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STOICHIOMETRY

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BY

SYDNEY YOUNG, D.Sc., F.R.S.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF DUBLIN

WITH NINETY-THREE FIGURES IN THE TEXT

SECOND EDITION

LONGMANS, GREEN AND CO.

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PREFACE TO THE SECOND EDITION.

NOT long after the publication of the first edition, the International Committee on Atomic Weights decided to adopt a somewhat lower value for the atomic weight of silver than that found by Stas. This change had been advocated by Guye, but, owing to the immense amount of care bestowed by Stas on this determination, the Committee were reluctant to make the change until the evidence in favour of the new value seemed to be incontrovertible. I have therefore re-written Chapter V., giving only a short summary of the work of Stas, and devoting more space to the more recent determinations of the atomic weights of silver, nitrogen, chlorine, and lead.

A short account of modern views on the nature of atoms is given in Chapter VI., and the bearing on the Periodic Law of recent researches on the Radio-elements and of the theories of Soddy and Fajans is there described. As regards the definition of the term "element," the recommendations of Paneth are provisionally adopted.

The results of the extensive researches of Professor J. Livingston R. Morgan and his co-workers on the relation of the weight of a falling drop to the surface tension of a liquid are described in Chapters VIII. and XVII.

The section on the Absorption of Gases by Solids has been re-written.

The very important researches on Osmotic Pressure carried out by Morse and his collaborators in America and by the Earl of Berkeley and E. G. J. Hartley in England are described and discussed.

I have derived much assistance from the valuable Annual

Reports on the Progress of Chemistry issued by the Chemical Society, and from the excellent monographs on the Chemistry of the Radio-elements by Professor Soddy and on Osmotic Pressure by Professor Findlay.

S. Y.

April, 1918.

PREFACE.

THE determination of the relative atomic weights of hydrogen and oxygen is attended by great experimental difficulties, and, in arriving at a final decision as to the value to be adopted, chemists have placed even greater reliance on physico-chemical investigations of the properties of the gases than on the purely chemical determination of the equivalent of oxygen.

It was also in consequence of the determination of the specific gravities of nitrogen and oxygen by Lord Rayleigh and by Leduc that doubt was first felt as to the accuracy of the value found by Stas for the atomic weight of nitrogen, and it is chiefly owing to further investigations of the physical properties of these gases, and of other gaseous compounds of nitrogen, that the lower value has been definitely adopted.

I have therefore thought it best, after describing the laws of chemical combination, to give a detailed account of the properties of gases before proceeding to a discussion of the methods of determining atomic weights.

The importance of the generalizations of Van der Waals regarding corresponding temperatures, pressures, and volumes is now so fully recognized that no apology is, I think, necessary for the amount of space devoted to this subject, and to a description of the methods of determining the critical constants.

It seems almost unnecessary to express my indebtedness to Ostwald's great "Lehrbuch der allgemeinen Chemie". I have also derived much valuable assistance from Nernst's "Theoretische Chemie," and from D. Berthelot's memoir

"Sur les Thermomètres à Gaz". The original papers to which reference is made in the footnotes have, in the great majority of cases, been consulted.

S. YOUNG.

TRINITY COLLEGE, DUBLIN,
October, 1907.

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SYMBOLS.

p = observed or real pressure of gas or vapour.

$\mathbf{p}$ = observed osmotic pressure.

P = calculated pressure (for perfect gas).

p_C = critical pressure.

π = reduced pressure.

t = Centigrade temperature.

T = absolute temperature.

t_c or T_c = critical temperature (Centigrade or absolute).

θ = reduced (absolute) temperature.

v = observed volume (v_L = volume of liquid, v_V of vapour).

v = volume of a gram (specific volume).

V = molecular volume = M × v.

v_c, v_c, V_c = critical volume.

ϕ = reduced volume.

s = observed density or specific gravity = $\frac{1}{v}$.

S = calculated density or specific gravity (for perfect gas).

d = observed vapour density (density of $O_2 = 16$ at same temperature and pressure).

D = calculated vapour density = $\frac{M}{2}$.

m = mass or weight (in grams).

μ = mass or weight $\left(\text{in gram-molecules} = \frac{m}{M}\right)$.

M = molecular weight.

L = heat of vaporization.

L′ = heat of fusion.

L″ = heat of volatilization (of solid).

c = specific heat.

C = molecular heat.

ϵ = increase of internal energy per unit rise of temperature.

E = molecular rise of boiling point.

E′ = molecular depression of freezing point.

CHAPTER I.

FUNDAMENTAL LAWS OF CHEMICAL COMBINATION.

Elements and Compounds.—All chemical substances are divided into two great classes—elements and compounds. The term "element" was employed by the ancient philosophers and alchemists, but rather in the sense of a principle or property than of a definite chemical substance, and it is to Robert Boyle (1627-1691) that we are indebted for the first precise scientific definition of the elements as substances which are themselves not capable of further separation, but which can be obtained from a combined body, and out of which the compound can again be prepared.

Since the time of Boyle until quite recently this definition has been universally accepted, and those substances have been classed as elements which up to the present time have resisted all attempts to decompose them. Compounds, on the other hand, may be formed by the union of elements, and may be decomposed by the action on them of other chemical substances or by heat or electricity.

The Conservation of Mass.—It is believed that the total amount of matter in the universe remains unaltered, whatever changes may occur in its distribution. It has been believed, also, that the total amount of each element is equally unalterable, although, if the element is able to combine with others, the amount existing in the free state or in any particular state of combination may vary considerably from time to time.

No direct experimental proof of the law or doctrine of the conservation of mass is possible, but all quantitative analyses are based on the assumption that when a chemical change occurs, there is no alteration in the total mass of the reacting substances. It is, indeed, possible to put this matter to the test of experiment by allowing a chemical reaction to take place in a sealed glass tube. A very minute alteration could be detected by weighing the tube on a very delicate balance before and after the chemical change had occurred.

This subject has been very carefully investigated by H. Landolt,[1] and also by Heydweiller[2] and others. In most cases the minute differences observed were within the limits of experimental error, but a slight loss (maximum 0·199 mgrm. in Landolt's experiments, and 0·217 mgrm. in Heydweiller's) was noted with certain reactions. No gain of anything like this magnitude was observed by either experimenter; in fact, the gains were always within the limits of experimental error. Landolt[3] afterwards concluded that the loss was due to two causes:—(1) When a glass tube is warmed, a little of the film of moisture on the surface of the glass is expelled, and it is only after a couple of days that the amount of moisture again becomes normal. It is advisable, he considers, always to wipe the glass vessel and the glass counterpoise with a damp cloth before the weighings are taken. (2) When a glass vessel is warmed, it expands, but on cooling it does not quite recover its initial volume until after a considerable time, perhaps a fortnight. Correcting for these sources of error, Landolt finds that in forty-eight determinations—relating to fifteen different chemical changes—there was a minute increase in weight in twenty-five cases and a minute decrease in twenty-three cases. The actual alterations in weight varied from ± 0·001 mgrm. to 0·030 mgrm., the highest value being just within the limits of experimental error.

Still further precautions have been taken by Manley,[4] who succeeded in raising the limit of accuracy in weighing from 0·03 to 0·006 mgrm. Landolt found the mean apparent change in mass during chemical reaction to be not greater than 1 in 1×10^7. Manley, in one very fully investigated case in which barium chloride and sodium sulphate were the reacting bodies, found that the apparent change in mass was not greater than 1 in 1×10^8.

Definition of an Element.—The extension of the doctrine of the conservation of mass to that of the conservation of each element is justifiable so long as Boyle's definition of an element is strictly applied. The suggestion has been made from time to time that the bodies which are now classed as elements have in the first place been formed by the condensation of one or of a very few primordial forms of matter; but even if this were proved to be the case, the

[1] *Zeitschr. physik. Chem.*, **55**, 589 (1906).
[2] *Drude's Ann.*, **5**, 394 (1901).
[3] *Sitz.-ber. d. k. Pr. Akad. d. Wiss.*, **16**, 354 (1908).
[4] *Proc. Roy. Soc.*, **87**, 202 (1912).

definition would remain valid until some means of reconverting the "elements" into the primordial substances, or of producing a simpler from a more complex "element," had been discovered.

If decomposition or disintegration of any of the substances now classed as elementary should be found to occur, it would be necessary either to remove these substances from the list of elements or to modify the definition so as to bring it into harmony with the facts, and at the same time to limit the law of conservation to matter as a whole. There can be no doubt that the bodies now termed elements form a class apart from those which are termed compounds, and it is probable that, as a matter of convenience, the term "elementary" will still be employed even if disintegration should be found to be a phenomenon of frequent occurrence.

The question whether the decomposition of certain elements can be brought about at will may, perhaps, still be regarded as an open one, but there can be no doubt about the spontaneous disintegration of a few of them.

It was observed in 1896, by Becquerel, that uranium salts possess the property of emitting rays which are able to pass through thin plates of metal and other opaque substances, and to act on a photographic plate. The study of the radio-activity of uranium compounds led to the discovery of the element radium by M. and Mme. Curie in 1898.

The compounds of this element were found to emit rays of three distinct kinds, and also a gaseous emanation, which is itself intensely radio-active. An immense number of researches have been carried out on this subject, for an account of the earlier of which reference may be made to Rutherford's "Radio-activity" (1905). It will be sufficient to mention that Rutherford and Soddy advanced the theory that the atoms of radio-active substances are undergoing spontaneous disintegration, with formation of a series of radio-active substances which differ in chemical properties from the parent substances and from each other, and that the radiations to which reference has been made accompany the breaking up of the atoms.

The emanation from radium is a gaseous substance which can be transferred from one vessel to another; its products are luminous and strongly radio-active, and, like radium itself, it undergoes disintegration, one of the products formed, as shown by Ramsay and Soddy,[1] being the monatomic gas helium.

[1] *Proc. Roy. Soc.*, 73, 346 (1904).

The metals uranium, thorium, and actinium are all radio-active, and all undergo very slow disintegration, and it is considered probable by Rutherford that radium is derived in this way, not directly, but after intermediate stages, from uranium; and also that the metal lead may be derived from radium by a similar disintegration process. Thus lead would be the final disintegration product of uranium. But thorium undergoes a similar process, and it has been predicted that the lead derived from uranium would have an atomic weight about one unit lower, and that from thorium about one unit higher than that of ordinary lead. The results obtained by Richards and Lembert,[1] Soddy,[2] Hönigschmid and Horovitz,[3] Richards and Wadsworth,[4] and Hönigschmid[5] afford evidence in favour of the correctness of this prediction, for the atomic weight of the lead from an East African uranium ore was found to be 206·046, and from bröggerite, which contains 79 per cent. of U_3O_8 and 4·5 per cent. of ThO_2, 206·063; that of the lead from thorite was 207·77, while that of ordinary lead is 207·20. Intermediate values were found for the lead from other radio-active minerals.

The densities also showed proportional variations, the atomic volumes being the same for all.

These different varieties of lead possess identical chemical properties and spectra, and are said to be *isotopic*. The existence of isotopes was predicted by Soddy and by Fajans.

Hevesy and Paneth[6] state that they have obtained visible quantities of a metal and its peroxide, chemically identical with lead and lead peroxide, by the decay of radium emanation.

It appears that among the known isotopes of lead there is a maximum variation in atomic weight of eight units, that being the difference between 214·1 (lead from Thorium B) and 206·1 (Radium G).

The changes undergone by radium are accompanied by the liberation of a relatively enormous amount of energy; it is found, for example, that the temperature of a mass of a radium salt (the metal has not yet been separated) is always higher than that of the

[1] *Journ. Amer. Chem. Soc.*, **36**, 1329 (1914).
[2] *Nature*, **94**, 615 (1915); *Engineering*, May 28, and Oct. 1, 1915.
[3] *Monatsch.*, **36**, 355 (1915).
[4] *Journ. Amer. Chem. Soc.*, **38**, 221 and 1658 (1916).
[5] *Chem. Soc. Ann. Report* for 1916, vol. xiii., p. 272.
[6] *Ber.*, **47**, 2784 (1914).

surrounding matter, yet the diminution in weight is exceedingly minute, although the gaseous emanation has been collected and its volume measured. It is safe, indeed, to assert that, had it not been for the great activity of the rays emitted by radio-active substances, radium would not have been discovered, and the disintegration of the atoms would not have been demonstrated. It has not been found possible to hasten or to retard the disintegration of any of the radio-active substances; the process goes on spontaneously, and each substance has its own definite and measurable rate of disintegration.[1]

On the other hand, Ramsay[2] has stated that in presence of water the gas formed by the disintegration of radium emanation is not helium but neon, and that in presence of a solution of copper sulphate it is argon. The copper, either as sulphate or nitrate, appeared at the same time to suffer disintegration to a minute extent, the residue, after removal of the copper, showing the spectrum of the allied metal lithium faintly. Ramsay and Cameron[3] and Ramsay and Usher[4] obtained similar results, and also state that by the action of the emanation on compounds of silicon, titanium, zirconium, thorium, and, to a much smaller extent, lead, small quantities of carbon dioxide and in some cases carbon monoxide were formed: they attribute their presence to the disintegration of the atoms of the elements of higher atomic weight in the same group as carbon.

Ramsay and Collie[5] found that on heating deeply stained Röntgen-ray bulbs, small quantities of helium and traces of neon were evolved, and Collie and Patterson and I. Masson[6] state that helium and neon are formed by bombarding fluorspar and other substances with kathode rays.

Inasmuch, however, as the results obtained by other observers[7]

[1] Becquerel, *Compt. rend.*, **133**, 199 (1901); Curie, *Soc. de Physique*, March 2, 1900; Rutherford, "Radio-activity," 2nd edit., p. 210; Schuster, *Nature*, **76**, 269 (1907); Eve and Adams, same reference; Danysz and Werthenstein, *Compt. rend.*, **161**, 784 (1915), and other observers.

[2] *Nature*, **76**, 269 (1907); *Trans. Chem. Soc.*, **95**, 624 (1909); **101**, 1367 (1912).

[3] *Trans. Chem. Soc.*, **91**, 1593 (1907); **93**, 966 and 992 (1908).

