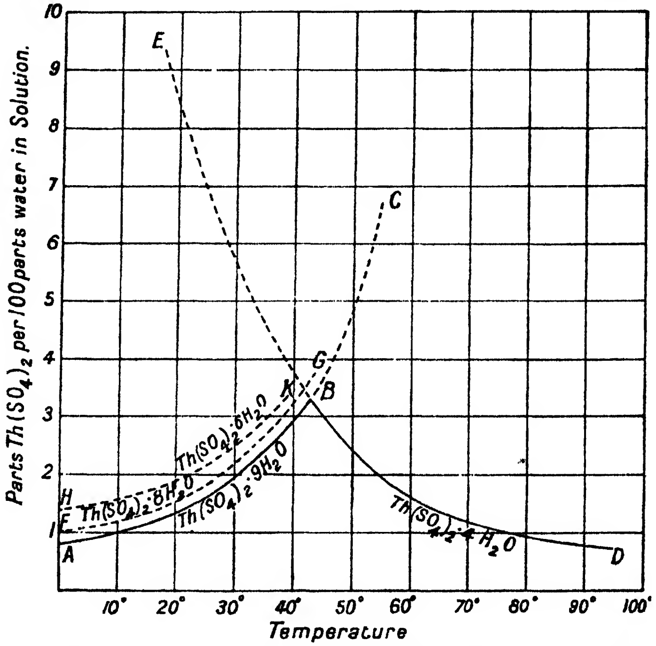


FIG. 149.—Solubility Curves of the Hydrates of Thorium Sulphate.

the dodecahydrate; at 37° C. this hydrate melts, and from this point on to C the curve is retroflex, and represents the fusion curve of the dodecahydrate. It will be observed that each hydrate has a definite melting point, a direct solubility curve and a retroflex solubility or fusion curve.

The solubility curves of the hydrates of thorium sulphate are shown in fig. 149. The ennea- and tetra-hydrates present a contrast in properties, since the solubility of the former increases with rise of temperature, whilst that of the latter decreases. The two curves intersect at B, at which point both salts are in equilibrium with one and the same saturated solution. If the temperature is lowered from this point the enneahydrate will separate out; if raised, the tetrahydrate will separate. Nevertheless, each hydrate can exist in a metastable state, so that the solubility curve of the enneahydrate has been traced up to 55° C. (C) and that of the tetrahydrate down to 18° C. (E). Thus, whilst the true equilibrium between these two salts and their saturated solution occurs at B, there is not necessarily a transformation of the one salt into the other through the medium of the solution when this temperature is departed from, though the further the temperature is removed from B towards E or C the more likely is it that the respective transformation into the ennea- or tetrahydrate will take place. Under conditions favourable to the production of the enneahydrate it frequently happens that the octahydrate is obtained. The solubility of this hydrate is given by the broken line FG, and that of the hexahydrate by HK. As both these salts are metastable in contact with water, they are gradually converted into the enneahydrate, but the rate of change is slow.

Breaks in the solubility curves with rise of temperature are by no means confined to aqueous solutions. Thus, in fig. 150 a break is seen to occur at 17·4° C. in the curve for lithium chloride in ethyl alcohol, the solid phase below this temperature being the tetra-alcoholate, whilst above 17·4° C. anhydrous lithium chloride is the stable phase in contact with the solution.

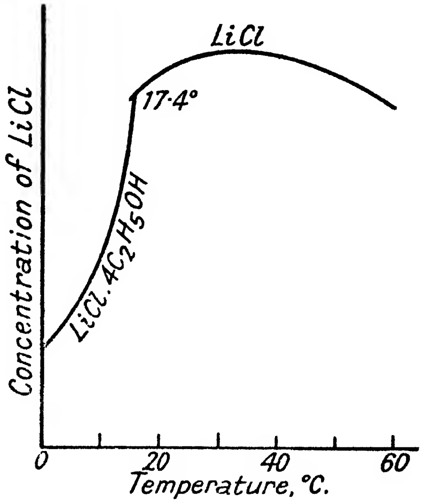


FIG. 150.—Solubility of Lithium Chloride in Ethyl Alcohol (Turner and Bissett, 1913).

Influence of Pressure upon Solubility.—In 1863 Sorby concluded that a rise of pressure increases the solubility of those substances which dissolve in a liquid with contraction of volume, but that it decreases the solubility of such substances as dissolve with an increase in volume. This is in harmony with the theorem of Le Chatelier (see p. 23) and is illustrated by the following data:

The Effect of Pressure on Solubility.
(von Stackelberg, 1896.)

Salt.	Change of Volume on Solution in Water.	Grammes of Salt in 100 grammes of Solution at 18° C.		
		1 Atmos. Pressure.	400 Atmos. Pressure.	500 Atmos. Pressure.
Sodium chloride .	Contraction	26·4	..	27·0
Ammonium chloride	Expansion	27·2	..	25·8
Alum . . .	Contraction	11·5	14·2	..

Physical Condition of the Solid Phase.—As long ago as 1870, Stas observed that the solubility of silver chloride varies with its method of preparation, the following results being obtained:

	Solubility.
Flocculent silver chloride .	0·0140 gramme/litre at 20° C.
Powdered ,, ,, .	0·0060 ,, ,, 17° C.
Granular ,, ,, .	0·001 ,, ,, 15° C.

Clearly the smaller the particles of the salt, the greater the solubility. This is further supported by data obtained for the sulphates of calcium and barium at 25° C.:

Influence of Size of Particle upon Solubility at 25° C.

(Hulett, 1901.)

Salt.	Diameter of Particles supposed Spherical.	Solubility at 25° C. (Mass per Litre.)
Calcium sulphate . .	2 μ	2·085 grammes.
	0·3 μ	2·476 ,,
Barium sulphate . .	1·8 μ	2·29 mgrms.
	0·1 μ	4·15 ,,

Before, therefore, the absolute solubility of a salt in water at any stated temperature and under, say, atmospheric pressure, can be given, the size of the particles of the solid phase must be known. This has an intimate connection with the phenomenon of supersaturation (see p. 376), for it is clear that a saturated solution of barium sulphate prepared in contact with particles of diameter 0·1 μ is supersaturated with respect to particles of diameter 1·8 μ, and, upon introduction of such particles, the excess would be precipitated out.

In most ordinary cases, however, variation in the size of the solute particles is not sufficient to cause any serious variation in the solubility. It is usual, in practice, to crush to a powder of sufficient fineness to allow of easy stirring in the saturation bottle (p. 374).

Influence of Dissolved Substances.—The presence of a dissolved substance in a liquid may influence materially the solvent action of that liquid towards a second substance. The problem has already been discussed in connection with the solution of gases in liquids (see p. 351) and of liquids in liquids (p. 360). Neutral gases, owing to their slight solubility, exert but little influence on the solubility of solids in water. Chemically active gases may, of course, exert an enormous influence; thus carbon dioxide greatly increases the solubilities of magnesium and calcium carbonates in water, this being attributable to chemical change, the soluble bicarbonates of the metals being formed.

The solubility of a solid in a mixture of two liquids is a more complicated problem, inasmuch as the salt may be soluble in either or both of the liquids, and the two liquids themselves may either be completely miscible, or only partly miscible. If the two liquids are practically insoluble in each other, or if, being only partly miscible, they are present in such quantities as to form two layers, it is evident that a solid, soluble in both liquids, will distribute itself between them in accordance with the **Partition Law** (see p. 377). If the two liquids are completely miscible, or if one of two only partially miscible liquids be present in such quantity as will completely dissolve in the first liquid only, the effect of such admixture upon the solubility of a solid will depend very largely upon the relative solvent powers of the liquids for the solid. For example, the solubility of sodium chloride in pure ethyl alcohol is very small—only 0·065 gramme per 100 grammes of alcohol at room temperature, whereas the corresponding figure for the salt in water is 36 grammes. Hence the solubility curve for the salt in water-alcohol at constant temperature steadily falls as the percentage of alcohol rises. If, therefore, alcohol is added to a concentrated aqueous solution of salt, some of the salt is precipitated. Physical precipitation of this kind is frequently of use in the preparation of pure substances, and is a favourite method of obtaining substances in the colloid state (see p. 469). Conversely, on adding common salt to a solution of ethyl alcohol in water, the alcohol separates as an upper layer and may be removed with a separating funnel.

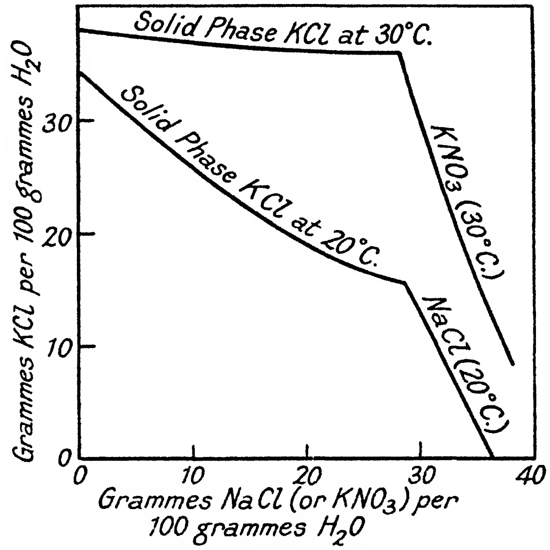


FIG. 151.—Solubility of Potassium Chloride in Aqueous Solutions of Potassium Nitrate at 30° C., and of Sodium Chloride at 20° C., and *vice versa* (Leather and Mukerji, 1913).

It sometimes happens that a dissolved solid enhances the solvent power of a liquid for certain other solids, but in most cases this is attributable to some kind of chemical change. Thus, for example, silver cyanide is insoluble in water, but it readily dissolves in an aqueous solution of potassium cyanide, because a complex salt is formed, namely, potassium argentocyanide, $K[Ag(CN)_2]$, which happens to be soluble in water. Similarly, iodine readily dissolves in potassium iodide solution owing to the formation of soluble potassium tri-iodide, KI_3. In most cases of purely physical solution, however, a dissolved solid will tend to reduce the solubility of a second solid in the same liquid. Thus the solubility of potassium chloride in water is reduced by the presence of dissolved potassium nitrate or sodium chloride. Similarly the solubility of potassium nitrate or of sodium chloride is reduced by the presence of potassium chloride. This is shown in fig. 151, together with the compositions of the solid phases in contact with the saturated solutions. This principle is frequently made use of in "salting out." For example, soap is salted out of solution by the addition of brine.

Rate of Dissolution.—The rate at which a solid will dissolve in a stationary liquid depends upon two factors, namely :

(i) The reaction between the solute and the solvent, and
(ii) The diffusion of the dissolved solute from the seat of dissolution.

If the former reaction is very rapid in comparison with the latter, it is clear that the latter must become the determining factor; the rate of solution will thus be proportional to the rate of diffusion, and this, by **Fick's Law** (1855), depends upon the amount of solid that has already passed into solution (p. 381).

Let A be the area of the film of solution in contact with the solid, and c its concentration, x being the concentration of the more dilute layers at any time θ; then, if A remains constant,

$$\frac{dx}{d\theta}=k_1A(c-x)$$

and this, upon integration, gives

$$k_1=\frac{1}{\theta}\cdot\frac{1}{A}\log_e\frac{c}{c-x}$$

The rate of solution under quiescent conditions should thus obey the monomolecular law if the foregoing assumptions are correct.

Experiment shows that this is the case when benzoic acid dissolves in quiescent water (Noyes and Whitney, 1897). If the water is agitated, the thickness of the film is reduced and the rate of diffusion and hence of dissolution is increased. The rate of dissolution of salts in water is reduced by the presence of emulsoids, such as gum arabic and glue. This phase of the subject is considered on p. 473.

Volume Changes on Dissolution.—When a solid dissolves in a liquid the volume of the solution may differ appreciably from the combined volumes of the solute and solvent. Aqueous solutions offer peculiar difficulty to systematic study, for not only may hydration of the solute take place, but both ionisation of the solute and depolymerisation of the water molecules introduce disturbing factors.

In so far as solutions in organic solvents are concerned, **Lumsden's Law** (1907) states that

if V_0 and V are the volumes of pure solvent and solution respectively, then if $V-V_0$ is taken as the volume occupied by the substance in solution it is either the same as that of the pure substance at the same temperature and in the liquid state, or, if it is not identical, it differs by a constant amount at all temperatures.

Instead of directly determining the alteration in volume when a solid dissolves, it is usual to determine the densities of the solvent and solution respectively.

The molecular volume, V_m, of the substance in solution, is then readily calculated by the usual formula:

$$V_m=\frac{M+m}{d}-\frac{m}{d_0}$$

where M is the molecular weight of the solute, m the mass in grammes of solvent per gramme-molecule of solute, and d_0 and d the densities of the pure solvent and solution respectively.

Writing v as the number of litres in which one gramme-molecule of substance is dissolved,

$$m = 1000vd - M$$

and

$$V_m = \frac{M}{d_0} - 1000v \cdot \frac{(d - d_0)}{d_0}$$

This gives us another method of arriving at the same data.

Experiment shows that when naphthalene is dissolved in toluene the increase in volume of the liquid is almost identical with the volume which the naphthalene would occupy if it were free and in liquid form at the same temperature. On the other hand, when thymol is dissolved in benzene, the increase in volume of the liquid is appreciably greater than the volume which the thymol would occupy if it were free and in the liquid state at the same temperature. If, now, the changes in volume are observed at various temperatures, both below and above the melting point of the pure solute, continuous curves are obtained on plotting the results as shown in fig. 152. There is no break at the normal melting point, neither is there any break at the normal boiling point of the solute. With naphthalene the curve above the melting point (79° C.) is practically identical with the molecular volume curve of the free liquid substance; with thymol the corresponding curves are practically parallel.

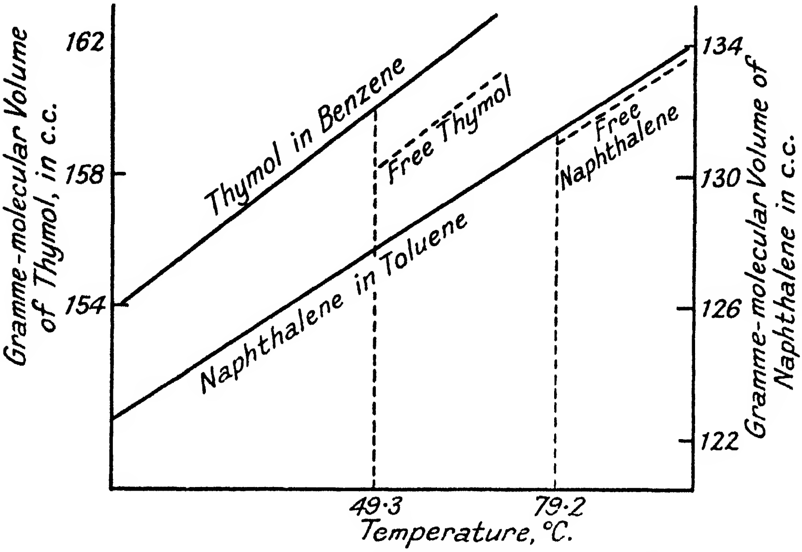


FIG. 152.—Molecular Volumes in Solution (Lumsden, 1907).

We have here, therefore, a method of determining approximately the molecular volumes that the substances would have if it were possible to supercool them in liquid form to the ordinary temperature.

Methods of Determining Solubilities.—One or both of two methods may be followed in determining the solubility of easily or moderately soluble substances, namely, agitation of the solid and liquid in a vessel maintained at the temperature desired, or heating the two substances to a higher temperature than required and then cooling to the temperature of investigation. In either case excess of the solid must be present, not only to ensure saturation, but also to prevent supersaturation. The same value for the solubility ought to ensue whichever method is adopted.

For either of these methods the apparatus shown in fig. 153 is convenient to use. The powdered solute, together with a sufficiency of solvent, is placed in the saturation bottle A and vigorously agitated with a mechanical stirrer for several hours at constant temperature in a thermostat. At the ordinary temperature saturation is usually a slow process and is not attainable in the course of a few minutes only. The thermometer T should be graduated to 0·1° C. When the solution is saturated it is drawn through the filter F into the weighing bottle B, which is subsequently detached and weighed. If the density of the solution is also required, a small density bottle may be inserted in B and weighed when full of liquid. The amount of dissolved solid may be determined by evaporation to dryness, or by some chemical method, as occasion serves, and, in the case of most soluble salts, may be expressed as grammes per 100 grammes of solution, S_s, or grammes per 100 grammes of solvent, designated as S_w where the solvent is water.

For very sparingly soluble salts, such as the silver halides and the sulphates of lead and barium, special methods have been adopted. A few of the more important are:

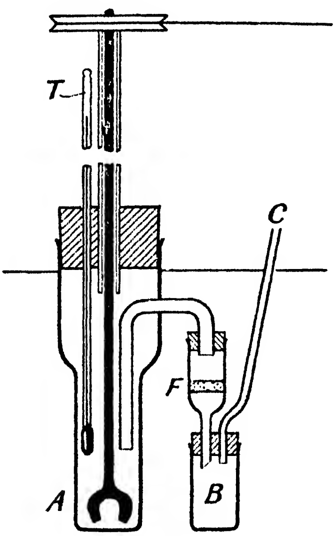


Fig. 153.—Apparatus for Determination of Solubility (Friend, 1930).

(*a*) Measurement of the specific electric conductivity of a saturated solution (see Vol. II).

(*b*) Determination of the electromotive force of a concentration cell containing the salt in solution.

(*c*) Colorimetric methods. These methods have been applied, for example, to lead sulphate, which is converted to the sulphide and the quantity in solution determined by comparing the depth of colour with that of a standard solution.

(*d*) Radioactive method. A solution of a soluble salt of the metal, whose sparingly soluble salt is to be investigated, is activated with a known quantity of a suitable radioactive indicator (Vol. II). The sparingly soluble salt is then quantitatively precipitated out of solution by addition of suitable reagents. The precipitate carries down with it the radioactive indicator. It is washed, dried and weighed. A portion is now agitated with water until a saturated solution has been obtained, using an apparatus similar to that shown in fig. 153, and a portion removed, taken to dryness and the activity of the residue determined electroscopically. The activity clearly is directly proportional to the quantity of salt present, and the solubility can thus be calculated in the usual way. The solubility of lead chromate has been determined in this way, using RaD as indicator. The value $1{\cdot}2 \times 10^{-5}$ gramme per litre at 25° C. was obtained (Hevesy and Paneth, 1913). The method is very sensitive, and a quantity of 10^{-10} gramme of RaD may be measured electroscopically. Further, there is less danger of included impurities affecting the result than with the methods previously described.

The Dissolution of Solids in Solids.

The term "solid solution" was applied by van't Hoff to certain substances which separate in the crystalline state from liquid solutions on cooling, the crystals not being the pure solvent or solute but a homogeneous mixture of solvent and solute—in short, a solid solution. A striking example of this came to light in the investigation by Beckmann and Stock in 1895 of the molecular weight of iodine in benzene solution. It was found that iodine always separated with the benzene in the solid state. Moreover, the ratio of the average concentration of iodine in the liquid to that in the solid was roughly constant, that is to say, Henry's Law held for the solid solution. If C_1 is the mean value—before and after freezing—of the concentration of iodine in the liquid, and C_2 the concentration in the crystals, each concentration being expressed in terms of iodine per 100 grammes of benzene, then, for three different concentrations of solution, the following figures were found :

C_1.	C_2.	C_2/C_1.
3·39	1·279	0·377
2·587	0·925	0·358
0·9447	0·317	0·336

Apart from the cases arising from freezing point measurements, however, miscibility in the solid state has been known for a considerable time. Until recently it was believed that only isomorphous substances possess the power of crystallising out together, and, in turn, isomorphism was recognised by the power of mutual overgrowth and of forming **mixed crystals**, as, for example, in the case of the alums. It is now known, however, that overgrowths may occur with substances that are not isomorphous (see p. 190).

Miscibility in the solid state varies with the nature of the substances and the temperature. The simplest case is that in which the substances can mix in all proportions, as exemplified by zinc sulphate, $ZnSO_4.7H_2O$, and magnesium sulphate, $MgSO_4.7H_2O$. Salts of the rare earths possess this property to a remarkable extent, and as the solubilities of the corresponding salts of two adjacent rare earth metals are frequently closely similar, it may be extraordinarily difficult to obtain pure specimens of each even by the most careful fractionation (see p. 401). In cases of limited solubility, two series of solid solutions are formed, each a solution of the one substance in the other, corresponding to conjugate liquid solutions.

As has already been explained (p. 190) the term "mixed crystals" used above is not altogether a happy one. It does not mean that the solid phase consists of a mixture of separate crystals of the individual substances, but that the composition of each crystal is a mixture; in other words, a solid solution of the one substance in the other.

Many pairs of metals are capable of forming solid solutions. Thus silver and gold, cobalt and nickel, antimony and bismuth, are examples of pairs of metals that can mix in all proportions in the solid state. On the other hand, copper and nickel, aluminium and zinc, gold and nickel, are miscible only to a limited extent. Solid solutions play a most important part in the metallurgy of iron and steel, and also of other metals.

An interesting example of solid solution is that of tungsten in metallic salts, to which reference has already been made (p. 70).

The formation of solid solutions, or the occlusion of the reagent or other salts by a precipitate, appears also to occur in many cases where precipitation from solution is effected. Thus, for example, when ferric hydroxide is precipitated in the presence of certain proportions of manganese salts, manganese hydroxide is co-precipitated, and the two hydroxides appear to be in part in solid solution. Precipitates of barium sulphate are likewise very prone to contamination with dissolved salts, and a similar contamination of his silver halide precipitates led Stas, in his classical researches on the atomic weight of silver (*circa* 1865), to obtain too high a value, namely 107·930, whereas the accepted value is now (1931) 107·880. As was mentioned in the analogous case of gases dissolved in solids, it is difficult to separate the phenomena of adsorption and absorption (see p. 356). The former, being a surface phenomenon, probably is the first to take place, being followed later by absorption or true solution in the above-mentioned cases.

SUPERSATURATION.

When a solution of a solid in a liquid, already saturated at a given temperature, is heated up with more of the solid until all the solid passes into solution, on cooling to the original temperature the excess of the substance in solution is not always deposited, crystallisation or precipitation being suspended. The solution obviously holds a greater quantity of substance than corresponds to the ordinary solubility, and is said to be **supersaturated.** Such solutions can readily be prepared by heating up sodium thiosulphate, sodium acetate, sodium sulphate, etc. with water, and allowing to cool without agitation.

Supersaturated solutions, however, are always liable to crystallise spontaneously, particularly on exposure to air. Löwel, in 1850, apparently was the first to show, however, in the case of sodium sulphate, that crystallisation was not induced by contact with air that had previously been passed through water, sulphuric acid, caustic alkalies, glass wool, or even through a series of empty flasks. It was afterwards observed that the spontaneous crystallisation of supersaturated solutions of sodium sulphate in contact with air is due to the presence of minute crystals of the salt in suspension in the air, which serve as nuclei, stimulating crystallisation. Hence by washing or filtering the air Löwel had removed these suspended nuclei, and in consequence retarded crystallisation.

Not only can minute crystals of the same substance serve as nuclei, but crystals of isomorphous bodies yield precisely the same result. It is now known also that this property is shared by many substances that are not strictly isomorphous with the dissolved salt, provided their molecular volumes are closely similar. Ostwald showed that nuclei weighing only 10^{-10} to 10^{-8} gramme were usually quite sufficient to induce crystallisation of supersaturated solutions. Furthermore, it appears from numerous researches that mere mechanical friction is sufficient to induce crystallisation, such crystallisation taking place in the complete absence of crystalline nuclei. This is tacitly recognised in qualitative analysis in testing a solution for potassium by the addition of chloroplatinic acid. If potassium is present its precipitation as hexachloroplatinate, K_2PtCl_6, is frequently accelerated by scratching the watch glass used with a glass rod.

Some substances yield supersaturated solutions with greater ease than others. Thus potassium chloride supersaturates only with difficulty, whilst borax does so readily. This is made use of in one commercial method of separating the two salts. A solution containing both is cooled fairly rapidly, whereby potassium chloride crystallises out, the borax remaining in supersaturated solution. After centrifuging to separate the potassium chloride, the clear solution is allowed to stand for some hours to enable the gradual, spontaneous crystallisation of the borax to take place.

Supersaturated solutions of liquids in liquids have been realised only in a few cases, but supersaturated solutions of gases in liquids are not uncommon. Tap water saturated with air at 7° C. can be incubated at 18° C. for six days without appreciable loss of oxygen. At this higher temperature it is, of course, supersaturated, but so long as the containing vessel is not shaken, and chemical actions such as fermentation are excluded, no appreciable loss of oxygen occurs. The addition of any powdered substance to such a solution, however, will break down the supersaturation, since the gases in the pores of the powder act as nuclei. Supersaturation of this kind differs from that considered above, inasmuch as the nuclei immediately escape from the liquid, whereby their influence is severely limited.

DISTRIBUTION OF A SOLUTE BETWEEN TWO IMMISCIBLE SOLVENTS.

Let us now consider how a solute will comport itself when added to a mixture of two immiscible liquids. If we denote the two solvents by A and B, and the solubilities of the solute in these by S_A and S_B respectively, the solute will distribute itself between the two liquids in proportion to its relative solubilities, assuming no association or dissociation occurs. We may therefore write

$$\frac{S_A}{S_B}=\frac{C_A}{C_B}=\text{constant}$$

where C_A and C_B are the concentrations of the solute in A and B respectively. The constant is termed the **Partition Coefficient**, and the formula is an expression of the **Partition Law**.

An example is afforded by succinic acid divided between ether and water, in which latter it is only very slightly ionised. Thus

C_{water}	0·024	0·070	0·121
C_{ether}	0·0046	0·013	0·022
$\frac{C_w}{C_e}$	5·2	5·4	5·5

the concentrations being expressed as grammes of acid per 10 c.c. of solvent.

The foregoing law is the principle upon which the extraction of products from dilute solution by shaking with different solvents is based. For example, aniline is very soluble in ether, and upon shaking an aqueous extract of aniline with ether, the latter takes up almost the whole of the aniline. Theoretically it cannot take it all, for the partition coefficient represents an equilibrium, and there will always be some aniline dissolved in the water, in equilibrium with the ether solution, although its amount may be negligibly small. If several solutes are present in the system, each molecular species behaves as though the others were not present, provided, of course, they are chemically neutral towards each other.

The problem now arises—given a solution and a definite quantity of an extracting solvent, is it more efficient to use the whole of the extractor for one separation or to extract several times with small portions of the extractor?

Let us assume that a substance S is twice as soluble in ether as in water, and that we have 100 c.c. each of aqueous solution and pure ether to work with. If we mix the two liquids together, shake and allow to stand until separation into two layers has been effected, the ether layer contains 66·7 per cent. of the solute S. If now we take the 100 c.c. of solution, but only 50 c.c. of ether, the ether layer contains half of S, the other half remaining in the water. Upon treating the latter with the remaining 50 c.c. of pure ether the ether layer again extracts half of S, or 25 per cent. of the original amount. The two ether extracts, therefore, contain 75 per cent. of S, as opposed to 66·7 per cent. in the former case. In actual practice, of course, there must be a limit to the number of extractions that can be made in any particular case, and a compromise is effected between theoretical efficiency and practicability.

Probably no two liquids are absolutely insoluble in each other, so that the equation

$$\frac{S_A}{S_B} = \frac{C_A}{C_B}$$

is not rigidly true, although it may be sufficiently so for practical purposes.

If the substance is associated in one of the solvents and not in the other, or if chemical combination takes place, the foregoing equation must be modified (Nernst, 1891). Suppose, for example, the substance is associated in solvent A but normal in solvent B. If x is the degree of association (p. 269), then the partition coefficient k is given by

$$k = \frac{C_A}{C_B^x} = \frac{\sqrt[x]{C_A}}{C_B}.$$

This affords a method of determining the molecular state of a substance in solution. A good example is afforded by benzoic acid (Nernst, 1891) which, in water, apart from slight ionisation, is represented by the simple formula C_6H_5COOH, whereas in benzene it is associated to double molecules. Since $x = 2$, the above equation becomes

$$k=\frac{C_B}{C_W^2}$$

where C_B and C_W are the concentrations in benzene and water respectively. Thus

C_W . . .	0·0150	0·0195
C_B . . .	0·242	0·412
$\frac{C_B}{C_W^2}$ . . .	1075	1084

Chemical combination between two solutes can frequently be detected in a similar manner. Thus, from the distribution ratio of hydrogen peroxide between ether and aqueous molybdic acid the existence in solution of permolybdic acid has been adduced (Brode, 1901).

CHAPTER XVIII.

DIFFUSION AND OSMOSIS.

THAT a close analogy exists between the gaseous and the dissolved states is evident from a consideration of the process of diffusion in the two cases. A given quantity of a gas will expand to fill any space into which it is introduced, whether the space has previously been evacuated or contains some other gas. If another gas is present, the rate at which the added gas distributes itself is considerably retarded. The diffusion or expansion may occur even against gravitation, as when a heavy gas or vapour, such for example as bromine, is introduced at the bottom of a cylindrical vessel. Like a gas, a substance in solution distributes itself throughout the whole volume of solvent. If a beaker of concentrated copper sulphate solution is placed in a large trough and the latter carefully filled with water, the salt gradually diffuses in all directions until the solution is of uniform concentration throughout. Similarly, if two miscible liquids are introduced into a cylindrical vessel in such a manner that the denser liquid lies beneath the lighter, then, as with gases, diffusion will take place until the whole liquid possesses a uniform composition. The time required to arrive at complete mixture may be very prolonged, for the rates at which liquids diffuse are extremely slow as compared with gaseous diffusion, owing to the great resistance to movement encountered. This we should expect, as molecular movement in liquids must of necessity be much slower than in gases.

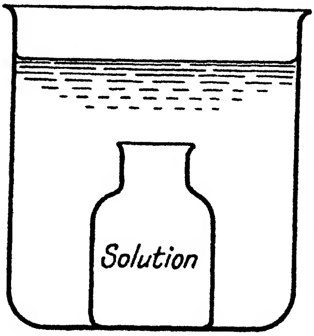


FIG. 154.—Graham's Experiment.

The first systematic experiments on the subject were those of Graham (1851), who introduced a small, wide-mouthed bottle, filled with a given solution, into a larger vessel containing water (fig. 154). After a certain time, samples of liquid were withdrawn from different layers and analysed. It was found that the velocity of diffusion

(i) varies with the temperature,
(ii) varies with the nature of the solute,
(iii) is directly proportional to the concentration of the solute.

A solution of ordinary alum in water behaves as if it were a mixture of aluminium and alkali sulphates, and as these diffuse at different rates, it is possible to effect a partial separation of them.

It was observed that solutes in water may be divided into two general groups, according to their rates of diffusion. Those which diffused with relative rapidity were found in general to yield crystalline solids; these were termed by Graham **crystalloids**. Those which diffused very slowly were gluey in character and were in consequence termed **colloids** (Greek *kolla*, glue) (see Chapter XXII).

Fick's Law.—In 1855, Fick, guided by Fourier's Law of the conduction of heat or "diffusion" of temperature, gave a mathematical interpretation to diffusion, which may be explained as follows: Consider a vertical cylinder containing a solution the concentration of which falls uniformly as we pass upwards, but remains uniform in any horizontal layer. If A is the cross-section of the cylinder (fig. 155), C the concentration of the solute at a given level and $C-dC$ the concentration at a level dl cm. above that level, then, if dS is the quantity of solute passing in the time $d\theta$ across the area A, we have

$$dS = -DA\frac{dC}{dl} \cdot d\theta,$$

D being termed the **diffusion coefficient.** It represents the number of grammes of solute crossing one square centimetre of area in one second for a concentration gradient of one gramme per centimetre. D is approximately constant for a given solute in a given solvent at the same temperature, varying only slightly with the concentration.

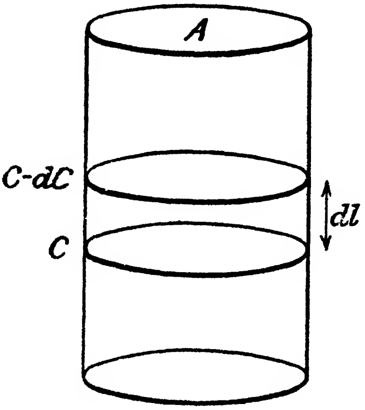


FIG. 155.

Determination of the Diffusion Coefficient.—Lord Kelvin used glass beads of different densities. These were introduced into a cylindrical vessel containing two miscible liquids, the denser liquid forming at first a uniform layer at the bottom, so that initially the beads floated at the horizontal junction of the two liquids. As diffusion proceeded the beads separated. The main objection to this procedure is the formation of air bubbles on the beads, which disturbs their apparent densities.

Weber verified Fick's Law for zinc sulphate in aqueous solution by determining the change in electromotive force (see Vol. II) between two amalgamated zinc plates suspended in the liquid. Comparing the results with those obtained with solutions of known concentration it was easy to calculate the rate of diffusion.

More recently, optical methods have been employed, such, for example, as measuring the change in refractive index of the liquid. This possesses the advantage that no foreign body is introduced into the system, so that diffusion can proceed undisturbed for long periods, during which changes in concentration may be determined as frequently as desired.

In the following table are given the diffusion coefficients for several solutes in different solvents, the coefficients being expressed in grammes per square centimetre per second. The concentration C is given in gramme-equivalents per litre.

Solute.	Solvent.	Temp., °C.	C.	$D \times 10^5$.
Sodium chloride .	Water	18	0·1	1·24
			1·0	1·24
			2·5	1·33
			5·0	1·50
Potassium nitrate .	Water	18	0·1	1·43
			1·0	1·24
			2·5	1·17
		0	1·0	0·87
		24	1·0	1·54
Potassium chloride .	Water	18	1·0	1·59
Hydrochloric acid .	,,	18	1·0	1·6
Zinc sulphate .	,,	15	1·0	0·27
Silver nitrate .	Water	15	0·2	1·28
	Ethyl alcohol	14	0·1	0·41
Potassium iodide .	Water	15	0·05	1·49
	Ethyl alcohol	14	0·05	0·47
Iodine . . .	Carbon disulphide	16	0·1	3·0
	Benzene	20	0·1	1·9
Gold . . .	Mercury	11	. .	0·8
	Lead	550	. .	3·7
	Tin	555	. .	5·4

It will be observed that the diffusion coefficients of salts of the alkali metals in water under analogous conditions do not differ very greatly. Increase in the concentration of the solute sometimes raises the value of *D*, as with sodium chloride, and sometimes reduces it, as with potassium nitrate. *D* invariably rises with the temperature, as is well shown with potassium nitrate. Change of solvent greatly influences the value of *D*. In general, salts diffuse less rapidly in ethyl alcohol than in water. Gold is seen to diffuse more rapidly in tin than in lead, and iodine more rapidly in carbon disulphide than in benzene. As the value for *D* as given above is very small, the unit of time θ is frequently taken as 24 hours. The value of *D* is then increased $60 \times 60 \times 24$ times.

Diffusion through a Membrane.—If the experiment shown in fig. 154 is repeated in every detail save that the wide-mouthed bottle containing the solution is closed with a membrane of parchment paper tied tightly round the neck, diffusion will still proceed as before, since the parchment paper is permeable not only to the water but to the solute also. This is termed **dialysis.** Colloidal substances do not readily pass through parchment, and a suitable piece of apparatus for illustrating this difference between " crystalloids " and " colloids " is shown in fig. 181 (p. 443).

The question arises as to whether or not a membrane can be found that will allow a solvent to pass through, but will prevent a " crystalloid " from so doing. Such membranes are known and are termed **semipermeable**—a term due to van't Hoff (1886).

In 1748 Abbé Nollet filled a bladder with alcohol (spirits of wine) and immersed the whole in water. The latter liquid entered the bladder, causing it to distend and ultimately burst. The bladder thus was functioning as a partially semipermeable membrane, allowing the water to pass in but retarding the outward passage of the alcohol. In 1826 Dutrochet showed that water diffuses into a pig's bladder containing a salt solution, setting up a hydrostatic pressure. Both Dutrochet, and later Vierordt (1848), observed also that the rate of passage of the water into the bladder varied both with the nature and concentration of the salt.

The first artificial semipermeable membrane was made by Moritz Traube in 1867 by immersing non-setting glue in a solution of tannic acid, when it became coated with a skin of semipermeable material. Non-setting glue is obtained by prolonged boiling of glue with water, say for some 30 hours. On cooling, unless very highly concentrated, the liquid does not set or gelatinise. The membrane thus obtained was permeable to ammonium sulphate and chloride, but not to potassium ferrocyanide; in other words, its action was selective. Other membranes were tried, notably copper ferrocyanide, which was found to be impermeable to many solutes, and which is, at the present time, one of the most widely used membranes.