[4] *Ber.*, **42**, 2390 (1909).

[5] *Nature*, **89**, 502 (1912); *Trans. Chem. Soc.*, **103**, 264 (1913).

[6] *Chem. News*, **107**, 78 (1913); *Proc. Roy. Soc.*, **90**, 554; **91**, 30 (1914); *Trans. Chem. Soc.*, **103**, 419 (1913).

[7] Strutt, *Proc. Roy. Soc.*, **89**, 499 (1914); Merton, *ibid.*, **90**, 549 (1914); Egerton, *ibid.*, **91**, 180 (1915).

have up to the present time been negative in all cases, the question must be regarded as an open one.

In the light of our present knowledge it is almost impossible to give a satisfactory definition of the term "element," but perhaps the recommendations of Paneth [1] may be provisionally adopted. The idea of elements previously held would be retained, and all the isotopes of any one element or a mixture of them would be spoken of as an element. The light and X-ray spectra would be the distinguishing criteria of a chemical element, which would be defined as a substance which cannot be decomposed by any chemical process. Atoms would be defined as the ultimate particles of matter, unchangeable by chemical analysis, which represent the limit of chemical decomposition. Elements might be defined as pure or mixed according as they are made up of the same kind of atoms or of different kinds of isotopic atoms.

Two elements should be denoted by the same name if, once mixed, they cannot be separated by any chemical process. But, as Soddy points out in the *Annual Report of the Chemical Society* for 1916, p. 252, difficulties must arise. Thus radium and mesothorium would be regarded as the same element, and should have the same name, as also should thorium and ionium.

With regard to the question whether it is possible to separate the isotopes of an element by any known process, Richards and Norris [2] have shown that a thousand fractional crystallizations of the nitrates are insufficient to effect any appreciable separation of either radium G or radium D from ordinary lead, as indicated by the atomic weight on the β-ray activity.

The Law of Definite Proportions.—In the latter half of the eighteenth century, Richter (1762-1807) showed that, in the formation of any given salt, the acid and the base combine together in definite proportions. Berthollet,[3] however, considered that in the chemical union of two substances, the composition of the product would vary with that of the original mixture, unless any exceptional circumstances, such as precipitation or escape of gas, stood in the way of this mass action. Proust, on the other hand, held the view that the composition of a chemical compound is perfectly definite, and by careful experiments, carried out from 1799 to 1807, he was

[1] *Zeitschr. physik. Chem.*, **91**, 171 (1916).
[2] *Journ. Amer. Chem. Soc.*, **39**, 531 (1917).
[3] *Essai de Statique Chimique* (1803).

able to prove the correctness of his conclusions. The truth of the law of definite proportions has since been confirmed by innumerable experiments.

The Law of Multiple Proportions.—It had long been known that certain metals could form more than one oxide or sulphide, but while Berthollet considered that such a metal could unite with any quantity of oxygen within certain limits, forming an indefinite number of oxides, Proust held that the number of oxides was limited, and that the composition of each was invariable. He showed, for example, that tin forms two oxides with the percentage composition—

	I.	II.
Tin	88·15	78·81
Oxygen	11·85	21·19
	100·00	100·00

John Dalton (1766-1844) pointed out that if, in such a case, the amount of one element is taken as constant, the quantities of the other bear a very simple ratio to each other. Thus, in the case considered, taking 7·44 as the constant weight of tin, the composition of the two oxides would be—

	I.	II.
Tin	7·44	7·44
Oxygen	1·00	2·00

As a result of his experiments on the compounds of carbon with oxygen and with hydrogen, and of nitrogen with oxygen, Dalton was able to formulate the law of multiple proportions, which may be stated as follows:—

If one element forms with another several combinations, the weights of the second element which unite with a constant weight of the first vary in the different compounds according to simple numerical proportions.

It is to be noted, however, that the compounds of carbon with hydrogen and the derivatives of the hydrocarbons are exceedingly numerous, so that the "numerical proportions" may be very far from simple.

Carbon forms two well-known gaseous compounds with oxygen, and taking the constant weight of carbon as 0·75, the weights of oxygen are 1 and 2.

Again, phosphorus and chlorine form two compounds which have the composition—

	I.	II.
Phosphorus . . .	0·2915	0·2915
Chlorine	1·0	1·$\dot{6}$

But 1 : 1·$\dot{6}$ :: 3 : 5, or the weights of chlorine that unite with 0·8745 part by weight of phosphorus are 3 and 5.

The Law of Equivalent Weights.—Richter observed that when two neutral salts, AB and CD, react together to form two new salts, AD and BC, one of which is insoluble, the solution remains neutral; he concluded, therefore, that if solutions of the two salts are mixed in such proportions that the quantity of the component D is just sufficient to unite completely with A, there must be exactly the requisite amount of C present to combine with the whole of B, because any excess of B or C would cause the solution to become either alkaline or acid.

Later, Richter made quantitative, but not very accurate, determinations of the relative quantities of various acids and bases which react to form salts. He found, for example, that 1000 parts by weight of sulphuric acid would saturate 859 parts of soda or 1605 of potash, and that 859 parts of soda would neutralise 1405 of nitric acid. But 1405 parts of nitric acid neutralise 1605 of potash, so that 859 parts of soda, 1605 of potash, 1000 of sulphuric acid, and 1405 of nitric acid, may be regarded as equivalent quantities.

Again, it has been shown that if a given substance A forms compounds with other substances B, C, D, m_A parts by weight of A uniting with m_B parts of B, m_C of C, and m_D of D respectively, and if B, C, and D form compounds with each other, the weights of C and D which unite with m_B parts of B are either m_C and m_D, respectively, or simple multiples or submultiples of these amounts.

For example, 1 gram[1] of hydrogen unites with 35·5 grams of chlorine to form hydrogen chloride, with 23 of sodium to form sodium hydride, with 8 of oxygen to form water, and also with 16 of oxygen to form hydrogen peroxide. And it is found that 23 grams of sodium combine with 35·5 of chlorine to form common salt, with 8 of oxygen to form sodium oxide, and also with 16 of oxygen to form sodium peroxide; lastly, chlorine and oxygen form two compounds

[1] More exactly 1·008 gram.

containing, for each 35·5 parts of chlorine, 8 and 32 parts respectively of oxygen.

Thus the quantities of oxygen which unite with 1 part by weight of hydrogen, with 23 parts of sodium, or with 35·5 of chlorine, are either 8, 16, or 32 parts, all of them simple multiples of 8.

Wollaston proposed the term "equivalent" to denote the amount of an element that unites with or displaces 1 part by weight of hydrogen, and the Law of Equivalent Weights may be stated as follows:—

When two or more elements unite to form a compound, the weights of these elements are proportional to their equivalents or to simple multiples of them.

The Atomic Theory.

Ancient Atomic Theory.—The idea that matter is not infinitely divisible, but that it is composed of minute indivisible particles or *atoms*, is a very old one. It is to be found in the works of Leucippus and Democritus, written twenty-four centuries ago, and was more fully developed by Lucretius. The views of these philosophers were, however, purely speculative, and were not in any way founded on observation or experiment. The chief conclusions arrived at by Lucretius may be shortly stated as follows:—[1]

1. *Atoms have different shapes; but the number of shapes is finite, and there is an infinite number of atoms of each shape.*

2. *Nothing whose nature is apparent to sense consists of one kind of atom only.*

3. *The atoms move through space at a greater speed than does sunlight.*

Dalton's Atomic Theory.—At the beginning of the nineteenth century, John Dalton brought forward the great theory which forms the basis of modern chemistry. The new atomic theory, unlike those of the ancient philosophers, was based on facts ascertained by experiment, and was concerned, not with the shapes or relative sizes of atoms, but solely with their relative weights.

It may be of interest to compare the views of Dalton with those of
is etius. A single verbal alteration—the substitution of *weights* for
th is all that is required in the first statement of Lucretius,
becomes—

M

[1] "Recent Advances in Physical Science," 1876.

1. *Atoms have different weights; but the number of weights is finite, and there is (practically) an infinite number of atoms of each weight.*

In conformity with Boyle's definition of an element, Dalton considered that—

2. *Chemical elements consist of one kind of atom only.*

3. Dalton himself did not take into consideration the motions of the atoms, but we now know that the smallest particles or molecules of a gas move with velocity many thousand times smaller than that of light (*vide* p. 175).

Dalton made determinations of the composition of a number of compounds, but his results were not very accurate. He stated that 1 part by weight of hydrogen united with 5·5 parts of oxygen to form water, and he assumed, as the simplest possible case, that, in the formation of the smallest particle of water, 1 atom of hydrogen combines with 1 atom of oxygen. Dalton employed the term "atom" to denote the smallest particle, not only of an element, but also of a compound, and he spoke of a binary, ternary, or quaternary atom according to the number of elementary atoms composing it.

Now if, on the one hand—

1 part by weight of hydrogen combines with 5·5 parts of oxygen,

and, on the other hand—

1 atom of hydrogen combines with 1 atom of oxygen to form a binary atom of water,

it follows that, taking the weight of an atom of hydrogen as unity, that of the atom of oxygen must be 5·5.

In this way Dalton calculated the atomic weights of a number of elements.

Wollaston objected to the use of the term "atomic weight," on the ground that there was no justification for the assumption that the smallest particle of water contained an equal number of atoms of the component elements; and, in order to avoid all theoretical considerations, he proposed to substitute the term "equivalent weight" or "equivalent," as defined on p. 9, for atomic weight. He did not believe that it would ever be possible to ascertain the relative number of atoms of two or more elements which unite together to form the smallest particle of a compound, and he therefore consid[illegible] that the atomic weights of the elements could never be deter[illegible]

It is true that, when Dalton brought forward the ato[illegible] no facts were known which threw any light on the ch[illegible] of compounds, and it was therefore doubtful whe[illegible] em[illegible] the

of any given element or a multiple or submultiple of the equivalent should be taken as the atomic weight. Wollaston's objection was so far justified, but he was mistaken in supposing that the problem could never be solved.

In order to find the atomic weight of an element, it is usual (*a*) to make an accurate determination of its equivalent by analytical methods; (*b*) to ascertain the relation between the equivalent and the atomic weight.

It is not, however, essential that the equivalent should be determined, and, indeed, in the case of helium, neon, argon, krypton, and xenon, which appear to be incapable of entering into combination, such a determination would obviously be impossible.

In order to find the atomic weights of these elements a knowledge of the properties of gases is requisite.

CHAPTER II.

THE PROPERTIES OF GASES.

The Solid, Liquid, and Gaseous States of Matter.—Matter exists in three forms or states of aggregation, the solid, the liquid, and the gaseous, which may be readily distinguished from each other by the following characteristic properties :—

A solid substance retains its shape unless acted upon by some external force. The amount of force required depends on the nature of the solid—whether soft or hard—and on its original shape. Thus, a piece of lead is more easily bent than a similar piece of iron, and a strip of tinfoil more easily than a thicker strip of sheet tin. If the force applied is not too great, the solid recovers its original shape when freed from its action, and is said to be elastic as regards shape. The volume of a solid at constant temperature can only be very slightly altered even by exposure to enormous pressure. In other words, a solid is almost incompressible.

The shape of a liquid, on the other hand, is very easily altered, as, for example, when water or alcohol is poured from one vessel into another. Under ordinary conditions a substance in the liquid state is only slightly compressible, more so, however, than when solid.[1]

Not only is the shape of a gas more easily altered than that of a liquid, but when placed in any vessel the gas has the property of completely filling and therefore of taking the shape of that vessel. Moreover, the volume of a gas is readily changed by altering the pressure to which it is exposed, unless that pressure is already very high.

Gases and liquids have no elasticity as regards shape, but at constant temperature they recover their original volume when, after compression, the added pressure is removed. In other words, gases and liquids are perfectly elastic as regards volume.

[1] Near the *critical point* a liquid is even more compressible than a gas at the ordinary temperature and pressure (p. 166).

The volume of a gas is affected by change of temperature to a much greater extent than that of a liquid or solid, and the volume of a liquid more than that of a solid.

The gaseous state of matter is also distinguished from the liquid or solid state by the much greater simplicity of the relations between temperature, pressure, and volume; and, in studying these relations, it is therefore convenient to consider the behaviour of gases first.

Boyle's Law.—The influence of pressure on the volume of air was first studied by Robert Boyle in 1662, and, later, by Mariotte in 1679. Boyle determined the relation between the volume and pressure of a given mass of air at constant temperature between 4 and $\frac{1}{13}$ atmos., and found that the volume varied inversely as the pressure.

The same law has been found to hold for other gases, and it may be stated generally that, under moderate or low pressures and at sufficiently high temperatures, *the volume of a gas at constant temperature varies inversely as the pressure.*

This statement is known as Boyle's law; it may be expressed by the equation—

$$\frac{v}{v'} = \frac{p'}{p}$$

$$\text{or } pv = p'v'$$

$$= \text{const. at constant temperature.}$$

The density of a gas s may be defined as the mass of 1 cubic centimetre of it, and its specific volume v as the volume of 1 gram.

$$\text{Hence } v = \frac{1}{s}$$

$$\text{and } p = cs \text{ at constant temperature}$$

where c is a constant; or *the density of a gas at constant temperature is directly proportional to the pressure.*

The relation between the pressure and volume of a gas at constant temperature may be represented graphically by measuring the pressures as ordinates and the volumes as abscissæ, as in Fig. 1. At any given temperature, say t_1, let the distance ao be proportional to a certain pressure p of the gas, and co to the volume v which it occupies under that pressure; from a and c draw the straight lines ab and cb perpendicular to the axes ox and oy respectively. Then the point b measures the volume v of the gas under the pressure p and at the temperature t_1. Similarly, the point b' measures the volume v' of

Mem.

the gas under pressure p' at the same temperature, and so for any other points on the curve passing through b and b'. The curve is termed an *isotherm*, or line of constant temperature; its form is that

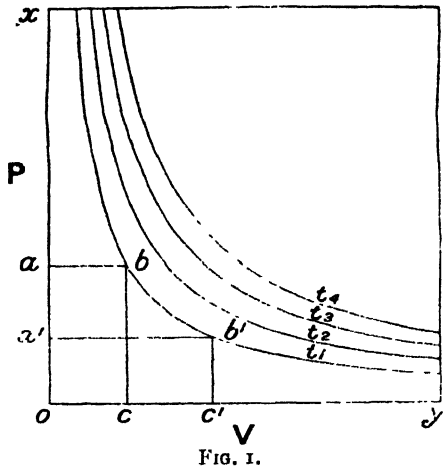


FIG. 1.

of a rectangular hyperbola, the rectangles $abco$ ($= pv$) and $a'b'c'o$ ($= p'v'$) being equal.