Osmotic Pressure.—It will be clear that if a solution is contained in a " cell " the walls of which are semipermeable membranes, and the cell is immersed in a vessel containing the pure solvent, the passage of the solvent into the cell will set up a hydrostatic pressure. Traube's experiments were qualitative in that he did not measure these pressure effects. Measurements were first carried out with any pretence to accuracy by Pfeffer in 1877, whose cell consisted of a cylindrical vessel of " biscuit," that is, unglazed porcelain or earthenware (fig. 156), the walls of which were impregnated with copper ferrocyanide. The " biscuit " thus served to support the copper ferrocyanide membrane, which was precipitated in the pores by filling the cell with potassium ferrocyanide solution and immersing in copper sulphate solution so that the two reagents diffused into the walls. The cell was filled with a solution of cane sugar and connected as shown with a mercury manometer to register the pressure. On immersing in water, the latter passed in until the hydrostatic pressure within the cell was such that equilibrium was attained, as much water then passing into the cell in unit time as passed out. Owing to the entrance of water, the pressure registered was not that of the original solution, and to prevent the entrance of anything more

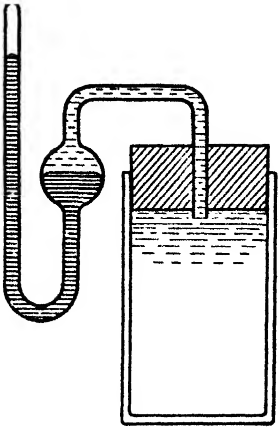


FIG. 156.—Pfeffer's Cell.

than a trace of water Pfeffer's later measurements were made with a closed air manometer of capillary tubing containing an index of mercury, the pressure being measured by the compression of the air.

The pressure registered in this way is known as the **osmotic pressure** (Greek *osmos*, a push) and is defined as *the pressure exerted on a boundary surface separating a solution from the pure solvent when there is at the surface in question a membrane which allows of the passage of the solvent only, and not of the solute.*

Since the pioneer work of Pfeffer, many investigators have carefully measured the osmotic pressures of solutions. Methods of preparing the copper ferrocyanide membrane have been improved, and include an electrolytic process in which copper sulphate and a platinum electrode are placed within the cell with potassium ferrocyanide solution and a copper electrode surrounding the cell, the solutions both being fifth- or tenth-normal. On the passage of a current, a membrane is formed between the inner and outer walls, which can be made strong enough to withstand a pressure of many atmospheres. So perfect are the membranes obtained in this manner that osmotic pressures of 12 atmospheres have been maintained for 60 days without perceptible leak.

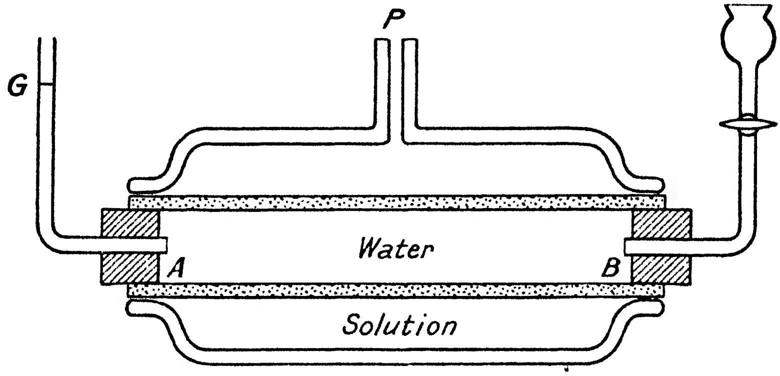


FIG. 157.—Berkeley and Hartley's Apparatus.

Mention may be made of the work of Lord Berkeley and Hartley, whose apparatus is shown diagrammatically in fig. 157. A copper ferrocyanide membrane was deposited on the outside of a cylindrical "biscuit" tube AB, which contained the pure solvent and was enclosed in a gun-metal case containing the solution. Pressure was applied through P until equilibrium was obtained, under which condition the level of the solvent in G remained constant, as the solvent passed out of the solution at the same rate as it entered. The applied pressure was thus equal to the osmotic pressure of the solution. Pressures up to 135 atmospheres were measured.

Frazer and Myrick (1916) used the apparatus shown in fig. 158 and measured the osmotic pressure directly. Up to 100 atmospheres the measurements were made with glass manometers, but these broke at higher pressures and an electrical resistance manometer was used, based on the principle that an almost linear relationship connects the electrical resistance of certain conductors with the pressure to which they are subjected. Copper ferrocyanide was deposited on the outer surface of the porous cell AB, which was kept filled with water. This cell was contained in a bronze cylinder filled with the solution. Feet were attached to the screw plug at the bottom so that the apparatus could stand vertically without additional support.

Indirect Methods of Measuring Osmotic Pressure. - The osmotic pressures of different solutions may also be determined by comparison methods. The contents of plant cells are enclosed in semipermeable membranes, and if the cells are placed in strong salt solutions the protoplasmic contents shrink away from the cell walls, which latter do not alter their shape. If the cells are now placed in pure water, the protoplasm swells out again and completely fills the cells. From this it is clear that if the osmotic pressure of the solution is greater than that of the cell sap, the protoplasm contracts —that is, **plasmolysis** occurs. If, on the other hand, the osmotic pressure of the solution is less than that of the cell sap, the protoplasm does not separate from the cell wall. Two solutions therefore are prepared, one of which just causes plasmolysis, whereas the other just does not. The mean of these concentrations gives a solution of osmotic pressure equal to that of the cell sap—in other words, the solution is **isotonic** with the cell sap. Solutions of other salts may be prepared in a similar manner, and these are then not merely isotonic with the cell sap but also isotonic with one another. By noting the dilutions required, the relative osmotic pressures of the original solutions can readily be calculated.

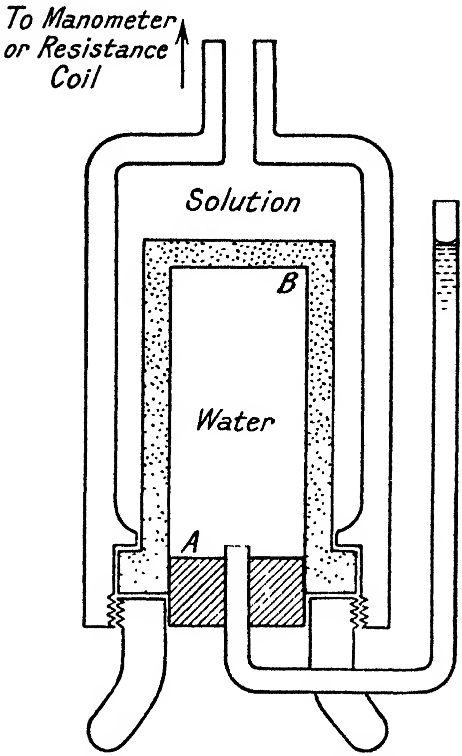


FIG. 158.—Frazer and Myrick's Apparatus.

In a somewhat analogous manner isotonic solutions may be prepared by the aid of blood corpuscles.

Typical Results for aqueous solutions of cane sugar at various temperatures are given in the table on p. 386. The concentrations are expressed as gramme-molecules of sugar per 1000 grammes of water—the so-called *weight molecular concentration*—and not as gramme-molecules of sugar per 1000 c.c. of solution—the more usual *volume molecular concentration.*

An instructive experiment illustrating the diffusion of a solvent through a membrane consists in inserting, with the aid of a glass tube, a drop of a saturated solution of potassium ferrocyanide into the top

Mean Osmotic Pressures (in Atmospheres) of Cane Sugar Solution at Various Temperatures.

(Morse.)

Concentration, gramme-molecules per 1000 grammes of Water.	0° C.	10° C.	25° C.	60° C.
0·1	2·46	2·50	2·63	2·71
0·2	4·72	4·89	5·15	5·43
0·4	9·44	9·79	10·30	10·87
0·6	14·38	14·86	15·63	16·54
0·8	19·49	20·16	21·25	22·34
1·0	24·83	25·69	27·05	28·37

of a two-thirds saturated solution of copper sulphate contained in a vertical glass cylinder. The drop of ferrocyanide solution is immediately coated with a semipermeable membrane of copper ferrocyanide. Being denser than the copper sulphate solution the drop steadily falls to the bottom of the jar, but after a few moments begins to rise again as water from the copper sulphate solution diffuses into it and renders it less dense.

Osmotic Pressure in Gases.—Gas pressure is readily measured at the surface or envelope which isolates the gas, and is due to the bombardment of the surface by the molecules. Although it is easy to measure total gas pressure, it is not easy to determine the pressure set up by a single gas present in a mixture. The measurement is possible if the pressure due to one gas can be eliminated by bringing it to some fixed value, for example, atmospheric pressure. To this end it is necessary for the containing vessel to be constructed of some material which exerts a selective action, allowing one gas to pass through it but not the other. The possibility of determining the pressure of nitrogen in a mixture of this gas with hydrogen was demonstrated by Ramsay in 1894. A palladium tube containing the mixture was closed by a manometer and surrounded by an atmosphere of hydrogen at 280° C., at which temperature hydrogen diffuses rapidly through the metal, whereas nitrogen is quite unable to do so. Hydrogen therefore passed in until its partial pressure within was equal to the pressure without—namely, atmospheric. The total pressure now registered exceeded one atmosphere, the excess being due to the nitrogen.

Osmosis and the Gas Laws.—Pfeffer's experiments with sugar solutions showed that:

(i) The osmotic pressure, Π, of a solution is approximately proportional to the concentration C of the solute, provided this is not too high and the temperature is constant. Since the concentration is inversely proportional to the volume of the solution, this is equivalent to the statement that

$$\Pi V = \text{constant}.$$

This expression is analogous to Boyle's Law for gases, and the following results are illustrative:

Osmotic Pressures of Sugar Solutions at 0° C.

(Berkeley and Hartley.)

Sugar.	Concentration, grammes of sugar per litre of solution, C.	Observed Osmotic Pressure, Π (atmos.).	Volume of solution containing one gramme-molecule, M, of sugar. $V=\frac{M}{C}$.	ΠV.
Sucrose (Cane sugar)	2·02	0·134	169·3	22·7
	10·0	0·66	34·2	22·6
	20·0	1·32	17·1	22·6
	45·0	2·97	7·6	22·6
	93·75	6·18	3·65	22·5
Glucose	99·8	13·21	1·804	23·8
	199·5	29·17	0·902	26·3
	319·2	53·19	0·564	30·0
	448·6	87·87	0·401	35·2
	548·6	121·18	0·328	39·7

It will be observed that for low concentrations of sucrose ΠV shows great constancy. But just as gases deviate from the gas laws under high pressures, so do we find that ΠV ceases to be constant for the more highly concentrated solutions, as illustrated by glucose in the foregoing table.

(ii) The osmotic pressure rises with the temperature, and is approximately proportional to the absolute temperature, which suggests that Charles' Law may be applied to substances in solution. This is illustrated by the following data taken from the table on p. 386, referring to a weight-molecular concentration of 0·4 gramme of cane sugar per 1000 grammes of water :

Temperature, °C. .	0	10	25	60
Absolute temp., T .	273	283	298	333
Pressure, Π . .	9·44	9·79	10·30	10·87
$\frac{\Pi}{T}$	0·0346	0·0346	0·0346	0·0327

The quotient Π/T shows remarkable constancy, but it will be noted that the concentration is expressed as weight-molecular and not as volume-molecular, which latter, strictly speaking, the gas laws require. The difference is for present purposes, however, negligibly small.

(iii) Equimolecular concentrations of different substances at the same temperature are found to yield approximately the same osmotic pressure, provided no disturbing action such as association or dissociation takes place. Avogadro's Hypothesis, originally framed for gases, would thus appear to apply to solutions.

If, now, we combine statements (i) and (ii) in the form of an equation, we have :

$$\begin{aligned}\Pi V &= \text{constant} \times T\\ &= R'T.\end{aligned}$$

This equation is identical in form with the ordinary gas equation. But what about the numerical value of R' ?

For a 1 per cent. solution of sucrose at 6·8° C. the osmotic pressure is 0·664 atmosphere, or $0{\cdot}664 \times 76 \times 13{\cdot}6 \times 981$ dynes per sq. cm., and V, the volume which contains 1 gramme-molecule (342 grammes) of sucrose, is 342×100 c.c. Further, $T = 273 + 6{\cdot}8$. Hence,

$$R' = \Pi V/T = \frac{0{\cdot}664 \times 76 \times 13{\cdot}6 \times 981 \times 34200}{(273 + 6{\cdot}8)}$$
$$= 8{\cdot}23 \times 10^7 \text{ C.G.S. units.}$$

This value is in such excellent agreement with that of R in the gas equation as quite to justify van't Hoff's statement that *the osmotic pressure of a substance in dilute solution is equal to the pressure that it would exert if it were converted into a gas at the same temperature as, and made to occupy the same volume as, that of the solution.* In the main, this statement has been fully confirmed by later workers.

The osmotic pressure of a dilute solution of a *salt* is not proportional to the concentration, and compared with a non-electrolyte a molecular quantity of a salt always exerts a much higher osmotic pressure. Dilute solutions of binary salts such as sodium chloride, for example, have an osmotic pressure approximately twice the calculated value. Accordingly, at the time when van't Hoff showed, from his interpretation of Pfeffer's osmotic pressure measurements, that the equation $PV = RT$ holds alike for gases and solutions, he was obliged to introduce into the equation, where electrolytes were concerned, a factor i, where

$$i = \frac{\text{Observed osmotic pressure}}{\text{Calculated osmotic pressure}},$$

the solution being of normal concentration. For salt solutions of this strength, accordingly, the gas equation became $PV = iRT$. i is known as **van't Hoff's factor**. The explanation of this phenomenon, put forward by Arrhenius in 1887, is given by the Theory of Electrolytic Dissociation, or the Ionic Theory, and will receive detailed treatment in a subsequent chapter (see Vol. II).

Finally it should be added that the nature of the membrane has no influence on the magnitude of the osmotic pressure. This we should expect, for the nature of the containing vessel has no influence upon the pressure of a gas within it.

Pfeffer, who carried out numerous experiments with different membranes made of such materials as Prussian blue, copper ferrocyanide and gelatin tannate, found that the magnitude of the osmotic pressure of a given solution apparently varied with the nature of the membrane. This, however, was due to the fact that his membranes were not truly semipermeable, but allowed some of the solute to pass through, so that the apparent osmotic pressures varied according to the extent to which the membrane "leaked."

It is easy to realise why solutions in cells whose walls consist of perfectly semipermeable membranes will yield the same values for their osmotic pressures irrespective of the nature of the membrane. Suppose, for example, they did not do so. Let us imagine that a solution in a cell surrounded by a membrane A possesses a higher osmotic pressure than the same solution surrounded by membrane B.

Upon arranging the system shown in fig 159, if the solution in the central cell is in equilibrium with the solvent in the first cell through the membrane A, then, by our first assumption, it possesses a greater hydrostatic pressure than corresponds to the value of the osmotic pressure in equilibrium with the solvent in cell 3. Some of the solvent will therefore pass out from cell 2 to cell 3 through the membrane B. As soon, however, as the hydrostatic pressure in cell 2 is lowered, more solvent passes in from cell 1 through membrane A. A continuous flow of solvent is thus set up in the system, in the direction from A to B, and as this will continue indefinitely, it may be made to perform work. In other words, we are getting something for nothing. As this is contrary to experience, we cannot but conclude that our initial assumption is wrong and that the two membranes A and B must behave alike. That is to say, provided the membrane is perfectly semipermeable, the osmotic pressure of a solution is independent of the nature of the membrane.

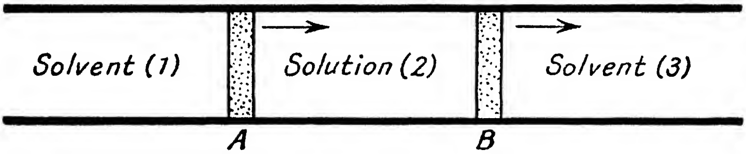


FIG. 159.

Molecular Weight Determination from Osmotic Pressure.— From the analogy already discussed between the gaseous and dissolved states, a close resemblance between the methods of determining molecular weights in these two states is to be expected, and although the resemblance may not at first be obvious, a little consideration makes it clear.

The molecular weight of a gas is obtained by finding what weight of it occupies, at 0° C. and 760 mm., a volume of 22,400 c.c. The measurements made are temperature, pressure and density (or concentration).

With a solution the problem is exactly the same, it being necessary to determine what weight of the substance, dissolved in 22,400 c.c. of the solvent, exerts at 0° C. an osmotic pressure of 760 mm. Again the measurements are temperature, pressure (osmotic) and concentration (or, as it may be termed, the density, or mass of substance per unit volume).

The molecular weight of a dissolved substance could, of course, be obtained without any knowledge of the osmotic pressure laws, for Raoult's empirical laws, which are dealt with later, concerning the depression of the vapour pressure and of the freezing point make this possible. Indeed, the principles and methods introduced by Raoult are extensively used in molecular weight determination in solution. These principles, however, have their theoretical basis in the laws of osmotic pressure, and a measurement of depression of vapour pressure or of the freezing point of a solvent is only an indirect measurement of the osmotic pressure of the substance in solution.

All that we require to know in order to calculate the molecular weight of a solute are the temperature, the osmotic pressure and the concentration. As the results obtained with aqueous solutions of inorganic substances are abnormal, a phenomenon to be discussed later, some measurements made by Morse and Frazer on cane sugar may be used as an illustration. A solution of 6·84 grammes of this substance in 100 grammes of water was found to exert at 15° C. an osmotic pressure of 4·91 atmospheres.

It is required, then, to find the weight of sucrose, which, in 22,400 grammes of water, would exert at 0° C. an osmotic pressure of 1 atmosphere. Since the gas equation is true for dilute solutions, this weight M is given by

$$M = \frac{6\cdot 84 \times (273+15) \times 22{,}400}{273 \times 100 \times 4\cdot 91}$$

$$= 329\cdot 2,$$

as compared with the theoretical value 342 calculated from the formula $C_{12}H_{22}O_{11}$ and the atomic weights of the elements. The error is no greater than is found in many cases when the molecular weights are derived from vapour pressure determinations.

Osmotic Pressure and Temperature.—We have already seen that, in the case of cane sugar, the quotient Π/T shows great constancy. This, however, is not the case with all substances, and a moment's consideration will suffice to indicate that several disturbing factors may be involved. There is the question, for example, of the heat of dilution, Q, of the solution. For a perfect gas the heat of dilution is nil, and P/T is independent of the temperature. In the case of osmosis, Π/T also will only be independent of the temperature when Q is negligibly small. For dilute solutions of cane sugar this is practically the case, and the Law of Charles applies to them.

When, however, Q is not negligible, the manner in which it varies with the temperature affects the form of the equation connecting osmotic pressure with the temperature, and the relationship may be very complex. When a very pronounced evolution of heat occurs on dilution, the value of Π obtained is abnormally high as compared with an ideal solution; the molecular weights calculated from these values of Π are in consequence too low. An apt example is afforded by aqueous solutions of sulphuric acid, for which Q is positive and relatively large. The apparent molecular weight of the acid as calculated from the osmotic pressures of solutions containing from 6 to 70 per cent. of acid is found to *decrease* as the concentration increases, if the effect of Q is neglected. If, however, due allowance is made for Q, the apparent molecular weight rises with increase in concentration, as indeed we should expect.

Other disturbing factors are the possible association or dissociation of the solute and solvent, as also the possibility of combination between the two, yielding, in the case of aqueous solutions, for example, a certain amount of hydration.

Osmotic and Vapour Pressures.—Let us assume that a solution is confined in a cell (fig. 160), one side of which is the piston P and the other a semipermeable membrane A. When the system is in equilibrium the solution is pressing on the membrane and on the piston with a pressure Π. If we push the piston in the direction of the arrow, so that the volume of the solution is reduced by dV, the work done is given by

$$W = \Pi dV. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and dx gramme-molecule of solvent is forced out of the solution through the membrane A.

But the volume of the solution could have been reduced in another way, namely, by isothermal distillation. If p and p' are the vapour pressures of the solvent and solution respectively, the work done is given by the expression

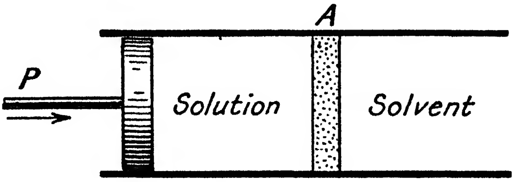


FIG. 160.

$$W = dxRT \log p/p' \quad . \quad . \quad . \quad . \quad (2)$$

The work must be the same in these two reversible processes, so that, combining equations (1) and (2), we have

$$\Pi = \frac{1}{dV} \cdot dxRT \log p/p' \quad . \quad . \quad . \quad (3)$$

Assuming the solution is so dilute that no change in the total volume occurs when dx is added to the solution, we have

$$dV = \frac{M'}{d} \cdot dx \quad . \quad . \quad . \quad . \quad (4)$$

since dV must represent the volume occupied by the dx gramme-molecule of solvent, M' being the molecular weight and d the density of the solvent.

Inserting this value for dV into equation (3) we find :

$$\Pi = \frac{d}{M'} RT \log p/p' \quad . \quad . \quad . \quad . \quad (5)$$

If $p - p'$ is small

$$\log p/p' = \frac{p - p'}{p'} = \frac{p - p'}{p} \text{ (approx.)}$$

and equation (5) simplifies to

$$\Pi = \frac{p - p'}{p' \text{ (or } p)} \cdot \frac{d}{M'} \cdot RT \quad . \quad . \quad . \quad . \quad (6)$$

An example will make this clear : On dissolving 2·47 grammes of ethyl benzoate in 100 grammes of benzene at 80° C. the vapour pressure of the benzene was reduced from 751·86 to 742·60 mm., that is, by 9·26 mm. The density of benzene at 80° C. is 0·8149, and the molecular weight is 78.

Since

$$R = \frac{PV}{T} = \frac{1 \times 22{,}400}{273} = 82{\cdot}1 \quad \text{(p. 40)},$$

we may insert the foregoing values into equation (6) and calculate the value of Π, namely,

$$\Pi = \frac{9{\cdot}26}{742{\cdot}6} \cdot \frac{0{\cdot}8149}{78} \cdot 82{\cdot}1(273+80)$$
$$= 3{\cdot}78 \text{ atmospheres.}$$

Osmotic Pressure and the Boiling Point.—It is usually more convenient to determine the elevation of the boiling point of a solvent on addition of a solute than the vapour pressure depression.

Upon integration, the Clausius-Clapeyron equation (p. 78) gives

$$\log p = -\frac{L}{RT} + \text{constant} \quad . \quad . \quad . \quad (7)$$

where L is the molecular latent heat of evaporation, assumed constant.

If T and T' are the absolute boiling temperatures of solvent and solution respectively, p and p' being the corresponding vapour pressures :

$$\log p/p' = \frac{L}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) . \quad . \quad . \quad . \quad (8)$$

Inserting this into equation (5) we find :

$$\Pi = \frac{d}{M}LT\left(\frac{1}{T} - \frac{1}{T'}\right)$$
$$= \frac{d\,l\,E}{T} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where E is the elevation of the boiling point, namely, $T' - T$, and l is the latent heat of evaporation per gramme, and equal to $\frac{L}{M}$. T' is replaced by T in the denominator.

If l is expressed in gramme-calories, and d refers to 1 c.c., we must multiply the right-hand side of the equation by 1000 and divide by 24·24 to convert the result to litre-atmospheres (p. 20), thus

$$\Pi = \frac{1000}{24{\cdot}24} \cdot \frac{d\,l\,E}{T} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Reverting, by way of illustration, to our previous example, the elevation of the boiling point of pure benzene on the addition of 2·47 per cent. of ethyl benzoate was 0·403° C. The latent heat of evaporation of benzene at 80° C. is 94·0 calories, whence

$$\Pi = \frac{1000}{24{\cdot}24} \cdot \frac{0{\cdot}8149 \times 94{\cdot}0 \times 0{\cdot}403}{(273+80)}$$
$$= 3{\cdot}61 \text{ atmospheres}$$

a figure which differs by about 4 per cent. from that calculated by the previous method, namely, 3·78 atmospheres.

Osmotic Pressure and the Freezing Point.—In a somewhat similar manner it can be shown that

$$\Pi = \frac{dl_m\delta}{T} . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where l_m is the heat of fusion of the solvent and δ the depression of the freezing point on addition of a solute. Thus, the freezing point of benzene (100 grammes) is lowered by 0·840° C. on addition of 2·47 grammes of ethyl benzoate. At its freezing point, 5·5° C., the density of pure liquid benzene is 0·8875 and its latent heat of fusion 29·9 calories. Inserting these data into equation (11), we have :

$$\Pi = \frac{1000}{24{\cdot}24} \cdot \frac{0{\cdot}8875 \times 29{\cdot}9 \times 0{\cdot}840}{(273 + 5{\cdot}5)}$$
$$= 3{\cdot}30 \text{ atmospheres.}$$

How does the Semipermeable Membrane Function?—Several answers have been given to this question. An early assumption was that the membrane acts as a filter, allowing the solvent molecules to pass through the pores, but holding back the larger, and possibly hydrated, molecules of solute. The membrane is struck on both sides by solvent molecules, but fewer free solvent molecules are present on the solution side, so that in unit time more solvent molecules strike the membrane from the solvent side and pass through. This goes on until equilibrium is attained, when, owing to the increased pressure, as many solvent molecules pass from the solution side to the solvent as *vice versa*. This explanation is unsatisfactory, however, for whilst it is true that the pores in a copper ferrocyanide membrane, for example, are exceedingly fine, ranging from 8 to 60 $\mu\mu$ in diameter, the average being from 15 to 20 $\mu\mu$, solute molecules are even smaller. Further, if the process is purely one of mechanical filtration, an explanation has still to be sought for the selective action of certain membranes.

In 1855 Hermite suggested that the membrane is permeable to bodies that dissolve in it, but impermeable to those that do not. The action may be illustrated by taking a cylindrical glass jar, pouring into it some chloroform, on top of this some water and, finally, pouring ether on top of the water. Three layers of liquid are thus produced. On closing and standing it will be observed that the chloroform layer increases in bulk, but the ether layer diminishes. This is due to the fact that the ether is slightly soluble in water, and more so in chloroform ; it therefore passes into solution through the water with the chloroform. The chloroform does not, in turn, pass up into the ether, as it is insoluble in water.

A third suggestion (Callendar, 1908) explains osmotic action on the assumption that the membrane consists of capillaries which function as vapour sieves. That is to say, they are not actually wetted by the liquid, but vapour passes through them. As the solvent has a higher vapour pressure than the solution, its vapour distils into the solution until the hydrostatic pressure is such that the vapour pressure of the solution equals that of the solvent.

CHAPTER XIX.

FUSION OF MIXTURES AND FREEZING POINTS OF SOLUTIONS.

In 1788 Blagden observed that the freezing point of a solution of a salt in water lies below that of water itself, the extent of the depression being proportional to the concentration of the dissolved salt. This is known as **Blagden's Law.** Later workers, notably Raoult (1882 to 1886), studied this phenomenon in greater detail.

Raoult's experiments on freezing points were not confined to solutions of salts in water, but included investigations of other classes of substances dissolved in a variety of solvents. From his results the general conclusion may be drawn that within certain limits, to be considered below, the addition of any substance to a solvent brings about a lowering of the freezing point of that solvent, the extent of the depression increasing with the amount of substance added. This statement, it may be noted, is true only so long as the substance which separates out on freezing is the pure solvent. The solute and solvent must not form solid solutions or compounds with each other.

For present purposes it is convenient to divide solutions into three types, as follows :

Type I. No compounds formed and no solid solutions.
Type II. Compounds formed, but no solid solution.
Type III. No compounds formed, but constituents soluble in both the liquid and solid states.

Type I. No Compounds Formed and No Solid Solutions.—This is the simplest case and may be illustrated by a consideration of what occurs when a dilute solution of a salt—sodium chloride, for example—is cooled from 0° C. downwards. Freezing first occurs at a temperature below 0° C., depending on the amount of salt added, and the solid which separates is pure ice. Hence, by this process, the salt solution left is more concentrated than the original one, and will have a still lower freezing point. By continued cooling, then, the water continuously separates as ice, and the remaining solution becomes more and more concentrated until saturation is reached. Obviously, at this point, separation of ice must also be accompanied by a deposition of salt, and solvent and solute separate out side by side. Moreover, since the concentration of the solution is maintained at a constant value, the freezing point must also remain constant during the separation of ice and salt together. Guthrie (1875), who investigated the continued action of cooling on a solution of sodium chloride, believed that the ice and salt separated together as a compound, to which he gave the name **cryohydrate,** since complete solidification occurred always at $-22°$ C., and the amount of salt present was 23·6 per cent.

The substance separating at the **cryohydric point** (Greek *kruos*, frost; *hudor*, water) or, as it is now frequently termed, for reasons stated on p. 396, the **eutectic point** (Greek *eu*, easily; *tekein*, to melt) is, however, not a compound, but a mixture. This is evident from the following :

(1) The ice can be removed by a simple physical operation such as washing with alcohol.

(2) The heat of solution of the cryohydrate is the same as that of the sum of both components separately.

(3) The density or specific volume is the same as that calculated by the method of mixtures.

(4) Microscopic examination reveals the separate existence of the two components.

The cryohydric temperature, or temperature at which complete solidification occurs, obviously is the lowest temperature to which a solution of sodium chloride can be cooled. All salts dissolved in water behave similarly, the actual cryohydric point depending on the nature of the salt.

Instead of starting with a dilute solution of salt and concentrating it by removal of ice, we may proceed by continuously adding the salt in small quantities at a time, making a determination of the freezing point after each addition. In this way a freezing point curve may be traced (fig. 161), plotting temperature of freezing against concentration. Starting from 0° C., the lower limit of the curve will be reached when the solution is saturated and the cryohydric point is reached. This point must also lie on the solubility curve of the salt in water, so that the cryohydric point is the point of intersection of the freezing point curve and the solubility curve.

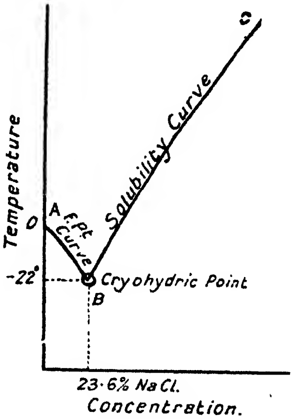


FIG. 161.—Freezing Point Curve of Sodium Chloride in Water.

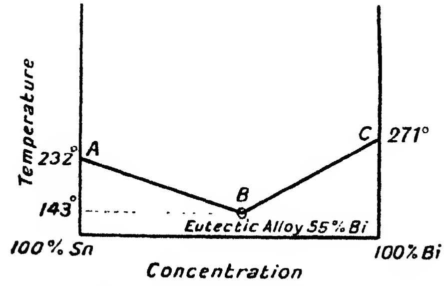


FIG. 162.—Freezing Point Curve, Sn–Bi.

The solubility curve may be regarded as a second freezing point curve, for just as the original freezing point curve represents the series of equilibria at different temperatures between ice and the salt solution, so the solubility curve deals with the equilibria between the solid salt and the solution. On cooling, ice separates out along AB, and salt along CB. The curve CB may be likened, therefore, to the freezing point curve of a solution of water in salt.

The two freezing point curves can also be realised if solutions containing components other than salt and water are studied. Many metal alloys behave exactly like a salt solution when the liquid alloy is cooled. Fig. 162 represents the freezing point diagram for tin and bismuth. If bismuth is continuously dissolved in molten tin, the freezing point of the latter falls gradually until saturation is reached, and then deposition of the two metals at a constant temperature and in constant proportion occurs. This point cannot be termed the cryohydric point, since water is not involved; the general term **eutectic** is employed, the alloy which solidifies here having the **eutectic composition.** For bismuth and tin this eutectic composition is 45 per cent. Sn and 55 per cent. Bi, the eutectic temperature being 143° C. By starting with bismuth and adding tin, a second freezing point curve is obtained ending at the eutectic point as before. Along AB crystals of tin separate when the solution is cooled, along CB crystals of bismuth.

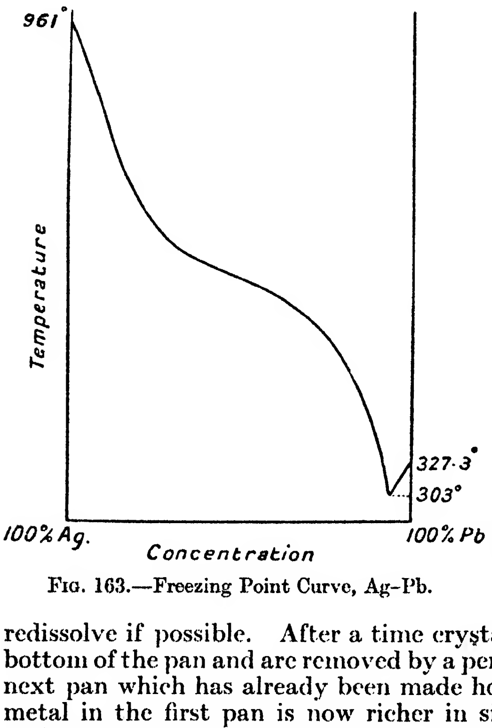
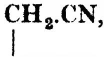


FIG. 163.—Freezing Point Curve, Ag-Pb.

Fig. 163 represents the diagram for lead and silver mixtures. The eutectic temperature is 303° C. and the eutectic alloy contains 2·25 per cent. of silver. This is the basis of **Pattinson's Process** (1833) for the desilverisation of lead. The process is carried out in a series of iron pans each heated over a fire. The lead is melted in the first pan, skimmed and then allowed to cool. As solid lead separates it is pushed beneath the surface of the molten metal so that it may redissolve if possible. After a time crystals of lead accumulate at the bottom of the pan and are removed by a perforated ladle and placed in the next pan which has already been made hot enough to melt them. The metal in the first pan is now richer in silver than before, whilst that in the second pan is richer in lead. The second pan is worked similarly; and so on. By successive crystallisations and transference to series of pans, the original alloy is gradually separated into silver-free lead at one end and an enriched alloy at the other. From a crude lead containing only 10 ounces of silver per ton, an alloy containing from 600 to 700 ounces per ton, or about 1·7 to 1·9 per cent. of silver, is obtained, and this is cupelled. The silver content of the enriched alloy cannot rise beyond 2·25 per cent. by weight.

It will be noticed that the last-mentioned alloy (see following table) has a very low melting point.

In the two systems we have already discussed, namely, Sn–Bi and Pb–Ag, only one liquid phase was present. We have now to consider the case where **two liquid phases** may co-exist. The system water–succinonitrile,  $\begin{array}{l}CH_2.CN\\|\\CH_2.CN\end{array}$, affords a good example (fig. 164). On addition of succinonitrile to the system ice–water at 0° C., the temperature falls to the cryohydric or eutectic point, $-1{\cdot}2°$ C. On raising the temperature

Cryohydric or Eutectic Points.

System.	Eutectic Point, °C.	Approximate Percentage Composition.
NaCl–Water . . .	– 22	23·60 NaCl.
NaBr–Water . . .	– 24	41·33 NaBr.
KI–Water . . .	– 22	52·07 KI.
$NaNO_3$–Water . . .	– 17·5	40·80 $NaNO_3$.
$(NH_4)_2SO_4$–Water . .	– 17	41·70 $(NH_4)_2SO_4$.
NH_4Cl–Water . . .	– 15	19·27 NH_4Cl.
NaI–Water . . .	– 15	59·45 NaI.
KCl–Water . . .	– 11·4	20·03 KCl.
$Pb(NO_3)_2$–KNO_3 . .	+207	46·86 $Pb(NO_3)_2$.
Pb–Bi	+122·7	44·4 Pb.
Sn–Bi	143	45·0 Sn.
Cd–Bi	144	40·8 Cd.
Zn–Bi	248	7·15 Zn.
Bi, Pb, Cd, Sn . . .	+ 71	47·8 Bi, 13·5 Cd, 18·6 Pb, 20·1 Sn.

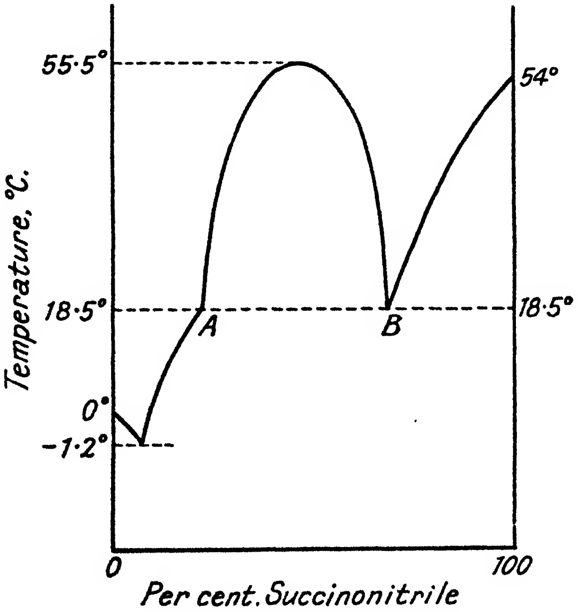


Fig. 164.—System Water–Succinonitrile.

and adding more of the nitrile, the melting point, A, of the latter under water is reached ultimately at 18·5° C. Two liquid phases now appear, the one a solution of water in the nitrile, the other of the nitrile in water. On still further raising the temperature the critical solution point is reached at 55·5° C., above which the nitrile and water are completely miscible in all proportions. On cooling and adding more nitrile the point B is reached at 18·5° C., and then on heating we progress along the fusion curve of the nitrile to the melting point of the pure solid at 54° C.