At higher temperatures, t_2, t_3, the relations between pressure and volume are represented by curves of similar form, but lying to the right of and above the first isotherm.

Gay Lussac's Law.—The expansion of air under constant pressure was first investigated by Dalton and by Gay Lussac, but Dalton's results were not sufficiently accurate to enable him to draw a correct conclusion from them. Gay Lussac showed that the volume of a gas increases by $\frac{1}{273}$ of its volume, measured at 0° C., for each rise of 1° C., or $v_t = v_0 (1 + \alpha t)$, where α, the coefficient of expansion, $= \frac{1}{273}$ or 0·00367.[1]

But the measurement of temperature is by no means so simple as that of pressure. It is customary to take the melting point of pure ice under atmospheric pressure and the boiling point of pure water under a barometric pressure of 760 mm. of mercury as standard temperatures; and on the Centigrade scale the melting point of ice is called zero, and the interval of temperature between the two poi[nts] is divided into a hundred parts or degrees, which should be of eq[ual] value. But changes of temperature are most conveniently indicat

[1] Charles appears to have been the first to discover that the coefficient a expansion is nearly the same for the more commonly occurring gases.

by the expansion or contraction of liquids, gases, or occasionally solids, and for ordinary and very many scientific purposes the mercurial thermometer is employed. The position of the mercury in such a thermometer, however, depends not only on the expansion of the mercury, but also—to a much smaller extent—on that of the glass. Now, two mercurial thermometers, made of different kinds of glass, which gave correct readings at 0° C. and at 100° C., would not register exactly the same temperature at, say, the boiling point of ethyl alcohol, 78·3° C., because the coefficients of expansion would not be quite the same for the two kinds of glass.

Similarly, two thermometers, containing liquids of sufficiently high boiling point, say mercury and bromonaphthalene, although both correct at 0° and 100°, would give slightly different readings at intermediate temperatures.

The coefficient of expansion of air is more than 20 times as great as that of mercury, and about 145 times that of glass, and an air thermometer is therefore not only much more delicate than a mercurial one, but the alteration in the volume of the glass vessel containing the air is of relatively small importance. Moreover, many gases have almost exactly the same coefficient of expansion under ordinary or low pressures, and it is reasonable, therefore, to assume that the relation between the temperature and the volume of a gas is a very simple one.

Using a mercurial thermometer, it is found that the coefficient α remains very nearly constant between 0° and 100°, and it is assumed that the slight variation is due to the errors in the thermometric scale, and that the true coefficient is really constant.

Suppose, then, that a quantity of air or other gas were enclosed in a perfectly cylindrical tube by an air-tight and frictionless piston, and that the volume of air, as indicated by the piston, were to be marked on the tube, firstly, with the air thermometer immersed in melting ice; and, secondly, in the steam from water boiling under a pressure of 760 mm. We should thus obtain the two fixed points 0° C. and 100° C. on the thermometer. By dividing the linear distance between the two fixed points into 100 equal parts we should mark out 100 equal volumes, since the tube is cylindrical, and it is assumed that, making the small correction for the expansion of the glass, each of these divisions is *exactly* one degree.[1] If, now,

[1] D. Berthelot ("Sur les Thermomètres à Gaz," pp. 80-99; *Travaux et Mem. du Bur. Int. de P. et Mes.*) has shown that the maximum error between 0°

divisions of the same length were to be marked from the zero point to the bottom of the tube, there would be found to be 273 of them; or the volume corresponding to a single division would be $\frac{1}{273}$ of the total volume at 0° C. If we call each division a degree, there will be 273 degrees on the thermometric scale below 0° C., and the temperature − 273 is called the absolute zero on the Centigrade scale.

A more rational method of expressing temperature is to start

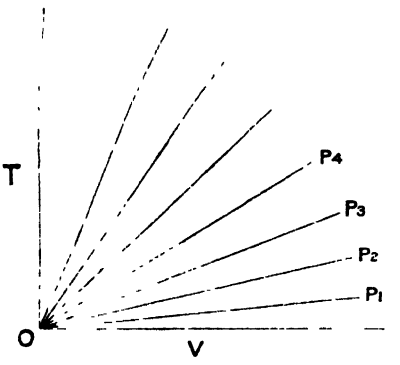


FIG. 2.

from the absolute zero instead of the arbitrary zero of the Centigrade scale. On this *absolute scale* of temperature the melting point of ice will be 273°, and the boiling point of water under normal pressure will be 373°; and, generally, the absolute temperature is obtained by adding 273 to the Centigrade temperature or $T = t + 273$.

$$\begin{aligned} \text{Thus } v_t &= v_0(1 + \alpha t) \\ &= v_0\left(1 + \frac{t}{273}\right) \\ &= v_0 \frac{273 + t}{273} \\ &= \frac{v_0 T}{273} \\ &= cT \end{aligned}$$

In words, the volume of a gas under constant pressure varies directly as the absolute temperature.[1]

and 100° at 760 mm. pressure is for the air or nitrogen thermometer, 0·018"; for the hydrogen thermometer, 0·001°; for CO_2, 0·143°.

[1] The absolute scale of temperature, as derived from the air thermometer, agrees almost exactly with the thermodynamical scale, which is independent of the nature of the body considered. The hydrogen and helium thermometers show

The relation between volume and absolute temperature is shown graphically in Fig. 2.

The straight lines of equal pressure, or *isobars*, radiate from the zero of temperature (absolute) and volume.

Similarly, if the volume is kept constant while temperature and pressure vary, it is found that the pressure varies directly as the absolute temperature, or $p = cT$ at constant volume. This relation is shown graphically in Fig. 3.

The straight lines of equal volume (or density), *isochors* or *isometrics*, radiate from the zero of pressure and absolute temperature.

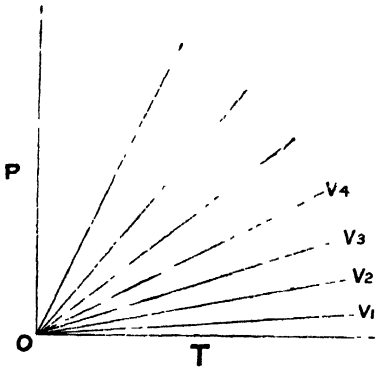


FIG. 3.

Combining the laws of Boyle and Gay Lussac, when both pressure and temperature vary, we have the equation—

$$\begin{aligned} pv &= p_0v_0(1 + \alpha t) \\ &= \frac{p_0v_0T}{273} \\ &= RT \end{aligned}$$

where R is a constant depending on the units of pressure, temperature, and mass, and on the nature and mass of the gas.

If the volume v_1 of a quantity of gas has been measured at a (Centigrade) temperature t_1 and under a pressure p_1, it may be required to know what the volume v_2 would be at another temperature t_2 and under the pressure p_2. Converting the Centigrade temps. t_1 and t_2 into T_1 and T_2 respectively, the ratio between the two volumes is given by the equation—

still closer agreement and can be employed for temperatures lower than the liquefying point of air.

$$\frac{v_2}{v_1} = \frac{T_2}{T_1} \times \frac{p_1}{p_2}$$

$$\text{or } v_2 = v_1 \times \frac{T_2}{T_1} \times \frac{p_1}{p_2}.$$

Thus 100 c.c. of air measured at 10° C. and under a pressure of 740 mm. would become at − 20° and under the pressure 800 mm.—

$$v_2 = 100 \times \frac{273 - 20}{273 + 10} \times \frac{740}{800} = 82{\cdot}7 \text{ c.c.}$$

Perfect Gases.—A gas which followed the laws of Boyle and Gay Lussac exactly would be called a *perfect* gas, but the most careful experiments have shown that, under ordinary conditions of temperature and pressure even the gases which are most difficult to condense, such as hydrogen, oxygen, and nitrogen, show slight deviations from these laws; and that the deviations are more marked in the case of gases which are more easily condensed.

Deviations from Boyle's and Gay Lussac's Laws.—As regards Boyle's law, for example, Lord Rayleigh,[1] taking the value of pv as unity when the pressure is 1 atmos., finds the following values of $p'v'$ when the pressure is reduced to 0·5 atmos.

	t° C.	p_1.	Critical temperature (absolute)
			°
Hydrogen . . .	10·7	0·99974	32
Nitrogen . . .	14·9	1·00015	127
Air	11·4	1·00023	—
Carbon monoxide . .	13·8	1·00026	134
Oxygen	11·2	1·00038	154
Nitrous oxide . . .	11·0	1·00327	309
Ammonia . . .	?	1·00632	406

The value of pv for hydrogen, a gas which cannot be liquefied at temperatures higher than 32° abs., becomes greater as the pressure rises; the values for the other gases in the list fall with rise of pressure, and the diminution is more and more marked as the maximum temperature of liquefaction (critical temperature) is higher.

Behaviour of Gases under High Pressure.—The compressibility of gases under higher pressures has been studied by very many observers. Pouillet[2] compared the compressibilities of eleven gases with that of air up to pressures of from 40 to 80 atmos. and found

[1] *Phil. Trans.*, **204**, 351 (1905). [2] *Elem. de Phys.*, **1**, 327.

that the volumes of SO_2, NH_3, CO_2, N_2O, CH_4, and C_2H_4 became smaller and smaller as compared with that of air as the pressure rose. The experiments, however, were not sufficiently accurate to show any marked differences in the case of O_2, H_2, N_2, NO, and CO. In 1842 Regnault[1] determined the compressibility of a number of gases, starting at different pressures (which were measured directly with a column of mercury), and reducing the volume in each case to one half. Regnault found that no gas followed Boyle's law exactly, and that the value of pv for every gas except hydrogen diminished with rise of pressure; he described hydrogen as a gas *plus que parfait.*

Ten years later Natterer[2] showed that at very high pressures the behaviour of all gases is similar to that of hydrogen under moderate pressures, the compressibility being smaller than is required by Boyle's law. At the enormous pressure of, roughly, 3600 atmos. the values of pv obtained were as follows, taking the value under normal atmospheric pressure as unity in each case:—

$N_2 = 5{\cdot}1$	$CH_4 = 4{\cdot}2$
$CO = 4{\cdot}9$	$H_2 = 3{\cdot}5$
Air $= 4{\cdot}5$	

Determinations of the compressibility of various gases were made by Cailletet[3] by very ingenious methods, but by far the most extensive and valuable researches in this direction are those of Amagat,[4] who took direct readings of pressure on a column of mercury in a vertical steel cylinder of 327 metres length, giving a maximum pressure of 430 atmos. The steel manometer could be taken to pieces and a glass tube inserted at the top, so that readings at various heights could be taken. The compression pumps contained mercury and glycerine, and were connected with the manometer and the glass volume tube, which consisted of a wide cylinder fused to a graduated and calibrated capillary tube of about 1 mm. internal and 10 mm. external diameter, and 500 mm. in length. Three different tubes were employed, so that the volume of gas should always be large enough to allow of accurate results being obtained.

The compressibility of air (or of hydrogen, nitrogen, or any other

[1] "Relation des Expériences" (1847).

[2] *Journ. pr. Chem.*, **56**, 127 (1852).

[3] *Compt. rend.*, **70**, 1131 (1870); **83**, 1211 (1877); **84**, 83 (1877); **88**, 61 and 411 (1879).

[4] "Mémoires sur l'élasticité et la dilatabilité des fluides jusqu'aux très hautes pressions," *Ann. Chim. Phys.*, Series VI., vol. xxix., 1893.

gas) having been determined by this method up to a pressure of 430 atmos., an air or gas manometer could afterwards be employed for the measurement of pressures up to that limit. For higher pressures it was necessary to employ some mechanical method of measurement, and Amagat modified the apparatus originally devised by Gally-Cazalat on the principle of the hydraulic press, in such a manner that accurate results could be obtained by means of it. The apparatus was provided with a series of pistons ranging from 12 cm. to 5·527 mm. in diameter, the ratio of the lower pressure—measured by a column of mercury—to that on the compressed gas being equal to the ratio of the cross-sections of the two pistons in use.

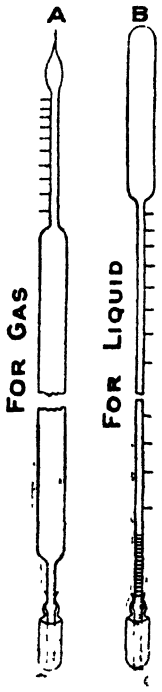


FIG. 4.

In this way pressures up to 3000 atmos. could be calculated from readings on a mercury column not exceeding 5·2 metres in height. A preliminary comparison with air and nitrogen manometers up to 430 atmos. showed good agreement. Up to 430 atmos. it was possible to compress the gases or liquids in thick-walled capillary glass tubes with no compensating external pressure beyond that of the atmosphere. For higher pressures, however, it was necessary to enclose the volume tubes in a pressure chamber so as nearly to equalize the internal and external pressures. In order to ascertain the volumes of gas the method of electrical contacts was employed, the mercury as it rose in the volume tube making contact successively with each one of a series of platinum wires fused through the walls of the tube. The form of the volume tubes employed for gases and liquids is shown in Fig. 4, A and B.

Further modifications were required for the determinations at high temperatures, and a method was devised by which direct readings could be taken so long as the pressure did not exceed 1000 atmos. The gases examined by Amagat were oxygen, nitrogen, air, hydrogen, carbon dioxide, ethylene, and methane.

In all cases except that of hydrogen the product pv diminishes at first with rise of pressure, reaches a minimum, and then increases again. With hydrogen only the last of these relations was observed, the product pv increasing throughout with rise of pressure; and

with nitrogen at 100° and 200° there was no minimum pv, though it was observed at 0° (Fig. 5).

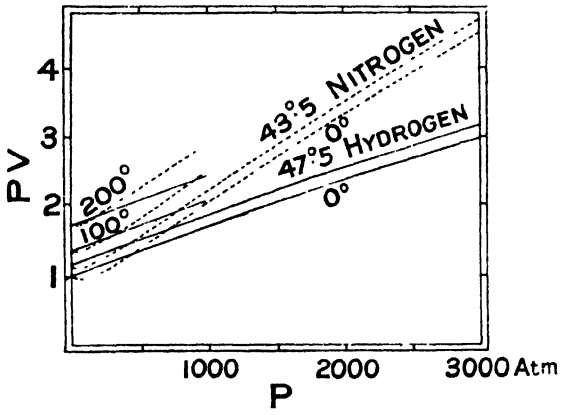


FIG. 5.

In the diagram (Fig. 6) the values of pv for carbon dioxide up to 1000 atmos. are mapped against the pressures at a series of tempera-

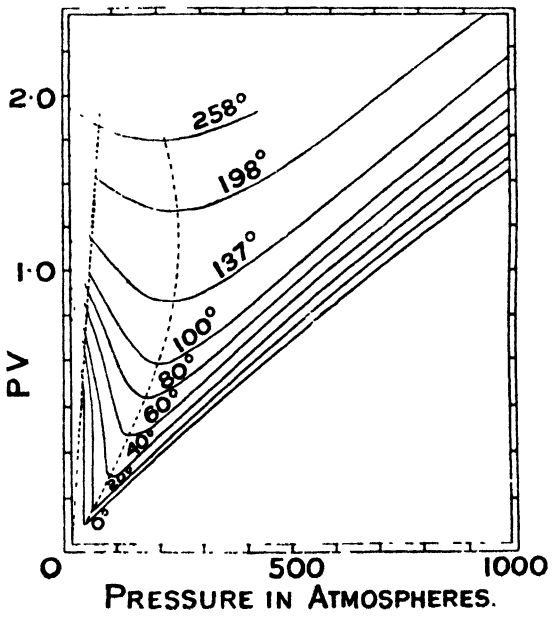


FIG 6.

tures from 0° to 258°. The value of pv at 0° and 1 atmos. is taken as unity, but no determinations were made under low pressures, and

the isothermals on the left side of the diagram were constructed by extrapolation, and are therefore indicated by dotted lines.

The values of pv up to 250 atmos. are shown on a wider scale in Fig. 7. In this diagram it will be seen that at temperatures up to a little over 30° (crit. t. = 31·35°) each isothermal consists of three distinct parts: starting from the lowest pressures there is (*a*) a curved line sloping downwards, (*b*) a straight line passing vertically downwards, (*c*) a nearly straight line sloping upwards. The vertical straight line (p = constant) shows what occurs during the liquefaction

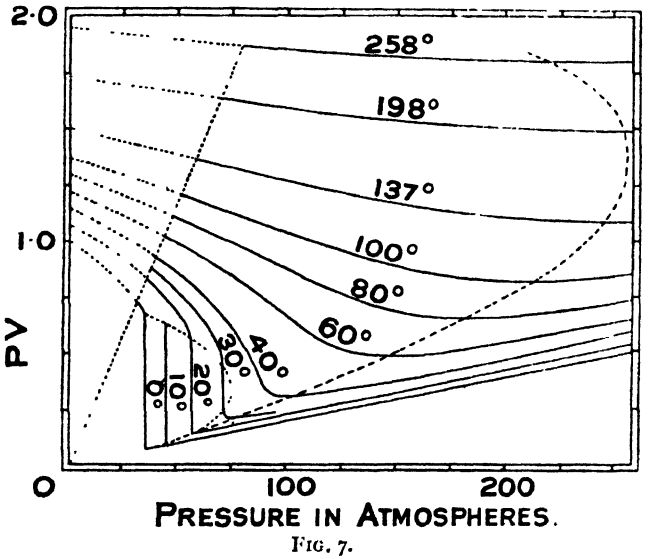


FIG. 7.

of the gas, and this part of the diagram will be considered in Chapter VIII.

Above 31·35° the isothermals show continuous curvature, and it will be observed that as the temperature rises, the depression in the isothermals becomes less marked, though it is still quite obvious, especially in Fig. 6, at 258°.

Minimum Values of pv.—For each isothermal on the diagrams there is a minimum value of pv, and the broken line (Figs. 6 and 7) passes through these minima. It will be seen that as the temperature rises the pressure corresponding to the minimum pv increases gradually, reaches a maximum, and then falls. The behaviour of ethylene is very similar to that of carbon dioxide at the same temperatures, but the experiments were made only up to 198°, and the

maximum pressure was not quite reached. With oxygen, however, a gas which is much more difficult to condense, the maximum has been passed at 0°, as will be seen from the table below.

	CO_2.		C_2H_4.		O_2.	
T°	*p*.	Minimum *pv*.	*p*.	Minimum *pv*.	*p*.	Minimum *pv*.
0	31·5	0·0740	42	0·1570	175	0·9120
15	—	—	—	—	165	0·9910
30	76	0·2185	87	0·3900	—	—
60	143	0·4830	125	0·6245	—	—
100	210	0·8140	161	0·9220	100	1·3750
137	245	1·0850	185	1·1660	—	—
198	255	1·4920	188	1·5340	—	—
258	218	1 8100	—	—	—	—

Although in the case of hydrogen at 0° there is no minimum *pv*, the whole isothermal sloping upwards as a nearly straight line, the isothermals at lower temperatures show minima, which become more pronounced as the temperature falls.

Thus, Witkowski[1] has determined the isothermals for hydrogen from + 100° C. to − 212° C., and Kamerlingh Onnes and Braak[2] have made very accurate measurements between − 104° C. and − 217° C. The following data are taken from their paper:—

Temperature.	Minimum *pv*.	*p*.
− 182·81	0·32663	32·57
− 195·27	0·27348	50·07
− 204·70	0·22945	54·67
− 212·82	0·18782	54·09
− 217·41	0·16342	42·54

The minimum values of *pv*, plotted against the corresponding pressures, fall on a parabola, the summit of which gives the maximum pressure. This was found to be 55·61 atmos., the temperature being − 208·8° C., and the value of *pv* 0·20826 (*pv* at 0° C. and 1 atmos. = 1). The earlier results obtained by Witkowski agree fairly well with those of Onnes and Braak.

[1] *Acad. Sci. Cracovie Bull.*, **6**, 305 (1905).

[2] *Comm. Phys. Lab. Leiden*, No. 97, 99*a* and 100*a* (1907); *Kon. Akad. Wet. Amsterdam*, **10**, 413 (1908).

Again, for air, Witkowski [1] has shown that the pressures corresponding to the minimum values of pv reach a maximum at − 75°, the pressure at this temperature being 124 atmos.

It appears, from what has been stated, that there must be a particular temperature for each gas at which the depression in the isothermal just disappears, so that the isothermal is horizontal through a considerable range of pressure. At this temperature the gas follows Boyle's law exactly up to a fairly high pressure, and behaves to this extent like a perfect gas. For hydrogen this temperature is found by Onnes and Braak [2] to be − 165·72° C.

It may also be said that each isothermal is practically horizontal for a short distance just as it reaches and passes the minimum pv, and that the gases behave like perfect gases, so far as Boyle's law is concerned, under these conditions also.

The isothermals at very high pressures approximate in form to straight lines, nearly parallel to each other. There is, however, slight curvature, as shown by the values of $\frac{p'v' - pv}{p' - p}$ given in the table below for hydrogen and oxygen at 0°.

Pressures.	Hydrogen.	Oxygen
500-1000 atmos. . . .	0·000732	0·001158
1000-1500 ,, . . .	690	1106
1500-2000 ,, . . .	638	1054
2000-2500 ,, . . .	612	1015
2500-3000 ,, . . .	579	0971

As regards the influence of temperature, the values of $\frac{p'v' - pv}{p' - p}$ are distinctly higher at 100° than at 0° for CO_2 and C_2H_4 at pressures from 200 to 1000 atmos., and for nitrogen and air there seems to be a slight rise with rise of temperature, but with hydrogen the values at 0°, 100°, and 200° show no decided variation.

Coefficient of Dilatation under Constant Pressure, $\frac{1}{v} \cdot \frac{dv}{dt}$.—Amagat tabulates the values of $\frac{1}{v} \cdot \frac{\Delta v}{\Delta t}$ ($= \alpha$), where v is the volume at the lower of the two temperatures in each case, not the initial volume at 0° C.

[1] *Acad. des Sci. de Cracovie* (1891). [2] *Comm.*, 100*a* (1907).

The values of a for CO_2 and C_2H_4 at each temperature rise at first with rise of pressure, reaching a maximum, and then falling again. The higher the temperature the higher is the pressure at which the maximum occurs. Thus, in the table for CO_2 from 40° to 50° the maximum (0·07566) occurs at 90 atmos.; from 90° to 100° the maximum (0·01247) is at 150 atmos.; and from 198° to 258° the maximum (0·00364) is at 300 atmos.

The fall in value of a with further rise of pressure for a given temperature interval continues, with O_2, H_2, N_2, and air, up to 3000 atmos.

As regards the variation of a with temperature at constant pressure, it is found that the values increase to a maximum and then fall. The higher the pressure the higher is the temperature at which the maximum occurs, but at high pressures the rise is less marked than at low ones. In the tables for CO_2 and C_2H_4 the maximum is not reached at pressures above 400 and 300 atmos. respectively, but the results obtained with oxygen, hydrogen, nitrogen, and air indicate that it would be attained at higher temperatures. These maxima do not differ greatly from those observed at constant temperature with rise of pressure.

Amagat states that at any pressure and at sufficiently high temperatures $\frac{\Delta v}{\Delta t}$ becomes constant as in the case of perfect gases, but the volume is not directly proportional to the absolute temperature, but to the absolute temperature diminished by a constant, or $v = cT - a$. The constant a diminishes as the pressure falls, and becomes zero at low pressures, when $v = cT$ at constant pressure, and the gas follows Gay Lussac's law.

Pressure Coefficients at Constant Volume.—Amagat considers the two coefficients, $\beta = \frac{1}{p} \cdot \frac{dp}{dt}$ and $B = \frac{dp}{dt}$. For the first he adopts the old name, "coefficient of dilatation at constant volume"; the second, which is simply the differential of pressure with regard to temperature, he calls the coefficient of pressure. It will be better, however, to employ the terms "coefficient of increase of pressure" for β, and "differential of pressure" for B.

Considering a series of constant volumes, the coefficient β, for a given temperature, increases with diminution of volume to a maximum and then falls. The maximum is most pronounced at low temperatures.

The differential B increases rapidly as the volume diminishes.

At any constant volume the differential B remains nearly constant; the slight variations tend to disappear at sufficiently high temperatures, and even at all temperatures under sufficiently high pressures. Thus, at constant volume the pressure is nearly proportional to the absolute temperature minus a constant, or $p = cT - a$. The constant a diminishes as the volume increases, and is zero for perfect gases.

This law, which was found by Ramsay and Young and by Barus to apply, approximately at any rate, to liquids as well as gases, and which also follows from the equation of state of Van der Waals (p. 187), will be considered more fully in Chapter XI.

The compressibilities of CO_2, SO_2, C_2H_4, and NH_3 were compared with those of nitrogen by Roth,[1] but the pressures to which the gases were subjected were not high enough to show the minimum values of pv at constant temperature.

Very important investigations on the properties of gases have been and are being carried out by Kamerlingh Onnes and his co-workers at Leiden.[2] Schalkwijk has determined the values of pv for hydrogen at 20° very accurately from 20 to 60 atmos., and gives the formula

$$pv_{20} = 1{\cdot}07258 + 0{\cdot}000667d + 0{\cdot}0000098d^2$$

where $d\left(=\frac{1}{v}\right)$ stands for the density of the gas with regard to that at 0° and 1 atmos. at 45° N. Lat.

Behaviour of Gases under very Low Pressures.—It has been stated (p. 18) that at ordinary temperatures even the gases which are most difficult to condense, such as hydrogen, oxygen, and nitrogen, do not follow the laws of Boyle and Gay Lussac exactly; that the deviations are more marked in the case of gases such as carbon dioxide, which are more easily condensed; and that, starting from atmospheric pressure, the deviations generally increase with rise of pressure.

It is clearly a matter of importance to ascertain whether the deviations continue to diminish, and whether they finally disappear on reducing the pressure below that of the atmosphere. Many deter-

[1] *Wied. Ann.*, **11**, 1 (1880).

[2] *Communications from the Phys. Lab. at the Univ. of Leiden*, No. 70 (cont.), 1901; 102*a* and *c* (1908); 119 (1910); 127*c* (1912); 146*b* (1915); 147*d* (1915); also Holborn and Schultze, *Ann. d. Physik*, **47**, 8 and 1089 (1915).

minations of the compressibilities of gases and a few determinations of their expansions under very low pressures have been made, but the experimental difficulties increase and the sources of error become very serious when the pressure is greatly reduced, and many of the results obtained by different observers are very discordant.

In the first place, it is evident that a given error in reading pressure which would be insignificant with a total pressure of, say, 1 atmos. might render an experiment worthless when the total pressure was reduced to, say, 1 mm. But beyond the mere difficulty experienced in reading the exact difference between the heights of two columns of mercury, there is the fact that the shape of the mercury meniscus, and with it the correction for capillarity, alters with the pressure, and possibly, as suggested by Ramsay and Baly, differs for different gases under the same pressure.

It is also well known that certain gases, notably carbon dioxide, are adsorbed to some extent by glass, and that when the pressure is greatly reduced, and especially when the glass is heated, this gas is slowly expelled again.

Conversely, if carbon dioxide is brought into contact with glass from which the condensed gas has been completely removed, some of the carbon dioxide will be adsorbed.

It is very probable that some kinds of glass adsorb gases much more freely than others, and some of the discrepancies between the results obtained by different observers may well be due to this cause.

Again, at exceedingly low pressures, the vapour pressure of mercury, even at 0° C., ceases to be negligible.

Another cause of error is that mercury adheres to some extent to glass, and it may be necessary to tap a manometer before reading in order that the true pressure may be indicated by the observed height of the column of mercury.