Type II. Compounds Formed, but No Solid Solutions.—When compounds are formed, for every compound produced, an additional branch containing a maximum point is obtained in the freezing point curve if the compound has a definite melting point under the prevailing pressure. Thus, with lead and magnesium (fig. 165), magnesium separates out between A and B as cooling occurs, but at B the eutectic alloy deposited is found to consist not of pure Mg and Pb, but of Mg and crystals of a new substance. If the eutectic alloy be remelted and more lead added, the freezing point rises and the crystals separating on freezing are neither pure Pb nor Mg, but the new substance. At the maximum point C the compositions of the liquid and the crystals separating are the same, so that at this point also, solidification occurs as a whole and at constant temperature. Since we are dealing at C with only one crystalline form, the point C must represent the melting point of the compound produced, namely $PbMg_2$. Further addition of lead lowers this melting point, crystals of the compound continuing to separate as we pass from C to D, until a second eutectic is reached, representing the new compound and lead. The curve ED is obtained either by remelting this second eutectic mixture and continuing the addition of lead, or by starting out with lead and adding magnesium. The crystals separating along ED are those of lead.

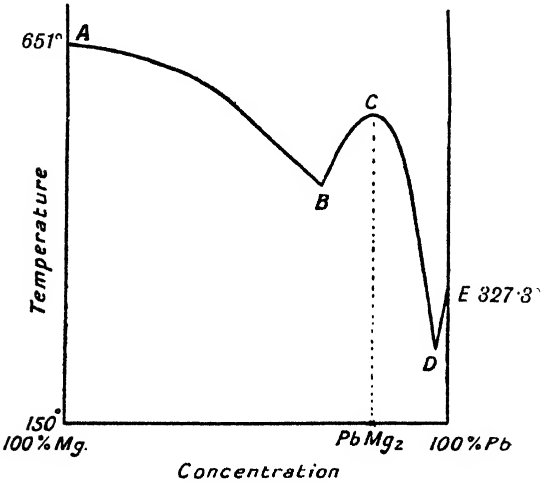


FIG. 165.—Freezing Point Curve, Mg-Pb.

Whenever compounds can be frozen out from solution and the phenomena are not complicated by the formation of solid solutions between the compound and one or other of the single components, an extra branch of the freezing point curve and an extra eutectic point appear on the diagram for each compound formed. The maximum point on each added branch gives the melting point and the composition of the compound. Thus with nitric acid and water, two compounds are formed, namely, $HNO_3.3H_2O$ and $HNO_3.H_2O$ (see fig. 166). With ferric chloride and water, four hydrates, $Fe_2Cl_6.12H_2O$, $Fe_2Cl_6.7H_2O$,

$Fe_2Cl_6.5H_2O$ and $Fe_2Cl_6.4H_2O$, are known, and each possesses a definite melting point. These points are indicated by maximum points on the Fe_2Cl_6–H_2O curve (see fig. 148, p. 367).

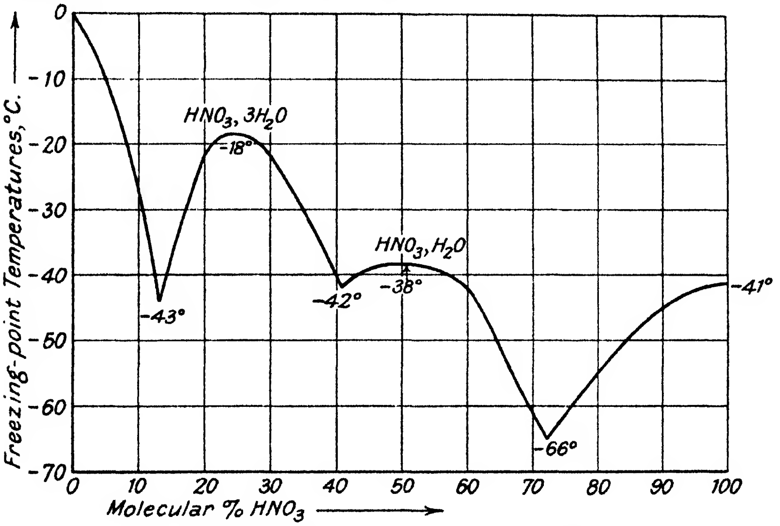


FIG. 166.—Freezing Point Curve of Aqueous Nitric Acid.

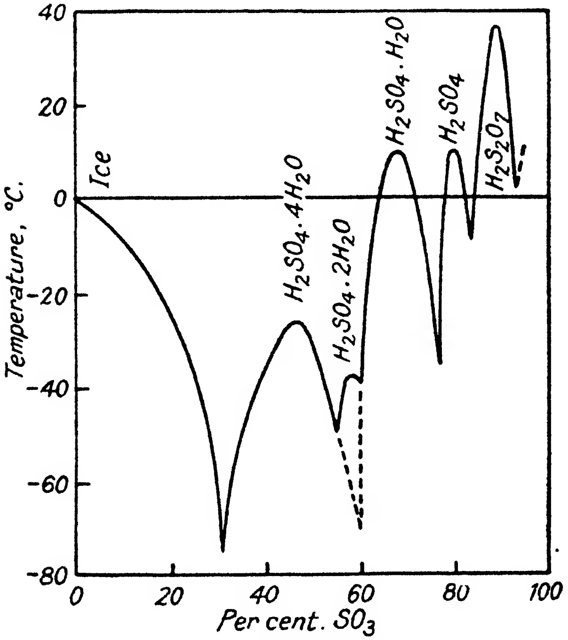


FIG. 167.—Freezing Point Curve for SO_3–H_2O.

Finally, the freezing point curve for sulphur trioxide and water has afforded clear evidence of hydrate formation, as shown in fig. 167.

A study of the freezing point curve is one of the most frequently used means of testing whether or not two substances, when mixed together in the liquid state, unite chemically.

Type III. No Compounds Formed, but Components Soluble in Both the Liquid and the Solid States.—This third type of freezing point curve represents the behaviour of liquid mixtures of substances which are soluble in one another both in the liquid and in the solid state, so that when freezing occurs the crystals deposited contain both constituents, and are thus " mixed crystals " or solid solutions.

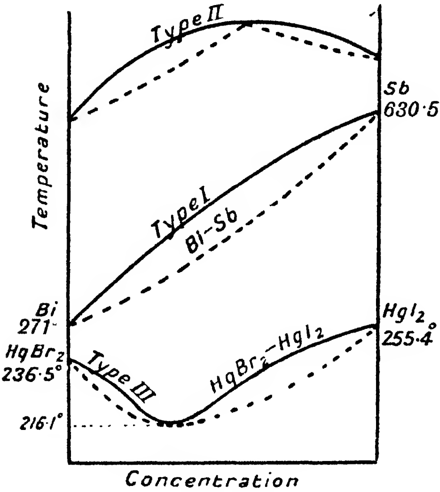


FIG. 168.

If the two substances are soluble in one another in the solid state in all proportions, the freezing point curve takes one of the three forms drawn in fig. 168. Most pairs of inorganic substances follow class I, Bi–Sb, Pt–Au, Ag–Au and Co–Ni providing examples. Mixtures of mercuric bromide and mercuric iodide have a freezing point curve of class III, which exhibits a minimum point. But little is known of examples of class II. It will be noticed that the three types of curves correspond with those which represent the vapour tensions of liquid mixtures (fig. 173).

In order to understand thoroughly the behaviour of mixtures of isomorphous substances, or those which form solid solutions, two curves are necessary, giving the composition of the solid phase (solidus curve) and of the liquid phase (liquidus curve). These curves coincide at the maximum and minimum points.

If the solubility of the two components in the solid state is limited, the freezing point curve is not a continuous line ; a break occurs, and the break is more pronounced the more limited the series of " mixed crystals."

In addition to the three types of freezing point curves already given, cases occur in which compounds are produced and form solid solutions with either or both of the components. The curves for these can be deduced by constructing a full diagram to include the separate curves for the two binary mixtures, namely, compound and component A and compound and component B.

Purification by Fractional Crystallisation or Liquation.—Crystallisation as a means of separating two substances in a state of purity from a mixture is comparatively simple when each component, acting as the solvent, freezes out in the pure state ; but when the substances form " mixed crystals," separation can be effected only by a lengthy repetition of the process, as with fractional distillation, and there are certain cases in which no separation can be brought about. The process necessary will be understood by reference to fig. 169, which shows a portion of the freezing and melting point curves of mercuric bromide and iodide. Since the curves are temperature-concentration curves, it is obvious that the solid separating contains more of the bromide than the remaining liquid. At the temperatures t_1, t_2 and t_3 the concentrations of mercuric iodide in the crystals are represented by A, C and E respectively, and in the liquid by B, D and F. As the temperature falls from t_1 to t_3, both the liquid and the deposited solid vary in composition. If, on the other hand, the solid separating at t_3 be isolated and heated, the temperature must be continuously raised before complete melting is obtained. Starting with crystals of composition E, and applying heat, there will be present at temperature t_2 a liquid of composition D and unmelted solid of composition C. If this still unmelted portion be isolated and heated to t_1, the solid now remaining is still richer in mercuric bromide. By a methodical repetition of these processes many times, on each fraction obtained, uniting portions that are similar in composition, it is possible to obtain finally a specimen of crystals which contains practically no iodide. A mixture of mercuric bromide and iodide can thus be separated into two portions, either bromide and the mixture of bromide and iodide of minimum freezing point, or iodide and the minimum freezing point mixture, according as one starts with a mixture rich in bromide or iodide respectively. Only with a curve of class I (*e.g.* Bi–Sb) can a separation into the two pure constituents be made. Thus, the process is strictly analogous to the distillation of liquid mixtures. If the composition of the mixture be that corresponding to the maximum or minimum point, where the freezing and melting point curves coincide, no separation can be made (unless the pressure be varied), the mixture behaving as a chemical compound of definite melting point.

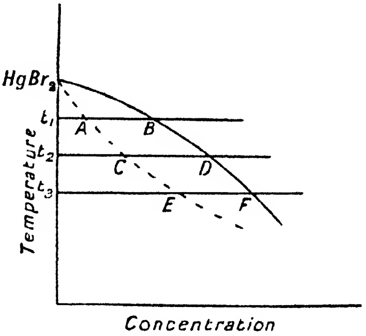


Fig. 169.—Fractional Crystallisation of Isomorphous Mixtures.

Purification by Fractional Crystallisation from Solution.—Fractional crystallisation is a simple matter when two or more salts present in a mixed solution possess widely different solubilities. But if their solubilities are closely similar, the process of fractionation may be long and tedious. Fractionation of the ammonium double sulphates of zirconium and hafnium is frequently used to separate these two closely similar elements. The zirconium salt, $(NH_4)_4Zr(SO_4)_4$, is less soluble than the corresponding hafnium salt, $(NH_4)_4Hf(SO_4)_4$, and after each crystallisation the latter tends to accumulate in the mother liquor and the zirconium salt in the crystals, until ultimately a crop of pure crystals of zirconium salt is obtained on the one hand, and a mother liquor free from zirconium on the other.

The process is even more complicated when the mixed solution contains closely similar salts of several different metals, as, for example, in the case of the rare earths. Fractional crystallisation of salts of the rare earth metals is adopted largely in order to effect the separation of these metals. For example, in separating the elements of the cerium group, namely, lanthanum (atomic number 57), cerium (58), praseodymium (59), neodymium (60) and samarium (62)—element 61 (illinium) is so extremely rare that it need not be considered here—either the magnesium double nitrates, of general formula $3Mg(NO_3)_2 \cdot 2R(NO_3)_3 \cdot 24H_2O$, or the ammonium double nitrates, $2NH_4NO_3 \cdot R(NO_3)_3 \cdot 4H_2O$, are frequently made use of. The different members in each series are isomorphous, crystallising in the trigonal and monoclinic systems respectively. The solubility of the salts increases very slightly as we pass from lanthanum to samarium, but only very slightly with each successive member of the series, so that a very large number of crystallisations may be necessary to obtain any one of the salts in a pure condition. The general procedure is as follows:

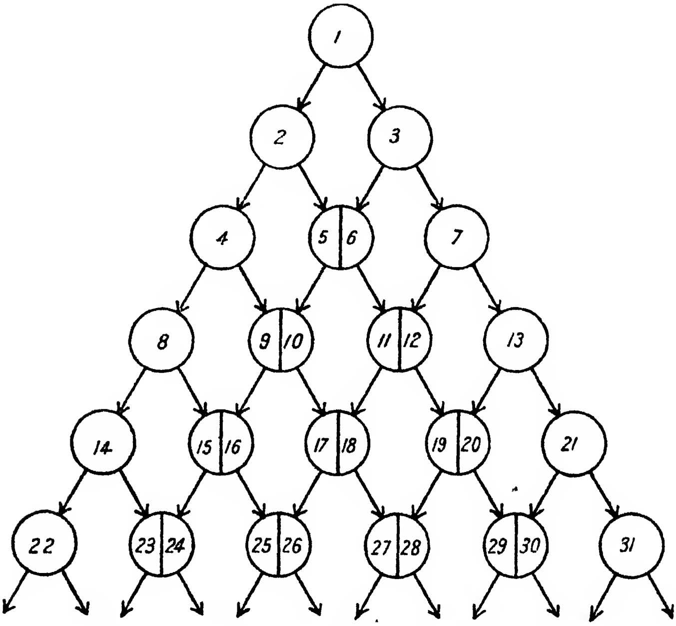


FIG. 170.—Illustrating Fractional Crystallisation.

The initial mixture of salts, from which the cerium may or may not have been removed by chemical methods, contained in some suitable vessel such as a flask or an evaporating dish (1), fig. 170, is crystallised from dilute nitric acid solution, about half the mixture being left in solution. Crystals (2) and mother liquor (3) are thus obtained and separated. Each in turn is re-crystallised. The crystals (2) give place to crystals (4) and mother liquor (5); the mother liquor (3) becomes divided into crystals (6) and mother liquor (7). Liquor (5) and crystals (6) are united into one fraction and this, together with crystals (4) and liquor (7), constitute the three fractions into which the material is now divided. By further crystallisation crystals (4) yield crystals (8) and liquor (9); fraction (5, 6) gives crystals (10) and liquor (11); and liquor (7) supplies crystals (12) and liquor (13). The following combinations are then effected: (9) with (10), and (11) with (12), the method being to pour liquor (13) into a fresh vessel, then liquor (11) on to crystals (12), and finally liquor (9) on to crystals (10).

Resolution into four fractions is thus accomplished. The subsequent operations are closely analogous. In the diagram (fig. 170) the arrows indicate how each fraction is subdivided and the juxtaposition of two numbers represents the mixing of two fractions. By this method the initial mixture is expanded into some 20 or 30 fractions, according to the nature of the mixture, the crystals separating along the even numbers (2), (4), (8), etc., which constitute the " head " fractions of the corresponding horizontal series, the mother liquors being in the direction of the odd numbers (3), (7), (13), etc., which constitute the " tail " fractions. We have now reached the end of the first stage of the process ; but it may be necessary to fractionate many more hundreds of times before we obtain pure fractions of any one salt. The next stage of the process is as follows :

Suppose, for example, that 20 fractions have been prepared, numbered in serial order from (1) to (20), beginning with the least and ending with the most soluble fraction. Each is re-crystallised. The mother liquor from (20) is poured into a new vessel (21), the liquor from (19) into (20), that from (18) into (19), and so on until the liquor from (1) is poured into (2). From (2) to (20) the vessels are heated until the crystals dissolve in the liquids, and then allowed to cool slowly. Fresh solvent is added to (1) for the crystallisation, but (21) is left alone. After crystallisation has occurred, the previous process of decantation is repeated, commencing as before by pouring the liquor from (20) into (21). For the next crystallisation a further quantity of solvent is added to (1), but fraction (21) is still untouched. After a few series of crystallisations fraction (1) has dwindled to a small amount. It is made to miss the next crystallisation. After the decantation of mother liquors, fraction (1) is then added to the crystals in (2), which thus becomes the new " head " fraction. By this time, however, fraction (21) has become sufficiently large to yield a new " tail " fraction (22). The fractionation proceeds as before, until the new " head " fraction (2) has dwindled so much as to require incorporation in (3), and (22) can now yield a new " tail " (23). In this way, as fractions (2), (3), (4), etc. successively disappear, new " tails " (22), (23), (24), etc. appear, so that the number of fractions remains constant. Ultimately a " head " fraction is obtained which consists of the pure, least soluble component. In the example chosen this would consist of the pure lanthanum salt, if the cerium had previously been removed, or of a mixture of the lanthanum and cerium salts, in either case free from the green-coloured praseodymium salt. If cerium is present, it can be removed by oxidation to insoluble ceric hydroxide and the pure lanthanum salt obtained. Proceeding in an analogous manner, samples of each of the praseodymium, neodymium and samarium salts can be isolated in a pure state.

The Freezing Points of Dilute Solutions.—As indicated on p. 394, Blagden and subsequent workers found that the lowering of the freezing point of a solution was proportional to the concentration of the solute, provided always that the substance separating out on freezing was the pure solvent. Raoult made a thorough test of this relationship, using a variety of solvents and including many organic solutes, as well as, in aqueous solution, the salts which previous investigators had studied. Blagden's Law, that the lowering of the freezing point is proportional to the concentration, was found to be true, provided the solutions used were dilute ; and it was further shown by Raoult that when the same solvent is used

equimolecular quantities of different solutes produce equal depressions of the freezing point.

This is **Raoult's Law.**

If a gramme-molecule, M, of the solute is dissolved in a fixed quantity of solvent, say 100 grammes, then the depression of the freezing point is constant, whatever the solute. This constant is termed the **molecular depression,** K, or, alternatively, the **cryoscopic constant** of the solvent. By applying Blagden's Law we see that, if m grammes of solute dissolved in 100 grammes of solvent depress the freezing point by $\delta°$ C.,

$$M : m = K : \delta$$

or

$$K = \frac{M\delta}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Conversely, having once determined the value of K, the molecular weight of a solute in solution may be determined, since

$$M = \frac{Km}{\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Electrolytes depart from these laws of dilute solution just as they do from the laws of vapour pressure (p. 418). The explanation is given in Vol. II.

Since a knowledge of the molecular weights of substances in solution is frequently of great value, we may now pass on to consider how cryoscopic investigations of this character are carried out. As ordinarily practised, the method used contains various devices and improvements introduced by Beckmann, but the essential process is that of Raoult, and consists in measuring the freezing point of a solvent before and after adding a known weight of the substance whose molecular weight is required.

For very dilute solutions, platinum resistance thermometers give the most accurate results. Ordinarily, the Beckmann mercury in glass thermometer, graduated to 0·01°, is employed (fig. 171). This thermometer usually has a scale reading of only 5° to 6°, and to obviate the necessity of having a large number of instruments suitable for different temperatures, the thermometer is so constructed as to be available for use at different temperatures. For this purpose the upper end of the capillary bore opens out into a large reservoir into which mercury can be driven. If, for example, the amount of mercury in the bulb is sufficient to cause the thread to appear on the scale at 50° C., less mercury will be required if the temperature to be measured is 60° C. The instrument accordingly is heated to about 64° C. until the excess of mercury has been driven into the reservoir, and it will be found on cooling that the thread is visible on the scale at 60° C. A slight correction is needed for the varying amount of mercury in the bulb.

The freezing point apparatus (fig. 172) consists of a stout glass tube fitted with a side-tube, and closed at the top by a cork, through which pass the thermometer and stirrer (preferably of platinum). The side-tube, also closed by a cork, serves for the introduction of the substance under investigation. Surrounding the freezing point tube is a wider tube which serves as an air jacket and so prevents too rapid a fall of temperature, and finally we have the cooling bath, which may contain a freezing mixture, water only or other material, according to the freezing point of the solvent. A known weight of the solvent is introduced into the freezing point tube and the freezing point determined, whenever possible, by the method of supercooling. For this purpose the solvent is cooled directly in the cooling bath until solid begins to separate. The tube is then quickly dried, placed in its jacketing tube, the liquid stirred slowly, and the temperature read off when it has become constant. An approximate value for the freezing point thus being obtained, the tube is withdrawn from its mantle and the frozen solvent allowed to melt. It is then replaced in its jacket and the liquid stirred slowly while the temperature falls. When the temperature has fallen to 0·2-0·5° below the approximate freezing point the liquid is stirred more vigorously, when crystallisation commences, and the temperature rises. If crystallisation does not begin, the liquid may be inoculated with a tiny crystal of the solvent. The liquid being stirred slowly, the temperature is read off every few seconds, the thermometer being tapped before each reading. The highest temperature reached is recorded as the freezing point of the solvent. The freezing point should be determined in three independent experiments and the mean value adopted.

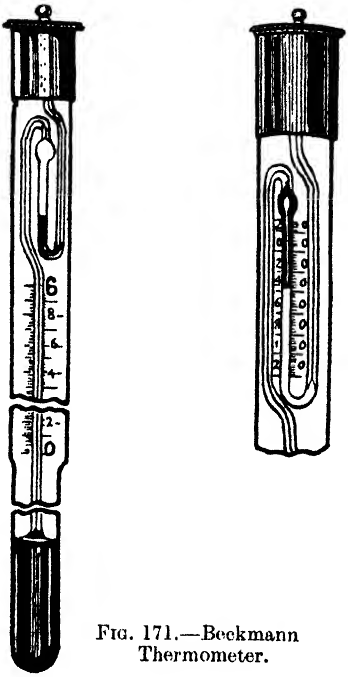


Fig. 171.—Beckmann Thermometer.

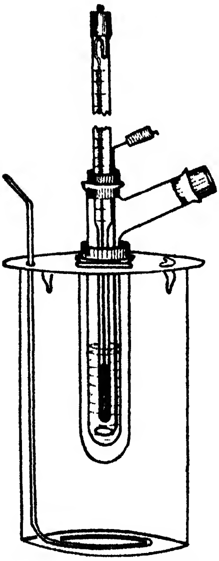


Fig. 172.—Beckmann Freezing Point Apparatus.

A weighed quantity of the solute (usually compressed by means of a small tabloid press) is then introduced through the side-tube into the solvent and allowed to dissolve. The freezing point of the solution is then determined as already described, an approximate value and then four or five accurate values being found.

A further addition of solute and another freezing point determination are then made.

In order that reasonably accurate results may be obtained, the cooling bath should not be more than 3° below the temperature at which the solvent freezes, the amount of supercooling of the solution should not exceed 0·2 to 0·5°, stirring should be uniform and not too rapid, and the thermometer should always be tapped sharply before a temperature is read.

The calculation is made as follows: If w grammes of a substance, dissolved in W grammes of solvent, lower the freezing point of the latter by δ° C., the molecular weight M of the solute is given by

$$M = \frac{100Kw}{\delta W} \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where the value of the constant K depends only on the solvent. K is not merely a number; it represents a definite temperature effect.

In the second column of the following table the values of the cryoscopic constant for some commonly used solvents are given, as determined experimentally:

Cryoscopic Constants.

Substance.	K (Observed).	l_m.	T_m.	$K = \frac{0{\cdot}01985 T_m^2}{l_m}$.
Water . .	18·4	79·7	273	18·56
Acetic acid .	39	43·7	289·6	38·10
Palmitic acid .	44	51·03	335·7	43·8
Stearic acid .	44	47·5	342·3	49·0
Benzene . .	49	29·92	278·5	51·46
Naphthalene .	71	34·66	353·1	71·4
Phenol . .	74	29·06	315·7	68·1
Benzophenone .	95	21·70	320·9	94·2

Van't Hoff's Equation.—The molecular weight of a dissolved substance may, as we have seen, be obtained without any knowledge of the osmotic pressure laws, for Raoult's empirical law concerning the depression of the freezing point makes this possible. Indeed, the principles and methods introduced by Raoult are extensively used in molecular weight determination in solution. The law, however, has its theoretical basis in the laws of osmotic pressure, and a measurement of the depression of the freezing point of a solvent is only an indirect measurement of the osmotic pressure of the substance in solution.

We have already seen (equation (11), p. 392) that

$$\Pi = \frac{dl_m\delta}{T_m} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

which equation connects the osmotic pressure, Π, with the depression of the freezing point and the latent heat, l_m, of the solvent. If V is the volume of solution containing a gramme-molecule of solute,

$$RT_m = \Pi V = \frac{dVl_m\delta}{T_m} \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

Since the molecular concentration of the solute in the solvent is $\frac{m}{M}$ (equation (1)), and dV is the mass of solvent containing 1 gramme-molecule of solute, it follows that

$$dV = \frac{100M}{m}$$

whence

$$RT_m = \frac{100M}{m} \cdot \frac{l_m \delta}{T_m}$$

or

$$\delta = \frac{RT_m^2}{100l_m} \cdot \frac{m}{M} \quad . \quad . \quad . \quad . \quad (6)$$

When $m = M$, δ becomes the molecular depression, K, and writing R as 1·985 calories, equation (6) becomes

$$K = \frac{0{\cdot}01985T_m^2}{l_m} \quad . \quad . \quad . \quad . \quad (7)$$

This is **van't Hoff's equation** and gives us a method of calculating the cryoscopic constant. Reference to the preceding table shows that the observed and calculated values of K are in general very concordant, the values for phenol showing the greatest divergence.

Influence of Concentration.—Theoretically, Raoult's equation (No. 1, p. 404) applies only to exceedingly dilute solutions. At higher concentrations K ceases to be constant. This is unfortunate, since at great dilutions the depression of the freezing point is small and the experimental error is proportionately great. Better results are obtained by taking into consideration the concentration of solute, not in grammes per 100 grammes of solvent, but in gramme-molecules per " molecule " of solution. Thus

$$\delta = \frac{Cn}{N+n} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where C is the new cryoscopic constant, and N and n are the numbers of " molecules " of solvent and solute respectively.

Since $n = w/M$ and $N = W/M'$, where M' is the molecular weight of the solvent, the other letters having the same significance as on p. 406, it is easy to show that equation (8) gives the same result as equation (3) at such great dilution that n is negligible compared with N. Under these conditions

$$\delta = \frac{Cn}{N+n} = \frac{Cn}{N} = CM' \cdot \frac{w}{WM} = K\frac{100w}{WM}$$

and the new cryoscopic constant, C, is related to K as follows (Brown and Bury, 1924):

$$C = \frac{100K}{M'}$$

The following data (p. 408) illustrate the superiority of this method of calculation at high concentrations. The concentrations of benzil have been carried much higher than is usual in ordinary cryoscopic determinations; nevertheless the calculated molecular weight approaches the theoretical value with extraordinary closeness.

Molecular Association.—It has hitherto been assumed that when the solute dissolves in the solvent there is no molecular change in

Molecular Weight of Benzil as Determined Cryoscopically in Nitrobenzene as Solvent.

(Theoretical M.wt. of benzil, 210·1.)

Grammes Benzil per 18·22 grammes Nitrobenzene.	Observed Depression of Freezing Point.	Molecular Weight of Benzil.	
		Raoult's Formula, $K=68{\cdot}7$.	Brown and Bury's Formula, $C=55{\cdot}8$.
0·1238	0·222	210·2	209·3
0·3421	0·605	213·1	210·7
0·9188	1·604	216·0	209·7
1·7351	2·955	221·4	209·6
2·3496	3·924	225·8	209·9

either and no combination between the two. If the value of K for a given solvent is known—and it may be determined either by calculation or by dissolving a substance of known molecular weight, which is believed not to undergo association or any other change in solution, and noting the depression of the freezing point—the value of the apparent molecular weight, M', in solution is given by equation (3). Dividing this by the simplest molecular weight, M, the extent of association in solution is obtained. This method, for example, has been applied to water with the following results :

Molecular Weight and Degree of Association of Water.

(Oddo.)

Solvent.	Melting Point, °C.	Molecular Weight.	Mean Degree of Association.
Phenol	42·7	21·2	1·18
p-Toluidine . . .	44	33·4 to 38·8	2·00
Chloracetic acid . .	63	21·1 to 29·1	1·40
Cyanamide . . .	44	26·1 to 33·0	1·64
Acetic acid . . .	16·7	22·3 to 39·9	1·73

The extent of association is appreciably lower than that as determined by surface tension methods (p. 269), possibly for the reasons given on p. 270.

Separation of the Solute with the Solvent.—Cryoscopic determinations of the apparent molecular weight of iodine dissolved in benzene lead to values ranging from 350 to 360, whereas the formula I_2 requires 2 × 127 or 254, and there is no other evidence of association.

The reason is that iodine yields a solid solution in benzene so that, as the latter freezes out, some iodine separates with it and the concentration of the iodine in the still liquid portion is thus reduced. The fall in temperature therefore is too small and the apparent molecular weight too high.

If the extent to which the solute separates with the solvent is known, the true amount in solution can be calculated. If x is the amount of solute which separates with the solvent, the concentration w in solution is reduced to $(w - x)$, so that equation (3) (p. 406) becomes

$$M = \frac{100K(w - x)}{\delta W} \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

x corresponds to the partition coefficient and can easily be determined experimentally.

If the solute is not associated, the observed molecular weight as calculated from equation (3) is independent of the concentration, although consistently higher than the normal. This is well illustrated by solutions of thiophen in benzene, data for which are as follows :

Conc. of Thiophen (per cent.) . . .	0·51	1·12	2·16	3·25
Apparent Molecular Weight (equation (3)) .	133	133	133	134

When the necessary correction is made for the amount of thiophen separating out with the benzene, the mean molecular weight, as calculated from equation (9), becomes 78·1, the theoretical value being 84·1.

Combination with Solvent.—It sometimes happens that the molecular weight of a solute appears to fall with increasing concentration. This is usually attributed to combination between solute and solvent, the amount of "free" solvent thus being reduced, thereby concentrating the solution and thus abnormally increasing the depression of the freezing point and leading to a low value for the molecular weight.

General Conclusions.—In solution in metallic solvents, such as molten tin, many metals appear to be monatomic. This is, in general, in accordance with their condition in the vapour state as judged by their vapour densities. Thus Heycock and Neville in 1890 found sodium, magnesium, zinc, copper, nickel, lead, palladium, silver, gold and thallium to be monatomic, whilst aluminium appeared to be diatomic. Slight association was observed with calcium, cadmium, mercury, indium and bismuth.

In the case of metallic salts, however, it frequently happens that the vapour state appears to be more complex than the solution. Thus at 1650° C. cuprous chloride molecules are associated to Cu_2Cl_2 (p. 131), but cryoscopic determinations in pyridine, in quinoline and in fused bismuth chloride indicate that in solution the molecules are represented by CuCl.

Non-metallic elements frequently appear to be associated in solution. This is particularly the case with phosphorus, sulphur and selenium. The following data (p. 410) are illustrative. The low value obtained for phosphorus in iodine is attributable to combination between the two.

A few data of general interest in connection with organic solutions

Molecular Weights in Solution as Determined Cryoscopically.

Substance.	Solvent.	Melting Point of Solvent, °C.	Apparent Molecular Formula of Solute.
Sulphur	Methylene iodide	5·7	S_8
	Iodine	113·5	S_8
	Anthraquinone	277	S_8
Selenium	Methylene iodide	5·7	Se_{10}
	Phosphorus	44·1	Se_8
	Anthraquinone	277	Se_8
	Iodine	113·5	Se_2
Tellurium	Iodine	113·5	$Te + Te_2$
Phosphorus	Methylene iodide	5·7	P_4
	Iodine	113·5	P
Iodine	Methylene iodide	5·7	I_2

are given in the table opposite. In the fourth column is given Raoult's cryoscopic constant for the solvent, assuming the solute has its normal, simple molecular weight. In the final column is given the degree of association of each solute, assuming the cryoscopic constant calculated with the aid of van't Hoff's equation for each solvent to be correct.

In general it appears that the degree of association of a solute is determined by several factors, the more important of which may be summarised as follows :

(i) The nature of the groups present in the molecule of the solute. Solutes containing the hydroxyl group are most highly associated, the order of influence of certain other groups being

OH,	COOH,	CN,	NH_2,	CHO,	CO.
(Most influence)					(Least influence)

(ii) The position occupied by these groups in the solute molecule may be important. For example, amongst aromatic substances the *para*-substituted compound is most affected, and the *ortho*-body least. Again, primary alcohols are more highly associated than tertiary alcohols.

(iii) In homologous series the degree of association falls with increasing molecular weight. Thus, for example, ethyl and methyl alcohols, formic and acetic acids, and formamide and acetamide are the most highly associated in their respective series.

(iv) The nature of the solvent also is most important in determining the actual degree of association, as a glance at the foregoing table will show. The dielectric constant of the solvent appears to be an important factor in this connection. Association is very usual in solvents of low

Substance.	Normal Formula.	Solvent.	K (Observed).	Degree of Association, $\frac{K \text{ (calc.)}}{K \text{ (obs.)}}$.
Hexane . .	C_6H_{14}	Benzene (calc. K = 51·46)	51·3	1·00
Naphthalene .	$C_{10}H_8$		50·0	1·03
Chloroform . .	$CHCl_3$		51·1	1·01
Carbon disulphide .	CS_2		49·7	1·04
Carbon tetrachloride	CCl_4		51·2	1·00
Acetone . .	$(CH_3)_2CO$		49·3	1·04
Aniline . .	$C_6H_5NH_2$		46·3	1·11
Phenol . . .	C_6H_5OH		32·4	1·59
Acetic acid . .	CH_3COOH		25·3	2·03
Benzene . .	C_6H_6	Nitrobenzene (calc. K = 68·7)	70·6	0·97
Naphthalene .	$C_{10}H_8$		73·6	0·93
Acetone . .	$(CH_3)_2CO$		69·2	0·99
Acetic acid . .	CH_3COOH		36·1	1·91
Naphthalene .	$C_{10}H_8$	Acetic acid (calc. K = 38·10)	39·2	0·97
Acetone . .	$(CH_3)_2CO$		38·1	1·00
Ethyl alcohol .	C_2H_5OH		36·4	1·05
Phenol . . .	C_6H_5OH		36·2	1·05

dielectric constant; but it also occurs in liquids of high dielectric constant.

Electrolytic solutions behave somewhat differently, the phenomena being complicated by ionisation. This branch of the subject is dealt with in Vol. II.

Examination of Milk.—Elevation of the natural freezing point of milk is sometimes used to detect adulteration with water and even to estimate the extent of adulteration. Pure milk freezes at −0·530° C. or slightly lower, different samples showing remarkably small fluctuations for a natural product. Addition of water raises the freezing point. The first prosecution in the Midlands based on this method occurred in 1931, the milk samples complained of freezing at −0·496° and −0·413° C., indicating that 9 and 31 per cent. of water respectively had been added to the milk.

CHAPTER XX.

VAPOUR PRESSURES OF LIQUID MIXTURES AND SOLUTIONS.

PROBLEMS connected with the vapour pressures of liquid mixtures and solutions present many features of both theoretical and practical importance. We shall confine our discussion to mixtures of two liquids only. Such mixtures may conveniently be divided into three classes, namely :

Class I. Two Immiscible Liquids.—Theoretically we should expect that if two liquids are entirely insoluble in each other, the vapour pressure of the mixture at any given temperature should be the sum of the vapour pressures exerted separately by the two components. This reminds us of Dalton's Law of Partial Pressures, each vapour behaving as an indifferent gas to the other. In practice, of course, no two liquids are absolutely insoluble in each other, and, as we have seen (p. 342), Dalton's Law of Partial Pressures is not absolutely true. Nevertheless, the agreement between theory and practice is often very gratifying. For example, in an actual experiment Young observed that a mixture of chlorobenzene and water distilled at a mean temperature of 90·30° C. under a pressure of 740·2 mm., which figure represents the total vapour pressure of the mixture. The individual vapour pressures at this temperature were 210·59 and 531·56 mm. respectively, the sum of which is 742·15 mm. The result speaks for itself.

Class 2. Two Partially Miscible Liquids.—In this case the vapour pressure of the mixture at any given temperature is usually not the sum of the independent vapour pressures. As an example, a mixture of aniline and water may be considered. The two components are appreciably soluble in each other at 100° C. A mixture of the two was found by Young to distil at 98·75° C. under a pressure of 764·4 mm., which figure represents, therefore, the total vapour pressure. The individual vapour pressures at this temperature were 43·6 and 726·8 mm. respectively, the sum of which is 770·4 mm. or 6 mm. in excess of that observed.

Class 3. Completely Miscible Liquids.—In the case of liquids that can mix in all proportions, the curve representing the relation between the vapour pressure of the solution and molecular concentration, at constant temperature, follows one of three general types, as shown in fig. 173. The simplest is **type I**, lying evenly between the pressure values for the separate constituents and in the limit a perfectly straight line, so that the vapour pressure admits of calculation if the composition of the mixture is known. The more closely alike in chemical and physical behaviour the two liquids are, the more closely does the vapour pressure curve of their mixtures conform to this type. Examples are afforded by

Water and methyl alcohol.
Ethyl chloride and ethyl bromide.
Chlorobenzene and bromobenzene.
Liquid nitrogen and liquid oxygen.

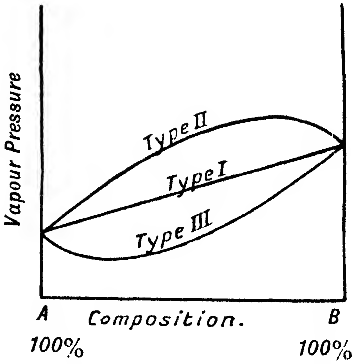


FIG. 173.—Vapour Pressure - Molecular Concentration Curves for Completely Miscible Liquids.

Van der Waals (1900) considered that this relationship would hold provided

(*a*) the critical pressures of both liquids are identical ; and

(*b*) the molecular attractions may be represented by the formula

$$a_{AB} = \sqrt{a_{AA} \times a_{BB}}$$

where a_{AB} represents the attraction between a molecule of substance A and one of B, a_{AA} that between two molecules of A, and a_{BB} that between two molecules of B.

The vapour pressure of a mixture of A and B containing x per cent. gramme-molecules of A, and hence $(100 - x)$ per cent. gramme-molecules of B, can be calculated for any given temperature from the formula :

$$100p = xp_A + (100 - x)p_B \quad . \quad . \quad . \quad (1)$$

where p is the vapour pressure of the mixture and p_A, p_B, that of component A and component B respectively. The boiling points of such mixtures, under a given pressure p, can be calculated in the following manner, provided we know the vapour pressures of each component over the necessary range of temperature. Equation (1) may be written

$$x = \frac{100(p_B - p)}{p_B - p_A} \quad . \quad . \quad . \quad . \quad (2)$$

and the value of x calculated for a series of temperatures for which the values of p_A and p_B are known. By plotting x against the temperature, the curve obtained by connecting up the points gives the desired connection between the molecular composition of the mixture and the boiling point under pressure p.

In fig. 174 are given curves connecting the vapour pressures of aqueous solutions of several alcohols with the molecular concentrations. For the sake of convenience the temperature chosen for each mixture is such that the vapour pressure of the alcohol is 400 mm. The curve for methyl alcohol and water shows only a very slight convexity upwards and closely approximates to the ideal type I (fig. 173). With ethyl alcohol solutions the curvature is more pronounced, whilst *n*-propyl and *iso*butyl alcohols with water yield curves with distinct maximum values, corresponding to **type II** (fig. 174). There is thus a gradual passage from type I to type II as the difference in properties between the two components of the mixture becomes greater.

For binary mixtures of type II:

$$a_{AB} < \sqrt{a_{AA} \times a_{BB}} \quad . \quad . \quad . \quad . \quad (3)$$

and

$$100p > xp_A + (100 - x)p_B \quad . \quad . \quad . \quad (4)$$

The greater the difference between a_{AB} and $\sqrt{a_{AA} \times a_{BB}}$, the more pronounced is the convexity of the curve.

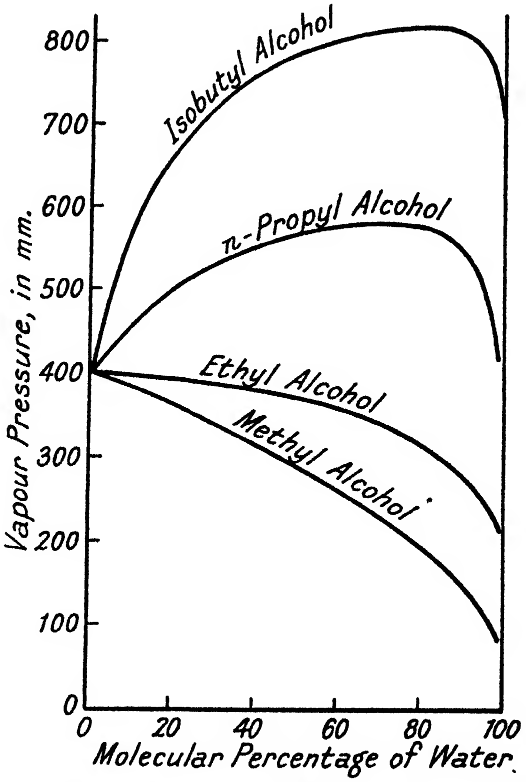


FIG. 174.—Vapour Pressure-Molecular Concentration Curves for Aqueous Solutions of Alcohols.

Curves of the nature of **type III** show a minimum value for the vapour pressure. These are less usual, and in most cases one of the components is acid whilst the other is basic. Examples are afforded by

Water and an acid, *e.g.*, formic, nitric, hydrochloric or hydrobromic acid.
Methyl ether and hydrochloric acid.
Pyridine and formic or acetic acid.

For binary mixtures of this type

$$a_{AB} > \sqrt{a_{AA} \times a_{BB}} \quad . \quad . \quad . \quad . \quad (5)$$

and

$$100p < xp_A + (100 - x)p_B \quad . \quad . \quad . \quad . \quad (6)$$

A fourth type is theoretically possible, namely, one in which both a minimum and a maximum vapour pressure occur. This has not as yet been realised experimentally.

Solutions which have an identical vapour pressure at a given temperature are termed **isopiestic** (Greek *isos*, equal; *piezo*, I press).

Determination of the Boiling Point of a Mixture.—This is conveniently carried out with the aid of an apparatus such as that shown in fig. 175. The thermometer T, surrounded by a guard tube, perforated at A, is supported in a flask fitted with a side-tube and condenser. B is connected with an exhaust and compression pump, and also to a gauge which enables the pressure to be determined. The guard tube prevents the condensate returning from the reflux condenser coming into contact with the thermometer.

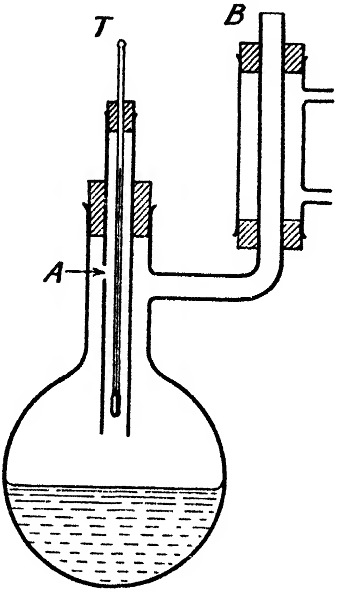


Fig. 175.—Boiling Point Apparatus for Miscible Liquids (Young, 1902).

Azeotropic Mixtures.—A solution boils when its total vapour pressure equals the external pressure. The composition of the vapour which passes over depends on the character of the liquids mixed. Thus, with liquids giving the curve of type II, the vapour pressure of any mixture is always greater than that of the component in excess of what is required to form the mixture of maximum vapour pressure. Therefore, when such a solution is distilled, there is no separation into the two components; the liquid which comes over first as distillate is a mixture of the two components, and the residue continually approximates in composition to the component in excess. Thus, the boiling points of water and propyl alcohol respectively are 100° C. and 97·2° C. at 760 mm., but mixtures may distil at temperatures below 97·2° C. For instance, the mixture containing 71·7 per cent. by weight of propyl alcohol corresponds with the maximum point on the vapour pressure curve for 87·7° C., and at that temperature its vapour pressure is 760 mm. Hence the mixture distils as a whole at 87·7° C. without change of temperature or composition. Any two substances giving a curve of type II give what is known as a "constant boiling mixture" or mixture of minimum boiling point. Such mixtures were once thought to be compounds, but with alteration of the pressure the compositions of the distillate and residue were found to vary, thereby characterising the liquids as mere solutions.

Liquid mixtures giving a vapour pressure curve of type III distil in such a way that the distillate first coming over is mainly the component in excess. The residue, therefore, continually approximates in composition to the mixture of lowest vapour pressure, and eventually there distils a second type of constant boiling mixture—namely, a mixture of maximum boiling point.

Solutions such as these, that possess a constant boiling point, whether maximum or minimum, are termed **azeotropic** (Greek *a*, not; *zeein*, to boil; *tropos*, direction) **mixtures** (Wade and Merriman, 1911) or, less frequently, **hylotropic** (Greek *hule*, matter) **mixtures** (Ostwald).

Hitherto we have considered binary mixtures only. Many ternary azeotropic mixtures of minimum boiling point are also known; typical examples are afforded by several of the lower fatty alcohols with benzene and water.

In the following table the compositions and boiling points under a pressure of 760 mm. of a few typical azeotropic binary mixtures are given:

Azeotropic Mixtures.

Type.	Component A.	Component B.	Boiling Point, °C.	Percentage of A by weight in Mixture.
II. Minimum boiling point.	Water	Ethyl alcohol	78·15	4·43
	,,	*n*-Propyl alcohol	87·72	28·30
	Ethyl alcohol	Benzene	68·24	32·37
	Acetic acid	,,	80·05	2
	Carbon disulphide	Ethyl acetate	46·1	97
	Pyridine	Water	92·6	57
III. Maximum boiling point.	Water	Nitric acid	120·5	32
	,,	Hydrochloric acid	110	79·76
	,,	Hydrobromic acid	126	52·5
	,,	Formic acid	107·2	22·5
	Acetone	Chloroform	64·7	20
	Formic acid	Pyridine	149	18

Standard solutions of hydrochloric acid for volumetric analysis are sometimes prepared by boiling aqueous solutions of the acid under a known pressure until the temperature reaches a constant value. The composition of the resulting mixture is known, and with suitable dilution a standard solution is obtained.

Distillation.—The composition of the distillate depends upon the nature of the liquids in the mixture. If two liquids are completely immiscible, boiling takes place when the sum of their vapour pressures equals the external pressure, and distillation proceeds, yielding a distillate of constant composition until one of the liquids disappears from the original mixture. This is the principle underlying **steam distillation,** which is used largely in organic chemistry. A familiar example is afforded by the system nitrobenzene–water, which boils at 99° C. under a pressure of one atmosphere. The vapour pressures of nitrobenzene and water at this temperature are 27 and 733 mm. respectively, and the molecular weights 123 and 18. The relative amounts of nitrobenzene and water in the vapour, and therefore also in the distillate, are given by the ratio

$$\frac{\text{Nitrobenzene}}{\text{Water}} = \frac{27 \times 123}{733 \times 18} = \frac{1\cdot0}{4\cdot0} \quad \text{(approx.)}.$$

One-fifth of the total distillate, therefore, is nitrobenzene, although at the temperature of distillation the vapour pressure of the nitrobenzene is only one twenty-seventh that of water. This is due to the low molecular weight of water, which is thus an excellent liquid for the purpose.

If two liquids are partially miscible, a distillate of definite composition is obtained until one of the layers disappears from the original solution; distillation then proceeds as with completely miscible liquids.

In so far as completely miscible liquids are concerned, it is only with liquids giving a curve of the first type that separation into the two components is theoretically possible. The distillate always contains more of that component possessing the higher vapour pressure and obviously the residue more of the other component. The boiling point steadily rises, reaching in the limit that of the component with the lower vapour pressure.

The distillation of binary mixtures of types II and III has already been discussed (p. 415).

Fractional Distillation.—Even when the liquids have a vapour pressure curve of type I, perfect separation is, in practice, impossible. If the distillate first obtained be redistilled or separated again into distillate and residue, the second distillate will be richer than the first in the more volatile component; and further treatment of the first residue in similar manner will leave a residue of the second component in a still purer state. By continuous repetition of these processes, separation may be made almost complete. Or, instead, the distillate may be collected in a number of separate receivers, in which case the first runnings will be very rich in one component, and the residue rich in the second component. Such a process is known as fractional distillation and, in principle, bears a considerable resemblance to fractional crystallisation (p. 400). If the mixed vapours be passed up a column, or through a still-head consisting of a series of bulbs, and thereby cooled, the higher boiling component is condensed more than the other, so that the vapour passing out of the head of the column consists mainly of the lower boiling component. Fractional distillation is used largely in chemistry as a method of purification.

Vapour Pressures of Dilute Solutions.—The preceding sections have been concerned with the vapour pressures of solutions of any concentration, and it has been seen that when dissolution occurs the pressure of the mixed vapours frequently is less than the sum of the separate pressures. When the solute is non-volatile, the vapour pressure of the solution is always less than that of the pure solvent. The earliest investigations on the vapour pressures of solutions dealt with non-volatile solutes. Thus, von Babo in 1848 discovered that the ratio p'/p, where p' and p are the vapour pressures of an aqueous solution and of water respectively, is independent of the temperature, and Wüllner, in 1856, found that the lowering of vapour pressure produced by a non-volatile solute was proportional to the concentration. These regularities were tested further by various workers, but most thoroughly by Raoult (1886 to 1890), who used a variety of solvents in addition to water, and many types of solute He found von Babo's Law to be true, and, for solutions which were not concentrated, Wüllner's Law also. Much more striking than these regularities was Raoult's discovery that the molecular lowering of vapour pressure of any one solvent is the same for different substances. The laws regarding the vapour pressure of dilute solutions may therefore be stated as follows:

1. The ratio of the vapour pressure of the solution to that of the solvent is independent of temperature (von Babo's Law).
2. The lowering of vapour pressure (for a non-volatile solute) is proportional to the concentration at constant temperature (Wüllner's Law).
3. Equimolecular quantities of different substances dissolved in a fixed quantity of the same solvent produce equal depression of the vapour pressure, provided the temperature remains constant.

The **molecular depression of vapour pressure** is a constant, C, defined by the equation

$$C = \frac{p - p'}{p} \cdot \frac{M}{m} \qquad . \quad . \quad . \quad . \quad (7)$$

where M is the molecular weight of the solute, m the amount of it per 100 grammes of solvent, and p and p' the vapour pressures of the solvent and solution respectively.

Raoult found that the relative depression $\left(\frac{p-p'}{p}\right)$ is equal to the ratio of the number of molecules of solute (n) to the total number of molecules present in solution, *i.e.*

$$\frac{p - p'}{p} = \frac{n}{N + n} \qquad . \quad . \quad . \quad . \quad (8)$$

where N is the number of molecules of the solvent. For dilute solutions this reduces to

$$\frac{p - p'}{p} = \frac{n}{N} \qquad . \quad . \quad . \quad . \quad . \quad (9)$$

with sufficient accuracy. This is the mathematical expression of **Raoult's Law.** Owing to ionisation (see Vol. II), acids, bases and salts give abnormal values for the molecular depression and do not follow Wüllner's Law.

We can derive Raoult's empirical law from theoretical considerations. If n gramme-molecules of solute dissolve in W grammes of solvent, then, applying the gas laws to the solution :

$$\Pi V = nRT \qquad . \quad . \quad . \quad . \quad . \quad (10)$$

that is

$$\Pi = \frac{nRT}{V}$$

$$= \frac{ndRT}{NM'} \qquad . \quad . \quad . \quad . \quad . \quad (11)$$

since $V = W/d$, d being the density of the solvent, and $W = NM'$, where N is the number of solvent molecules of molecular weight M'.

Combining this with equation (6) (p. 391) connecting the osmotic pressure with the vapour pressure, we find

$$\frac{p - p'}{p} \cdot \frac{d}{M'} \cdot RT = \frac{ndRT}{NM'}$$

or

$$\frac{p - p'}{p} = \frac{n}{N}$$

which is Raoult's Law (equation (9)).

Molecular Weight by the Depression of Vapour Pressure.—Raoult's Law of depression of vapour pressure for dilute solutions of non-volatile solutes (equation (9)) may be written

$$\frac{p-p'}{p}=\frac{wM'}{WM} \quad . \quad . \quad . \quad . \quad (12)$$

where w is the weight of the solute dissolved in W grammes of solvent, the other letters having the same significance as before. Clearly M can be found from measurements of the vapour pressure.

The method is not used very extensively. Two sets of bulbs are connected in series, the first set containing the solution, the second solvent only, all being kept at constant temperature. If now a current of dry air is bubbled through the liquids, it will take up an amount of vapour proportional to the vapour pressure. From the first set it will remove a quantity (which can be arrived at by weighing before and after the experiment) proportional to p', and from the solvent, which has a higher vapour pressure, a further quantity proportional to the difference of vapour pressure, $p-p'$. The total amount removed is thus proportional to p. Hence, by substituting these values, and knowing the concentration of the solution, the molecular weight of the solute can be found.

Ramsay, in 1889, made a series of direct determinations of the depression of the vapour pressure of liquid mercury at the boiling point, *c.* 357° C., produced by dissolving various metals in it. In calculating the molecular weights of the metals it was assumed that the mercury was monatomic, so that M' in equation (12) was 200. The apparatus used is shown diagrammatically in fig. 176. A U-tube containing the mercury or amalgam was suspended in a bath of mercury vapour. The shorter end of the U-tube was closed and the other end connected with a gauge so that the pressure could be altered slightly and various separate readings of pressure taken. A source of error was found to lie in the tendency of the curved surface or meniscus in the closed limb to differ from that in the open limb, but the general concordance of the results was regarded as an indication that the error was not serious. The following metals were found to be monatomic: lithium, sodium, magnesium, zinc, cadmium, gallium, tin, lead, manganese, silver and gold. Antimony and aluminium gave high results, suggesting slight association, possibly to Sb_2 and Al_2, as also did lead and tin in the more concentrated solutions. Low values were obtained with calcium, barium, potassium and thallium, as also with high concentrations of sodium. As atomic dissociation is out of the question, it appears

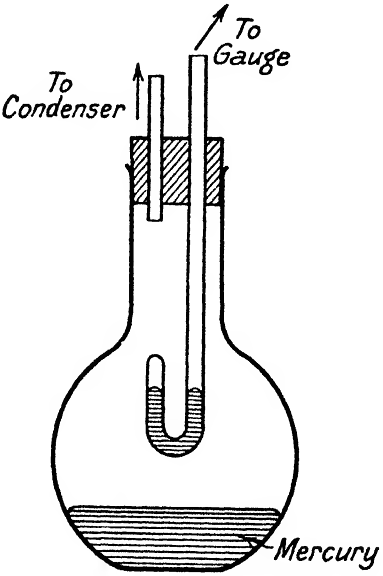


FIG. 176.—Ramsay's Mercury Molecular Weight Apparatus.

probable that a certain amount of combination with the solvent had taken place (compare p. 409). It is instructive to compare these results with those obtained for the molecular weights of metals dissolved in molten tin, as determined by Heycock and Neville by the freezing point method (p. 409).

MOLECULAR WEIGHT FROM THE ELEVATION OF THE BOILING POINT.

Instead of measuring the depression of vapour pressure, it is more usual to determine the elevation of boiling point which, for dilute solutions, is proportional. For, in fig. 177, suppose the three curves represent the vapour pressure of the solvent I, of a solution II, and of a more concentrated solution III. At a common pressure indicated by the line ABC, the boiling points are t_1, t_2 and t_3, such that $t_2 - t_1$ (AB) is the elevation for the first solution, and $t_3 - t_1$ (AC) for the second solution. If dilute solutions only are considered, the curves are very short, and may be considered straight and parallel.

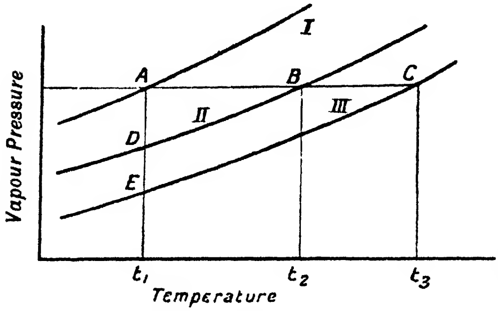


FIG. 177.—Showing Elevation of Boiling Point Proportional to Lowering of Vapour Pressure.

Hence

$$AC : AB = AE : AD,$$

or, the elevation of boiling point is proportional to the depression of vapour pressure.

The molecular weight of the solute is calculated from a formula very similar to that used for freezing point measurements, viz.

$$M = \frac{100Cw}{EW}$$

where E is the elevation of the boiling point and C is the molecular elevation. The constant C in this equation may, like the corresponding freezing point constant, be calculated from a theoretical equation, namely,

$$C = \frac{0{\cdot}01985T^2}{l}$$

where T is the boiling point (absolute) of the solvent and l its latent heat of vaporisation in gramme-calories per gramme (see p. 82).

For some common solvents the following are values of the constant C, that for ammonia being the lowest known :

Ebullioscopic Constants.

Chloroform	39·0	Acetone	17·0
Benzene	27·0	Ethyl alcohol	11·7
Carbon disulphide	23·7	Water	5·2
Sulphur dioxide	15·0	Ammonia	3·4

The foregoing process gives results which should not vary more than ± 5 per cent.

Beckmann's Method.—A convenient form of apparatus for general laboratory use is shown in fig. 178. The boiling point tube A has two side-tubes t_1 and t_2. Through t_1, which is closed by a ground-glass stopper, the substance under investigation is introduced as required. The tube t_2 is longer than t_1, and carries a water condenser to return condensed vapour to the boiling point tube, and an upright tube containing fused calcium chloride, giving access to the air. A stopper at V carries the Beckmann thermometer, which dips into a known weight of the solvent.

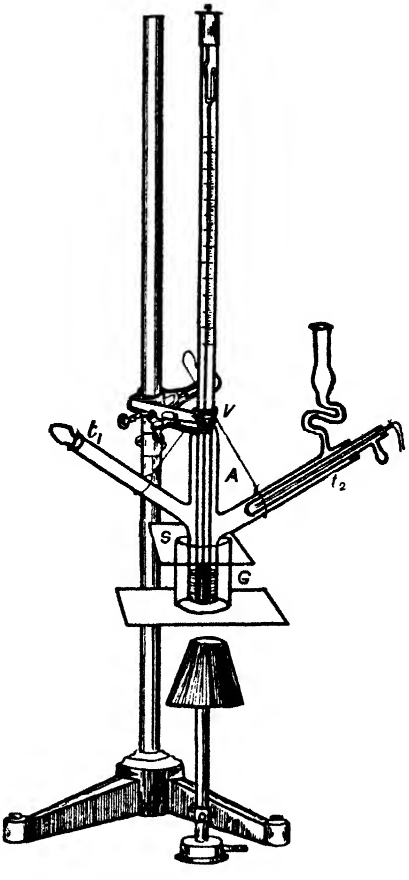


Fig. 178.—Beckmann's Boiling Point Apparatus.

The boiling point tube stands on a square of asbestos millboard, and is protected from cooling effects by surrounding it with a cylindrical glass mantle G containing air, a square of mica, S, cutting off radiant heat and hot-air currents from the exposed part of the thermometer. As a source of heat a small gas flame or an electrically heated coil may be used; in the former case, superheating is avoided by introducing glass beads, garnets, pieces of granite, or, best of all, small pieces of platinum foil bent into the form of tetrahedra.

The boiling point of the solvent is first noted. Some little time is generally needed before the temperature becomes steady to within 0·01° C. When this condition has been attained, the temperature is noted and the height of the barometer read. The apparatus is then allowed to cool a few degrees before the introduction (best in the form of a small pastille) of a known weight of the substance, and afterwards the measurement of boiling point is repeated with the solution. Several additions of material may be made and readings taken. The boiling points should be corrected for variations in barometric pressure during the experiment.

The Landsberger-Sakurai Method.—Instead of heating the liquid either by a flame or by electrical means, it can be raised more rapidly to its boiling point by passing in vapour of the solvent. Sakurai (1892) first used this method in molecular weight determinations, and the same principle is adopted in the better known Landsberger method (1898). The method, as used by the latter, was not intended to give results of great accuracy, but the improvements introduced by Turner

(1910) provide a means of obtaining accurate results at a greater speed than is possible with the ordinary Beckmann apparatus. The latest modification (fig. 179), employed by Turner and Pollard (1913), consists of the molecular weight tube AB fitting at a ground-glass joint *b* into the boiler CD, which also serves as a constant temperature jacket. Vapour passes from the boiler through E and issues through two perforations at F into the liquid whose boiling point is being measured. From AB vapour escapes through KL into a condenser, connection being made at the ground-glass joint *c*. Into the molecular weight tube a ground-glass stopper with two tubulures fits at *a*, one tubulure providing the vapour exit, the other an entrance for a short-stemmed Beckmann thermometer.

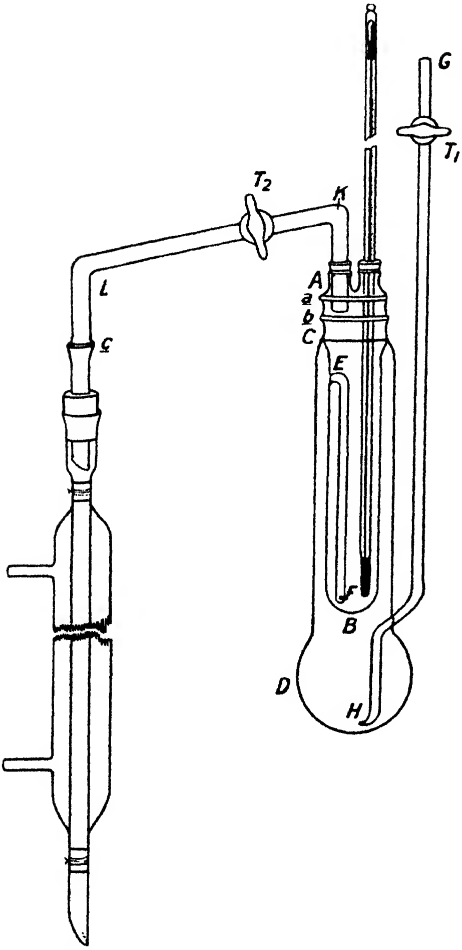


FIG. 179.—Turner and Pollard's Modification of the Landsberger-Sakurai Apparatus.

In carrying out a determination, the molecular weight tube, together with the stopper, vapour exit tube and thermometer, is weighed and a small but undetermined quantity of solvent then added, a second and larger quantity being placed in the boiler with two or three pieces of porous pot to induce steady boiling. Vapour passes into the liquid in the molecular weight tube, during which process the tap T_1 is usually kept closed, and by its condensation raises the temperature to the boiling point, indicated by the constancy of the thermometer reading. Most of the solvent is now returned to the boiler, a known weight of the substance to be tested is placed in the tube, and the process repeated. After reading the temperature, the apparatus is quickly disconnected and the tube, with its attachments and contents, again weighed, T_2 being closed. The weight, less that of the apparatus and solute added, gives the quantity of solvent present. By connecting the apparatus again, and continuing the passage of vapour, a series of readings at different concentrations can be made. It will be noted that in this process the amount of solvent is increased, whereas in the Beckmann method the amount of solvent is fixed, and that of the solute varied as desired.

Consideration of the Results.—The results obtained by ebullioscopic methods for the molecular weights of solutes in general closely resemble those obtained by cryoscopic methods ; they are affected also by closely analogous factors, such as concentration, combination with the solvent, dissociation and association. The value of the ebullioscopic constant, *C*, can be calculated with the aid of van't Hoff's equation, or can be determined experimentally by dissolving a substance of known molecular weight, which does not undergo association or any other change in solution, and noting the elevation of the boiling point. Once *C* is known the molecular weight of a given substance can be determined, and hence its degree of association ascertained, as already explained for cryoscopic methods. A few typical results are given in the two following tables:

Molecular Weights in Solution as Determined Ebullioscopically.

Substance.	Solvent.	Boiling Point of Solvent, °C.	Apparent Molecular Formula of Solute.
Sulphur	Iodine	184·4	S_7
	Diphenyl	255	S_8
	Disulphur dichloride	138	S_8
Selenium	Iodine	184·4	$Se + Se_2$
	Diphenyl	255	Se_8
Tellurium	Iodine	184·4	$Te + Te_2$
Phosphorus	Iodine	184·4	P
	Carbon disulphide	46·3	P_4
Nitrogen sulphide	Carbon disulphide	46·3	N_4S_4
Disulphur dichloride	Carbonyl chloride	8·2	S_2Cl_2
Sulphuryl chloride	Sulphur dioxide	−10·0	SO_2Cl_2
Aluminium chloride	Ether	34·5	$AlCl_3$
Ferric chloride	Ether	34·5	$FeCl_3$
	Ethyl alcohol	78·5	$FeCl_3$
Ferrous chloride	Pyridine	115·4	$FeCl_2$
Aluminium bromide	Bromine	58·8	Al_2Br_6
Cuprous chloride	Pyridine	115·4	$CuCl$
	Quinoline	241	$CuCl$
Cuprous bromide	Pyridine	115·4	$CuBr$
Cuprous cyanide	Pyridine	115·4	$Cu_2(CN)_2$
Stannous chloride	Ethyl sulphide	92·6	$SnCl_2$
	Pyridine	115·4	$SnCl_2$
	Urethane	184	$SnCl_2$
Arsenic trichloride	Carbonyl chloride	8·2	$AsCl_3$
Antimony trichloride	Carbonyl chloride	8·2	$SbCl_3$

Association in Solution as Determined Ebullioscopically.

Substance.	Normal Formula.	Solvent.	Boiling Point of Solvent, °C.	Association Factor.
Phenol . .	C_6H_5OH	Ether	34·5	1·0
Benzoic acid .	C_6H_5COOH	Benzene	79·6	2·0
		Ether	34·5	1·0–1·2
		Carbon disulphide	46·3	2·0–2·2
Tartaric acid .	$(CHOH)_2(COOH)_2$	Ethyl alcohol	78·5	1·0
Mandelic acid .	$C_6H_5.CHOH.COOH$	Water	100·0	1·0
		Benzene	79·6	1·4–1·7
Acetamide .	CH_3CONH_2	Acetone	56·1	1·1–1·2
Acetanilide .	$C_6H_5.NH.COCH_3$	Chloroform	61·2	1·3
		Benzene	79·6	1·5
Urea . .	$CO(NH_2)_2$	Ethyl alcohol	78·5	1·0
Aniline . .	$C_6H_5NH_2$	Ether	34·5	1·0
Naphthalene .	$C_{10}H_8$	Ethyl alcohol	78·5	1·1–1·2

The effect of **concentration** is well shown by the following data for the apparent molecular weight of phosphorus dissolved in carbon disulphide :

Grammes Phosphorus per 100 grammes CS_2	1·581	3·723	7·44	10·84	18·86
Apparent Molecular Weight ($P_4 = 124$)	129	134	142	150	170

In salts the degree of association depends both on the **positive and negative radicals**, an increase in the mass of the positive radical, when a series of similar salts is considered, bringing about a decrease in the degree of association. Thus, in chloroform solutions, each containing 0·025 gramme-molecule of solute in 100 grammes of solvent, tetraethylammonium bromide has an approximate molecular formula of $[(C_2H_5)_4NBr]_{7\cdot2}$, and tetrapropylammonium bromide $[(C_3H_7)_4NBr]_{3\cdot78}$. In like manner, ammonium iodide is more strongly associated than potassium iodide, and this, in turn, more than rubidium iodide.

In general, ebullioscopic methods involve higher temperatures than freezing point methods for the determination of molecular weights. This must, of course, always be the case when the same solvent is used. Since rise in temperature tends, in general, to reduce the molecular complexity of the solute, molecular weights as determined ebullioscopically are frequently slightly lower than those obtained by cryoscopic methods.

As in cryoscopy, when **chemical combination** between solute and solvent occurs, the results obtained for the apparent molecular weight are too low. This is the case, for example, with phosphorus in iodine, and is not merely a temperature effect due to the higher boiling point of iodine.

Where chemical action is absent, the solvent may exert an influence of another kind. Solvents have generally been classed as associating solvents or dissociating solvents according as they allow or prevent the formation, by substances dissolved in them, of aggregates of simple molecules. To the class of so-called "associating solvents" belong benzene, carbon disulphide, chloroform and bromoform, etc., and to that which prevents association or actually dissociates the molecular complexes of added substances belong water, methyl and ethyl alcohols, and others. It has been shown that the degree of association depends largely on the dielectric constant or specific inductive capacity of the medium, media of high dielectric constant preventing association, whilst those of low value most readily permit of association. A medium of high dielectric constant weakens the attractive forces between molecules, whereas one of low dielectric constant allows these forces freer play, and does not hinder their mutual attractions.

CHAPTER XXI.

ADSORPTION.

When a sponge is dipped into water or blotting-paper into ink, the liquid is absorbed and penetrates into the absorbent. If, however, a piece of glass is strongly heated and cooled in a vacuum and then brought into contact with the air, minute quantities of gas or vapour collect on its surface, forming an **adsorbed layer.** This layer may only be of the order of one molecule thick, and it may not be possible to detect its presence optically. It does not penetrate into the glass, and is thus purely a surface phenomenon.

Adsorption, therefore, may be defined as *the unequal distribution of a substance at the boundary separating two phases.* It is a universal phenomenon.

Characteristic Features of Adsorption.

1. It is a surface phenomenon and hence **a function of the specific surface** (p. 12), so that the more finely divided a solid is, the greater is its adsorptive power. Since substances in intimate contact tend to diffuse into one another and yield solutions, it is not always easy to determine where adsorption ends and dissolution begins. This is particularly the case when gases, liquids or solids are adsorbed by solids. Several references to this occur in the sequel.

2. **Low temperatures** favour adsorption, and in certain cases critical temperatures exist above which adsorption cannot take place. Thus mercury is not ordinarily adsorbed by glass above $-135°$ C., neither is silver above $+575°$ C. The adsorption of gases by porous solids is very pronounced at low temperatures (p. 357) and is utilised commercially.

3. Adsorption increases with the **concentration** or, in the case of gases, with the pressure. The relationship between the two is given by the adsorption law (p. 438). Hence, in order to remove any adsorbed layers from solids it is usual to raise the temperature and reduce the concentration. Thus, heating a solid *in vacuo* will effectively remove adsorbed gases; and repeated boiling of a precipitate with pure water will tend to remove many adsorbed impurities.

4. Adsorption does not necessarily imply chemical change, although it is frequently accompanied by such change. For example, the dye known as Congo red is an acid, and the acid is blue in colour. When aluminium hydroxide is added to the blue solution in water a blue suspension is obtained, the blue dye being adsorbed on to the hydroxide surface. On warming, combination takes place and the precipitate turns red. Sometimes the union between adsorbent and adsorbate is

so firm that the product appears to lie intermediately between a mixture and a compound. It is then termed an **adsorption compound**.

5. When not accompanied by chemical change, adsorption is a **reversible process**, equilibrium being established between the adsorbed layer and the bulk of the unadsorbed material, much in the same way as in the case of a solute distributed between two immiscible solvents (p. 377).

6. Adsorption may be **selective**. Thus solids frequently exert a preferential adsorptive effect upon certain gases. For example, charcoal adsorbs ethylene preferentially to coal gas. Numerous examples are known of selective adsorption of solutes from liquid solutions by solids, particularly from electrolytic solutions. Thus, when ferric hydroxide is precipitated from solution it is usually electropositive and tends to adsorb selectively electronegative ions (p. 459). Similarly, arsenious sulphide is usually electronegative when thrown out of solution and tends to adsorb selectively electropositive ions. Charcoal adsorbs many colouring matters from aqueous solution and is used in refining sugar (p. 432). Colloidal silica selectively adsorbs dissolved impurities from such liquids as petroleum oils, motor spirit and waxes.

Adsorption of Gases by Solids.—If a bottle half-filled with magnesia or zinc oxide is shaken, the solid powder surges like a liquid. The particles actually do not touch one another; they are separated by adsorbed gas.

Adsorption is favoured by low temperature, and we have already seen that at low temperatures porous substances like charcoal can absorb very large quantities of gas (p. 357). (For this reason the containers of the gas masks used by our troops during the Great European War (1914 to 1918) contained nut-charcoal to effect the removal of poison gas.) It is difficult in these cases to draw the line between adsorption and absorption, but adsorption must precede absorption in point of time. In this connection it may also be of interest to mention that in the production of high vacua the apparatus, which has already been attached by hermetic sealing to a bulb containing coconut charcoal, is filled with carbon dioxide; the bulb is immersed in liquid air and the carbon dioxide is absorbed so rapidly and completely that the pressure may almost immediately be reduced to a fraction of a millionth of an atmosphere.

Langmuir's Theory of the Mechanism of Gaseous Adsorption (1918).—Mention has already been made of the fact that purely physical adsorption is a reversible process, and is the result of the reaching of a state of equilibrium between the processes of condensation and evaporation. We may assume that the adsorbed layer is usually monomolecular, as, for example, in the case of the permanent gases under low pressures, although evidence is not wanting that in certain cases, such as the adsorption of readily condensible vapours, the films may be multimolecular in thickness.