The compressibility of gases under reduced pressures has been studied by Mendeléeff,[1] who finds that for hydrogen the value of pv diminishes steadily as the pressure falls from 2200 to 20 mm. For air, carbon dioxide, and sulphur dioxide, pv was found to increase slightly with fall of pressure until a maximum was reached, after which it appeared to diminish again. The pressures corresponding to these maxima were about 650 mm. for air, 180 mm. for CO_2, and 60 mm. for SO_2.

[1] *Ber.*, **7**, 486 and 1339; **8**, 774, **9**, 1312 and 1341 (1874-1876).

Siljeström[1] obtained quite different results; he found that the value of pv for air increased steadily with fall of pressure from 759 to 7 mm., and he obtained similar results with oxygen and carbon dioxide.

Mendeléeff, however, considers that Siljestrom's methods were inaccurate, and that he misinterpreted his results; Mendeléeff, in fact, argues that Siljeström's results, properly corrected and interpreted, really lead to the same conclusion as his own.

Amagat[2] determined the compressibilities of air, hydrogen, and carbon dioxide, the pressure being reduced in the three cases to 0·295 mm., 2·288 mm., and 3·375 mm. respectively, and he arrived at the conclusion that for these gases at very low pressures the deviations from Boyle's law were practically within the limits of experimental error.

The apparatus employed by Amagat is shown in Fig. 8. It consists essentially of two glass bulbs, A and B, sealed below to a vertical tube immersed in the mercury in the wide tube C, and connected above with a differential manometer MM'. The bulbs could be exhausted and any gas admitted by means of the side tube provided with a stopcock *d*.

The limb M of the manometer was exhausted, the other, M', connected with A and B. After filling the bulbs with gas under greatly reduced pressure, the difference in level of the mercury in M and M' was read when, by adjusting the height of the reservoir C, the mercury in the bulb tube stood firstly at *b* and secondly at *a*.

Bohr[3] determined the compressibilities of oxygen at pressures between 15 mm. and 0·01 mm. at temperatures between 11° and 14°. Bohr finds that at these low pressures the relation between pressure and volume is represented by the equation $(p + \alpha)v = k$, in which α is a constant between certain limits of pressure. From 15 to 0·7 mm. $\alpha = 0{\cdot}109$, but below 0·7 mm. $\alpha = 0{\cdot}07$. There is apparently a sudden change in the behaviour of oxygen at the pressure 0·7 mm. Bohr contends that the observed deviation cannot be explained by errors of experiment.

Van der Ven, in 1889, found that the values of pv for air diminished as the pressure fell from 248 to 16 mm. Taking $pv = 1{\cdot}000$ at pressure 248 mm., the following values were found:—

[1] *Pogg. Ann.*, **151**, 451 (1874).
[2] *Ann. Chim. Phys.* [5], **28**, 480 (1883).
[3] *Wied. Ann.*, **27**, 459 (1886).

p	pv
62	0·9873
31	0·9811
16	0·9740

These results are in the same direction as Mendeléeff's.

Ramsay and Baly[1] attempted to determine the compressibilities of oxygen, nitrogen, hydrogen, and carbon dioxide under very low pressures by means of a pair of McLeod gauges, but they found that, on account of the adsorption of gases by glass, trustworthy results could only be obtained with hydrogen, and then only after condensed gas had been very carefully removed from the glass by long-continued exhaustion and frequent heating to a high temperature.

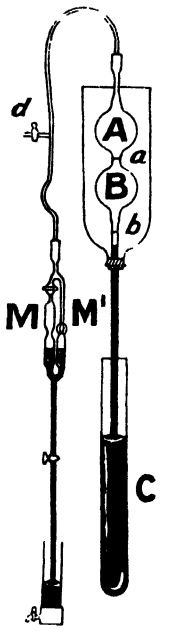


FIG. 8.

In the case of hydrogen, the values of pv were found to be constant within the limits of experimental error between 650 and 2·5 mm.

Moreover, if v is the volume of the apparatus, and v' that of the pumps, the pressure after and before a stroke of the pump should be in the ratio $v : v + v'$ if Boyle's law holds good. In other words, the ratio of the real pressures after and before each stroke should be equal to $\frac{v}{v + v'}$, and this was found to be the case within the limits of experimental error down to exceedingly low pressures.

It was not found possible to determine the compressibilities of other gases (O_2, N_2, CO_2) by means of the apparatus, but by a modification of the method the coefficients of expansion at constant pressure were determined at a series of low pressures. Ramsay and Baly found that the results with oxygen were erratic when the pressure was about 0·75 mm.

Battelli,[2] employing both glass and iron vessels, found that hydrogen followed Boyle's law down to a pressure of 0·02 mm. But he observed a deviation with air at pressures between 2 and 5 mm., and with oxygen a break at about 0·7 mm. Carbon dioxide was found to be more compressible than is required by Boyle's law, but

[1] *Phil. Mag.* (Sept. 1894), p. 301.

[2] *N. Cimento*, 1, 5 and 81 (1901); and *Phys. Zeitschr.*, 3, 17 (1901).

Battelli attributes this deviation to absorption by the walls of the vessels. Thiesen[1] pointed out that Bohr's and Battelli's results do not really agree, and he himself observed no break with oxygen at low pressures. After filling one of his balloons with glass wool, some peculiarities were observed with oxygen, but Thiesen saw no reason for assuming any anomaly at 0·7 mm.

Rayleigh[2] devised a manometer suitable for very low pressures, which were ascertained with very great accuracy by tilting the forked manometer (Fig. 9) until the fine pointers—one in each arm—just touched the surface of the mercury at B, B. The tube A was connected by flexible tubing with a reservoir of mercury, and the manometer was set at first with the pointers touching the mercury when both limbs were completely exhausted. The angle through which the manometer was tilted was measured by the angle of rotation of the mirror M, which was fixed to the platform N, resting on the three points L (shown in plan below). The mirror, stand, and manometer were rigidly attached to a board, which could be rotated on a horizontal axis parallel to the face of the mirror, lying approximately in the mirror surface and at about the middle of the height of the operative part.

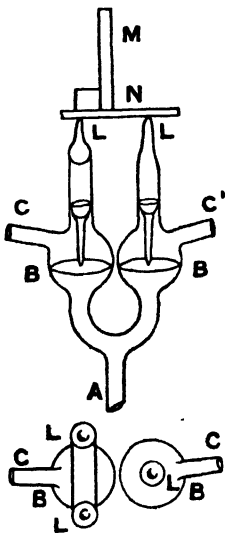


FIG. 9.

Between 1·5 mm. and 0·01 mm. hydrogen, nitrogen, and oxygen were found to follow Boyle's law within the limits of experimental error. The mean error in pressure from that required to make pv equal to the mean value in any series was usually less than 0·001 mm., and the + and − errors were generally well distributed.

In the following year Rayleigh,[3] employing a quite different form of manometer, determined the relation between the values of pv at 75 and 150 mm. for five gases. Calling the larger volume and the smaller pressure v_1 and p_1 respectively, $p_1v_1 = B \cdot p_2v_2$.

The values of B observed were as follows :—

[1] *Ann. d. Physik*, **6**, 2, 280 (1901). [2] *Phil. Trans.*, **196**, 205 (1901).
[3] *Ibid.*, **198**, 417 (1902).

	B.
Air	0·99997
H_2	0·99997
O_2	1·00024
Argon	1·00021
N_2O	1·00066

The results with oxygen were not so satisfactory as with the other gases, the individual values varying from 1·00005 to 1·00044. It is, therefore, quite possible that the mean value may be a little too high. Referring back to the values of B for hydrogen, nitrogen, oxygen, and air (p. 18) for the pressures ½ atmos. and 1 atmos., the conclusion to be drawn from the whole of Lord Rayleigh's results, and from those of Regnault, Amagat, Leduc and Sacerdote,[1] Jaquerod and Scheuer,[2] and others, is that the values of B approach and finally reach unity as the pressure falls, those for hydrogen rising and for the other gases falling. For the pressure range 75 to 150 mm., the differences from unity are quite negligible in the case of hydrogen, air, and presumably nitrogen. There is probably still a slight difference with oxygen, but this disappears at still lower pressures. In the case of nitrous oxide, B has still a fairly high value between 75 and 150 mm.

It is easy to understand how, by the introduction of moderate experimental errors or other disturbing factors, a simple physical relation may be transformed into an apparently complex one, but it is in the highest degree improbable that the transformation of a really complex relation into an apparently simple one could be thus brought about.

Again, the fact that so many observers have obtained practically concordant results with hydrogen, but very discordant results with oxygen, seems to prove that there is some cause of disturbance other than ordinary experimental error, peculiar to the latter gas, but no satisfactory explanation of the anomalies observed by Bohr, Battelli, and Ramsay and Baly has yet been suggested.

The general results obtained with gases under moderate or low pressures may be stated as follows:—

1. Comparing different gases at the same temperature, say 0°, and through the same range of pressures, say from 0·5 to 1 atmos., $\frac{\delta(pv)}{\delta p}$ changes from a relatively large negative value to a small posi-

[1] *Compt. rend.*, **125**, 297 (1897). [2] *Ibid.*, **140**, 1384 (1905).

tive value as we pass from the more easily to the less easily condensable gases.

2. Comparing any one gas at a series of temperatures and through the same range of pressure, $\frac{\delta(pv)}{\delta p}$ changes from a relatively large negative value to a small positive value as the temperature rises. For example it may be noted that for nitrogen at 0°, $\frac{\delta(pv)}{\delta p} = -0{\cdot}000571$ per metre of mercury; at about 52° $\frac{\delta(pv)}{\delta p} = 0{\cdot}000000$, and at 100° the value is $+ 0{\cdot}000347$.

Thus for a moderate range of pressure nitrogen follows Boyle's law accurately at about 52°, but not at 0° or 100°.

3. For the less easily condensable gases, such as hydrogen and nitrogen, $\frac{\delta(pv)}{\delta p}$ at any constant temperature above, say, 0° remains constant or nearly so from zero pressure to 3 or 4 atmos., but for the more easily condensable gases, such as carbon dioxide, there is distinct variation.[1]

4. If $\frac{\delta(pv)}{\delta p}$ is constant and small for a gas between, say, 0 and 3 or 4 atmos., the value of $\frac{p_1v_1}{p_2v_2}$ between these limits of pressure will be practically constant for a given value of δp whatever the actual pressures, and will approach more and more closely to unity as δp becomes smaller. The fact, therefore, that Rayleigh found no measurable variation in the value of pv between 1·5 mm. and 0·01 mm. in the case of hydrogen, nitrogen, and oxygen need not be taken to prove that $\frac{(\delta pv)}{\delta p} = 0$ between those limits of pressure, but that its value remained very small. In other words, Rayleigh's results do not prove that these gases follow Boyle's law absolutely at very low pressures, but that the deviations are too small to be detected even in experiments of such remarkable accuracy.

Coefficients of Expansion and of Pressure.—In the equation—

$$v_t = v_0(1 + \alpha t) \text{ at constant pressure}$$

α is the coefficient of expansion; and in the equation—

[1] D. Berthelot, "Sur les Thermomètres à Gaz," p. 7.

$p_t = p_0(1 + \beta t)$ at constant volume

β is the coefficient of increase of pressure.

The values given below have been obtained for various gases, p being the constant pressure at which α was determined, and p_0 the initial pressure in the determination of β.

Gay Lussac was of opinion that all gases had the same coefficients of expansion (α) under constant pressure; that they all followed Boyle's law; that they therefore all had the same coefficients of increase of pressure (β) at constant volume; and, lastly, that $\alpha = \beta$.

Regnault showed that no real gas is *perfect*, but he concluded that the coefficients for different gases become more and more nearly equal as the pressure falls, and that the statement that the coefficients are equal may be taken as correct only for very low pressures.

Gas.	Observer.	p.	$\alpha(0^\circ - 100^\circ)$.	p_0.	$\beta(0^\circ - 100^\circ)$.
Hydrogen	Regnault	1 atmos.	0·003661	1 atmos.	0·003668
,,	Chappuis	1 metre	0·00366004	1 metre	0·00366254
,,	K. Onnes and Bondin			1 ,,	0·0036627
,,	Richards and Marks	1 atmos.	0·0036609		
,,	Travers and Jaquerod			700 mm.	0·00366255
,,	,,			500 ,,	0·0036627
Helium	,,			700 ,,	0·00366255
,,	,,			500 ,,	0·0036628
Nitrogen	Regnault			1 atmos.	0·003668
,,	Chappuis	1 metre	0·00367313	1 metre	0·0036744
,,	,,	1·387 metre	0·00367750	793·5 mm.	0·0036718
,,	,,			530·8 ,,	0·0036683
Air	Regnault	1 atmos.	0·003671	1 atmos.	0·003665
Oxygen	Makower and Noble		mean values	663·38	0·0036738
,,	,,			353·99	0·0036698
Carbon monoxide	Regnault	1 atmos.	0·003669	1 atmos.	0·003667
Carbon dioxide	,,	,,	0·003710	,,	0·003688
,,	Richards and Marks	,,	0·0037282		
Sulphur dioxide	Regnault	,,	0·003903	1 atmos.	0·003845
Nitrous oxide	,,	,,	0·003719	,,	0·003676
					$\beta(0^\circ - 1067^\circ)$.
Nitrogen	Jaquerod and Perrot			240	0·0036643
Air	,,			230	0·0036643
Oxygen	,,			180-230	0·0036652
Carbon monoxide	,,			230	0·0036648
Carbon dioxide	,,			240	0·0036756
,,	,,			170	0·0036713

D. Berthelot[1] points out, as already stated, that for the gases formerly called *permanent* the values of $\frac{d(pv)}{dp}$ on any isotherm at about the ordinary temperature are small, and may be regarded without sensible error as constant up to pressures of 3 or 4 atmos. In other words, up to pressures of 3 or 4 atmos. the isotherms may be regarded as straight lines. Berthelot shows that the coefficients of expansion and of increase of pressure, α and β, may be conveniently studied by consideration of the pv—p diagram.