Langmuir (1918) suggested that when gas molecules impinge on a solid (or liquid) surface, they usually condense, being adsorbed by forces akin to those holding the atoms of the solid together. If these forces are strong, the rate of evaporation of the molecules may be so retarded that the solid surface becomes virtually covered with a monomolecular layer of the adsorbed gas molecules. If the forces are weak, the " life " or period of attachment of the adsorbed molecules to the solid surface is brief, so that the total number of molecules adsorbed at any instant is relatively small, and the whole area of the solid surface is not covered.

The surface of a crystal may be regarded as resembling a checkerboard. Upon adsorption, gas molecules orient themselves with respect to the surface lattice of the crystal, and thus tend to form a new lattice above the old one. Each unit of area of a crystal will thus contain a definite number of "elementary spaces," as Langmuir terms them, each capable of holding one adsorbed atom or molecule. It is hardly to be expected that these "elementary spaces" will all be alike; often there may be several kinds of such spaces on the surface of a crystal of complex chemical composition. In a mica crystal, for example, it may be that both oxygen and hydrogen atoms, arranged in a regular lattice, constitute the surface, and that different "elementary spaces" are surrounded by different numbers or arrangements of atoms. Thus, for example, the following is a conceivable arrangement:

$$\begin{matrix} \mathrm{H} & \mathrm{O} & \mathrm{H} & \mathrm{H} & \mathrm{O} & \mathrm{H} \\ \mathrm{H} & \mathrm{H} & \mathrm{O} & \mathrm{H} & \mathrm{H} & \mathrm{O} \\ \mathrm{O} & \mathrm{H} & \mathrm{H} & \mathrm{O} & \mathrm{H} & \mathrm{H} \\ \mathrm{H} & \mathrm{O} & \mathrm{H} & \mathrm{H} & \mathrm{O} & \mathrm{H} \end{matrix}$$

and so on.

If we assume that the adsorbed atoms take up positions over the squares formed by four adjacent atoms in the lattice, the diagram gives two kinds of "elementary spaces," namely,

$$\begin{matrix} \mathrm{H} & \mathrm{O} \\ \mathrm{H} & \mathrm{H} \end{matrix} \quad \text{and} \quad \begin{matrix} \mathrm{O} & \mathrm{H} \\ \mathrm{H} & \mathrm{O} \end{matrix} .$$

If, on the other hand, the adsorbed atoms arrange themselves directly above the surface atoms, there will still be two kinds of "elementary spaces." The tendencies of the different "elementary spaces" to adsorb molecules will not necessarily be identical; in that case, some lattices will become more quickly filled than others, and upon increasing the pressure of the gas the different kinds of spaces will become successively filled with adsorbed molecules. It may happen that the gas molecules are slightly too large for the "elementary spaces," so that only by crowding together can they be made to occupy adjacent spaces, which may make the complete saturation of the surface a matter of difficulty. Such a phenomenon is a form of steric hindrance.

The surface atoms of amorphous substances like glass probably are not arranged in a regular lattice formation, so that an indefinite number of different kinds of "elementary spaces" may exist.

Langmuir has attempted to develop his theory of adsorption quantitatively. From the rate of effusion of gases through small pores, he calculates that the rate at which gas molecules come into contact with a surface is given by the equation

$$m = P\sqrt{\frac{M}{2\pi RT}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where m is the mass in grammes of the gas of molecular weight M impinging on each square centimetre of surface per second, under a pressure of P atmospheres at $T°$ abs. R, the gas constant, is taken as $8{\cdot}32 \times 10^7$ ergs.

If n is the number of gramme-molecules of gas striking each square centimetre per second, then

$$n = \frac{m}{M} = \frac{P}{\sqrt{2\pi MRT}} = 43{\cdot}75 \times 10^{-6} \times \frac{P}{\sqrt{MT}} \quad . \quad . \quad (2)$$

Of the molecules impinging on the surface we may assume that the fraction a will condense and remain held by surface forces until it evaporates away again. The rate at which the gas condenses will thus be an.

Let N_0 represent the number of "elementary spaces" per square centimetre of surface; then, if the adsorbed layer is monomolecular, N_0 represents the largest possible number of adsorbed molecules. When a molecule strikes a portion of the surface already covered, Langmuir assumes that it evaporates away so quickly as for the process to be, in effect, equivalent to a reflection. Therefore the rate of condensation on the surface is anq, where q represents the fraction of the surface uncovered. Similarly the rate of evaporation of the molecules from the surface is given by $\nu(1-q)$ where ν is the specific rate of evaporation, that is, the rate at which the gas would evaporate if the surface were completely covered, and $(1-q)$ is the fraction of the surface actually covered.

When equilibrium has been established, the rates of evaporation and condensation are equal, and

$$anq = \nu(1-q) \quad . \quad . \quad . \quad . \quad (3)$$

whence

$$1 - q = \frac{an}{an + \nu} \quad . \quad . \quad . \quad . \quad (4)$$

Denoting the "relative life" or period of attachment of the adsorbed molecules to the surface by λ, we have

$$\lambda = \frac{a}{\nu} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Substitution of this in equation (4) gives

$$1 - q = \frac{\lambda n}{1 + \lambda n} \quad . \quad . \quad . \quad . \quad (6)$$

If x is the number of gramme-molecules of gas adsorbed per square centimetre of surface, and N is Avogadro's number, then

$$x\frac{N}{N_0} = 1 - q = \frac{\lambda n}{1 + \lambda n} \quad . \quad . \quad . \quad . \quad (7)$$

Since, from equation (2), $n \propto \sqrt{P}$, both n and x can be determined experimentally, so that N_0 and λ can be calculated.

Now the "average life" of the atoms condensing on the surface is given by $N_0/N\nu$, whilst the average life, τ, of all the atoms striking the surface is $aN_0/N\nu$. So that, from equation (5),

$$\tau = \frac{aN_0}{N\nu} = \frac{\lambda N_0}{N} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

so that

$$x = \frac{\tau n}{1 + \lambda n} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

For very low pressures

$$x = \tau n \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

since λn is negligibly small with reference to unity. At high pressures λn becomes very large with respect to unity, so that x approaches a saturation value given by

$$x = \frac{\tau}{\lambda} = \frac{N_0}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

corresponding to the case where every "elementary space" contains one adsorbed molecule. At these high pressures the amount of gas adsorbed will not vary with the temperature except in so far as N_0 is dependent on the temperature.

In the foregoing it is assumed that the plane adsorbing surface contains only one kind of " elementary space," and that each space can hold only one molecule. The equations become more complicated when more kinds of " elementary spaces " than one are supposed to exist, and when each space can hold more than one adsorbed molecule.

Langmuir points out that there is good reason to believe that the forces holding adsorbed molecules act primarily on the individual atoms rather than on the molecules. If these forces are sufficiently powerful it may happen that the atoms leaving the surface have become paired in a different manner from that in the original molecules.

Let us, for example, consider the adsorption of a diatomic gas like oxygen, and assume that each atom occupies one " elementary space." In order that a given molecule impinging on the surface may condense and be retained for an appreciable time, two adjacent " elementary spaces " must be vacant ; the rate of condensation is thus anq^2, and when equilibrium is established

$$anq^2 = \nu(1 - q)^2$$

and the number of gramme-molecules, x, of oxygen adsorbed per unit area is given by

$$\frac{2xN}{N_0} = 1 - q$$

In the following table are given values for the " relative lives," λ, of several gases adsorbed on glass at 90° abs. as determined experimentally by Langmuir. The approximate number of molecules required to form a monomolecular layer can be estimated from the density of the " gas " when in the liquid state. This number is always less than the value found for N_0 from adsorption experiments, as shown in the final column of the table, where

$$\beta = \frac{\text{Experimental } N_0}{\text{Calculated } N_0}$$

and thus represents the fraction of the saturated solid surface covered by adsorbed molecules.

"Relative Lives" of Gas Molecules Adsorbed on Glass at 90° Abs.

(Langmuir, 1918.)

Gas.	λ (seconds).	N_0.	β.
Nitrogen . . .	101,000	0.174×10^{15}	0·26
Oxygen . . .	97,000	0.108×10^{15}	0·14
Argon	70,000	0.151×10^{15}	0·20
Carbon monoxide . .	95,000	0.208×10^{15}	0·32

Adsorption of Hydrogen by Tungsten Filaments.—When a tungsten filament is raised to a high temperature electrically in hydrogen gas at very low pressures, the gas apparently disappears, but is found to be adsorbed on the walls of the containing bulb in a chemically active condition. The explanation appears to be as follows: Of the hydrogen molecules that strike the heated filament a certain proportion condenses on the metal as dissociated atoms which evaporate off again only slowly. When any two such atoms occupy adjacent "elementary spaces" they can unite to re-form molecules of hydrogen which evaporate off rapidly. But a considerable proportion of the atoms will occupy isolated spaces; their lives or periods of attachment will be longer than those of hydrogen molecules because of their unsaturation. Eventually, however, they evaporate off as atoms and become adsorbed as such on the walls of the bulb, where they retain their chemical activity for an appreciable time, even after the tungsten filament has been allowed to cool. They will, for example, interact with gaseous oxygen at the temperature of the room. The proportion of the hydrogen gas dissociated at various temperatures has been calculated, with the following results:

At 1700° C.	0·33 per cent.
,, 2200° C.	3·1 ,,
,, 3200° C.	34 ,,

In the presence of a trace of water vapour, a volatile oxide of tungsten is produced which condenses on the walls of the bulb, where it is reduced by the adsorbed atomic hydrogen, water vapour being re-formed and a deposit of tungsten left on the glass. The trace of water may thus catalytically cause the transfer of a large quantity of tungsten from the filament to the glass.

Adsorption of Liquids by Solids.—Solids are only "wetted" by liquids when adsorption takes place. Under ordinary conditions mercury does not wet or adhere to glass. In order that a liquid may wet a solid it must remove the layer of adsorbed gases. If the adsorbed gas be removed with the aid of a high vacuum, mercury may be made to adhere to glass. The effective removal of adsorbed gases from pigments is one of the problems confronting the manufacturer. The pigment is subjected to a prolonged grinding with linseed oil because, to obtain a good paint, it is essential that the gases adsorbed on the surface of the pigment shall be displaced by the oil, so that intimate contact between the two may be established.

Adsorption plays a most important part in the lubrication of machinery. It is found that the addition of 1 to 2 per cent. of fatty acids to a mineral oil increases its lubricating power. The acids lower the surface tension of the oil, and thus accumulate at its surface in accordance with principles already discussed (p. 256). It is supposed that the carboxylic groups of the acids attach themselves by what may be termed the latent valences of the oxygen to the metal, with their hydrocarbon chains floating out into the mineral oil, much in the way that a caterpillar frequently clings to a twig with its prolegs and allows its body to project into the air. The resistance to shear is then between the hydrocarbon tail of the fatty acid and the molecules of the mineral oil, accompanied by little or no movement on the actual surface of the metal. Friction is thus reduced.

One of the best methods of eliminating traces of oil from boiler feed waters consists in adding aluminium sulphate and sodium carbonate to them. A gelatinous precipitate of aluminium hydroxide is produced, which adsorbs the particles of oil. The precipitate may be removed by sedimentation or filtration, and the water is completely freed from the oil.

Adsorption from Solutions.—It is well known that if ordinary brown vinegar is shaken with charcoal and filtered, a colourless filtrate is obtained. The brown colouring matter has been selectively adsorbed by the charcoal. In the refining of sugar, the warm, brown-coloured solution of raw sugar is admitted to " char cisterns," that is, cast or wrought iron cylinders fitted with perforated false bottoms and charged with animal charcoal. The whole is usually allowed to " settle " for several hours, and when the taps at the bottom are opened, the colourless liquor flows out.

The adsorption of dissolved substances from solutions by solids plays a very important part in many chemical reactions. In quantitative analysis it frequently happens that a precipitate carries down with it appreciable quantities of other substances, these either being adsorbed, or in solid solution. Thus, in estimating alkali sulphates by precipitation as barium sulphate by addition of barium chloride, the barium sulphate is contaminated with appreciable quantities of barium chloride and/or alkali salt, according to circumstances. Similarly, when hydroxides of iron, chromium and aluminium are precipitated in the course of a systematic qualitative analysis, they tend to adsorb zinc and calcium, and these latter elements may be entirely overlooked as the analysis proceeds. The adsorption is rendered less serious by employing dilute solutions, with only a slight excess of ammonium hydroxide, and sufficient ammonium chloride. When ferric hydroxide is precipitated from solution in the presence of an alkali arsenite, some arsenic is adsorbed ; indeed, if the arsenite solution is dilute and iron is present in great excess, the whole of the arsenic may be removed from solution by adsorption in this way. Bunsen first directed attention to this in 1834, and freshly precipitated ferric hydroxide has long been recommended as an antidote for cases of arsenical poisoning (see p. 439).

Adsorption has been utilised very effectively in the separation of radioactive elements. These usually are present in the raw material in minute quantities only, so minute that it would be impossible to separate them by the ordinary process of precipitation followed by filtration. The difficulty is overcome by adding precipitable quantities of what may be termed a "type" element. Thus, for example, radium and barium both belong to Group II of the Periodic Table and both yield insoluble sulphates (p. 362). If, therefore, a given solution contains traces of radium, on addition of barium chloride and precipitation with sulphuric acid, radium sulphate is precipitated along with the barium sulphate. In a similar manner polonium may be precipitated along with bismuth as sulphide, and so on.

In his classical researches on the atomic weights of the elements, the Belgian chemist Stas, working during the middle of last century with an accuracy which then was almost phenomenal, used large quantities of material for his precipitations. In the case of silver, for example, he used from 70 to 405 grammes. The result was that his precipitates were contaminated owing to adsorption of reagents from the solutions, a source of error not recognised at the time. The atomic weights determined by Stas thus were slightly less correct than they would otherwise have been in view of the great care with which the experiments were carried out. The atomic weight of silver, for example, was given by Stas as 107·93 (O = 16), whereas the accepted value to-day (1931) is 107·880. This error was particularly unfortunate, for the atomic weight of silver may be regarded as a "key" value, as the determination of many other atomic weights involves a knowledge of that of silver.

The nature of the solvent is very important in determining the extent to which a solid can adsorb a dissolved solute. Thus, for example, an aqueous solution of Crystal Violet may be shaken with charcoal until colourless; but if the water is poured off and alcohol added, the liquid becomes coloured, for some of the dye is extracted from the charcoal, the equilibrium concentration in the alcohol being greater than in the water.

In general it may be said that substances which are themselves readily adsorbed tend as solvents to prevent the adsorption of solutes dissolved in them. If, for example, to charcoal suspended in phenol as solvent other substances such as methyl alcohol, stearic acid or benzene be added as solutes, these solutes are not adsorbed by the charcoal (Richardson and Robertson, 1925).

Davis (1907) found that the amount of iodine adsorbed by sugar charcoal from equivalent concentrations in different solvents increased with the nature of solvent as follows:

Alcohol,	Benzene,	Ethyl acetate,	Toluene,	Chloroform.
(Least)				(Most)

The order of relative adsorption was not the same for other forms of carbon, namely, animal charcoal and coconut charcoal.

If we assume that the adsorbent is able to adsorb both solute and solvent an explanation is to hand for the interesting fact that adsorption of the solute may be positive, nil, or even negative, for this will depend upon whether the solute is more strongly, equally or less strongly adsorbed than the solvent (Williams, 1914). In the last-mentioned case a solution shaken up with the adsorbent actually increases in concentration owing to the selective adsorption of the solvent.

As in solid-gas systems, it may not be easy to determine where adsorption ends and dissolution begins. Whilst adsorption will precede dissolution, it does not follow that adsorption will be complete before dissolution begins, although it may be so rapid that it is complete before dissolution is appreciable. Thus Davis (1907) showed that the absorption of dissolved iodine by various charcoals from solution in organic solvents consists of adsorption which is very rapid and is quite complete after some hours, followed by diffusion into the interior, which proceeds for weeks or months, yielding a solid solution.

Measurement of the electrical conductivity of aqueous solutions of ferric chloride shows a gradual increase after dilution, a definite maximum conductivity being reached ultimately for each concentration of the salt. The time required to reach a final stage of equilibrium varies with the concentration. For a 0·0001-normal solution some three hours are required, whilst a week is usual for a 0·0006-normal solution. This increase in conductivity is due to hydrolysis,

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl,$$

but the difficulty is to understand the extreme slowness with which the equilibrium is attained, for the hydrolysis should take place with rapidity. The suggestion has been made that the hydrolysis proceeds stepwise, thus

$$FeCl_3 \longrightarrow FeCl_2(OH) \longrightarrow FeCl(OH)_2 \longrightarrow Fe(OH)_3.$$

It is not indicated, however, why any one of the steps should require so long a time for completion. A suggestive theory, supported by ultramicroscopic examination, has, however, been advanced by Wagner (1913), according to which hydrolysis is instantaneous, but the gradual change in conductivity is due to changes in the surface areas of the colloid particles. At first these particles are small, so that the specific surface (p. 12) is enormous, and practically the whole of the liberated acid is adsorbed. With time the particles gradually increase in size, becoming less numerous, so that the specific surface falls, liberating proportionate amounts of the adsorbed acid. The conductivity thus rises.

The adsorption of emulsoids by solids is dealt with later (p. 472).

Adsorption of Liquids by Liquids.—The conditions that must be satisfied before one liquid can spread by surface action over another have been discussed (p. 255), and it was mentioned that such spreading occurs in monomolecular layers, that is, in layers of superficial solution in which the spreading liquid is one molecule in thickness. In the case of organic acids and bodies containing hydroxyl groups floating on water, Langmuir suggested that the molecules in the film are orientated on the surface of the water, the oxygenated groups being attracted by forces akin to, or identical with, chemical valency, and thus held more or less rigidly to the surface of the water, their hydrocarbon chains having no tendency to dissolve, but remaining projecting vertically as explained in connection with the lubrication of solid surfaces (p. 432).

Adsorption Layers of Solutions.—This may be regarded as a special case of solution. We have already seen that when a substance dissolves in a liquid, the surface tension of the latter is altered. If the solute lowers the surface tension of the solvent, it will tend to accumulate in the surface layers ; but if it raises the surface tension the surface layers will be less concentrated, for the solute will accumulate in the bulk of the liquid. These differences in concentration are particular cases of adsorption, which is regarded as positive in the first case and negative in the second.

Let the concentration of the solute in the bulk of the solution be represented by C, and the excess concentration in unit area of the liquid surface by u ; it can be shown that

$$C\frac{d\sigma}{dC} = -u\frac{d\Pi}{dC} \quad . \quad . \quad . \quad . \quad (1)$$

where Π is the osmotic pressure and $\frac{d\sigma}{dC}$ is the differential coefficient of the function connecting the surface tension and the concentration of the solution. It is here assumed that the solute is un-ionised and electrically neutral.

For dilute solutions

$$\Pi = RTC$$

as shown on p. 387 ; whence

$$d\Pi = RTdC.$$

Inserting this value for $d\Pi$ into equation (1) we have

$$u = -\frac{C}{RT} \cdot \frac{d\sigma}{dC} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This is the **Gibbs-Thomson formula.** It was tested qualitatively by Miss Benson (1903) with an aqueous solution of amyl alcohol. This alcohol reduces the surface tension of water and should therefore accumulate in the surface layers. A copious froth was produced on the liquid and its alcohol content compared with that in the bulk of the liquid. The results were as follows :

	C.c. alcohol per litre.
Original solution	4·00
Froth (mean of 4 expts.)	4·14

The froth thus contained some 3·5 per cent. excess of amyl alcohol over that in the bulk of the liquid.

A quantitative verification of the formula is much more difficult, for it is necessary to determine the value of $\frac{d\sigma}{dC}$ for a given concentration C, and also the area of the surface, so that the excess of solute in unit area, that is, the term u in equation (2), can be evaluated. The changes in concentration probably are confined to a depth of only a few Ångström units below the surface. The evaluation of u has not yet been very satisfactorily achieved. In 1911 Donnan and Barker experimented with a solution of nonylic acid in water. The ratio $d\sigma/dC$ was determined, adsorption being produced by passing air through the solution in such a manner as to give a known number of bubbles of definite size. Their results, however, gave too high a value for u, probably because the formation of the bubbles was too rapid, and did not allow sufficient time for equilibrium to be obtained between the surface and the bulk concentrations.

The Gibbs-Thomson formula assumes that the solute is un-ionised and electrically neutral. If the solute is ionised complications arise, which are dealt with later (Vol. II).

It will be obvious that whilst a solute may reduce the surface tension of a solution very appreciably, it can only increase it to a small extent. Thus a solute which decreases the surface tension tends to accumulate in the surface layers and may become highly concentrated in these layers, reducing the surface tension proportionately. But a solute which increases the surface tension accumulates in the bulk of the liquid, so that the surface tension effect is in part neutralised by the concentration effect.

Although in considering the Gibbs-Thomson formula we have chosen illustrations from liquid systems, no assumption was made in the calculation about the nature of the phases. The formula, therefore, holds for various kinds of boundaries, such as solid-gas, solid–liquid, liquid–liquid and liquid–gas.

METHODS OF DETERMINING THE EXTENT OF ADSORPTION.

The adsorption of gases and vapours by solids is usually determined by weighing, or by heating in a vacuum and measuring the volume of the evolved gases. Using powdered glass as his adsorbent, Mülfarth in 1900 determined with considerable accuracy the relative adsorptions of carbon dioxide, nitrous oxide, ammonia and other gases. To determine the absolute adsorption per unit area it is necessary, however, to know the surface area of the adsorbent. Glass wool is frequently used, therefore, since its surface area is easily determined if the fibres are of uniform diameter. In their experiments with carbon dioxide Evans and George (1923) packed a known weight of glass fibre into a glass vessel, B, which was then evacuated to the lowest vacuum obtainable and heated to 300° C. during the evacuation. In this way it was believed that any adsorbed vapours and gases were completely removed from the glass fibres, the surface area of which totalled 103,500 sq. cm. A second glass vessel, A, of known volume, contained carbon dioxide, the temperature and pressure of which were noted. A was then connected with B and the pressure was again noted. From the known volumes of A and B the resultant pressure was calculated on the assumption that no adsorption of carbon dioxide had taken place. The difference between this value and the observed pressure gave the pressure which the adsorbed carbon dioxide would have exerted in the volume A + B at the known temperature. It was easy, therefore, to deduce the amount of carbon dioxide adsorbed by the glass fibre in B.

Assuming the condensed gas to have the same density as liquid carbon dioxide, the thickness of the adsorbed layer could be calculated. This was found to be equivalent to 5·5 molecules at a pressure of 121 mm. at 0° C.

From the relative adsorbabilities of other vapours with reference to carbon dioxide the corresponding thicknesses of their adsorbed layers under analogous conditions have been calculated to be as follows:

Thicknesses of Adsorbed Vapour Layers.

(Evans and George, 1923.)

Vapour.	Molecular Diameter, cm.	Molecular Layer.
Carbon dioxide . .	$5{\cdot}1 \times 10^{-8}$	5·5 molecules
Ammonia . . .	4·02 ,,	39·9 ,,
Sulphur dioxide .	4·84 ,,	32·1 ,,
Nitrous oxide . .	4·38 ,,	4·5 ,,
Acetylene . .	5·09 ,,	3·5 ,,

The adsorption of solutes in liquids by solid bodies is usually investigated by methods involving filtration of the equilibrium mixture and subsequent estimation of the concentration of the solute in the filtrate. Thus, for example, an aqueous solution of acetic acid of known concentration is shaken with charcoal. After filtration the concentration of the acid is again determined by titration, the difference giving the amount of acid adsorbed by the charcoal.

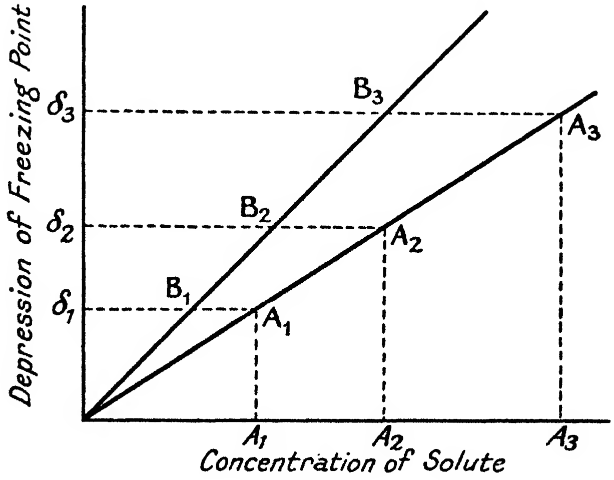


FIG. 180.

The extent of adsorption may be estimated also cryoscopically (Richardson and Robertson, 1925). One advantage of this method is that the rate of change of adsorption with concentration is easily followed. With the aid of the ordinary Beckmann freezing point apparatus (p. 405) the depression of the freezing point of the solvent by various additions, A_1, A_2, A_3, etc. (fig. 180) of solute in the presence of a given quantity of charcoal is determined. Curve $B_1B_2B_3$ connects the depression with the concentration in the absence of charcoal. The distances A_1B_1, A_2B_2, A_3B_3, etc., therefore give the concentrations of solute in the charcoal, and $B_1\delta_1$, $B_2\delta_2$, $B_3\delta_3$, etc., the concentrations of the solute in equilibrium with the charcoal, so that the desired ratio of the concentrations is easily determined.

The extent to which solutes are adsorbed in the surface layers of liquid solvents is by no means easy to determine with accuracy. Mention has already been made (p. 435) of Donnan's work in this connection.

The Adsorption Isotherm.—The distribution of a solute between two immiscible solvents has already been studied under the designation of the Partition Law (p. 377). We saw that, if C_1 and C represent the equilibrium concentrations of a solute in two solvents,

$$\frac{C_1^n}{C} = \text{constant} \quad . \quad . \quad . \quad . \quad (3)$$

where n gives the degree of association of the solute in the second solvent.

Equation (3) obviously may be written :

$$\frac{C_1}{C^{\frac{1}{n}}} = k \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and if we replace C_1 by x/m, where x is the mass adsorbed and m is the mass of adsorbent, equation (4) becomes

$$\frac{x}{m} = k\sqrt[n]{C} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is the equation of an ordinary parabola. This is termed the **Adsorption Law** or the **Adsorption Isotherm** of Freundlich.

If we logarise, we have

$$\log x - \log m = \frac{1}{n}\log C + \log k \quad . \quad . \quad . \quad (6)$$

The variables here are $\log x$ and $\log C$, and if these are plotted as abscissæ and ordinates respectively, a rectilinear curve is obtained. In general the exponent $\frac{1}{n}$ is found to lie between 0·2 and 0·5.

In the case of gases C is replaced by p, the pressure.

The value of k depends upon the units adopted, whilst n is a function of both the adsorbent and adsorbate or adsorbed material. The law is only approximately true, for n varies somewhat with the concentration. As the temperature is raised, $1/n$ approaches unity. The gradual rise in $1/n$ and rapid fall in the value of k with rise of temperature is well illustrated by the data given below for the adsorption of carbon dioxide by charcoal (Travers, 1906) :

Temperature, °C.	−78	0	35	61	100
k	14·29	2·96	1·236	0·721	0·324
$\frac{1}{n}$	0·133	0·333	0·461	0·479	0·518

Mention has already been made (p. 432) of the fact that freshly precipitated ferric hydroxide adsorbs arsenious acid from solution.

The extent of the adsorption is given by the equation

$$x = 0{\cdot}631\sqrt[5]{C}.$$

The following data illustrate the general agreement between the calculated and observed values of C for corresponding values of x (Biltz, 1904):

x . . .	0·251	0·415	0·549	0·712	0·824
C obs. . .	0·010	0·107	0·495	1·898	3·875
C calc. . .	0·010	0·123	0·498	1·829	3·797

The solubility of oxygen in blood does not follow Henry's Law (p. 345), according to which the solubility of a gas is proportional to the pressure. Experiment shows that large amounts of oxygen are absorbed at low pressures by blood as compared with at pressures of several atmospheres. The explanation usually offered is that the oxygen combines with the hæmoglobin of the blood to form the characteristically bright red oxyhæmoglobin of arterial blood, which readily dissociates when the pressure of the oxygen is reduced. This, however, cannot be the whole explanation for several reasons, one of which may be mentioned, namely, that complete absorption of oxygen is not effected even under a pressure of 10 atmospheres.

In 1907 Wolfgang Ostwald directed attention to the fact that the amounts of oxygen absorbed by the blood at various pressures are expressed by the adsorption formula

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

where the equilibrium concentration of the gas is denoted by the pressure p. The value of $\frac{1}{n}$ was found to be 0·34. It appears probable, therefore, that adsorption takes place, probably on the surface of the disperse phase in the blood.

It is interesting to note that the amount of oxygen thus taken up by the blood is very much greater than that absorbed by pure water. This is evident from the following data:

Solvent.	C.c. Oxygen measured at N.T.P. Absorbed by 100 c.c. of Solvent from the Atmosphere.
Water	0·7
Dog's blood	24
Human blood	18–19

The mean heat of reaction of oxygen with hæmoglobin at 22° C. is given as 6950 calories, whilst that of carbon monoxide and hæmoglobin is 14,700 calories. The difference is noteworthy in view of the well-known poisoning action of the latter gas.

The Properties of Adsorbed Gases.—Adsorbed gases usually manifest a greatly enhanced chemical activity. The adsorbed gas must be regarded as in a distorted molecular condition, and thus more ready to react chemically. Thus hydrogen adsorbed on to palladium shows much greater reducing power than the normal gas. Hydrogenated palladium precipitates mercury and mercurous chloride from an aqueous solution of mercuric chloride without any evolution of hydrogen. It reduces ferric salts to the ferrous state and potassium ferricyanide to ferrocyanide so completely that the reduction may be used for analytical purposes. It reduces chlorine water to hydrochloric acid, iodine to hydriodic acid, chromates to chromic salts, and ceric to cerous salts, whilst cupric, stannic, arsenic, manganic, vanadic and molybdic salts are also partially reduced by it. The reduction of a ferric salt to the ferrous condition may be demonstrated very effectively by an experiment described by Newth. A piece of palladium foil is heated to redness and then charged with hydrogen by making it the cathode in a cell containing acidified water through which an electric current is passed. When sufficient hydrogen has been adsorbed, the foil is withdrawn and dipped momentarily into a solution of ferric chloride. It is then suspended in a dilute, acidified solution of potassium ferricyanide, when the ferrous chloride formed by reduction betrays its presence by yielding an immediate blue coloration.

Reference is made on p. 442 to the chemical activity of oxygen adsorbed on charcoal at temperatures ranging from atmospheric up to 100° C.

The Heat of Adsorption.—Since rise of temperature reduces adsorption, it follows, from Le Chatelier's Theorem (p. 23), that adsorption is accompanied by the evolution of heat, quite apart from any thermochemical effects that may result subsequently from interaction of adsorbent and adsorbate. In the following table are given the heats of adsorption of a few gases on metals at 0° C. expressed as gramme-calories per gramme-molecule of gas:

Heats of Adsorption of Gases at 0° C.

Adsorbent.	Adsorbate.	Heat Evolved, Calories.
Platinum	Hydrogen	13,760
	Carbon monoxide	35,000
Palladium	Hydrogen	18,000
Nickel	Hydrogen	11,340 to 12,000
	Ethylene	5845
Copper	Hydrogen	9500

The heats of adsorption, Q, of many organic vapours by charcoal may be represented by the equation:

$$Q = mx^n \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where x is the number of cubic centimetres of vapour adsorbed, and m and n are constants (Lamb and Coolidge, 1920). A few data are as follows:

Vapour.	*m*.	*n*.
Carbon tetrachloride . .	0·893	0·930
Chloroform . . .	0·829	0·935
Carbon disulphide . .	0·752	0·920
Methyl alcohol . . .	0·742	0·938
Benzene	0·774	0·959

The following points are worthy of note :

(i) The constant n is very nearly unity, so that Q decreases only slightly with increasing adsorption ; in other words, the adsorptive forces show little evidence of fatigue.

(ii) The quantity of vapour adsorbed under comparable conditions of temperature and pressure is inversely proportional to the molecular volume of the adsorbate when in liquid form.

(iii) The greater the number of molecules adsorbed at a given pressure, the less is the heat of adsorption.

(iv) If we assume the adsorbed gas to be in the liquid state, the molecular heat of adsorption, H, less the molecular latent heat of condensation, L, gives what may be termed the " net " molecular heat of adsorption. Dividing this by the molecular volume, V cubic centimetres, of liquid adsorbate gives the net heat of adsorption per cubic centimetre. The value is found to be closely similar for all the liquids examined. The following table illustrates this point:

Net Heats of Adsorption on Charcoal.

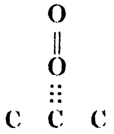
Substance.	H.	L.	$H-L$.	$\frac{H-L}{V}$.
Carbon tetrachloride . .	16,090	7077	9013	84·8
Chloroform . . .	14,930	8000	6930	87·5
Carbon disulphide . .	12,630	6830	5800	99·1
Methyl alcohol . . .	12,950	9330	3620	90·8
Benzene	15,170	7810	7360	85·0

This indicates that the heat of adsorption is due to the attractive force of the charcoal on the liquid, and that for a given volume of liquid, that is, for a given volume of filled capillary space, the heat liberated is nearly constant.

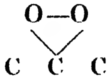
When the adsorbate unites chemically with the adsorbent, the normal heat of adsorption is enhanced by the heat of union. In this connection a study of the heat of adsorption of oxygen by charcoal is of interest (Garner and McKie, 1927). In view of its formation from cellulose or sugars, it is believed that the most probable structure of amorphous carbon is that of an interlocking network of carbon chains, and we may therefore represent a section of the surface by the scheme

C C C C C C C etc.

With this structure, adjacent carbon chains will touch at points irregularly along their length. Where contact occurs between carbon atoms of adjacent chains, powerful cohesive forces will keep the atoms together in a state resembling chemical combination; but there probably exist at other places atoms of carbon which are not fully saturated by neighbouring atoms, and which therefore possess an excess of potential energy. Such of this energy as occurs on the surface would tend to be liberated during adsorption. There are three simple ways in which oxygen molecules may be attached to the surface carbon atoms, namely,



I



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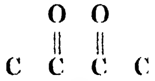

III

Of these the first represents a purely physical and reversible process. This occurs at low temperatures and under high initial gas pressures, since the adsorbed gas can be recovered as oxygen on decreasing the pressure or on raising the temperature (Dewar, 1904). Types II and III will yield carbon dioxide and carbon monoxide respectively on desorption. The heat of the first type of adsorption is only about 3 kilogram-calories per gramme-molecule of oxygen adsorbed. As the temperature is raised the heat of adsorption, Q, rises as shown below:

Relation between Q and Temperature.

Q (Kilogram-calories) .	70	91	108	114	116	154	224
t° C.	18	57	100	150	200	300	450

Upon desorption at 100° C., oxygen admixed with carbon dioxide is liberated. Probably as the temperature rises from atmospheric to 100° C. adsorption of type I with increasing amounts of type II occurs. Between these temperatures the physically adsorbed molecule of oxygen is probably somewhat distorted, as part of the adsorbed gas possesses unusual chemical activity. It will readily oxidise oxalic acid and amino-acids, which suggests that the union of the two atoms in the molecule has been weakened. Between 100° and 200° C. the value of Q is fairly constant and type II probably predominates, types I and III occurring, but to a less extent. At higher temperatures type III becomes increasingly predominant, the percentage of carbon monoxide in the desorbed gases rising.

CHAPTER XXII.

THE COLLOID STATE.

THE first systematic study of substances in what is now termed **the colloid state** originated with Graham in 1861. On pouring dilute aqueous solutions of various substances into small dishes made of parchment and floating on water, Graham observed that some of the dissolved substances readily diffused or **dialysed** (Greek *dia*, through; *lyein*, to loosen) through the parchment, whilst others did not. This difference in the behaviour of different substances may readily be illustrated by pouring a dilute solution of potassium iodide and starch into a small glass cylinder, the bottom of which is covered with parchment paper, as shown in fig. 181. The cylinder stands on a glass tripod in a crystallising dish containing distilled water. After a few minutes a portion of the liquid in A is removed and chlorine water added; a pale yellow colour due to iodine shows that potassium iodide has diffused through the parchment from B, but no starch. Addition of a little starch gives a deep blue colour, confirming iodine.

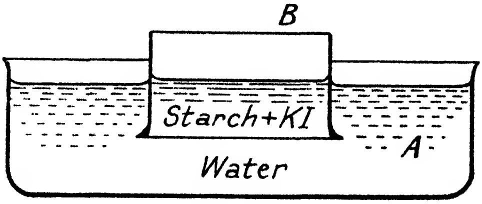

FIG. 181.

Graham found that the substances which diffused most readily were in general crystalline in the undissolved state; he therefore termed them **crystalloids.** Those bodies which did not diffuse readily were of a starchy or gluey nature; these he designated as **colloids** (Greek *kolla*, glue). The term " colloid " is now used in a much wider sense, as the sequel will show. It refers not to a type of substance, but to a condition of the dispersion of a substance in some medium, the peculiar characters of the substance depending upon the size of the particles.

CHARACTERISTIC FEATURES OF COLLOIDS.

1. Colloids are Polyphasic Systems.—A colloid consists of at least two phases, and thus constitutes a **polyphasic** or **heterogeneous system.** It contains a **continuous phase** or **dispersion medium,** in which are suspended minute particles of a second substance, termed the **discontinuous** or **disperse phase.** The particles of the disperse phase are too small to be seen, even with the aid of a microscope; they are believed generally to be spherical in shape, their diameters lying roughly between the limits of 1 $\mu\mu$ and 100 $\mu\mu$ (p. 8). If the particles are appreciably smaller than 1 $\mu\mu$ they become of approximately molecular dimensions, and the system is a solution or a so-called

molecular dispersoid. If the particles are appreciably greater than 100 $\mu\mu$, the system loses its characteristic colloidal properties and becomes a suspension or **macro-heterogeneous system.** Between the limits of 1 $\mu\mu$ and 100 $\mu\mu$ the disperse phase is stated to be in the "colloid state." The system is **micro-heterogeneous,** and is known as a **sol** (Latin *solvere,* to loosen). If water is the liquid medium the system is known as a **hydrosol,** or often as an **aquasol** ; if alcohol, an **alcosol** ; if glycerol, a **glycerosol** ; if benzene, a **benzosol** ; and so on. Or the more general term **organosol** may be employed when the continuous phase consists of some organic liquid. It is not essential, however, that the continuous phase shall be a liquid ; thus gaseous sols are known, as, for example, fogs and smokes. The continuous phase in these cases is the air, so these are termed **aerosols.** On the other hand, the beautiful rich colour of ruby glass is due to colloidal particles of gold dispersed throughout the glass, which thus constitutes what is virtually a solid continuous phase. Again, the disperse phase need not be a solid ; it may be a liquid, or it may even be a gas. Evidently, therefore, many different types of colloid systems are possible, closely analogous to the different solution systems which have already been discussed (Chapter XVII). They may be summarised as follows :

Colloid Systems.

SOLID	+SOLID	Blue rock salt (p. 467).
	+LIQUID	Adsorbed or occluded liquids.
	+GAS	Adsorbed or occluded gases.
LIQUID	+SOLID	Suspensoids.
	+LIQUID	Emulsoids.
	+GAS	Foams.
GAS	+SOLID	Smokes.
	+LIQUID	Fogs.

There is no GAS–GAS colloid system, since gaseous particles are already of molecular dimensions and thus yield true solutions only, being mutually soluble in one another to an unlimited extent.

The two phases of a colloid system need not be chemically different ; they may be allotropes, isomorphs or polymorphs of each other. A good example is afforded by liquid sulphur, which contains three allotropic forms in dynamic equilibrium, namely, sulphur λ, μ and π (p. 181). At the point of maximum viscosity at least one of these forms is presumed to be in the colloid state, the other form or forms constituting the continuous phase. Such a system is an **allocolloid.** An **isocolloid** system consists of isomorphs or polymorphs.

2. Diffusibility.—As has already been mentioned, the disperse phase of a colloid system does not readily diffuse through parchment or other suitable septa. Indeed, it was this peculiarity which led Graham to study those substances closely and to found the science of colloid chemistry.

3. Filtrability.—Colloid particles readily pass through all ordinary filters, and appear in the filtrate along with any dissolved materials. This is readily understood from the following data (Bechhold, 1908) :

	Diameter of Pores.
Ordinary thick filter-paper	3·3 μ
Filter-paper 556 (Schleicher and Schüll) .	1·7 μ
Filter-paper 602 („ „) .	0·89 to 1·5 μ
Chamberland filter	0·23 to 0·41 μ
Reichel filter	0·16 to 0·175 μ

A colloid particle thus will readily pass through these.

4. Visibility.—The particles of disperse phase in a sol cannot be seen individually even with the aid of a powerful microscope. A gold sol, for example, appears to be perfectly clear, just like a dilute solution of gold chloride, in which the disperse phase is of molecular dimensions. The reason for this is not far to seek. It is impossible actually to "see" a particle whose diameter is less than half the wavelength, λ, of the light used. The wavelength of the extreme visible violet end of the spectrum is not less than 3600 Å, that is 3600×10^{-8} cm. or 360 $\mu\mu$. Whence

$$\lambda/2 = 180\ \mu\mu$$

which is roughly double the diameter of the largest particles in a true colloid system. Such particles, therefore, are invisible.

5. The Tyndall Effect (1869).—When a beam of light is passed into a perfectly pure, optically void liquid, it apparently disappears. If passed into a sol, such as, for example, a gold sol, contained in a rectangular glass vessel, its path is indicated by turbidity, the appearance resembling fluorescence. This effect was noted by Faraday in 1857, but is usually named after Tyndall, who first applied it to the study of dust and mist in the air. By examining the beam with a Nicol prism it is found to be polarised, and although complete extinction may not occur, the variation in intensity of the illumination as the Nicol is rotated is very evident. Fluorescent solutions such as those of eosin or fluoresceïn do not show polarisation. The two phenomena, therefore, are quite distinct.

Instead of passing a parallel beam of light, a conical beam may be projected into the liquid, the apex of the cone lying within the liquid. This is frequently called the **Tyndall Cone.** Some sols do not show the Tyndall effect at all well; such, for example, are freshly prepared silicic acid, blood serum and alkali albuminates. They are "emulsoids" (see p. 447) and as such the disperse phase contains considerable quantities of the continuous phase and the difference between the refractive indices of the two phases is small. Similarly, coarsely powdered glass suspended in immersion oil, which has the same refractive index, does not exhibit turbidity in the Tyndall beam. With ordinary light the Tyndall effect ceases when the diameter of the particles falls to about 6 $\mu\mu$; in other words, molecular dispersoids ordinarily are optically void when pure. By the use of X-rays, however, the effect can be carried even into molecular regions, since the wavelength of the X-rays is very much smaller than the shortest visible rays.

6. Chemical Composition.—As a general rule complexity of chemical constitution favours formation of the colloid state, but there is no definite connection between the two. Glue, starch, albumin and gelatin are typical colloidal substances, and their constitutions are exceedingly complex. On the other hand, many substances which, in true solution, are regarded as simple, can readily be obtained in the colloid state. Thus colloidal forms of platinum, silver and gold have been known for many years. Even such a typical crystalloid as sodium chloride has been obtained in the colloid state. Undoubtedly under these conditions the substances are highly associated or polymerised.

7. The Colloid State a Universally Possible State of Matter.—From what has been said in the foregoing it is evident that the essential properties of colloidal substances are bound up with the size of the disperse particles, rather than with their chemical composition. There appears to be no reason, therefore, why all substances should not be capable of assuming the colloidal state, presuming a suitable continuous phase can be found for them. This was first emphasised by von Weimarn. It is just possible that the converse of this may be true also, namely, that all substances in colloid state may be capable of assuming the crystalline form given the right conditions. Thus, by very slow evaporation it has been found possible to prepare crystals of such typically colloidal substances as gelatin, agar, and even albumen.

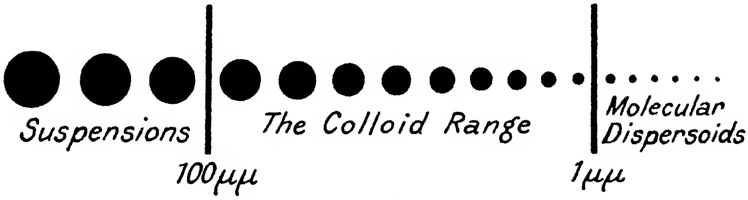

FIG. 182.

It is clear that we cannot speak of colloids in the same way, for example, as we speak of the inert gases or the rare-earth metals. It is better to speak of the colloid state, just as we refer to the solid, liquid or gaseous state.

The Colloid Range.—From what has been said it will be clear that the disperse particles of a sol are intermediate in size between coarse, optically visible particles, that is, mechanical suspensions, and particles of molecular dimensions. There is no sharp line of demarcation between mechanical suspensions and colloids, on the one hand, or between colloids and molecular dispersoids, on the other. Any dividing lines must of necessity be arbitrary. Where shall we draw them ? Fig. 182 shows diagrammatically the passage from suspensions to solutions. For several reasons it is usual to regard particles of diameter ranging from 1 $\mu\mu$ to 100 $\mu\mu$ as of colloid dimensions ; these reasons may be summarised briefly as follows : Firstly, as regards the upper limit, we have already seen that the limits of filtrability and of visibility under ordinary conditions lie with particles of diameter in the neighbourhood of 160 to 180 $\mu\mu$. These numbers are merely approximations and represent an extreme upper limit to the size of colloid particles. An early suggestion was that the upper limit should be taken as 140 $\mu\mu$, but there is no valid reason for choosing such a number in preference to the round figure of 100 $\mu\mu$. So this latter figure is usually accepted by colloid chemists as the **arbitrary upper limit.** Secondly, as regards the lower limit, molecular diameters ordinarily range from about 0·1 $\mu\mu$ to somewhat more than 1 $\mu\mu$. Some substances like starch, which have molecular diameters of the order of 5 $\mu\mu$ when dissolved in water, show well-defined colloid properties. It is convenient, therefore, to choose 1 $\mu\mu$ as our **arbitrary lower limit** for the diameters of colloid particles. The following molecular diameters calculated on the basis of the kinetic theory furnish an interesting comparison :

Chloroform	0·8 $\mu\mu$
Ethyl alcohol	0·4 $\mu\mu$
Carbon dioxide . . .	0·29 $\mu\mu$
Hydrogen	0·22 $\mu\mu$

These observations may be tabulated as follows :

Dispersed Systems.

Heterogeneous.		*Homogeneous.*
Macroheterogeneous. Mechanical Suspensions.	Microheterogeneous. Colloidal Solutions. Sols.	Molecular Dispersoids. True Solutions.
Diameter of particles > 100 $\mu\mu$. Particles can be examined microscopically ; do not pass through filter-paper.	Diameter of particles 100 $\mu\mu$ to 1 $\mu\mu$. Particles cannot be seen. They scatter but do not reflect light. They pass through filter-paper but do not diffuse or dialyse readily.	Diameter of particles < 1 $\mu\mu$. Particles cannot be seen. They do not yield a Tyndall effect. They pass through filter-paper and both diffuse and dialyse.

SUSPENSOIDS AND EMULSOIDS.

Two exceedingly important colloid systems are those known as **suspensoids** and **emulsoids** respectively. Reference to the table on p. 444 shows that whilst suspensoids are LIQUID–SOLID systems, emulsoids are LIQUID–LIQUID systems. These correspond in microheterogeneous systems to suspensions and emulsions in macroheterogeneous systems. Let us compare and contrast these two systems.

1. Chemical Composition.—Generally speaking the suspensoids contain an inorganic disperse phase, typical examples being platinum, silver and gold hydrosols. The emulsoids usually contain an organic disperse phase, well-known examples being starch, glue and gum arabic hydrosols. But this distinction is not complete. Silicic and titanic acids are typical inorganic substances, but their hydrosols behave in many ways like emulsoids.

2. Composition of the Phases.—In general the disperse phase of a suspensoid does not combine with or dissolve to any appreciable extent in the continuous phase. We do not, for example, regard either gold or platinum as in any way hydrated in their hydrosols, nor do we suppose that the continuous phase (water) contains appreciable quantities of dissolved metal. But the disperse phase of an emulsoid usually combines with or dissolves some of the continuous phase, and it usually also dissolves to some extent in the continuous phase. Metallic hydroxide hydrosols lie intermediately between the two. The disperse phase contains chemically combined water and a good deal of more loosely attached water as well; but the continuous phase may contain only inappreciable amounts of dissolved hydroxide.

3. Physical Condition of the Phases.—As already mentioned, the disperse phase of a suspensoid is regarded as solid, that of an emulsoid as liquid. Ferric hydroxide is probably liquid.

4. Density.—The density of suspensoids can be calculated from the law of mixtures. Thus, with the hydrosol of arsenious sulphide the following results were obtained by Linder and Picton (1895):

Per cent. Arsenious Sulphide.	Observed Density.	Calculated Density.
4·4	1·033810	1·033810
2·2	1·016880	1·016905
1·1	1·008435	1·008440

In the case of emulsoids one cannot calculate the density from the law of mixtures, for there is usually an alteration in volume when the sol is produced. Thus, for example, a sample of dry casein had a density of 1·318. On conversion into a hydrosol its density, as calculated by the method of mixtures, was 1·39. There had thus been appreciable contraction on preparing the sol. Similarly a contraction occurs when gelatin, starch and albumin take up water. Ferric hydroxide hydrosol shows emulsoid character in that a slight dilatation occurs when it is precipitated out.

5. Viscosity.—In general the viscosity of an emulsoid is greater than that of a suspensoid of equivalent concentration. The viscosity of dilute suspensoids is practically identical with that of the pure continuous phase, and is unaffected by passage through capillary tubes. As we shall see later, passage of an emulsoid through a capillary tube tends to break down its structure, so that "repeat" results cannot be obtained in this way. Special methods must therefore be adopted in determining the viscosities of emulsoids.

6. Surface Tension.—Suspensoids have usually the same surface tension as their pure continuous phase. The surface tension of emulsoids is usually less.

7. Precipitation.—In general the disperse phases of suspensoids are readily precipitated on addition of soluble salts. This is easily shown by adding a few crystals of sodium sulphate to ferric hydroxide sol. After a few minutes in the cold, or almost immediately upon warming, the sol becomes turbid, and ferric hydroxide separates out as a flocculent precipitate. If this precipitate is removed and shaken up with pure water it does not pass back into sol form. The hydroxide has been irreversibly precipitated. The precipitate is termed a **gel**, and the process of precipitation **gelation**. Emulsoids, on the other hand, usually require a high concentration of salt to effect their precipitation, and if the salt solution is replaced by pure water, in the case of hydrosols, the gel passes back into sol form. In other words, the gelation is reversible. For this reason suspensoids are sometimes termed hydrophobic or lyophobic, and emulsoids hydrophilic or lyophilic. These terms are hardly to be encouraged. The reversible gelation of emulsoids is utilised in the manufacture of soap, brine being added to the liquor in the tanks, whereby the soap is salted out.

8. **Concentration.**—In general, the concentration of the disperse phase in a suspensoid is very small indeed. A concentration of merely a few grammes of platinum per 1000 litres has frequently been used in research work. Increase in concentration tends to render the sol unstable, ultimately causing irreversible gelation. With emulsoids, owing to their greater stability, the concentration is not so restricted.

9. Metallic hydrosols frequently possess considerable **catalytic activity.** Thus platinum hydrosol stimulates the decomposition of hydrogen peroxide solution, a dilution of one gramme-atom of platinum in 70 million litres of water having a pronounced accelerating effect (see Vol. II). On the other hand, emulsoids tend to retard the catalytic activities of suspensoids and in general the velocities of such reactions, whether chemical or physical, as involve a change of state. This is attributable to adsorption (p. 474).

THE ULTRAMICROSCOPE.

Although we cannot actually see colloid particles, it is easily possible to obtain optical evidence of their existence. If a horizontal beam of light is passed into a small rectangular glass cell C (fig. 183) containing an optically void liquid, the beam apparently will disappear in the cell and reappear at the opposite side. On viewing the cell from above with a microscope M the field will be dark save for slight illumination due to scattering, etc. from the sides of the cell. If, however, a sol, such as gold hydrosol, is introduced into C, the field becomes illuminated with myriads of bright points. Each point represents the position of a colloid particle which is scattering some of the incident light. On looking down the microscope we think we see the particles, but we do not really do so; what we do see is the light scattered by the particles, and our eye pictures its various sources as round or spherical. Direct measurement of the shape or size of the particles thus is still impossible. The size of the "image" formed depends upon the intensity of the illumination and the qualities of the microscope, as well as upon the volume of the particle.

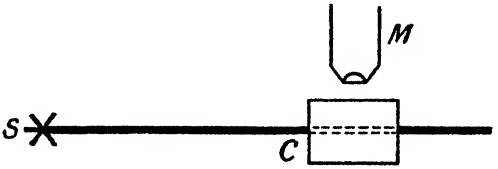

FIG. 183.

Instruments based on the foregoing arrangement are known as **ultramicroscopes**, the earliest being that of Zsigmondy. The instruments are so named (Latin *ultra*, beyond; Greek *mikros*, little, *skopein*, to look at) because they enable us to discover the presence, and watch the movements of, particles smaller than those which the microscope can render visible. We have already seen that with the microscope the limit of visibility with ordinary light is of the order of 180 $\mu\mu$. By means of the ultramicroscope we can detect the presence of particles of diameter not less than 5 $\mu\mu$. This is the lower limit of ultramicroscopic range with visible light. Particles smaller than this are sometimes termed **amicrons,** those whose diameters lie between 5 $\mu\mu$ and 100 $\mu\mu$, **submicrons,** and those from 100 $\mu\mu$ to 10 μ, **microns.**

A simple and very convenient form of ultramicroscope, suitable for qualitative work, is made by fitting what is known as a paraboloid condenser to an ordinary microscope. The condenser is made of a solid block of glass, paraboloid in shape but truncated so that its focus lies just above the surface of the glass slide S (fig. 184), on which a drop of the sol to be examined is placed, covered with a protective slip of glass, C. A ray of light AB entering the condenser is reflected to the focus, and, if it there meets a colloid particle, scattering takes place, and the scattered light entering the microscope M reveals the presence of the particle. A central disc DE covers the bottom of the condenser and prevents the entry of disturbing rays of light. Owing to the difficulty of measuring with accuracy the volume of the sol employed, the instrument cannot conveniently be used for quantitative work.

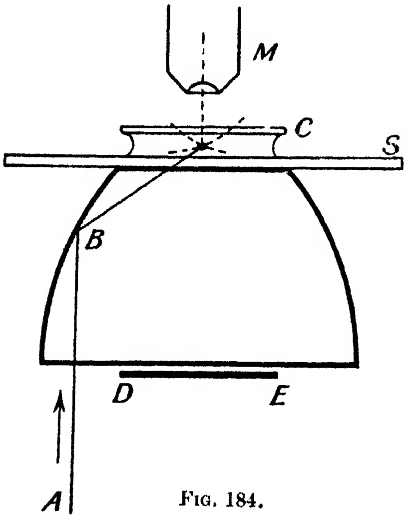

FIG. 184.

The intensity, I, of the light scattered by colloidal particles $\propto V^2$ where V is the volume of the particle, and also $\propto \left[\frac{\eta_d^2}{\eta_c^2} - 1\right]^2$ where η_d and η_c are the refractive indices of the disperse and continuous phases respectively. Whence

$$I = \text{constant} \times V^2 \left[\frac{\eta_d^2}{\eta_c^2} - 1\right]^2 \quad . \quad . \quad . \quad (1)$$

It is evident that, no matter how intense the illumination may be, the colloid particles may escape detection if η_d is not appreciably different from η_c, as the intensity of the scattered light may be too feeble. Emulsoids that do not show the Tyndall effect can hardly be expected to show well under the ultramicroscope.

The Brownian Movement.—Whilst examining under a microscope some pollen grains of *clarkia pulchella* suspended in water, Brown (1827) observed that the grains were continually moving. Curious to know if this was evidence of life, Brown next tested spores of mosses and equisetum a century old. Then he tried finely divided resins, glass, sulphur, etc, and observed that this motion was common to all;

it was not confined to living matter. In recognition of Brown's discovery the movement is known as the "Brownian Movement."

When Zsigmondy had arranged his ultramicroscope he noticed that the colloid particles were moving very rapidly, so rapidly indeed that he did not at first connect the phenomenon with the Brownian movement. The movement is persistent and irregular, as is well seen by photographing on to a cinematograph film; it is independent of such conditions as vibration and convection currents, and appears to depend mainly upon the size of the particles, the temperature and the viscosity of the continuous phase, and upon illumination.

The explanation offered by Wiener (1863) and others lies in the suggestion that the motion is due to molecular movements in the continuous phase, the molecules of which bombard the relatively large colloid particles; it is the recoils of these from the irregular bombardment that one observes in the ultramicroscope.

The energy of a molecule at $T°$ is given by $\frac{3}{2} \cdot \frac{RT}{N}$, or $0{\cdot}55 \times 10^{-13}$ erg at 0° C. This means that when a molecule is stopped at 0° C. sufficient energy is liberated to raise a drop of water, of diameter μ, to a height of nearly μ. We can readily understand, therefore, that the colloid particle subjected to a series of such bombardments will show continuous and erratic movement.

When viewed under the ultramicroscope the particles are seen to possess two types of motion, namely, translatory and oscillatory. By the **amplitude,** A, is meant the distance between the extreme and mean positions of the particle. The oscillation period, θ, is the time required by the particle to travel from one extreme position to the other and back again, that is, the time to complete one oscillation. If u is the velocity,

$$u = \frac{4A}{\theta} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The smaller the particle the greater the velocity will be, other things being equal. Thus Exner (1900), working with gamboge hydrosol, observed the following connection between the diameters of the particles and the velocities:

Diameter, μ. . . .	0·4	0·9	1·3	3	4
Velocity, μ per second .	3·8	3·3	2·7	Barely perceptible	None

Usually the Brownian movement ceases with particles of diameter about 5 μ.

The viscosity of the continuous phase is a most important factor. If the viscosity is very high, as, for example, with glass, no movement of the particles can be detected. Working with a series of platinum hydrosols and organosols, Svedberg (1906) showed that, for several liquid media, $A\eta$ is constant, η being the viscosity of the continuous phase and A the amplitude of the particles of platinum approximately 50 $\mu\mu$ in diameter. This is known as **Svedberg's Law.** The method of experiment consisted in allowing the sol to flow at a known slow velocity through the observation cell, the amplitude being noted with the aid of a micrometer eyepiece.

Rise of temperature accelerates the Brownian movement, and it also decreases the viscosity of the continuous phase. We can, however, distinguish between the two effects. According to Seddig (1908)

$$A^2 = \frac{kT}{\eta} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where T is the absolute temperature. Combining this with Svedberg's equation

$$A\eta = \text{constant} \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

we have

$$A = KT \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

that is, the amplitude of movement of the colloid particles is directly proportional to the absolute temperature when the viscosity is constant.

THE SIZE OF THE DISPERSE PARTICLES.

As we do not actually see the colloid particles under the ultramicroscope, for reasons that have already been given, we cannot observe directly either their size or their shape. There are, nevertheless, several methods by which the approximate sizes of colloid particles may be determined, and some of these we will proceed to consider.

1. **Ultrafiltration.**—Bechhold (1907) constructed a series of filters of different degrees of efficiency and measured the sizes of the pores they contained. The filters were made by soaking hard filter-papers either in a solution of collodion of known concentration in acetic acid, afterwards washing with water, which dissolved out the acetic acid and left a mass of nitrocellulose in the paper, or in gelatin (of various concentrations), which was subsequently hardened and rendered insoluble by soaking in cold formaldehyde for several days. Such filter-papers possessed pores of diameter varying between 930 and 21×10^{-6} mm., and by their use Bechhold was able to classify various colloids according to the sizes of their particles. The average sizes of the holes in the filter-papers were determined pneumatically by measuring the pressures required to force air through them under water. The size of the pores was easily varied by altering the concentration of the solutions.

As the foregoing filter-papers are not suitable either for high temperatures or for acetone sols, Manning (1926) prepared nickel membranes with pores ranging from 50 to 300 $\mu\mu$ by electro-deposition of nickel on a fine metal gauze of 200 mesh, the gauze merely serving as a support for the deposited nickel.

A convenient form of filter is shown diagrammatically in fig. 185. The filter F is supported on the gauze G held between washers WW round the circumference, and clamped between two flanged tubes bolted together with screws SS. Filtration can then proceed under such pressure as is desired.

The minimum size of the particles held back by such filters is probably, though not of necessity, about the same as the diameter of the filter pores. In the case of emulsoids filtered under pressure, one might imagine, for example, that a large spherical particle might be squeezed through a relatively small hole in consequence of deformation. That, however, is hardly likely to occur to any appreciable extent, for as the diameter of the particles falls to colloid dimensions the effect of surface tension increases enormously and great pressures are required to deform the drops sensibly. Thus, for example, whilst a small drop of oil may fall through a tube half its own diameter by its own weight, a similar drop 0·2 μ in diameter would require a pressure of 4·1 atmospheres to force it through a tube 0·1 μ in diameter. For drops of colloid dimensions much greater pressures still would be required.

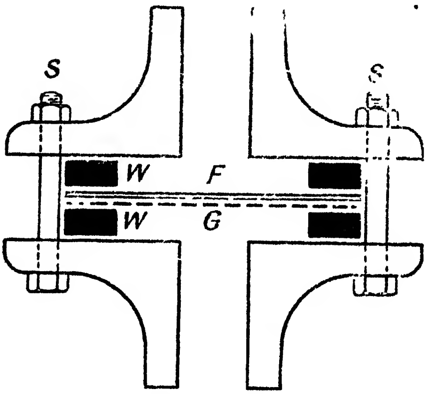

FIG. 185.—Filter for Ultrafiltration.

By finding which, of a series of filter-papers, will just permit the particles of a sol to pass into the filtrate, the diameter of the colloid particles, presumed spherical (see p. 456), can be ascertained. In general the results agree satisfactorily with those obtained by other methods.

2. By the Ultramicroscope. —The sol is first analysed chemically and found to contain, say, m grammes of disperse phase in unit volume. The number of particles, n, in unit volume is now estimated by counting those observable under an ultramicroscope in an aliquot portion of the solution. If d is the density, the average volume, v, of each particle is given by

$$v = \frac{m}{nd} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This, of course, assumes that the density of the compact substance is the same as that of the highly dispersed body, and probably in the case of suspensoids this is almost perfectly true. Assuming the particles to be spherical and of radius r,

$$\frac{m}{nd} = v = \tfrac{4}{3}\pi r^3$$

whence

$$r = \sqrt[3]{3m/4\pi nd} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

An example studied by Burton (1906) will make this clear. A portion of a silver hydrosol containing 6·8 mgrms. silver per 100 c.c. was diluted one hundred times. Of this solution 0·01 c.c. was examined in an instrument working on the same principle as the ultramicroscope, and the number of particles counted, this number being 300. Assuming the particles to be spherical and the density of silver to be 10·5, the average radius of the particles was found to be $1{\cdot}7 \times 10^{-5}$ cm.

3. From the Rate of Sedimentation.—In 1850 Stokes calculated that a particle, assumed to be spherical, moving through a medium of viscosity η at a velocity u, encounters resistance, R, the magnitude of which is given by the expression

$$R = 6\pi r\eta u$$

where r is the radius of the particle.

If the particle falls under the influence of gravity it will ultimately assume a steady rate of fall, when the following condition must be satisfied :

$$\tfrac{4}{3}\pi r^3 g(d_d - d_c) = R$$
$$= 6\pi r \eta u$$

where d_d and d_c are the densities of the particle (or disperse phase) and of the medium (or continuous phase). Whence

$$u = \frac{2}{9} r^2 g \frac{d_d - d_c}{\eta} \quad . \quad . \quad . \quad . \quad (8)$$

This is a very important equation.

It will be observed then, when $d_d = d_c$, the velocity of the particle is nil, and the particle remains stationary in the continuous phase. If $d_d < d_c$ the particle has a negative velocity ; that is, it rises.

Let us now consider a particle of gold of radius 10 $\mu\mu$ or 10^{-6} cm. and with the aid of equation (8) let us calculate its rate of sedimentation in water. Assuming its density is 19 and the viscosity of water at 20° C. is 0·01, we have

$$u = \frac{2}{9} \cdot 10^{-12} \times \frac{981(19-1)}{0{\cdot}01} \text{ cm./sec.}$$
$$= 3{\cdot}9 \times 10^{-7} \text{ cm. per sec.}$$
$$= 0{\cdot}014 \text{ mm. per hour}$$
$$= 10 \text{ mm. per month.}$$

In a similar manner the following rates of sedimentation have been calculated :

Diameter of Gold Particle.	Rate of Sedimentation.
$2 \times 5\ \mu$	3500 mm. per hour.
$2 \times \mu$	140 ,, ,,
$2 \times 10\ \mu\mu$	0·014 ,, ,,
$2 \times \mu\mu$	1·2 mm. per year.
$2 \times 0{\cdot}5\ \mu\mu$	30 mm. per century.

The rate of sedimentation of emulsoids will be appreciably slower than the foregoing for particles of similar size, since the density of the disperse phase is less widely different from that of the continuous phase. If the density of an emulsoid particle is 1·6, $(d_d - d_c)$ is only 0·6, and a particle of diameter 1 $\mu\mu$ will fall only 1 mm. in a century under the influence of gravity.

Although Stokes' Law yields fairly satisfactory results for particles near and above the upper colloid limit, its application to smaller particles is attended by considerable discrepancy. The reason is not far to seek. In the foregoing calculations we have assumed that the particle falls freely through the liquid without carrying any of the continuous phase with it. Such is not actually the case, however, for each colloid particle has a layer of adsorbed continuous phase all round it. Assuming this adsorbed layer to be of the order of one molecule thick, say $\delta\ \mu\mu$, the working radius of the particle is not r but $(r+\delta)\mu\mu$. If r is 10 μ, the error involved is small, but if r is only 10 $\mu\mu$ the effect may be appreciable.

4. From the Brownian Movement.—One very important consequence of the Brownian movement is that an equilibrium distribution of the colloid particles is ultimately reached. The smaller the particles, the more rapid their movement and the less the time required to reach equilibrium distribution. The true velocity of a colloid particle cannot be measured; the apparent rate varies enormously both in direction and magnitude, and the path followed is extremely complex—as, indeed, we might expect, seeing that the movement is a collision effect. At the suggestion of Einstein and Smoluchowski, each tackling the problem separately, it is now usual to choose, as a measure of colloid movement, the length of the straight line joining the initial and final positions of the given particle in a fixed time. This line is the **displacement** of the particle. By using an ultramicroscope the **horizontal displacement** of a particle can readily be determined.

On the assumption that the Brownian movement is mathematically irregular in all directions at right angles to the vertical, Einstein has shown that a sol diffuses like a true solution, so that the coefficient of diffusion, D, is given by the expression

$$D=\frac{1}{2}\cdot\frac{l^2}{\theta}\quad . \quad . \quad . \quad . \quad . \qquad (9)$$

where l is the displacement in time θ. The movement is not perfectly irregular in a vertical direction, owing to the pull of gravity on the particles.

Einstein has further shown that

$$D=\frac{RT}{N}\cdot\frac{1}{6\pi\eta r}\quad . \quad . \quad . \quad . \quad . \qquad (10)$$

where R is the gas constant, T the absolute temperature and N is Avogadro's Number. Combining these two equations, we have

$$r=\frac{RT}{N}\cdot\frac{\theta}{3\pi\eta l^2}\quad . \quad . \quad . \quad . \quad . \qquad (11)$$

which gives us a method of calculating r.

The smaller the radius the more accurate the observation, since l is greater. Even then, however, the method does not admit of a high order of accuracy. At least fifty observations are necessary, and as r varies inversely as l^2, it is evident that any error in l is seriously magnified.

5. From the Rate of Diffusion.—Sutherland (1905) modified equation (10) to

$$D=\frac{RT}{N}\cdot\frac{1+A\dfrac{\lambda}{r}}{6\pi\eta r}\quad . \quad . \quad . \quad . \quad . \qquad (12)$$

where A is a constant, approximating to 0·815, and λ is the mean free path of the molecules of the continuous phase. This equation applies to smaller particles than does equation (10). If the particles are large, λ/r vanishes and the equation resolves itself into equation (10). This method has been applied successfully to albumin sols, in which the particles were found to have radii ranging from 1·43 to 2·9 $\mu\mu$.

6. From the Equilibrium Distribution.—It is a matter of common knowledge that as we ascend vertically from sea level the density of the air becomes gradually less, the concentration of air molecules falling off in geometrical progression. Perrin has shown that the vertical equilibrium distribution of colloid particles in a hydrosol down to a depth of about 0·1 mm. is identical with that of a gas of similar concentration. Perrin used sols of gamboge and mastic, the particles of which had been rendered uniform in size by centrifuging. A drop of the sol was placed in a hollow slide of depth 0·1 mm. and given a plane surface with a cover glass (fig. 186). The number of particles was counted at various depths in a restricted field with the aid of a microscope, M. The relation between the size and numbers of the particles at different levels is given by the equation (see Vol. II)

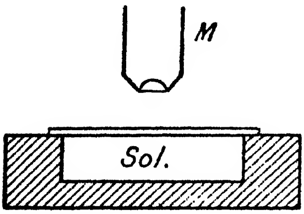

FIG. 186.

$$\log_e \frac{n_0}{n} = \frac{N}{RT} \cdot \frac{4}{3}\pi r^3 gh(d_d - d_c) \quad . \quad . \quad . \quad (13)$$

where n_0 and n represent the numbers of particles at levels 0 and h, and d_d and d_c the densities of the disperse and continuous phases, the other letters having their usual significance. From equation (13) the value of r can readily be calculated. For very small particles a correction for adsorbed continuous phase would appear to be necessary. Perrin worked with particles approximately 0·37 μ in radius; the concordance of his results, and the good value obtained for Avogadro's Number, namely, $6{\cdot}82 \times 10^{23}$, by calculation from equation (13), indicate that in his experiments adsorption did not interfere seriously. As mentioned on p. 32 the value for Avogadro's Number, according to the most accurate methods of measurement, is $6{\cdot}064 \times 10^{23}$.

7. From the Intensity of Scattered Light.—Rayleigh (1871) showed that the intensity of the light scattered by a suspension from a beam of known intensity, I, is given by the expression

$$I_s = Anr^6/\lambda^4 \quad . \quad . \quad . \quad . \quad (14)$$

where I_s is the intensity of the scattered light, λ the wave-length, n the number of particles and A is a constant depending on I and on the refractive indices of both phases and the angle at which the beam is viewed.

If we keep λ and n constant,

$$I_s \propto r^6.$$

The intensity of the light is measured photographically.

THE SHAPE OF THE DISPERSE PARTICLES.

As already explained (p. 449), we do not actually see the colloid particles under the ultramicroscope. We are compelled, therefore, to arrive at their shape indirectly.

Emulsoids.—Owing to mutual combination or solution of the disperse and continuous phases, the interfacial surface tension may be small. Probably, however, in the majority of cases it will be ample to cause the disperse particles to assume a spherical shape.

Suspensoids.—A considerable amount of evidence has been obtained in favour of the view that suspensoid particles, particularly those of metallic sols, may possibly possess a certain amount of crystalline structure. Thus, for example, suspensoids may initiate crystallisation in supersaturated solutions. In general, only crystalline substances can do this, although exceptions are not unknown. Very highly dispersed sols lose this power. Again, experiment shows that sol particles may coalesce and, after long standing, yield definite crystals. It is possible, therefore, that in certain cases large colloid particles do possess a certain amount of structure or crystallinity. But as the particles decrease in size the forces of surface tension may become so great as to overcome the forces of crystal orientation and the tendency will be for the particles to become spherical. It has long been known, from the microscopic examination of crystals, that globulites first form, which, after attaining a definite size, begin to assume a true crystalline form, crystals with rounded edges first appearing, and finally more perfect crystals. This is a strong argument in favour of the view that small suspensoid particles probably are spherical.

THE DISTRIBUTION OF COLLOID PARTICLES.

The question now arises as to how the colloid particles are distributed when in equilibrium in a vertical column of the sol measuring downwards from the surface. As we have already seen, Perrin found that down to depths of 0·1 mm. the particles arrange themselves just as gas molecules do, their concentration increasing in geometrical progression. But it is obvious that this increase in concentration cannot go on indefinitely, for even at a depth of 3 cm. the concentration would be 2^{1000} times the initial concentration—an impossible figure (Burton, 1922). Experiment shows that below a depth of about 2 mm. the concentration of a sol remains fairly constant. The curve connecting the number of particles with the depth is shown in fig. 187.

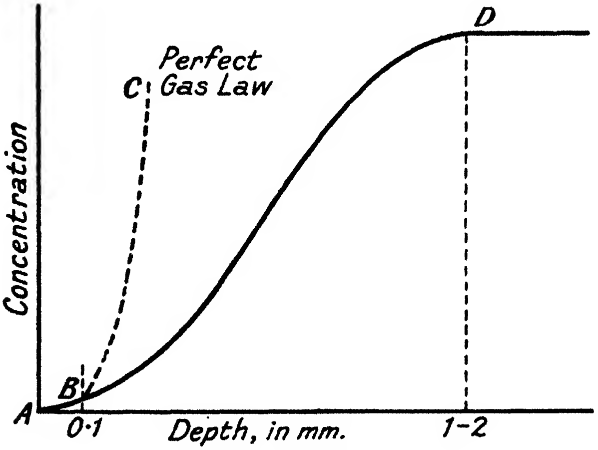

FIG. 187.—Curve showing Distribution of Colloid Particles.