In Fig. 10, let AA′ and BB′B″ be two isotherms relating to temperatures t_1 and t_2 respectively.

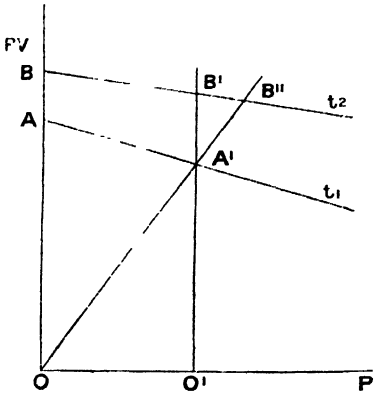


FIG. 10.

From the point O′ (OO′ = p) draw a straight line parallel to the axis of ordinates cutting the isotherms in A′ and B′. From O to A′ draw a straight line, and produce it to cut the second isothermal in B″. Then the lines AA′ and BB″ represent isotherms, O′B′ an isobar, and OB″ an isochor, or line of equal volume.

The angular coefficient of the isotherm AA′, or the coefficient of deviation from Boyle's law at $t°_1$, is—

$$\frac{d(pv)}{dp} = \frac{O'A' - OA}{OO'}.$$

The coefficient of expansion, α, under constant pressure between the temperatures $t_1 + t_2$ is—

$$\alpha = \frac{1}{t_2 - t_1} \times \frac{v' - v}{v} = \frac{1}{t_2 - t_1} \times \frac{A'B'}{O'A''}.$$

[1] *Loc. cit.*

The coefficient of increase of pressure, β, at constant volume is—

$$\beta = \frac{1}{t_2 - t_1} \times \frac{p' - p}{p} = \frac{1}{t_2 - t_1} \times \frac{A'B''}{\overline{OA}'}.$$

When the pressure (or density) decreases indefinitely, α and β tend towards a common limit, which may be termed γ, the coefficient of expansion (or increase of pressure) characteristic of the perfect gaseous state—

$$\gamma = \frac{1}{t_2 - t_1} \times \frac{AB}{\overline{OA}}.$$

In order to calculate γ, any three out of the four following constants must be known:—the angular coefficients of the two isotherms; α, giving the points A' and B'; and β, giving A' and B''.

The values of γ have been calculated by D. Berthelot for nitrogen and hydrogen from the determinations of Chappuis.[1]

Thus for nitrogen Chappuis finds—

(1) at 0°, $\frac{d(pv)}{dp} = -0{\cdot}000571$

(2) between 0° and 100° for $p = 1$ metre, $100\alpha = 0{\cdot}367313$

(3) between 0° and 100° for $p_0 = 1$ metre, $100\beta = 0{\cdot}367440$.

Hence at 100° $\frac{d(pv)}{dp} = +0{\cdot}000347$

and $100\gamma = 0{\cdot}366185$

From determinations by Chappuis between 0° and 100° of α for $p = 1386{\cdot}8$ mm. and of β for $p_0 = 793{\cdot}5$ mm. and $532{\cdot}9$ mm. respectively, three independent values of λ may be calculated. They are—

	Mean of all.
$100\gamma = 0{\cdot}366185,\ 0{\cdot}366184,\ 0{\cdot}366177$	$0{\cdot}366182$.

For the above determinations vessels of platinum-iridium or of hard glass were employed. Experiments with a porcelain vessel gave variable and evidently untrustworthy results.

In the case of hydrogen the data are less complete and the calculated values of γ less concordant. It is quite possible that a vessel of platinum-iridium may be unsuitable for hydrogen even at 100°, and the only determination of α was made in a vessel of this alloy. Only the third determination of β was carried out in a vessel of hard

[1] *Travaux et Mémoires du Bureau international des Poids et Mesures.*

glass. The three values of 100γ calculated by Berthelot for hydrogen are 0·366248, 0·366206, and 0·366169 respectively, of which he regards the last as the most correct. The mean of the five values, four for nitrogen and the last for hydrogen, would give—

$$\gamma = 0{\cdot}00366180 \text{ and } \frac{1}{\gamma} = 273{\cdot}090^{\circ}.$$

[The mean of all seven values would be $\gamma = 0{\cdot}00366193$ and $\frac{1}{\gamma} = 273{\cdot}080$.]

Kamerlingh Onnes and Braak,[1] from their own data with hydrogen at 0° C. and 100° C., deduce the value 273·10°, but consider that the true value may be 0·01° lower.

Buckingham[2] makes use of the measurements of the specific heat of nitrogen by Holborn and Austin,[2] and, as a result of his own calculations and of those of D. Berthelot, he deduces the value 273·13° C. for the melting point of ice on the centigrade thermodynamic scale of temperature.

[1] *Comm.* 101 *b* (1907).

[2] *Bull. of Bureau of Standards, Washington*, 3, 237 (1907).

CHAPTER III.

GENERAL PROPERTIES OF GASES (*continued*).

The Densities of Gases and Vapours.—The weight of a given body is proportional to its mass and to the force of gravity acting on it. The attractive force varies slightly with the latitude and with the height above the sea-level, but in any one locality weight is simply proportional to mass, and the terms are frequently employed as synonymous.

The density s of a substance may be defined as the weight (or mass) of unit volume of that substance. The gram is taken as the unit of weight, the cubic centimetre as the unit of volume. The specific gravity of a substance may be defined as its weight in terms of that of the same volume of some standard substance under specified conditions of temperature, and, if necessary, pressure.

In the case of liquids and solids, sometimes of gases also, it is customary and most convenient to take water at 4° C. as the standard substance, because the unit of weight, the gram, was originally defined to be the weight of 1 cubic centimetre of water at 4° C., that is, at its point of maximum density, and in practice the unit of volume is taken to be that occupied by 1 gram of water at 4°. That being the case, the density of a substance is numerically equal to its specific gravity.

The specific volume v is the reciprocal of the density or specific gravity, and may be defined as the volume occupied by 1 gram of a substance.

Of course, as the volume of a substance depends on the temperature and pressure, these should be mentioned in stating its specific volume or density, but as the volume of a solid or liquid under ordinary conditions is not appreciably affected by moderate changes of pressure, the temperature only need usually be mentioned.[1]

[1] Some chemists take water at 0° as the standard, others take water at the same temperature as that of the substance investigated; it is therefore advisable

Gases, under ordinary conditions, are so much lighter than liquids or solids that it is frequently convenient to state the weight of a litre instead of that of a cubic centimetre, and for many purposes it is useful to compare the specific gravity of a gas with that of another standard gas under the same conditions of temperature and pressure.

When a substance is liquid or solid under ordinary conditions, but can be vaporized by raising the temperature or reducing the pressure, and when the specific gravity of its vapour is compared with that of a standard gas at the same temperature and pressure, the ratio so obtained is always termed by chemists the *vapour density* of the substance.

There is thus some ambiguity in the use of the terms "density" and "specific gravity," but confusion is hardly likely to arise, because the magnitude of the value stated is a sufficient indication of what is meant.

At one time it was customary to express the specific gravity of a gas, and the vapour density of a liquid or solid, in terms of that of air taken as unity, but air is a mixture, and its composition is not absolutely constant. Many chemists preferred to take hydrogen as the standard gas, because the atomic weight of hydrogen was taken as unity. Within recent years, however, it has been thought better to take 16 as the atomic weight of oxygen, so that the recognized unit is $\frac{1}{16}$ of the atomic weight of oxygen, and not the atomic weight of hydrogen, which differs slightly from it.

Following this change, many experimenters have recently taken 16 as the specific gravity of oxygen, making this gas the standard.

The accurate determination of the density of a gas is a very difficult matter, for the gas must be contained in a vessel of large capacity and of relatively great weight. An error in weighing may therefore be negligible as regards the total weight of globe and gas, but of great importance as regards that of the gas itself.

Again, owing to the buoyancy of the air, the apparent weight of a large globe is greatly affected by changes in atmospheric pressure. The surface of glass, also, is slightly hygroscopic, and the apparent weight of a glass globe therefore depends to a slight extent on the hygrometric state of the air.

to state the temperature of the water thus—Sp. gr. at $\frac{15^\circ}{4^\circ}$, or at $\frac{15^\circ}{0^\circ}$, or at $\frac{15^\circ}{15^\circ}$. It is, of course, only in the first of these cases that the specific gravity is numerically equal to the density.

Regnault was the first to avoid some of these difficulties by employing as a counterpoise a second globe of as nearly as possible the same weight and capacity as that required for the gas.

Regnault, however, overlooked the fact, pointed out later by Rayleigh, that since glass is slightly elastic, the capacity of a globe is affected by changes of pressure, being slightly less when exhausted than when filled with gas. The weight of air displaced when the vessel is exhausted is therefore slightly less than when it is full, and the apparent weight of the exhausted globe is therefore a little too great. Regnault's actual globes of 10 litres capacity have been broken, but Crafts has estimated the correction as 3 mgrm.

In making the determinations, the utmost care must be taken to exhaust the globe completely before weighing it, and in order to avoid the introduction of impurities it is advisable to exhaust the globe two or three times after admission of small quantities of the gas under examination. The globe is then filled with the gas at a known temperature and pressure, and is again weighed.

The following are some of the best determinations of the weight of a litre of a few gases at 0° and 760 mm. at sea-level, at the latitude of Paris :—

	Rayleigh.	Morley.	Leduc.	Germann.
Oxygen	1·42905	1·42900	1·4288	1·42906[2]
Hydrogen . . .	0·08998[1]	0·08987	0·08982	
Nitrogen . . .	1·2507	1·2503		

Determination of Vapour Densities.—Various methods have been devised for the determination of the vapour density of a substance which is liquid (or solid) at the ordinary temperature. The three which have been most frequently employed are those of Dumas, Hofmann, and V. Meyer.

Dumas' Method.—Dumas employed a glass bulb with the neck drawn out to a fine tube. The bulb was first weighed full of air at a known temperature and pressure, and by subtracting the calculated weight of air, that of the empty bulb was ascertained. A quantity of the liquid was introduced by warming the bulb and holding the open end of the tube under the liquid. The bulb was then heated in a suitable bath to a temperature 20° or more above the boiling

[1] This value is admittedly a little too high.

[2] Scheuer obtained the same result as Germann.

point of the liquid, when brisk ebullition took place, and the air in the bulb was expelled by the vapour. When the escape of vapour ceased, the fine tube was sealed near the end, and the bulb was thus filled with the vapour at the temperature of the bath and under atmospheric pressure. After cooling, the bulb with the little tube that was drawn off was weighed again, and the weight of vapour thus ascertained. Finally, the capacity of the bulb was determined by breaking the end of the tube under recently boiled water and weighing the bulb full of water. The vapour density is equal to the weight of vapour divided by that of the same volume of the standard gas at the temperature of the bath and under the atmospheric pressure.

The chief advantage of Dumas' method is the simplicity of the apparatus required, but it is not suitable for substances which can only be obtained in small quantity, because a considerable amount of liquid must be evaporated in order to ensure complete expulsion of air from the bulb.

Hofmann's Method.—This is an improvement on a method devised by Gay Lussac. The apparatus consists of a eudiometer tube graduated in millimetres and calibrated, or graduated in cubic centimetres; a mercury trough; and a vapour-jacketing tube similar to B (Fig. 11). The eudiometer is filled with mercury, and if an accurate result is required, the mercury should be boiled in the tube to remove all air and the film of condensed gas adhering to the glass. The tube is then inverted in the trough of mercury. The substance is weighed in a small bulb, which is usually loosely stoppered or may be drawn out to a fine capillary tube, and the little bulb is passed up into the eudiometer, great care being taken to avoid loss of material or introduction of air. The bulb rises past the mercury, and the substance evaporates into the vacuous space either at once or when the eudiometer is heated by the jacketing vapour. The amount of substance required is very small, and the weight is determined directly. The temperature is that of the jacketing vapour; the volume is read on the eudiometer, but in exact work must be corrected for the expansion of glass; the pressure is the difference between the corrected heights of the barometer and of the column of mercury in the eudiometer. The corrections for pressure are, unfortunately, somewhat uncertain. In the first place, the heights of the two columns of mercury must be corrected to 0° C., but while the upper part of the mercury in the eudiometer is at the temperature of

the vapour, the lower part is at or about the temperature of the room, and it is impossible without a special appliance, such as the integrating thermometer of Ramsay and Steele,[1] to estimate with accuracy the temperature of the intermediate portion; in the second place, if the temperature is high, the vapour pressure of mercury cannot be neglected, but the diffusion of mercury vapour is a slow process, and unless considerable time is allowed, the maximum pressure may not be attained.

On the other hand, readings may be taken at different temperatures, and by replacing the open mercury trough by a closed cylindrical glass vessel A (Fig. 11), connected with a pump and pressure gauge, the external pressure may be altered, and a series of determinations may be made at different pressures and volumes.[2]

Victor Meyer's Method.—This method is the most convenient for ordinary purposes, and is the one which is most frequently employed. The long tube A (Fig. 12), which may be of glass, porcelain, platinum, or perhaps quartz, is carefully dried, and a little dry sand or fine asbestos is placed in it as a protection against fracture when the bulb containing the substance is introduced. The tube is closed above by a cork, and is heated below in a suitable bath B, or in a furnace to a temperature which must be well above the boiling point of the substance under investigation, the expanded air being allowed to escape in bubbles through the water in the trough C. The graduated tube D, previously filled with water and inserted in the trough, is then placed in position over the delivery tube, and the bulb containing a weighed quantity of the substance is introduced. This may be done by moving the cork, dropping in the tube, and replacing the cork at once; or the little bulb may be supported at the top of the tube while the cylindrical bulb is being heated, and may afterwards be released and allowed to fall by a mechanical arrangement without removing the cork.

Rapid evaporation takes place, and the vapour expels its own volume of hot air, which is finally collected at the temperature of the room in the graduated tube. As the air is collected over water it becomes saturated with moisture. If b is the barometric pressure, p' the vapour pressure of water at the temperature of the room, and p''

[1] *Zeitschr. physik. Chem.*, **44**, 348 (1903); *vide* also Brühl, *Ber.*, **9**, 1368 (1876); **12**, 197 (1879).