It may be divided into four regions, namely,

1. The Gibbs-Thomson surface layer.
2. The Perrin layer.
3. The Porter-Hedges layer.
4. The region of constant concentration.

The **Gibbs-Thomson Surface Layer** refers to depths of the order of one molecule thick. In the case of suspensoids there is no appreciable effect, as the presence of the suspensoid particles has little or no influence on the surface tension of the pure continuous phase. On the other hand some emulsoids, such as the hydrosols of gum acacia and starch, have a higher surface tension than water, whilst others, notably gelatin, egg albumen, glue and dextrin, have a lower surface tension. In accordance, therefore, with the general rule that the surface tension of a system will tend towards a minimum value (p. 255), there will be a greater concentration of the emulsoid particles of the latter group in the surface layers than in the bulk of the liquid. Sols of gum acacia and starch, on the other hand, will in accordance with the same rule have a diminished concentration in their surface layers.

These differences in concentration are given by the Gibbs-Thomson formula (p. 435):

$$u = -\frac{C}{RT} \cdot \frac{d\sigma}{dC} \quad . \quad . \quad . \quad . \quad (15)$$

u being negative when the surface tension rises with the concentration of the sol.

The **Perrin Layer** has already been referred to. In the figure it is represented by AB, and if Perrin's equation (No. 13, p. 456) were obeyed to greater depths than about 0·1 mm. the concentration would be represented by the broken line BC.

In the **Porter-Hedges Layer** (1922) the concentration of the particles steadily increases to a maximum at a depth of from 1 to 2 mm. and then remains constant. This is shown in the figure by the curve BD, which follows the mathematical expression

$$\log_e \frac{n}{1-bn} + \frac{1}{1-bn} = Kh + A \quad . \quad . \quad . \quad (16)$$

where n is the number of particles in unit volume, b is Avogadro's constant, h the height (or depth) in cm., K a constant and A the integration constant.

THE PRECIPITATION OF SUSPENSOIDS.

We have already learned (p. 448) that one of the main differences between suspensoids and emulsoids lies in the irreversible precipitability or coagulation of suspensoids on addition of soluble salts, whereas such gelation as emulsoids undergo with such treatment is generally reversible.

If we add a small quantity of sodium chloride to ferric hydroxide sol, the sol may remain apparently quite clear, though its particles may not now be able to pass through a porous plate. Addition of further quantities of sodium chloride will cause opalescence, turbidity and ultimately precipitation of ferric hydroxide gel. Addition of the salt has gradually caused the masses of the colloid particles to increase, until the system has become a mechanical suspension. Precipitation in this manner is a gradual process and can be followed under the microscope, the Brownian movement slowing up and ultimately ceasing.

The explanation is to be found in the fact that the sol particles are electrically charged; the ions of the dissolved salt tend to neutralise these charges and thus to effect precipitation. Ferric hydroxide sol, as usually prepared, is electropositive, and its precipitation is effected mainly by the negative ion of the dissolved salt. This is evident from the following data (Hardy, 1900), which represent the smallest quantities of a few electrolytes required to precipitate the sol under certain standard conditions:

Electrolyte.	Concentration, gramme-molecules per litre.	Electrolyte.	Concentration, gramme-molecules per litre.
NaCl	0·00925	K_2SO_4	0·00020
½$BaCl_2$	0·00964	$MgSO_4$	0·00022
KNO_3	0·0119	$K_2Cr_2O_7$	0·00019
½$Ba(NO_3)_2$	0·0140		

Doubling the valency of the positive ion has no appreciable effect, but doubling the valency of the negative ion has reduced the necessary salt concentration to approximately one-fiftieth.

In the following table, prepared by Freundlich (1903), the minimum concentrations of various salt solutions required to produce complete coagulation of arsenious sulphide after two hours are recorded, the concentrations being expressed in gramme-molecules per litre of solution, except for K_2SO_4, H_2SO_4 and $Ce_2(SO_4)_3$:

Electrolyte.	Concentration.	Electrolyte.	Concentration.
LiCl	0·0815	$CaCl_2$	0·000905
NaCl	0·0712	$Ca(NO_3)_2$	0·00095
KCl	0·0691	$BaCl_2$	0·00096
½K_2SO_4	0·0915	$ZnCl_2$	0·00096
NH_4Cl	0·0591	$AlCl_3$	0·00013
HCl	0·0429	$Al(NO_3)_3$	0·00014
½H_2SO_4	0·0420	½$Ce_2(SO_4)_3$	0·00013
$MgCl_2$	0·0010	$Th(NO_3)_4$	0·00013

These figures clearly prove what Schulze (1882) had previously found, that the precipitating effect on a negatively charged colloid is dependent on and increases with the valency of the positive ion; also, that the precipitating agents which yield the greatest concentrations of ions at a given dilution are most effective, so that the mineral acids have a much greater precipitating power than the organic acids. In analytical chemistry the formation of colloidal solutions of arsenious and antimony sulphides is prevented by passing hydrogen sulphide into solutions acidified with hydrochloric acid.

It is because of the foregoing effect that if Indian ink is diluted with ordinary tap water, the particles are precipitated and the ink becomes useless.

Since a salt, upon dissolution, yields both positive and negative ions, it is clear that its final effect upon a sol must be the algebraic sum of its cationic and anionic effects, for the cation will tend to stabilise a positive sol and an anion a negative sol.

Sols of opposite electrical charge tend to precipitate each other for very obvious reasons. Sols of the same kind of charge do not precipitate one another, indeed, the mixed sol acquires the stability of the more stable component (Henri, 1904).

Ultraviolet light may effect the precipitation of negative sols. Thus the catalytic activity of platinum hydrosol towards the decomposition of hydrogen peroxide solution is steadily reduced by exposure to the richly actinic light from a mercury vapour lamp.

Gold Numbers.—If sodium chloride is added in increasing amount to a red gold hydrosol, the colour gradually changes to blue and violet, and ultimately the gold is irreversibly precipitated as a gel. The colour change, like the precipitation itself, is caused by a gradual increase in the size of the colloid particles. Emulsoids tend to protect the gold sol from change of colour and precipitation in this manner, and are therefore frequently termed **protective colloids.** It is an adsorption effect, and emulsoids can be classified roughly according to their protective powers (Zsigmondy, 1901). By the **gold number** of an emulsoid is understood *the number of milligrams of emulsoid which just prevent turbidity or colour change to violet of 10 c.c. of red gold hydrosol on addition of 1 c.c. of 10 per cent. sodium chloride solution.* The gold sol should contain from 0·0053 to 0·0058 per cent. of gold. A high gold number obviously indicates that the protective effect of the emulsoid is but feeble.

Zsigmondy classed the emulsoids as follows :

(i) *Most Active*	Gelatin, glue, casein, isinglass.
(ii) *Medium Activity*	Gum acacia (gum arabic), albumen, gum tragacanth.
(iii) *Weak*	Dextrin, potato starch.
(iv) *Inactive*	Water glass, silicic acid.

Electrical Properties.

The fact that colloid particles carry definite electrical charges has already been elicited from the study of their precipitation or coagulation. The existence of these charges is demonstrated readily by suspending strips of filter-paper in gas jars containing a few cubic centimetres of hydrosols of various kinds (fig. 188). It will be observed that some of the sols rise up the paper through capillary attraction, whilst in other cases the colloid particles are precipitated on to the immersed portions of the filter-papers. Filter-paper in contact with water is electronegative, and therefore has no effect on sols the particles of which are negatively charged. But positively charged particles lose their charge in contact with the filter-paper and are precipitated thereon, although the continuous phase passes up as usual. It is thus possible to separate positively charged particles from their dispersion medium. This is the basis of what is termed **capillary analysis,** which is used in connection with mixed dyes. A positive dye is precipitated on the paper, whilst a negative one is free to diffuse or spread out over the paper. The following table gives the electrical characters of a few typical hydrosols :

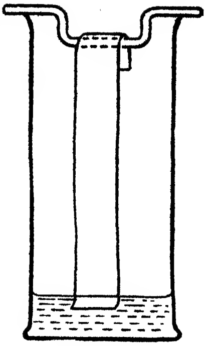

FIG. 188.

Electropositive.	Electronegative.
Metallic hydroxides.	Metallic sulphides.
Some metals, *e.g.* bismuth, lead, iron (possibly hydroxides).	Prussian blue.
Methyl violet.	Many metals, *e.g.* silver, gold, platinum.
Methylene blue.	Silicic acid, stannic acid.
	Mastic, gamboge, eosin.

The polarity depends not only on the disperse phase, but also on the dispersion medium. Thus, the metallic hydroxides are charged positively when in water, but negatively in turpentine.

Cause of Electric Charge.—The electrical properties of sols appear to be due to the presence of adsorbed ions. It is frequently possible to prepare suspensoids containing either charge at will. Thus, on adding potassium iodide solution to excess of dilute silver nitrate solution a positively charged silver iodide sol is obtained. If, on the other hand, the silver nitrate is added to an excess of dilute potassium iodide solution the resulting sol is negative (Lottermoser). Again, by the addition of aluminium sulphate solution, a negatively charged hydrosol, such as that of gold, may be neutralised or even charged positively.

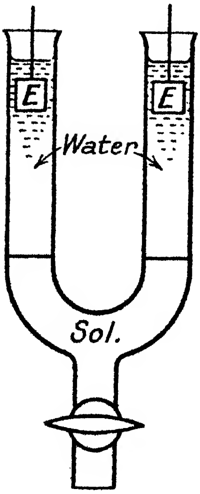

FIG. 189.

As usually prepared, ferric hydroxide sol is positive. It can, however, be prepared with a negative charge by adding slowly a dilute solution of ferric chloride to an excess of dilute caustic soda, the mixture being shaken continuously.

Cataphoresis (Greek *kata*, away ; *phero*, I bear) is the term used to indicate the migration of sols in an electric field. It was first observed by Linder and Picton (1892) in connection with arsenious sulphide hydrosol which, being negative, migrated to the anode, and in ferric hydroxide hydrosol, which migrated to the cathode. The phenomenon is now known to be of general occurrence.

The velocity of migration may be determined macroscopically, microscopically and ultramicroscopically. A convenient macroscopic method consists in filling partially with water a U-tube of the shape shown in fig. 189 and forcing a quantity of sol up through the tap so that it reaches equal heights in the limbs. A voltage of 60 to 200 volts is now applied by means of the platinum electrodes, E, which are surrounded by the water only. The movement of the sol is readily followed. The microscopic method consists in measuring the rate at which the particles move across the field of the microscope.

The velocity of migration, u, is given by the expression

$$u=\frac{\zeta H\epsilon}{4\pi\eta} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where ζ is the potential difference between the sol particles and the continuous phase—the so-called "double layer" (see Vol. II)—H the fall of potential between the electrodes expressed as volts per centimetre, ϵ the dielectric constant of the continuous phase and η the viscosity. The values obtained for a few sols are as follows :

Hydrosol or Ion.	Nature of Charge.	Diameter of Particles, $\mu\mu$.	Velocity in cm./sec. per 1 volt/cm.
Arsenious sulphide . .	−	50	22×10^{-5}
Gold	−	< 100	40 ,,
Platinum	−	< 100	30 ,,
Silver	−	< 100	33 ,,
Ferric hydroxide . .	+	< 100	30 ,,
Sodium ion . . .	+	. .	45 ,,
Lithium ion . . .	+	. .	35 ,,

It is interesting to note that the velocities of the colloid particles are closely similar to those of the slow-moving, heavily hydrated ions of sodium and lithium.

Emulsoid cataphoresis is usually slower than that of suspensoids, and shows interesting peculiarities. Thus, coagulated albumen does not migrate in neutral solution and is thus isoelectric with water ; in acid solutions it moves towards the cathode, but towards the anode in alkaline solutions.

Electro-endosmosis.—This term is employed to indicate the movement of the continuous phase of a sol across a diaphragm under the influence of a current of electricity, the particles remaining stationary. It is thus the reverse of cataphoresis. The extent of the endosmosis may be measured either by determining the hydrostatic pressure, P, which may be obtained by allowing the liquid phase to accumulate to a head in tubes, of radius r, when

$$P=\frac{2\zeta Hl\epsilon}{\pi r^2}=\frac{2\zeta E\epsilon}{\pi r^2} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where E is the potential difference between the electrodes, so that $E=Hl$, l being the distance between the electrodes.

Keeping the pressure constant and noting the volume, V, of liquid that escapes :

$$V = \frac{q\zeta E\epsilon}{4\pi\eta l} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where q denotes the area or cross-section of the diaphragm or tube, namely πr^2 if circular.

"MOLECULAR WEIGHTS" OF DISPERSOIDS.

Colloid particles are not, in general, merely simple molecules; they are physical aggregations of molecules and have not, therefore, molecular weights in the ordinary sense of the term. We may, if we like, regard them as associated molecules, but it is difficult to determine their molecular weights by the usual methods, such as the depression of the freezing point and other methods outlined in Chapter XIX, as the effect is so small. However, an indication may now be given of the kind of result that has so far been obtained.

Freezing Point Data.—These are somewhat uncertain; the high molecular weight of the particles leads to very small depressions of the freezing point, so that not only is the percentage error of observation high, but irregularities due to adsorbed ions or other impurities exert a disproportionately large effect. At best, therefore, the results can be but mere approximations. A few results are given in the table below. Sabanejeff (1891) divides colloids into two general groups, which he terms

(*a*) "Higher" or typical colloids, of molecular weight more than 3000.

(*b*) "Lower" colloids, of molecular weight less than 3000.

Molecular Weights of Colloids.

Hydrosol.	Molecular Weight.	Method.
Invertin	54,000	Diffusion.
Silicic acid	> 49,000	Freezing point.
Emulsin	46,000	Diffusion.
Starch	25,000	Freezing point.
Egg albumen	17,000	Diffusion.
,, ,,	13,000 to 14,000	Freezing point.
Pepsin	12,000	Diffusion.
Arsenious sulphide	6,000	,,
Ferric hydroxide	3,100	Freezing point.
Gum arabic	2570 to 4110	Osmosis.
,, ,,	1600 to 2000	Freezing point.
Caramel	1600 to 1750	,, ,,
Tungstic acid	1700	Osmosis.
Tannin	1100	Freezing point.
Tungstic acid	800	,, ,,

Osmotic Pressure Method.—This method is somewhat more sensitive than the freezing point method, since a depression of 0·001° C. corresponds to 9 mm. mercury or 125 mm. water, and these are readily measureable. The method should be good, for semipermeable membranes are less permeable by colloids than by ordinary solutes. The results, however, are variable. For gum arabic Pfeffer (1877) obtained values ranging from 2570 to 4110.

Diffusion Method.—By the use of Einstein's equation (No. 10, p. 455), namely,

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi r\eta},$$

we can calculate the molecular weight of a colloid particle, since

$$M = \frac{4}{3}\pi r^3 dN$$

assuming the particle to be spherical.

Substitution gives

$$M = \frac{dR^3T^3}{162\pi^2N^2\eta^3D^3} \quad . \quad . \quad . \quad . \quad (20)$$

at constant temperature.

For smaller masses use may be made of Thovert's equation (1902), namely,

$$M = k/D^2. \quad . \quad . \quad . \quad . \quad . \quad (21)$$

If D is expressed for an area of 1 as cm.^{2} per sec., k is 60×10^{-10}. For example, the coefficient of diffusion of arsenious sulphide sol was $0{\cdot}1 \times 10^{-5}$, whence the molecular weight was about 6000.

Distribution under Gravity.—Perrin's equation (No. 13, p. 456) may be written

$$\log_e \frac{n_0}{n} = \frac{N}{RT} mgh\left(1 - \frac{1}{d_{\mathrm{d}}}\right) \quad . \quad . \quad . \quad (22)$$

for a hydrosol, in which d_{c} is unity, and the colloid particles are assumed to be spherical. This enables us to calculate the mass m of the particle, and dividing by the mass of the hydrogen atom we obtain the molecular weight with reference to hydrogen. This is found to give very high values. Thus, for gamboge a mass of $\cdot 48 \times 10^{-15}$ gramme was found by Perrin. Taking the mass of an atom of hydrogen as $1{\cdot}64 \times 10^{-24}$ gramme, the "molecular weight" of the particle is 30×10^9.

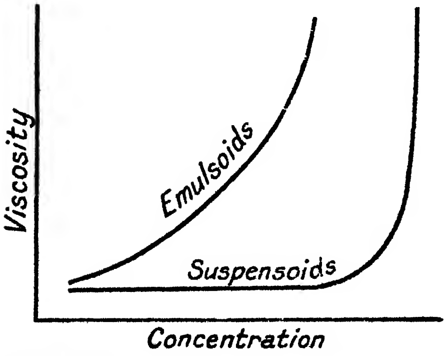

FIG. 190.—Rise of Viscosity with Concentration.

VISCOSITY.

As has already been mentioned (p. 448), the viscosity of dilute suspensoids is practically identical with that of the continuous phase. In general, the viscosity of an emulsoid is appreciably greater.

Capillary methods of determining the viscosity of an emulsoid are unsuitable; passage through a capillary tube tends to break down the emulsoid structure, so that satisfactory "repeat" results cannot be obtained. Hatschek's apparatus, described on p. 245, has proved very suitable.

Concentration.—The viscosity rises with the concentration, steadily with emulsoids, but only slowly at first with suspensoids, as shown in fig. 190. For ordinary soluble gelatin sol the following values have been obtained at 25° C. :

Concentration of gelatin, per cent.	0·25	0·5	1·0	3·0
η	1·10	1·22	1·75	2·96

At high concentrations the viscosity of a suspensoid rises suddenly to a very high value.

Age.—Viscosity varies with the age of the sol. In the case of suspensoids it falls with prolonged standing, in consequence of coagulation. With emulsoids the change may be rapid. The following results were obtained with a 2 per cent. potato starch hydrosol (Stock, 1917) :

Time.	Fresh.	After 5 minutes.	After 40 minutes.
η (water = 1) . . .	106·7	96·3	19·3

More usually, however, the viscosity of emulsoids rises with the time.

Temperature.—With rise of temperature the viscosity of a sol, as of the pure continuous phase, tends to fall. For suspensoids the viscosity is **thermostable** ; that is, it is a definite amount at a fixed temperature whether we approach that temperature from a higher or a lower one. In other words, the previous thermal history of the sol does not matter any more than for a pure liquid or a molecular dispersoid. The viscosity of emulsoids falls rapidly with rising temperature. By prolonged heating it is possible to change a hydrosol of gelatin or glue to what is known as the β-form (Traube, 1867), which will no longer set on cooling.

Electrolytes.—The addition of soluble electrolytes to suspensoid hydrosols reduces their viscosity in consequence of coagulation or precipitation. Emulsoids behave in various ways. On cooling a 2·5 per cent. gelatin sol, a gel is obtained. If the sol contains magnesium sulphate in solution a very stiff gel may result ; if, on the other hand, potassium iodide is present, the sol may refuse to gelate on cooling.

Hatschek's Equation (1911).—Considering the theoretical aspects of the viscosity of a liquid in which are suspended small particles, undeformably spherical in shape, Hatschek concludes that, if η is the viscosity of the system and η_1 that of the continuous phase,

$$\eta = \eta_1\left(1 + c\frac{v_d}{v}\right) \quad . \quad . \quad . \quad . \quad (23)$$

where c is a constant, equal to 4·5, v_d and v the volume of the disperse phase and of the system respectively, provided v_d/v is not greater than about 0·4. It will be noted that neither the radius nor the distance apart of the particles appears in this equation. The viscosity of the system is thus independent of the size of the particles, and is a linear function of the volume of the disperse phase only. A similar equation has been deduced by Einstein, the constant c being 2·5.

This formula has been tested experimentally with suspensions of starch granules of varying radii in water (Harrison, 1911). The viscosity was found to be independent of the size of the grains, as the formula demands, and in linear ratio to the volume of the disperse phase. The formula was found to hold up to 30 per cent. of the disperse phase. The numerical value of c was 4·75, however, instead of 4·5. Application of the formula to sulphur sols has not proved quite so successful (Sven Oden, 1912).

A second formula given by Hatschek as applicable to emulsions and emulsoids is:

$$\eta = \eta_1 \cdot \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1} \quad . \quad . \quad . \quad . \quad (24)$$

in which it is assumed that the volume of the disperse phase is at least 50 per cent. of that of the total system. A is here equal to v/v_d. On graphing η against A a curve is obtained, hyperbolic in appearance, η rising rapidly as A approaches unity. Experiments carried out with coarse emulsions of paraffin oil in soap solution have shown satisfactory agreement with this formula.

The difficulty in the case of emulsoids is to evaluate A, for the disperse phase swells in contact with the continuous phase and it is not easy to determine the amount of this swelling. It may be assumed, however, that the volume of the disperse phase is a constant multiple of the weight of the dispersed matter.

Transition Temperatures.—We have already seen that when a mixture of phenol and water, containing at least 36 per cent. of phenol, is allowed to stand, it separates into two layers, the upper one being a solution of phenol in water and the lower one a solution of water in phenol. On shaking, an emulsion is formed. On warming to 68·3° C. the liquid becomes clear, as at this critical solution temperature the liquids are mutually soluble to an unlimited extent. On slowly cooling the clear solution from a higher temperature down through 68·3° C. a faint opalescence appears, which becomes increasingly pronounced as the temperature falls and then gives place to a white turbidity, characteristic of coarse emulsions. As the clear liquid represents a molecular dispersoid, it is obvious that during the transition from solution to emulsion, the disperse phase must have passed through the range of colloid dimensions. Ultramicroscopic investigation shows

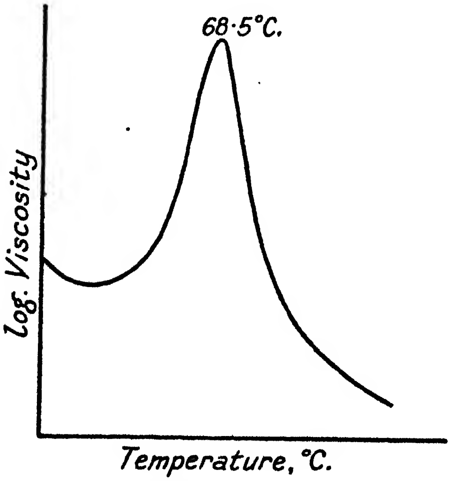

FIG. 191.—Viscosity and Temperature of Phenol-Water.

that the opalescent liquid is emulsoid in character, the particles of disperse phase being of colloid dimensions (Wo. Ostwald, 1907). Viscosity measurements on the emulsion at various temperatures indicate (fig. 191) that at first the viscosity falls as the temperature rises; it then rises rapidly as opalescence appears to a maximum at about 68·5° C., and ultimately falls, with the clear solution, to values lower than the initial ones.

A second interesting example is afforded by a starch suspension during heating (fig. 192). At first a normal decrease in viscosity is observed; it is strictly a linear function of the temperature. Then between 57° and 58·5° C., which is the temperature of gelation, there is a sharp change in the viscosity, which rapidly increases, as indicated.

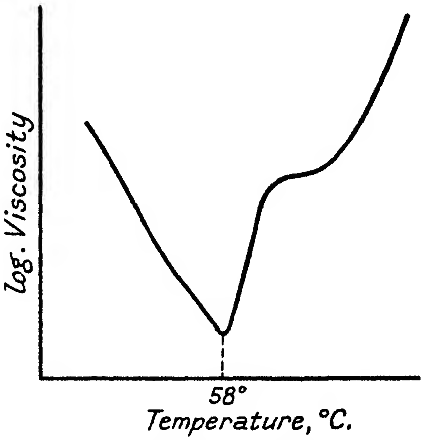

FIG. 192.—Effect of Heat on Starch Suspension.

COLOUR PHENOMENA.

Both opalescence and colour usually reach a maximum intensity in the colloid range. Thus, for example, molecularly dispersed solutions of gold are pale yellow in colour; indeed, very dilute solutions are practically colourless. When, however, these dilute solutions are treated with reducing agents which precipitate the gold in colloid form, an intense red or blue colour is developed, according to the degree of dispersion of the colloid particles. It has been suggested that the blue colour of certain specimens of rock salt (p. 444) is due to the presence of colloidal sodium, and that of ultramarine to colloidal sulphur.

As we might expect, different degrees of dispersion cause different colour effects. Usually the most highly dispersed particles give a yellow or orange effect, the larger ones giving violet. It has already been mentioned in connection with Zsigmondy's gold number (p. 460) that the addition of sodium chloride to red gold sol tends to turn it blue or violet in consequence of a gradual increase in size of the colloid particles. Silver hydrosols show similar changes in colour with variation in particle size, as indicated by the following data (Schaum and Lang, 1921):

Colour of Silver Sol.	Diameter of Particle.
Orange-yellow	60 $\mu\mu$
Orange-red	90 ,,
Purple	120 ,,
Violet	150 ,,
Bluish-green	180 ,,

The foregoing remarks apply more particularly to suspensoids. Emulsions of two liquids of similar refractive index but possessing different degrees of dispersion are chromatic, for the systems resemble vast collections of lenses. The effects sometimes are very beautiful. An example is afforded by glycerol dispersed in benzene. The system may be stabilised by addition of cellulose nitrate in amyl acetate. Such systems are known as **chromatic emulsions.**

THE PREPARATION OF SOLS.

Sols may be prepared by either of two different types of methods, namely :

A. Beginning with a system of low dispersion, the degree of dispersion is increased until colloid dimensions are reached. This is known as **peptisation** (Greek *peptein*, to digest) or simply as **dispersion.** The term "peptisation" was introduced by Graham because the process resembles that observed when solid proteins are peptised by ferments.

B. We may, on the other hand, begin with a molecular system and condense until colloid dimensions are reached. This is exactly opposite to the previous method and is known simply as **condensation.**

Condensation is more usual with suspensoids than peptisation ; it is usually more easy to effect, for the specific surface and hence the total surface tension effect is reduced, energy being liberated.

An interesting experiment was carried out by von Weimarn. An alcoholic solution of sulphur in a test-tube was frozen in liquid air. The sulphur remained in solution, probably as a molecular dispersoid, possibly partly in colloid form. On slowly warming, the following changes were observed :

(*a*) The solid became opalescent due to separation of colloidal sulphur.
(*b*) The whole became white, the sulphur particles now exceeding colloid dimensions.
(*c*) The suspension became faintly white as the suspended particles re-dissolved in the warmer alcohol and fell again to colloid dimensions.
(*d*) The solution became clear, the sulphur again being in molecular solution.

The first two changes, (*a*) and (*b*), illustrate condensation from a molecular dispersoid to a coarse suspension ; the next two changes, (*c*) and (*d*), illustrate the reverse, namely peptisation.

It has been pointed out (p. 466) that when an emulsion of phenol and water is warmed to its critical solution temperature, just before the liquid becomes a clear solution, an opalescence appears, due to the presence of globules of phenol of colloid dimensions in the water. Similarly on slowly cooling the clear solution the opalescence reappears. The difficulty, however, is to stop the peptisation or condensation, as the case may be, at the proper place. Let us see how this can be done.

A. Methods involving Peptisation or Dispersion.

From Gels.—In the preparation of emulsoids dispersion methods are frequently applied to gels. These usually consist in adding the requisite quantity of continuous phase to the gel. Thus, when the carpenter prepares his glue for application to wood, he warms the gel with water in a glue pot, which is essentially a water bath, until an emulsoid of requisite concentration is obtained. In preparing a sol of gum tragacanth the gum, in the form of a powder, is first moistened with alcohol and the mixture is then violently disrupted by a rapid stream of water obtained by turning on the tap rapidly and allowing water to burst into the mixture in its containing vessel. If water were simply added to the dry gum the outer portions would swell and protect the inner ones, and thus a sticky, unmanageable mass would be obtained. By making use of the solvent properties of alcohol in the manner described, this difficulty is overcome.

Mechanical Methods.—Sols of mercury can be made by forcing water, containing a trace of potassium citrate ($2{\cdot}5 \times 10^{-3}$ normal), which tends to prevent coagulation of the mercury, through mercury in such a manner that bubbles form on the surface of the mercury under water. These, on bursting, produce mercury hydrosols of a high degree of dispersion (Nordlund, 1918). A suitable form of apparatus is shown in fig. 193.

Chemical Methods.—As illustrating these, the preparation of **cadmium sulphide** hydrosol may be mentioned. Cadmium sulphide is first precipitated from ammoniacal solution with hydrogen sulphide. The precipitate is filtered off, washed, suspended in excess of water and hydrogen sulphide passed through. The suspension gradually becomes milky, then yields a clear, golden-yellow sol, with a slight red cast on its surface. On replacing the dissolved hydrogen sulphide with nitrogen, by bubbling this latter gas through the liquid, a very stable sol results.

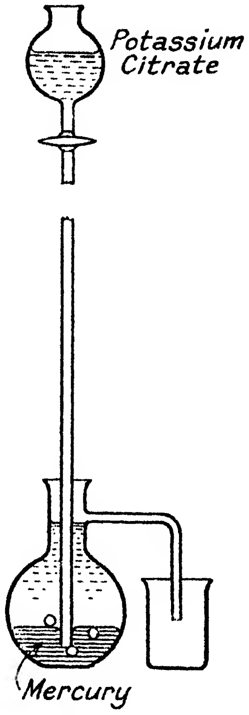

Fig. 193.—Apparatus for Production of Mercury Sols.

B. Methods involving Condensation.

These may be physical or chemical. A few illustrations will suffice.

Freezing.—Ice can readily be obtained as an organosol by rapidly cooling saturated solutions of water in organic media. When, for example, chloroform is saturated with water and rapidly cooled to −80° C. the ice separates out in particles of colloid dimensions, and the sol may be passed unchanged through filter-paper (von Weimarn, 1910).

Change of Solvent.—This is a very convenient method. **Sulphur,** for example, is practically insoluble in water, but dissolves in ordinary alcohol to the extent of about 0·05 gramme per 100 grammes at 18° C. Upon adding a saturated alcoholic solution to excess of water with vigorous stirring, the sulphur is precipitated out as a hydrosol, which is very stable, white in colour, with a bluish opalescence. Hydrosols of **phosphorus, gamboge, mastic,** etc. may be prepared in a similar manner. The gamboge sol is canary yellow in colour; the other two are white. An etherosol of **selenium** may be obtained by pouring a solution of crystalline selenium in carbon disulphide into an excess of ether. It has a beautiful rose-red colour, possessing a metallic sheen, and is stable for many days or weeks.

Chemical Precipitation is frequently employed. One of the simplest cases is the hydrolysis of ferric chloride. A couple of drops of saturated ferric chloride solution are added to about 300 c.c. of water in a beaker. This dilute solution, which is practically colourless, is now warmed to about 80° C., when it develops a well-marked orange-brown colour due to separation of **ferric hydroxide** in particles of colloid size. The sol is very stable, and illustrates very clearly the great intensity of colour that may be developed within the colloid range (p. 446). An orange-coloured sol of **antimony trisulphide** is readily obtained by adding ammonium sulphide to an excessively dilute solution of tartar emetic (potassium antimonyl tartrate). By passing hydrogen sulphide into dilute solutions of arsenious oxide and mercuric cyanide, sols of **arsenious** and **mercuric sulphides** are obtained respectively; the former is orange in colour, with a green surface effect in reflected light; the latter is brownish-black. Addition of a drop of ferric chloride solution to a jar of very dilute, acidified potassium ferrocyanide solution, with vigorous stirring, yields a clear blue sol of **Prussian blue.** In most of these cases the sol is rendered more stable by addition of a small quantity of an emulsoid, such as gelatin, 0·5 gramme of which, per litre, has proved very effective. In the preparation of metallic sols, chemical reduction is frequently employed. On warming a very dilute solution of gold chloride with a little tannic acid, a beautiful cherry-red colour develops, due to colloidal **gold**. The sol is fairly stable, and the tannic acid serves as a weak protective colloid as well as a reducer. If hydrazine chloride is used as reducing agent a blue or violet colour is developed, for the gold particles are of different size (p. 460) owing to the more powerful reducing activity of the hydrazine. Similarly a brown **silver** sol is obtained by reducing a very dilute ammoniacal solution of silver nitrate with tannic acid. A gel of gold and stannic acid possessing a rich purple colour by transmitted light is obtained by adding stannous chloride solution containing stannic chloride to dilute neutral gold chloride solution. It was first described by Andreas Cassius of Leyden in 1683, and is usually known as **Purple of Cassius.** When the precipitate is washed and dried it acquires a metallic lustre. When stannous chloride is added to dilute solutions of platinum salts a red coloration is produced due to the formation of so-called **red colloidal platinum,** which is kept in a fine state of division by the colloidal stannic acid present. In the absence of a protective colloid the red colour changes to brown. An interesting analogy may be traced between this red colloidal platinum and the better known Purple of Cassius referred to above.

As obtained by chemical methods such as the foregoing, the sols are contaminated more or less with other substances that may remain mostly dissolved in the continuous phase, but are also partially adsorbed on to the surface of the disperse phase. As we have already seen, adsorbed ions cause most, if not all, of the electric charge carried by sols, and the particular method of preparing a sol may determine whether that sol shall be charged positively or negatively (p. 461).

Electrical Methods.—In 1899 Bredig prepared hydrosols of platinum by sparking with a continuous current between two stout platinum wires immersed in ice-water. At first glance this might appear to be a dispersion method, but it is not really so. The metal is first vaporised by the intense heat of the arc and then condenses in the water. Sols of palladium, iridium, gold, silver, etc. have also been prepared in this way. By using pure water and pure platinum we expect to obtain a pure hydrosol; nevertheless it is always negatively charged. The old idea was that the charge was frictional, but this has been shown to be incorrect. The charge appears to be ionic, and it is thought that during disintegration in the arc some of the platinum is oxidised and during subsequent condensation some platinum particles and some oxidised particles coalesce. The oxidised platinum in contact with water acts as an electrolyte, perhaps as platinic acid, $PtO_2.4H_2O$ or $H_2Pt(OH)_6$, with the result that the growing particles develop into a complex anion in equilibrium with an equivalent quantity of hydrogen ions (Pennycuick, 1927).

Bredig's sols were prepared in open beakers or dishes. The arc thus was "free." By suitably surrounding the arc Svedberg has obtained what he calls an **enclosed arc**, the temperature of which is greater, the vaporisation of the metal being considerably increased. Of the two electrodes the anode is the more sensitive to thermal protection. Svedberg's apparatus is shown in outline in fig. 194. It has been used for the preparation of silver alcosols, and consists of a quartz tube AB provided with a small hole level with the arc between two silver wires of about 1 mm. diameter. A current of nitrogen enters through both ends of the tube AB and escapes through the small hole, carrying with it the silver vapour at a high temperature. By applying a magnetic field, the escape of the silver is facilitated. The metallic vapour condenses in the alcohol in the surrounding tube CD, yielding an alcosol. The sol, however, may contain appreciable quantities of colloidal silicic acid.

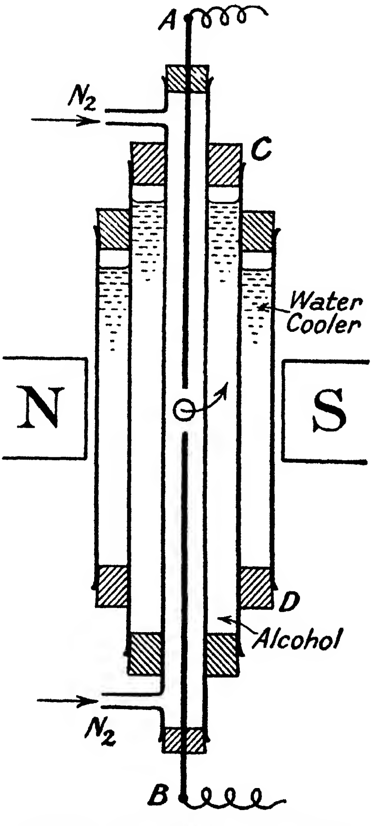

Fig. 194.—Svedberg's Enclosed Arc.

Concentration of the Disperse Phase.

The concentration of a sol is expressed by the ratio of the disperse phase to the continuous phase. Since, however, the colloid particles may vary in size, one should, strictly speaking, give the specific surface of the disperse phase as well as the concentration.

In the absence of a protective colloid, suspensoids can usually be prepared only in dilute sols, usually containing less than 0·5 per cent. of metal by weight in the case of metal sols. Higher concentrations of suspensoids other than metals have been obtained, as, for example, 4·4 per cent. of arsenious sulphide and 4·58 per cent. of sulphur in the corresponding hydrosols.

Emulsoids, on the other hand, are not so restricted. Indeed there appears to be no upper limit of concentration. Thus gelatin, by suitable regulation of the temperature, will retain its colloid form with progressively smaller quantities of water, and will not separate as a coarse mechanical system or emulsion.

EMULSOIDS.

Emulsoids are classified usually as organic and inorganic. The former are the more numerous; the latter are represented by silicic acid and a few other substances of analogous composition, such as stannic acid and titanic acid.

Gelation.—Emulsoids show considerable variation with regard to gel formation or gelation. They may be divided into three main groups, namely, where

(*a*) Gelation is reversible and may be produced by increasing the concentration or lowering the temperature. This is the case with agar and gelatin. Hysteresis (Greek *hysteros*, later) is usually manifested on setting, the setting point lying many degrees below the melting point (p. 476).

(*b*) Gelation may take place irreversibly on warming, as with albumen, or on addition of electrolytes, as with silicic acid.

(*c*) Gelation may not take place either on heating or on cooling. This is the case with most emulsoids in continuous phases other than water.

Adsorption of Emulsoids.—The disperse phase of emulsoids is very susceptible to adsorption by solids. The corrosion of metals immersed in water affords a good illustration, the presence of small quantities of typical emulsoids exerting a pronounced retarding effect. The following data refer to small sheets of iron, zinc and lead suspended in water and various emulsoids of concentration 0·2 per cent. The corrosion was determined by noting the loss in weight after an exposure for three weeks, the loss suffered by the metals in water alone being taken as 100 (Friend and Vallance, 1922).

Effect of Emulsoids on the Rates of Corrosion of Metals in Water.

Emulsoid.	Relative Corrosion of Iron.	Relative Corrosion of Zinc.	Relative Corrosion of Lead.
Water	100	100	100
Sucrose	112	129	5
Gum acacia	57	200	19
Gelatin	41	94	3
Tragacanth	23	26	2
Agar	3	0	1

These results are of considerable domestic importance, since in culinary operations emulsoids are produced largely. In this probably lies the explanation of the very marked resistance to corrosion offered by aluminium cooking utensils. The behaviour of sucrose is interesting, for in dilute solution it is not colloidal but molecularly dispersed. It shows a pronounced accelerating action on the corrosion of iron and zinc, but a powerful retarding action on that of lead. Lead is very susceptible to colloid retardation.

The rate of dissolution of salts in water is retarded by the presence of emulsoids, which appear to be adsorbed on to the crystal faces and so retard the solvent action of the water. The following results obtained with a few typical emulsoids at room temperatures are illustrative:

Effect of Emulsoids on the Rates of Dissolution of Salts in Water.

Emulsoid.	Percentage Concentration of Emulsoid.	Duration of Experiment, minutes.	Salt.	Percentage Retardation of Dissolution.
Agar . .	0·02	60	K_2SO_4	1·8
Gelatin . .	0·10	20	,,	1·51
Gum acacia .	0·10	20	,,	1·14
Agar . .	0·03	15	$KClO_3$	1·63
	0·10	15	,,	15·6

The retardation in the rate of solution is quite pronounced, and the order for the different emulsoids is substantially the same as in the corrosion experiments already mentioned. The retardation increases progressively with the concentration of the emulsoid, but if sufficient time be allowed the same amount of salt will be dissolved eventually as if no emulsoid were present.

In making casts with plaster of Paris, artists delay the setting of the plaster by addition of some emulsoid such as gum acacia. Experiment shows that the retardation with varying concentrations of the gum conforms very closely to the requirements of the adsorption law (p. 488). Many other reactions have been studied in a similar manner. Thus the liberation of iodine from potassium iodide solution by ammonium persulphate is similarly retarded. Agar, on the other hand, appears to have no influence on the velocity of the acid catalysis of methyl acetate. This suggests that the rates of reactions taking place in solution and concerned with molecular dispersoids only, without involving any change of state, are not appreciably affected by dilute emulsoids. Generally speaking, *emulsoids tend to retard the rate of such reactions, whether chemical or physical, as involve a change of state from solid to liquid or vice versa in one or more of the components.*

In photographic processes the part played by emulsoids and gels on the rate of chemical reactions is of paramount importance.

A very pretty lecture experiment is afforded by the precipitation of mercuric iodide on addition of the chloride to potassium iodide. If this is carried out in moderately dilute aqueous solution, the unstable yellow form is first precipitated, but changes rapidly from orange to red as it becomes converted to the more stable variety. If, however, the reaction is carried out in the presence of gelatin, say 1 per cent., the liquid first turns yellow momentarily, due to the formation of colloidal mercuric iodide, then becomes turbid, and a beautiful canary colour develops, which remains practically unchanged for half an hour or more, according to circumstances. Only very slowly does change occur to the red polymorph. The protective colloid retards the growth of the yellow particles. Sunlight accelerates the change markedly. With the aid of the ultramicroscope these changes may be seen beautifully. Drops of gelatin and dilute potassium iodide solution are mixed under the coverglass and the ultramicroscope focussed as usual. A drop of mercuric chloride solution is brought to the edge of the coverglass and is drawn under by capillary action. The field of the ultramicroscope becomes swept with a stream of luminous particles moving with dazzling velocity—the Brownian movement of the colloidal mercuric iodide. The movement slows down as the particles increase in size, until the colloid range has been passed, and after a few minutes a fine precipitate is obtained evincing hardly any movement.

Influence of Emulsoids on Suspensoid Catalysts.—The stabilising action of emulsoids on suspensions has already been referred to (p. 460). It is attributable to adsorption. It is not surprising, therefore, that the catalytic activity of suspensoids, protected in this manner, should be weakened. The decomposition of hydrogen peroxide, for example, is accelerated by the addition of even traces of colloidal platinum (p. 471), and the reaction is a convenient one to study since the rate of decomposition is followed readily by titration of aliquot portions of the reaction mixture with potassium permanganate. Addition of a little gelatin sol retards the catalytic activity of the platinum, as the following data (Groh, 1914) show. By θ is meant the relative time required to decompose 50 per cent. of the peroxide solution using the same concentration of platinum sol.

Gelatin, per cent. .	0·000	0·001	0·01	0·05	0·10
θ	100	437	460	620	983

If the retardation is regarded as proportional to the extent of adsorption by the sol, the data are found to conform to the requirements of the adsorption law (p. 438). The inhibitive effect of various other typical emulsoids upon the decomposition of hydrogen peroxide by colloidal platinum has been studied by Iredale (1921), and when these emulsoids are graded in the order of their inhibitive powers, the order is substantially the same as that obtained in the corrosion tests (p. 472). This is to be expected, as both are adsorption phenomena.

Colloidal Electrolytes.—This name has been given (McBain and Salmon, 1920) to solutions of salts in which one of the ions has been replaced by a charged, hydrated ionic micelle or colloid particle. The electrical conductivity of a colloidal electrolyte is comparable with that of an ordinary salt, since the colloidal ion is very heavily charged; but since the ionic colloid exhibits the low osmotic effects of an ordinary colloid, the total osmotic activity of a colloidal electrolyte may be much less than that of an ordinary electrolyte.

To this group of substances belong dyes, such as Congo red, various indicators, and gelatin salts; in short, many substances of high molecular weight, such as, for example, those containing long carbon chains, but which are able to cast off an ordinary ion.

In this connection soaps have been very carefully studied by McBain and his co-workers; they are particularly suitable for the purpose, since their chemical formulæ are known, no tautomerism takes place, and a truly reversible equilibrium is readily established in solution. Furthermore, the definite transition from a typical crystalloid electrolyte through a colloidal electrolyte ultimately to a neutral colloid may be demonstrated by changing the temperature and concentration. Let us choose sodium palmitate as our typical soap. For most concentrations the degree of hydrolysis in water is very small; in extreme dilution it is appreciable, but with concentrations ranging from decinormal upwards the concentration of hydroxyl ion, as determined by e.m.f. and by catalytic methods (see Vol. II), increases but slowly. The hydrolysis of sodium palmitate is represented as follows:

$$C_{15}H_{31}COONa + H_2O \rightleftharpoons C_{15}H_{31}COOH + NaOH,$$

and the actual extent of hydrolysis at 90° C. is found to be:

Concentration of Soap (Normality)	N	$0{\cdot}75N$	$0{\cdot}5N$	$0{\cdot}1N$	$0{\cdot}01N$
Hydrolysis (Per cent.) . .	0·20	0·30	0·37	1·28	6·6

Above decinormal, which is approximately 3 per cent. concentration, the hydrolysis is only a fraction of 1 per cent.

Despite this low hydrolysis, soaps, particularly in concentrated solutions, exhibit a high electrical conductivity, comparable with that, for example, of sodium acetate. As so little free alkali is present this must be a property of the soap itself.

McBain concludes that, in concentrated solution, a portion of the soap coalesces to form a neutral colloid particle, say $(NaP)_x$, where P stands for the palmitic acid radical. The anions also are supposed to combine similarly with one another, say to $(P')_n$, where P′ represents the palmitic ion, carrying one electric charge. These aggregates coalesce, together with water, to form a heavily charged colloid particle of general formula

$$(NaP)_x . (P')_n . (H_2O)_y .$$

Such aggregates constitute the micelles already referred to. Being of colloid dimensions they exhibit but little osmotic activity; but because of their large electric charge, n being at least 10, and probably much more, these micelles move rapidly in an electric field, and thus impart to the solutions a comparatively high electrical conductivity.

GELS.

A gel may be defined as *a solid, jelly-like system which may consist of two liquid phases or of one solid and one liquid phase.* As with sols, a suitable prefix indicates the nature of the continuous phase. The terms hydrogel, alcogel, benzogel are self-explanatory.

An ordinary table jelly is an excellent example of a hydrogel, and its method of preparation by allowing a warm emulsoid of sufficient concentration to cool to the ordinary temperature is a typical one. If such a gel is warmed, it becomes an emulsoid sol again; this is termed **solation.**

Gels are classed roughly as **rigid** and **elastic.** To the former class belong the inorganic gels such as silicic acid ; most jellies are elastic.

Physical State.—Gels appear to be solid, even when they contain upwards of 99 per cent. of water. They may be cut, bent, and even broken. When subjected to prolonged pressure they gradually flow, and in course of time a gel will assume the shape of its containing vessel.

Probably gels possess structure. We have already seen that emulsoids appear to possess a certain amount of structure, and that this is more or less broken down by passage through capillaries (p. 464). It is reasonable to suppose, therefore, that in gels this structure will be more definite. Microscopic examination, however, is not free from objection. The two phases of a gel possess closely similar refractive indices, and if stains or other substances are used to bring out the microstructure, it may well be argued that these agents may cause or modify that structure. Vapour pressure measurements indicate that gels have fine pores, 2·5 to 5 $\mu\mu$ in diameter, which suggests a fibrillar structure.

The structure of a gel may be more or less independent of the liquid continuous phase, since this latter may be replaced by other liquids of very diverse character and even by gas, with inappreciable shrinkage (Kistler, 1931). Ordinary evaporation of the liquid phase causes severe shrinkage (see p. 479), and the effect upon the structure may be very pronounced. Suppose, now, a gel is produced in a suitable liquid, and that liquid is more or less completely replaced by a second liquid, such as alcohol or propane, of low critical temperature and which does not dissolve the structure ; then, on placing in an autoclave with excess of the liquid and raising above the critical temperature whilst the pressure is maintained above the vapour pressure, so that sufficient evaporation of liquid cannot occur to cause contraction of the gel by surface capillary forces, the liquid is converted to gas without discontinuity. If the gas is allowed to escape, then, on cooling, a coherent gel is obtained, the volume of which is practically unchanged, whilst the continuous phase has been replaced by air. **Silica aerogel** has been obtained by Kistler in this way ; it is highly opalescent, displaying a glassy fracture and, when dropped, small pieces emit a metallic ring. In a similar manner aerogels of gelatin, agar, egg albumen, alumina, etc. have been prepared.

Melting Points.—Gels do not melt sharply like pure crystalline substances, so that the numerical value of the melting point must be a somewhat arbitrary figure. Usually the melting point is higher than the setting point, a phenomenon known as hysteresis (p. 472). This is illustrated by the hydrogels of agar and gelatin :

	Melting Point.	Setting Point.
Agar (approx. 1 per cent.) . .	100 to 105° C.	35 to 40° C.
Gelatin (approx. 5 per cent.) .	26° C.	18° C.

The melting point of a gel is determined conveniently by allowing it to set in a thin-walled test-tube with a glass rod R (fig. 195) embedded in it. On slowly warming the water bath the temperature is noted at which, on raising R, the test-tube begins to slide off the gel. If, now, the bath is allowed to cool, the setting point is the temperature at which the test-tube rises with R when the latter is lifted.

Diffusion.—Molecular dispersoids diffuse readily through gels. Graham, for example, found that sodium chloride diffused in gelatin almost as rapidly as in water. This applies only to dilute gels, up to about 3 or 4 per cent. of gelatin, or, in the case of agar, less than 1 per cent. At higher concentrations of the disperse phase the rate of diffusion is appreciably less.

The process of diffusion can readily be watched if coloured substances are used. For example, a test-tube may be half-filled with a gel of agar or gelatin by pouring the warm emulsoid into it and allowing to cool. If, now, a solution of some coloured salt, such as copper sulphate or cobalt chloride, be poured on top and allowed to stand, the characteristic colour will gradually penetrate down the gel as diffusion proceeds. If a dilute solution of ferric chloride is poured into a tube containing an agar gel to which a little alkaline phenolphthalein has been added, the red colour is bleached as the hydrochloric acid, produced by hydrolysis of the ferric chloride, diffuses downwards.

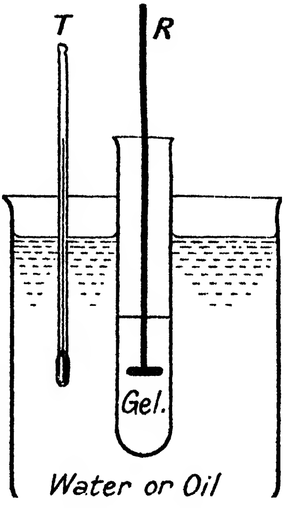

FIG. 195.—Apparatus for Determining Melting Point of Gel.

Some gels, however, offer considerable resistance to the passage of dissolved substances. Thus a fairly concentrated solution of sodium sulphate will deposit crystals if some pig bladder is introduced. The bladder imbibes the water, but not the sodium sulphate. Certain inorganic gels, such as copper ferrocyanide, refuse admittance to many dissolved molecules, and thus act as semipermeable membranes. These are widely used in osmosis investigations (p. 382).

Rhythmic Precipitation.—In 1869 Ord obtained stratified precipitates of calcium oxalate in the presence of colloidal substances. The subject was more fully investigated by Liesegang in 1896, and his name is usually coupled with the phenomenon. If a little dilute silver nitrate solution is poured into a test-tube containing gelatin hydrogel to which a small quantity of potassium dichromate has been added, a red patch of silver chromate is formed at the surface of the gel. Upon standing for a few hours it will be observed that a clear space occurs just below the top layer of silver chromate, followed by a band of more silver chromate; this is followed by alternate clear spaces and bands of precipitate for a considerable distance down the tube. The phenomenon is known as rhythmic or periodic precipitation.

The experiment may be varied by preparing a block of gelatin containing potassium dichromate and dropping it into a beaker containing silver nitrate solution. The silver salt diffuses into the block from all parts, and upon removing the block and cutting in two, rhythmic precipitation will be seen to have taken place, the banded structure closely resembling that of agates. It has been suggested that agates have been formed in Nature from silica gels in an analogous manner.

If a thin layer of chromated gelatin is spread on a sheet of glass and a drop of silver nitrate solution added at the centre, diffusion takes place outwards from the drop and rings of silver chromate are produced. These are known as Liesegang rings.

Measurement shows that, if $d_1, d_2, d_3 \ldots$ are the distances between successive rings, then the ratio

$$\frac{d_3 - d_2}{d_2 - d_1} = \text{constant}.$$

Periodic precipitation can be effected under suitable conditions in the entire absence of gels (Morse, 1931), although the formation is usually microscopic in size. The function of the gel in the foregoing experiments would thus appear to be merely to render more favourable the conditions of periodic precipitation and thus to induce effects that are macroscopic in size. Although many theories have been suggested, the simplest appears to be that the distance between successive rings is largely determined by the difference between the rates of diffusion and of precipitation in the gel. The gel retards the "release" of supersaturation and thus enhances the relative effect of diffusion, so that an increase in the distance between successive rings occurs, other things being equal, over that in the absence of the gel.

Turgescence.—Many gels tend to swell when exposed to certain liquids or vapours. This is termed turgescence (Latin *turgere*, to swell) or **imbibition** (Latin *in*, into; *bibere*, to drink). A similar phenomenon has long been known. The ancients quarried by hammering dried wooden wedges into cracks in the rocks. Water was then poured on, which caused the wood to swell and force the masses of rock apart. The bursting of fruit after a prolonged drought is much the same phenomenon, the skin being unable to keep pace with the turgescence of the fruit beneath.

In general the total volume of the gel and water falls, as can readily be shown in the case of gelatin by adding the latter to a flask with a long narrow neck, filling with water to a given level, and noting the fall in level some hours later when the gelatin has swelled.

Only certain liquids or vapours will induce turgescence. Thus rubber is practically unaffected by water, but immersed in benzene it expands enormously in a very few minutes. Every cyclist knows that the amount of rubber left on a tyre after evaporation of a fairly large bulk of rubber "solution" is very small.

Sometimes a certain temperature must be reached before turgescence takes place; this is so with ordinary potato starch. The water must be raised to about 58° C. When swelling occurs the viscosity suddenly increases very greatly (p. 467).

The effect of vapours in producing swelling is well illustrated by breathing on to thin sheets of gelatin. Unequal turgescence takes place and the gelatin foil coils up into various shapes. The swelling of animal hair in a moist atmosphere is utilised for hygrometers.

Turgescence is accompanied by heat evolution, as the following data show:

Dried Gel.	Gramme-calories evolved per gramme of Gel.
Gelatin	5·7
Starch	6·6
Gum acacia	9·0
Gum tragacanth	10·3

Syneresis—a term due to Graham—(Greek *syn*, together; *hairein*, to take) is the exact opposite of turgescence, and refers to the partial separation of the continuous phase from the gel. When a dilute gel is allowed to rest for several hours or days, protected against evaporation, and of course from any possible infection by micro-organisms, it separates into two layers, one being liquid and the other solid, as before, but containing a higher concentration of disperse phase. The liquid layer may be in the form of drops, and is usually termed "condensation water." This is not a good term, for it is not pure water, but a dilute sol; and it has not been condensed, but secreted from the gel. If unprotected from evaporation, the water will pass off as vapour and the gel will become drier.

When a gelatin sol is poured over glass, allowed to set and the whole warmed to, say, 100° C. in an oven, much of the water evaporates off rapidly, and the gel shrinks, but as it clings tenaciously to the glass, the gel tries to make the glass surface shrink with it and actually tears out shell-shaped pieces of glass.

When a dilute gel on a sheet of glass is surrounded by a freezing mixture, some of the water in the gel crystallises as frost figures. Upon thawing and allowing this water to drain away, the gelatin retains the impression of the crystals.

Effect of Strain.—In the unstrained state gels are isotropic; when strained, however, they become doubly refracting, like glass under strain. Quantitative experiments indicate that the extent of the double refraction is approximately proportional to the strain (Leick, 1904).

When rapidly stretched, gels become warm. Hence, by the theorem of Le Chatelier (p. 23), rapid warming of a stretched gel should cause it to contract. This may be illustrated by suspending a stretched piece of rubber tubing in the centre of a wide tube down which steam is subsequently passed (fig. 196). As the temperature of the rubber rises, the indicator A ascends the arbitrary scale.

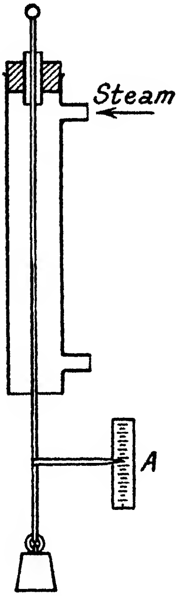

FIG. 196.

When violently shaken, a gel may become liquid, but return to its gel form again on standing. This change is known as **thixotropy** (Greek *thixomai*, I shall touch).

DISPERSE SYSTEMS IN GASES.

Disperse systems in which the continuous phase is gaseous are found to resemble, as closely as one could reasonably expect, the solid–liquid and liquid–liquid systems which have been discussed in the preceding pages. Systems of one component are known, of which a mist of liquid water in water vapour affords a good example. The most common systems, however, contain two components, and if the air is the gaseous phase and the disperse particles are of colloidal dimensions, the system is termed an **aerosol**. Such dispersions may be divided into two groups according as the disperse phase is solid or liquid. Examples are :

Solid disperse phase . .	Dust, fume, smoke.
Liquid ,, ,, . .	Cloud, mist, spray.

Formation of Disperse Systems.—Both dispersion and condensation methods may be employed. As examples of **dispersion methods**, grinding, spraying and explosion or detonation may be mentioned. The student will readily think of examples of these. In Nature these processes frequently occur on a grand scale. During the great eruption of Krakatoa in 1883 vast quantities of dust were hurled into the air, and for several years afterwards the sunsets were remarkable for their glow, indicating that particles of dust in a highly disperse condition continued to float in the atmosphere.

Preliminary dispersion may lead ultimately to **condensation** as a final stage. Thus, during the Great War, cloud screens were produced frequently by the detonation of hygroscopic substances such as stannic chloride. Atmospheric moisture condensed on the finely dispersed particles, yielding a mist. Some of the earliest smoke clouds produced were obtained by the combustion of white phosphorus. Other examples of condensation are afforded by the gradual cooling of a moist atmosphere, whereby a mist or cloud is produced, by the volatilisation of metals in an electric arc and their subsequent condensation in the surrounding air, by the union of two chemically reactive gases such as ammonia and hydrogen chloride—at first the product of the reaction will be of molecular dimensions, but condensation leads to the production of a fog.

In Nature, cloud particles range from about 6 to 17 μ in diameter; fog particles are larger, namely, from 14 to 35 μ. When the diameter reaches 40 μ, or 0·04 mm., the particles begin to precipitate out as fine rain. Rain drops vary in size from this to a maximum of about 6 mm. A cloud may be produced artificially by the sudden, adiabatic expansion of a moist atmosphere containing dust particles. The cooling due to the expansion causes deposition of moisture on the dust particles.

In many chemical reactions, notably in certain forms of oxidation or combustion, fumes are produced which yield fogs containing particles in a highly disperse condition. Thus, when roasting arsenical ores a fume of arsenious oxide is evolved; in the regulated combustion of crude oils a black smoke of carbon is evolved which, on condensation, yields the product known as lampblack or carbon black; combustion of coal and other fuels in factories and domestic grates yields vast quantities of smoke—thus a massive bank of smoke in London has been seen to rise to a height of several thousand feet and to be carried away in a sunlight-obscuring trail fifty miles in length.

Among the inorganic particles present in the air are minute crystals of sodium chloride which are believed to owe their origin to sea spray, and are found inland, hundreds of miles from the sea. Sodium sulphate particles are also present, and are formed probably by the interaction of sodium chloride with sulphurous acid vapour, with subsequent oxidation.

The Concentration of the Disperse Phase.—The amount of coarsely dispersed material in the air or in gases is frequently determined by aspiration of the air or gas through some porous material which functions as a filter and examining the residue **gravimetrically** or **colorimetrically**. This method is frequently used for determining the concentration of smoke in boiler flues and stacks. The apparatus shown in fig. 197 is fairly typical. A brass tube AB is fixed horizontally in the stack wall. It is closed at A, but a slit CD, some 3 inches long, admits the smoke, which is aspirated at the rate of about one litre per minute through the glass tube G containing a cotton plug, which is dried in a steam oven before and after exposure until constant weight is attained.

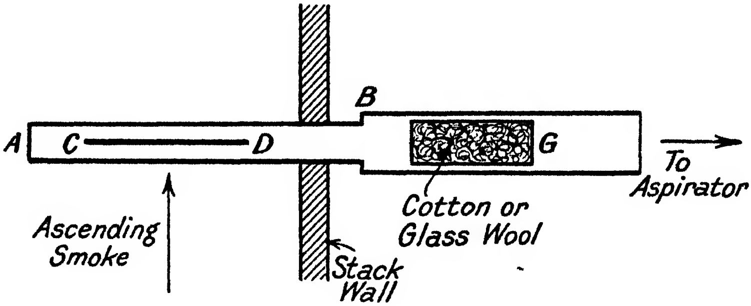

FIG. 197.

The first accurate work on the concentration of suspended organic matter in the air was that of Russell in 1885, who ignited his filter, which was of glass wool, with copper oxide, and estimated the carbon and nitrogen. He found that London air contained :

	Mgrm. Organic Matter per 100 cu. ft. Air.
In fine weather	0·35
Dull weather	1·03
Foggy weather	2·44

Results of a similar order were obtained in Leeds by Cohen in 1897, namely, 1·2 milligrams of general solid disperse phase per 100 cubic feet of air. Assuming this to be distributed uniformly up to a height of some 300 feet, it represents 2 cwt. of solid over each square mile.

Even the purest atmospheres contain minute particles of dust. It is rare to find air with fewer than 100 particles per cubic centimetre. In London the figure may rise to 100,000 or even 150,000. Swiss air, which is very clear, has more than 300, and the air over different seas has been found contaminated as follows :

	Particles per c.c.
Atlantic Ocean	2000
Mediterranean Sea	875
Pacific Ocean	245
Indian Ocean	243

In the following table are given some of the data obtained by Owens on the Norfolk Coast in a series of tests during August 1921 :

Examination of Air at Holme, Norfolk.

(Owens, 1922.)

Date, August 1921.	Number of Particles per c.c. of Air.	Average Diameter (Microns).	Remarks.
13	150	0·5	Fine dark-coloured dust. No crystals.
18	310	0·5 to 0·7	Very uniform in size. No crystals.
20	145	0·5	Some crystals.
25	304	0·5	All rounded. Some perfect spheres.
28	17	0·5	Irregular.

Smoke recorders are sometimes used ; in these smoke is made to impinge on a cold surface, such, for example, as white paper wrapped on a revolving water-cooled drum. The intensity of the stain produced is roughly proportional to the concentration of the disperse phase. For white dispersions, such as flour, black papers may be used.

Various **optical methods** have been tried. During the Great War the obscuring power of a smoke or cloud was defined as the number of square feet of landscape obscured by one pound of smoke material. It was measured by dividing the volume of smoke by the depth of the smoke layer necessary to obscure the filament of a standard lamp (40-watt Mazda). This, of course, was purely an arbitrary standard, and experience showed that, for a given concentration, a large number of small particles was a more effective obscurer than a smaller number of large particles.

Tyndallmeters have been tried (Tolman, 1919), in which a beam of light is made to pass through a column of smoke and the intensity of the emergent beam is observed through a telescope fixed at right angles to the direction of the beam. If the concentration of the disperse phase is not too great, it is regarded as inversely proportional to the intensity of the emergent beam, provided of course the particles undergo no appreciable change in size. The instrument may be standardised with a suspension of finely ground silica in water, and under uniform conditions can be made to yield very uniform results.

Perhaps the most satisfactory method of determining the concentration of the disperse phase consists in **electrostatic precipitation**, which was first suggested by Hohfield in 1824 as a means of preventing smoke nuisance, Lodge following up the subject more fully in 1883. The process is now carried out on a large scale in the precipitation of the suspended particles of commercial fumes and smokes. The Lodge-Cottrell precipitator in its simplest form comprises a number of vertical pipes or series of plates through or between which, for example, fumes from some metallurgical plant are passed. The pipes or plates form the anode, whilst the cathode may consist of a wire hung down the axis of the pipes or centrally between each pair of plates, and raised to 80,000 volts. The disperse particles in the gases become highly charged, and are repelled from the wire on to the pipes or plates, where they collect and finally fall down into hoppers. This method, modified as required to meet special conditions, is used for de-tarring coal gas as it leaves the retorts at the gas works, for the precipitation of fumes of sulphuric acid obtained during concentration of the acid, for the fractional precipitation of the constituents in smokes, and for many other similar purposes. Under suitable conditions precipitation of the disperse phase is so complete and efficient that the process may be adapted to a quantitative determination of this phase. A suitable apparatus for this purpose is shown in fig. 198. A fine platinum wire under tension and raised to 15,000 volts passes centrally through a glass tube, some 10 inches long, containing a weighed piece of thin aluminium foil wrapped cylindrically in position. The gases are passed through at the rate of 5 litres per minute. The increase in weight of the aluminium foil is noted.

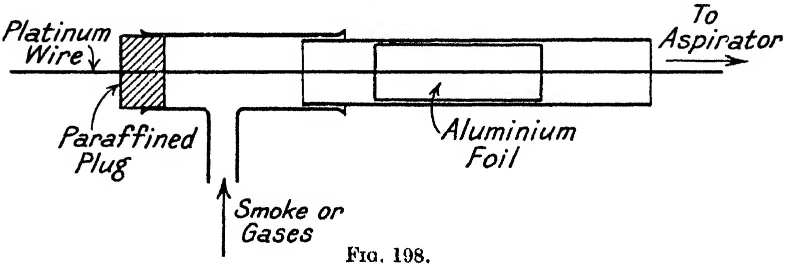

FIG. 198.

Brownian Movement in Gaseous Systems.—This was first studied by Bodaszewski in 1881, but it was not until 1909 that quantitative investigation was undertaken, namely, by de Broglie. The movements of particles of tobacco smoke were recorded on a photographic plate with the aid of an ultramicroscope. It was proved experimentally in this way that Einstein's equation (No. 10, p. 455) holds for gaseous systems.

Size of the Disperse Particles.—When the particles of the disperse phase are of microscopic size, they can of course be collected on a slide and their dimensions observed directly through the microscope. When, however, the particles are of colloid dimensions, indirect methods must be employed, as in the liquid systems already studied.

One method consists in noting the **rate of sedimentation,** in accordance with Stokes' Law (equation (8), p. 454). Owing to the low viscosity of gases—for air at 15° C. the viscosity is only $1{\cdot}81 \times 10^{-4}$ unit—the rate of sedimentation is proportionately high. It may be noted that, assuming the particles to be spherical, the law does not hold when their radii exceed 10^{-2} cm. The particles then fall like rain, the maximum velocity of which, falling through the air, is approximately 8 metres per second. Equation (8) also does not apply unless the particles are appreciably larger than the mean free paths, λ, of the gas molecules. For oxygen (p. 53) λ is $10{\cdot}2 \times 10^{-6}$ cm.; for particles of radius less than 10^{-4} in oxygen or air, therefore, equation (8) does not give accurate results.

When the particles are relatively large, say of radii lying between 10^{-4} and 10^{-2}, the mean or resultant effect of the molecular bombardment to which they are subjected when at rest by the gaseous molecules is that of a uniform and continuous pressure exerted normally over the whole surface area of the particle. Consequently, on falling under the influence of gravity, the particle encounters a continuous uniform resistance which increases with the velocity of the particle. Taking the viscosity of air as $1{\cdot}81 \times 10^{-4}$ at 15° C., and neglecting the density in comparison with that of water, equation (8) becomes

$$u = 120 \times 10^{4} \times r^{2} \text{ cm. per sec.,}$$

from which the following velocities for particles of water falling through air under gravity are readily calculated :

Radius of particle .	10^{-2}	10^{-3}	10^{-4}	10^{-5} cm.
Rate of fall . .	120	1·2	$1{\cdot}2 \times 10^{-2}$	$1{\cdot}2 \times 10^{-4}$ cm. per second.

The difficulty with the smaller particles is to avoid convection currents.

If, now, the particles are smaller than the mean free paths of the gas molecules, or, what comes to the same thing, when larger particles fall through a rarefied gas, they will tend to slip between the molecules, and the resulting velocity will be greater than that postulated by Stokes' Law. Cunningham (1910) and Millikan (1911) showed that the relation between the two velocities is given by the expression

$$\frac{u_{\text{obs.}}}{u} = 1 + A\frac{\lambda}{r} \quad . \quad . \quad . \quad . \quad (25)$$

where $u_{\text{obs.}}$ and u are the observed velocity and the theoretical velocity, according to Stokes' assumptions. A is a constant approximating to 0·817, and λ is the mean free path of the gas molecules. Stokes' equation thus becomes

$$u = \frac{u_{\text{obs.}}}{1 + A\frac{\lambda}{r}} = \frac{2}{9}r^{2}g\frac{(d_1 - d_2)}{\eta} \quad . \quad . \quad . \quad . \quad (26)$$

The size of the disperse particles may also be calculated from observations of the **Brownian movement** (equation (11), p. 455), from the **rate of diffusion** (equations (10) and (12), p. 455), from the **intensity of the scattered light** (equation (14), p. 456), and finally by Millikan's **oil-drop method** (1910), so called because it was first applied to minute drops of oil. This last method consists in observing the rate of fall, u_1, under the influence of gravity, of a charged particle of mass m suspended in a gas ; an electric field, X, is then applied, which partly or completely neutralises the effect of gravity or even reverses the direction of the particle and makes it rise. Assuming the particle to carry one electronic charge, e, and in almost every smoke some particles do carry this charge, if u_2 is the final velocity under the combined effect of the electric field and gravity,

$$\frac{u_1}{u_2} = \frac{mg}{Xe - mg} \quad . \quad . \quad . \quad . \quad (27)$$

which gives a method of calculating m.

Thermal Precipitation.—That solid particles are deposited more easily upon a cold surface than upon a hot one is shown readily by holding alternately a cold flask filled with mercury and a hot one filled with boiling water a few inches above a strip of burning magnesium. A deposit of magnesia is formed on the cold flask, but not on the hot flask. For this reason a cooled drum is used, as already mentioned, with certain smoke recorders.

If tobacco smoke is passed between two concentric tubes one of which is appreciably warmer, say by some 80° C., than the other, the disperse phase will be quantitatively deposited upon the cooler tube.

The air in rooms heated by pipes and radiators is warmer than the walls and furniture, so that suspended dust readily collects upon these. The accumulation of sooty patches above radiators, lamps and gas brackets on the walls and ceilings of rooms is sometimes very pronounced.

These facts are of considerable biological importance. The dust of a dusty atmosphere is cooler than the lungs, and this, coupled with the evaporation of moisture, tends to prevent the deposition of dust on the lungs. In this connection it may be mentioned that Lehmann (1912) has shown that when a dust-laden air is breathed through the nose, approximately 40 per cent. of the dust remains in the human system, either in the lungs or stomach, the remaining 60 per cent. either being respired or retained by the nose and mouth. If, however, the subject breathes through the mouth, some 80 per cent. is retained by the body. This illustrates the importance of breathing through the nose, but it also illustrates the necessity of reducing the dust in the atmospheres of public rooms and dwellings to the smallest possible amount, as no matter how careful the subject is, some of the dust finds its way into the human system.

Optical Properties.—The permanent gases are very transparent to light when free from dust and moisture ; but the introduction of a disperse phase effects great changes in this property, particularly in the presence of moisture. Tyndall (1868) ascribed the colours of sunrise and sunset to the selective scattering of light by minute particles of dust and/or water suspended in the atmosphere ; the optical effects observed after the eruption of Krakatoa support this view. Tyndall further showed that the light scattered by the disperse particles of smokes and clouds is polarised. Hence an atmospheric haze frequently disappears, or partially disappears, when viewed through a Nicol prism held at such an angle as to exclude the polarised light scattered by the particles.

Dust suspended in the atmosphere diminishes the transparency of the latter by an amount depending on the concentration of the disperse particles and upon the moisture content of the air. The effect of the moisture is caused by condensation on the dust particles, which increases their apparent size and hence their obscuring power. It has been calculated that 2000 particles per cubic centimetre will suffice to obscure a mountain at a distance of 50 miles, whilst 100,000 particles per cubic centimetre would render objects invisible at a distance of 1 mile. In the London area there is a loss of some 37 per cent. of sunshine due to dust and smoke, and the obscuring effects extend out to Kew, where the sunshine is reduced by 10 per cent. in consequence of the London smoke.

In 1870 Maxwell showed that a small particle is repelled by rays of light with a force proportional to the illumined surface. This is known as **photophoresis** (Greek *photos*, light; *phorein*, to bear). Maxwell suggested this as the reason why the tail of a comet is repelled from the sun, the pressure of the light on the minute particles composing the tail more than counterbalancing the gravitational effect. The head of the comet is made up of larger masses on which the effect of the light is small compared with that due to gravity.

Luminous Flames, such as those of a candle or coal gas, owe their luminosity to the presence of incandescent particles floating in gas. When an intense beam of light is projected on to the luminous portions of the flames the beam is both bent from its original direction and polarised. The flames are termed **stationary** but not stable dispersoid systems (von Weimarn, 1919). In a stable system the particles would not change, whereas in the flame they constantly disappear and are as frequently renewed.

GENERAL INDEX.

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