[2] Ramsay and Young, *Phil. Trans.*, **178**, 57 (1887); Young, *Proc. Phys. Soc.*, **13**, 658 (189-).

the pressure of the column of water in the graduated tube reduced to millimetres of mercury, the true pressure of the dry air $= b - p' - p'' = p$. If the heated vapour itself could be cooled to the temperature of the room without condensing, and if its coefficient of expansion were the same as that of air, its volume under a pressure p would be the same as that of the cooled air.

Calling the weight of substance m, the temperature of the room t,

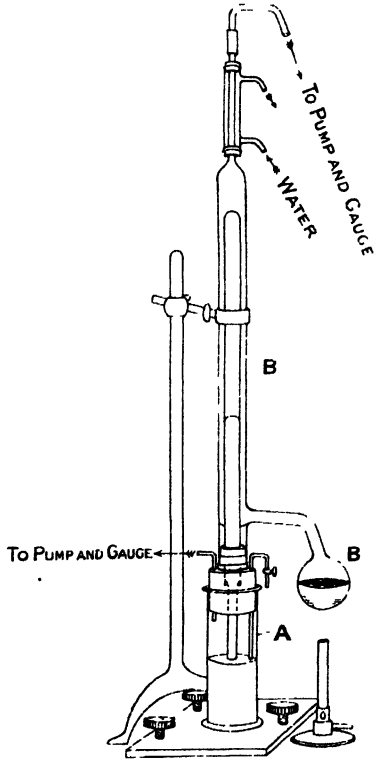


FIG. 11.

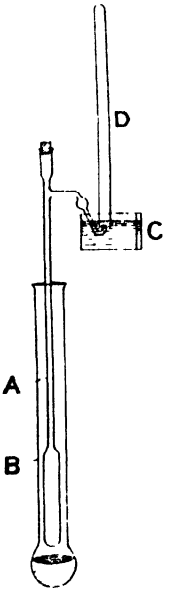


FIG. 12.

and the volume of air collected v, it may be stated that m gram of the substance would occupy as vapour v c.c. at $t°$ and under pressure p. The vapour density may therefore be calculated without knowing the temperature of the bath or furnace. The method can be employed up to temperatures which are limited only by the melting or softening of the material of the vapour-density tube.

Numerous modifications of these methods have been devised. A simple and convenient form of apparatus has been devised by

Menzies.[1] The vapour density is ascertained from the increase of pressure caused by the evaporation of a known weight of the substance into a closed space containing air. The apparatus is a modification of that shown in Fig. 81 (p. 292). The narrow, graduated tube is open below; the wider tube contains a little mercury and is not graduated; and there is an arrangement for breaking and dropping a small sealed bulb containing a weighed quantity of the substance under investigation. The increase in pressure is shown by the levels of the mercury in the narrow and wide tubes.

Special methods for determining vapour densities at high temperatures have been devised by Gibson[2] and at very high temperatures by von Wartenberg.[3]

Gay Lussac's Law of Volumes.—Cavendish in 1781 discovered that hydrogen and oxygen combine together to form water in the exact, or almost exact, ratio of 2 volumes of hydrogen to 1 volume of oxygen. Gay Lussac and Humboldt confirmed the correctness of this ratio in 1805, and Gay Lussac afterwards determined the volumetric composition of several compounds; he published in 1809 the generalization known as Gay Lussac's "Law of Volumes," which may be stated as follows: *When two or more gaseous substances combine together to form a compound, the volumes of the combining gases bear a simple ratio to each other and also to that of the compound when it is also a gas.*

Thus, for example, 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia gas.

Gay Lussac also showed how the density of the gaseous compound could be calculated from the densities of the component gases, and in some cases he found that there was a fair agreement between the calculated and observed densities.

It is clear, however, that, since under ordinary conditions of temperature and pressure no known substance behaves as a perfect gas, the law of volumes cannot in general be regarded as strictly true, neither can the observed and calculated densities of the gaseous compounds be expected to show exact agreement. But from what has been stated (p. 34), it may be concluded that the law would be found strictly applicable to gases under exceedingly low pressures, at any rate at sufficiently high temperatures. According to Cavendish, and

[1] *Journ. Amer. Chem. Soc.*, **32**, 1624 (1910).
[2] *Proc. Roy. Soc. Edin.*, **33**, 1 (1913).
[3] *Zeit. anorg. Chem.*, **56**, 320 (1907).

to Gay Lussac and Humboldt, the volumes of hydrogen and oxygen which unite to form water are in the ratio of 2 : 1, but the very accurate experiments of Morley,[1] Scott,[2] and Burt and Edgar[3] give a mean value of 2·00282 for the ratio. But the value of pv for hydrogen decreases, while that for oxygen increases, with fall of pressure, and at zero pressure the ratio would be—

$$\frac{2\cdot00282 \times \left(p_0v_0\right)_{II}}{\left(p_1v_1\right)_{O}}$$

which, with Lord Rayleigh's values of α_0 (p. 45) = 1·9999.

Avogadro's Hypothesis.—Shortly before the enunciation of the law of volumes Dalton had brought forward his atomic theory, according to which a simple ratio exists between the number of atoms of different elements which unite together to form a compound, and Gay Lussac attempted unsuccessfully to bring the atomic theory into harmony with the law of volumes by assuming that the densities of gases are proportional to their atomic weights. Bernoulli, in 1740, had attributed the pressure exerted by a gas to the impact of the rapidly moving particles against the walls of the containing vessel. Avogadro, in 1811,[4] and, independently but somewhat later, Ampère brought forward the hypothesis that equal volumes of different gases, measured at the same temperature and pressure, contain the same number of these particles, which Avogadro termed *molecules*.[5]

Molecular Weights.—If this hypothesis is true, the densities of different gases—at the same temperature and pressure—must be proportional to the masses of the molecules or the molecular weights (p. 57). But just as it is only at exceedingly low pressures that Gay Lussac's law of volumes can be said to be strictly true, so it is only at such pressures that Avogadro's hypothesis can be strictly applicable to real gases. If, however, the densities of two gases under ordinary atmospheric pressure and the values of $\frac{d(pv)}{dp}$ are known, it is easy to calculate what their densities would be if they behaved as perfect gases.

[1] *Smithsonian Contributions to Knowledge*, **29** (1895).

[2] *Trans. Roy. Soc.*, **184**, 543 (1893), corrected by Morley (*loc. cit.*).

[3] *Ibid.*, **216**, 293 (1916). [4] *Journal de Physique*, **73**, 58 (1811).

[5] The bearing of Avogadro's hypothesis on the determination of atomic weights will be considered later.

Thus the density of oxygen compared with that of hydrogen at 0° C. and 1 atmos. pressure was found by Morley to be 15·90. The corrected value would, however, be—

$$15{\cdot}90 \times \frac{\left(\frac{p_1 v_1}{p_0 v_0}\right)_O}{\left(\frac{p_1 v_1}{p_0 v_0}\right)_H}$$

where $p_1 = 1$ atmos. and $p_0 =$ zero pressure;

or

$$15{\cdot}90 \times \frac{(1 + \alpha_0)_O}{(1 + \alpha_0)_H}$$

where $\alpha_0 = \frac{1}{pv} \times \frac{d(pv)}{dp}$ at 0°

$= 2(1 - B_0)$, where $B_0 = \frac{p_{\frac{1}{2}} v_{\frac{1}{2}}}{p_1 v_1}$

$= 1 - B'_0$, where $B'_0 = \frac{p_0 v_0}{p_1 v_1}$

p_1, $p_{\frac{1}{2}}$, p_0 being 1 atmos., $\frac{1}{2}$ atmos., and zero pressure respectively.

The values of B for a few gases, at the temperatures stated in the table, are given on p. 18, under the heading $p'v'$. Correcting to 0° C., and calculating from B_0, Lord Rayleigh obtained the following values of α_0:—

Oxygen	− 0·00094
Hydrogen	+ 0·00053
Nitrogen	− 0·00056
Carbon monoxide	− 0·00081
Carbon dioxide	− 0·00668
Nitrous oxide	− 0·00747

For carbon dioxide Chappuis finds the value $\alpha_0 = -0{\cdot}00665$; and for hydrogen and nitrogen, from determinations of compressibility between 1 and 2 atmos., $\alpha_0 = +0{\cdot}00057$ and $-0{\cdot}00043$ respectively. From determinations at pressures between 400 and 800 mm. Jaquerod and Scheuer obtain the following values of α_0:—

Hydrogen	+ 0·00052
Oxygen	− 0·00097
Nitric oxide	− 0·00117

For neon Burt[1] finds $\alpha_0 = +0{\cdot}00105$, and for helium 0·00000; for hydrogen chloride Gray and Burt[2] find $\alpha_0 = -0{\cdot}00748$, and for oxygen − 0·000964.

[1] *Trans. Faraday Soc.*, **6**, 1 (1910). [2] *Trans. Chem. Soc.*, **95**, 1633 (1910).

Taking Lord Rayleigh's values of a_0 for oxygen and hydrogen, the corrected density of oxygen is—

$$15{\cdot}90 \times \frac{1 - 0{\cdot}00094}{1 + 0{\cdot}00053} = 15{\cdot}88.$$

The molecular weight of oxygen is therefore 31·76 if that of hydrogen is taken as 2; it is, however, more convenient to state the molecular weights of gases and vapours in terms of that of oxygen, which is taken as 32.

On this basis, the molecular weight of hydrogen is—

$$\frac{32}{15{\cdot}88} = 2{\cdot}015.$$

Adopting Lord Rayleigh's values for oxygen and nitrogen, the molecular weight of the latter gas is—

$$32 \times \frac{0{\cdot}96737}{1{\cdot}10535} \times \frac{1 - 0{\cdot}00056}{1 - 0{\cdot}00094} = 28{\cdot}016.$$

D. Berthelot has calculated the following values from the data obtained by Leduc and Sacerdote:—

	Molecular weights.
Hydrogen	2·0145
Nitrogen	28·013

The agreement with Lord Rayleigh's values is very satisfactory.

Value of R for Perfect Gases.—It is now possible to calculate the value of R in the equation for *perfect* gases.

$$PV = \frac{p_0 v_0}{273} \times T = RT.$$

If unit mass, say 1 gram, of gas be taken in each case, the value of R will depend on the molecular weight as well as on the units of pressure and volume, but if one gram-molecule (the molecular weight in grams) of each gas be taken, R will be constant for any given units of pressure and volume, for it is now known that 32 grams of oxygen, 2·0145 grams of hydrogen, or 28·015 grams of nitrogen would each occupy 22·41 litres at 0° C., and under normal atmospheric pressure if they behaved as perfect gases.

Taking the millimetre of mercury as the unit of pressure, and the cubic centimetre as the unit of volume, the equation will be, for any perfect gas—

$$pv = \frac{760 \times 22{,}410}{273} \times T$$
$$= 62{,}390\ T$$

or with the litre and the atmosphere as units of volume and pressure, respectively, the equation becomes—

$$pv = \frac{1 \times 22{\cdot}41}{273} \times T$$
$$= 0{\cdot}08209T.$$

According to D. Berthelot (*loc. cit.*), the constant is given with greater accuracy by taking the volume of a gram-molecule of gas as 22·412 litres, and the absolute zero of temperature as −273·09° C. The value of R for the two systems of units would then become 62,372 and 0·08207 respectively.

Specific Heats of Gases.—The specific heat of a substance is the amount of heat required to raise the temperature of unit mass (usually 1 gram) of it through 1° C. The unit of heat is called a calorie, and is taken to be the amount of heat required to raise the temperature of 1 gram of water through 1 C., either from 0° to 1° or from 15° to 16°.

If the volume of gas is kept constant when the temperature is raised, the pressure increases, and heat is required to increase the kinetic energy of rectilinear motion of the molecules and also the energy of vibration or oscillation, if any, of the molecules. If, on the other hand, the pressure is kept constant, the gas expands, and work must also be done against the external pressure. The heat required to raise the temperature of 1 gram of the gas through 1° C. in the first case is called the specific heat at constant volume, c_v, and in the second case, the specific heat at constant pressure, c_p.

If the increase in molecular or internal energy is the same in both cases, and if heat is not required to produce any other changes, the difference between the two specific heats, $c_p - c_v$, is the amount of heat equivalent to the external work done in expansion against pressure. In other words, if the energy of a gas at a given temperature is independent of the volume, the heat equivalent to the work done in expansion is equal to $c_p - c_v$.

Early experiments by Gay Lussac, and more accurate determinations by Joule, seemed to indicate that when air was allowed to expand into a vacuum, and therefore without developing mechanical

power, no change of temperature occurred. But it is evident that if there is a force of attraction between the molecules of a gas, this force will diminish as the distance between the molecules increases, and therefore, when the gas expands, some work must be done in overcoming this attraction, and there must always be a slight cooling on expansion due to this cause.

Again, work may be measured as the product of pressure and volume pv, and it has been shown that for the ordinary gases at constant temperature the product pv is not quite constant. For example, in the case of air at 0° C. the value of pv increases as the pressure falls, and hence there should be cooling on expansion; but with hydrogen at 0° the product pv diminishes with fall of pressure, and there should therefore be a slight heating on expansion. The actual heat change produced in any case should be the algebraic sum of the changes due to the two causes.

Experiments by Joule and Thomson, in which gases were forced through a porous plug, showed a decided cooling effect in the case of air and carbon dioxide even at 100°, but with hydrogen a small heating effect was observed both at 7° and at 90°. Thus, with hydrogen, the heating effect due to the change in value of pv was greater than the cooling effect due to molecular attraction.

The statement that the internal energy of a gas at constant temperature is independent of the volume is, in fact, only true for perfect gases; hence it is only for perfect gases that the difference between the specific heats at constant pressure c_p and constant value c_v is strictly a measure of the external work done in expansion.

The term *molecular heat* may be conveniently applied to the product of the specific heat into the molecular weight of any substance, and it may be proved that for a perfect gas the difference between the molecular heat at constant pressure C_p and that at constant volume C_v is equal to the gas constant R expressed in calories.

For if we raise the temperature of one gram-molecule of gas from T° to (T + 1)° at constant pressure, the volume increases from V to $V \times \frac{(T + 1)}{T}$.

But $V \times \frac{(T + 1)}{T} - V = \frac{V}{T}$.

And the external work is equal to the product of the pressure into the increase of volume $= \frac{PV}{T} = R$. Therefore $C_p - C_v = R$.

[1 litre atmosphere = 24·17 calories, and R = 0·08207 litre atmos. = 1·984 calorie; therefore $C_p - C_v = 1·984$ calorie, or, roughly, $C_p - C_v = 2$ calories.]

For the methods of determining the specific heats of gases reference may be made to Preston's "Theory of Heat" or Haber's "Thermodynamics of Technical Gas Reactions," trans. by Lamb, Longmans, 1908. A useful summary of the values of C_v for a number of gases at different temperatures is given by Lewis and Randall, *Journ. Amer. Chem. Soc.* **34**, 1128 (1912). Most experimenters have determined the specific heats at constant pressure, but Joly[1] has obtained accurate values for the specific heat at constant volume by means of the steam calorimeter, and has shown that for air and carbon dioxide the specific heat increases with the density, while for hydrogen it appears to diminish.

The methods in general use for the determination of the specific heats of gases may be divided into three groups: (1) The direct methods in which the hot gas is passed through a calorimeter. (2) The adiabatic methods of Clément and Desormes, Kundt and Warburg, and Lummer and Pringsheim, involving the changes of pressure, temperature, and volume due to adiabatic compression or expansion. (3) The explosion methods of Bunsen, Mallard and Le Chatelier, Berthelot and Vieille, and Langen, in which an explosive mixture of gases is ignited, and the maximum pressure thus developed is ascertained.

According to the kinetic theory of gases, the heat capacity at constant pressure of a gram-molecule of any monatomic gas should be independent of the temperature and equal to 4·97 calories per degree, and this was found to be the case for mercury vapour by Kundt and Warburg.[2] For argon and helium Lord Rayleigh and Ramsay[3] found the molecular heat to be about 5, while for argon Niemayer[4] obtained the constant value 4·99 from 0° to 100°, and Pier[5] the average value 4·96 for the range from 0° to 2350°. For helium Bein and Geiger[6] obtained the value 5·1, Eggert[7] the constant value 5·065 from −15° to 150°, and Scheel and Heuse[8] the

[1] *Proc. Roy. Soc.*, **41**, 352 (1886).
[2] *Pogg. Ann.*, **127**, 497 (1866); **135**, 337 and 527 (1868).
[3] *Proc. Roy. Soc.*, **57**, 265 (1895); Ramsay, *ibid.*, **58**, 81 (1895).
[4] *Diss., Halle* (1902).
[5] *Zeit. Elektrochem.*, **15**, 536 (1909).
[6] *Ber. physik. Gesell.*, **5**, 657 (1907).
[7] *Ann. d. Physik*, **44**, 643 (1914).
[8] *Ibid.*, **40**, 473 (1913).

value 4·993 at 18°, but these observers found the notably lower value 4·934 at −180°.

The conclusion had been arrived at by Le Chatelier[1] that the molecular heats of all gases at constant pressure may be expressed by the formula $C_p = 6{\cdot}5 + aT$, where a is a constant which increases with the complexity of the molecule. From a consideration of the data obtained by Holborn and Austin,[2] Holborn and Henning,[3] Pier,[4] Martini,[5] Strecker,[6] Thiesen,[7] Swan,[8] Furstenau,[9] Nernst,[10] Stevens,[11] and others, Lewis and Randall[12] conclude that the molecular heats of the diatomic gases may be represented by the formula proposed by Le Chatelier and adopted by Nernst, but that for those of the polyatomic gases in general the formula

$$C_p = A + aT + bT^2 \text{ is required.}$$

The following values of A, a, and b, are adopted by them with the reservation that they require confirmation in the case of the halogens and their hydrides and of hydrogen sulphide.

	A.	a.	b.
Monatomic gases	5·0	—	—
N_2, O_2, CO, NO, HCl, HBr, HI	6·5	+ 0·0010	—
H_2	6·5	+ 0·0009	—
Cl_2, Br_2, I_2	6·5	+ 0·001	—
H_2O and H_2S	8·81	− 0·0019	+ $0{\cdot}0_5222$
CO_2 and SO_2	7·0	+ 0·0071	− $0{\cdot}0_5186$
NH_3	7·5	+ 0·0012	—

It may be noted that the formulæ make the molecular heats of water vapour, hydrogen sulphide, carbon dioxide and sulphur dioxide nearly the same at 0°, and this equality is confirmed by the experiments of Thibaut.[13] The results obtained more recently by Moody,[14] Escher,[15] Mercer,[16] and Schulze and Rathgen[17] for air,

[1] *Zeit. physik. Chem.*, **1**, 456 (1887).
[2] *Abh. Phys. Tech. Reichsanstalt*, **4**, 131 (1905).
[3] *Ann. d. Physik*, **23**, 809 (1907).
[4] *Zeit. physik. Chem.*, **62**, 385 (1908); **66**, 759 (1909); *Zeit. Elektrochem.*, **15**, 536 (1909); **16**, 897 (1910).
[5] *Phil. Mag.*, [5], **39**, 142 (1895).
[6] *Ann. Physik.*, [3], **13**, 20 (1881).
[7] *Ibid.*, [4], **9**, 88 (1902).
[8] *Proc. Roy. Soc.*, **82**, 147 (1910).
[9] *Ber. physik. Gesell.*, **6**, 968 (1908); **7**, 137 (1909).
[10] *Zeit. Elektrochem.*, **16**, 96 (1910).
[11] *Ann. Physik.*, [4], **7**, 285 (1902).
[12] *Loc. cit.*
[13] *Ann. d. Physik*, **35**, 347 (1911).
[14] *Phys. Rev.*, **34**, 275 (1912).
[15] *Ann. d. Physik*, **42**, 761 (1913).
[16] *Proc. Phys. Soc.*, **26**, 155 (1914).
[17] *Ann. d. Physik*, **49**, 457 (1916).

hydrogen, nitrogen, oxygen and carbon dioxide at or not very far above the ordinary temperature agree fairly well with those calculated from the above formulæ, but those found by Scheel and Heuse [1] between − 180° and 0° for hydrogen, nitrogen, oxygen, air and carbon dioxide show wide differences.

Holborn and Jakob [2] have determined the specific heat of air at 59° at a series of constant pressures up to 200 atmospheres with the following results:—

Pressure in Kg. per cm.²	$c_p \times 10^4$.	
	Observed.	Calculated.
0	—	2413
1	2415	2416
25	2490	2485
50	2554	2556
100	2690	2694
150	2821	2819
200	2925	2925

These results agree well with the means of those of Joule and Thomson, Vogel, and Noell, but differ widely from those of Lussana.

Ratio of the Two Specific Heats.—This ratio, $\frac{c_p}{c_v} = \gamma$, which is of great importance in chemical theory, may be calculated from the velocity of sound in a gas by the formula of Laplace—

$$u = \sqrt{\gamma \times \frac{p}{s}}$$

where p is the pressure, s the density, and u the velocity.

The value of γ for air, calculated in this way, was found to be 1·408.

The ratio may also be determined by the method of Clément and Desormes, based on the adiabatic equation $pv^\gamma = \text{const.}$ Air at a pressure p_1, slightly lower than that of the atmosphere p_0, is enclosed in a large globe, provided with a very wide stopcock and a narrow pressure gauge. The stopcock is opened for a moment, so that air rushes in until the pressure rises to p_0, and at the same time the temperature, owing to compression of the air, rises slightly. The stopcock is at once closed and the temperature allowed to fall again, when the final pressure p_2 is measured.

[1] *Loc. cit.* [2] *Zeit. Vereins Deutsch. Ing.*, 58, 1429 (1914).

Then $$\gamma = \frac{\log p_0 - \log p_1}{\log p_2 - \log p_1}.$$

By this method Röntgen[1] obtained the value 1·4053 for dry air.

More recently the following values have been obtained: 1·4032, Partington;[2] 1·4011, Moody;[3] 1·4047, Escher.[3]

Leduc[4] dispenses with the pressure gauge and ascertains the pressures from the masses of gas found by weighing the flask at the different stages of filling and adiabatic expansion, the initial pressure being slightly higher than that of the atmosphere. He has also described another method of determining γ.[5]

Lastly, if the velocities of sound in two gases are compared at the same temperature and pressure, and if the value of γ for one of them is known, that of the other may be calculated.

For $$u_1 = \sqrt{\gamma_1 \times \frac{p}{s_1}} \text{ and } u_2 = \sqrt{\gamma_2 \times \frac{p}{s_2}}$$

$$\therefore \frac{u_1}{u_2} = \sqrt{\frac{\gamma_1 s_2}{\gamma_2 s_1}} \text{ and } \gamma_1 = \gamma_2 \frac{s_1}{s_2} \times \frac{u_1^2}{u_2^2}.$$

FIG. 13.

The method of Kundt has chiefly been employed for this purpose.

A glass rod AB (Fig. 13) is sealed at its middle point or fitted by a cork to the wide tube DC. The end of the rod at A is enlarged and flattened so that it nearly closes the tube. A small quantity of a light powder—lycopodium, cork-dust, or precipitated silica—is placed in the tube between D and A, and, by tapping the tube, is made to lie evenly along it. The tube may be filled with any gas by means of the side tubes E and F. When the rod is made to vibrate longitudinally by drawing a piece of cotton-wool moistened with alcohol firmly along it from C to B, the vibrations are communicated to the gas in the tube, and the fine powder tends to gather into little heaps along the tube. The piston G is moved backwards or forwards until the best position is found. The powder indicates the position of nodes and inter-nodes and the distance *l*

[1] *Pogg. Ann.*, **148**, 580 (1873).
[2] *Phys. Zeit.*, **14**, 969 (1913).
[3] *Loc. cit.*
[4] *Compt. rend.*, **155**, 909 (1912).
[5] *Ibid.*, **152**, 1752 (1911).

between two heaps measures the half wave-length of sound in the gas. The velocity is equal to the product of the wave-length into the number of vibrations in unit time, and since the rod AB always gives the same note, the velocities of sound in two different gases may be compared by placing them successively in the tube and measuring the distances l_1 and l_2 between the heaps.

These distances are proportional to the velocities u_1 and u_2, therefore—

$$\gamma_1 = \gamma_2 \times \frac{s_1}{s_2} \times \frac{l_1^2}{l_2^2}$$

or, if the densities are stated in terms of that of a standard gas, taken as unity—

$$\gamma_1 = \gamma_2 \times \frac{d_1}{d_2} \times \frac{l_1^2}{l_2^2}.$$

If the second gas is air, $\gamma_2 = 1{\cdot}405$.

The experimental results and their bearing on chemical theory are considered in Chapter X., p. 175.

CHAPTER IV.

DETERMINATION OF ATOMIC WEIGHTS.

Relation between Atomic Weight and Equivalent, or Quantivalence.—It has been stated (p. 11), that, in order to find the atomic weight of an element, it is usual (*a*) to determine its equivalent with the greatest possible accuracy, and (*b*) to ascertain the relation between the equivalent and the atomic weight.

The equivalent was first defined as the weight of an element that combines with or displaces 1 part by weight of hydrogen. The atomic weight of hydrogen was also taken as unity.

The best determinations indicate that 7·938 parts of oxygen unite with 1 part of hydrogen to form water, and the equivalent of oxygen is therefore 7·938 if that of hydrogen = 1. But the equivalents of a great number of elements are ascertained by direct comparison with that of oxygen, very few with that of hydrogen, and it is therefore convenient to adopt the even value 8 as the equivalent of oxygen, and to define the equivalent of any other element as the weight of it that combines with or displaces 8 parts by weight of oxygen or the equivalent weight of some other element. In the case of hydrogen this weight would be 1·0078.

It is convenient to adopt the same value for the atomic weight as for the equivalent of hydrogen, and it may therefore be stated that the atomic weight of hydrogen, according to the most exact determinations yet made, is 1·0078. But the experimental difficulties attending the determination of the exact ratio between the equivalents of hydrogen and oxygen are very great, and for the present the International Committee appointed to consider the question of atomic weights do not consider themselves justified in going beyond the third place of decimals, and they adopt the value 1·008 for the atomic weight of hydrogen.

With regard to oxygen, the even value, 8, being adopted as the equivalent, it remains to be ascertained whether 8 or, if not, what multiple or submultiple of 8 is to be taken as the atomic weight of that element.

In considering the ratio between the atomic weight and the equivalent of any element, the accuracy of the experimental determination of the equivalent is not a matter of importance, and, for the purposes of this discussion, it will be sufficient to adopt the whole numbers 1 and 8 for the equivalents of hydrogen and oxygen respectively.

The ratio of atomic weight to equivalent for any element having been ascertained, the equivalent—now determined with the greatest possible accuracy—must be multiplied by this ratio, in order to obtain the "exact" atomic weight.

Consider the case of an element A, which forms a compound with a second element B, the equivalent of which is known. The equivalent of A can then be calculated if the composition of the compound has been accurately determined. For example, the percentage composition of the native oxide of tin is:—

Tin	78·77
Oxygen	21·23
	100·00

The equivalent of tin is therefore $\frac{78{\cdot}77 \times 8}{21{\cdot}23} = 29{\cdot}68$.

If the ratio of the number of atoms of A to that of B in the smallest particle of the compound is a simple one, then the atomic weight of each element must bear a simple ratio to its equivalent.

The simplest case is that in which both the elements A and B and also the compound A_1B are gaseous or can be easily vaporized. Take, for example, the compound water, which is formed by the combination of 1 part by weight of hydrogen with 8 parts by weight of oxygen (approximately). In order to calculate the ratio between the atomic weights of hydrogen and oxygen the quantivalence of oxygen must be determined. To do this, it is necessary to ascertain the number of atoms of each element in the smallest particle of water—in other words, to find the values of x and y in the formula for water, H_xO_y.

It is found experimentally that 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of steam (approximately), if the constant temperature and pressure are such that the steam does not condense to liquid water.

Again, Dalton assumed that 1 atom of hydrogen unites with 1 atom of oxygen to form 1 binary atom of water.

The numerical relations are very simple in both cases, but there is a want of agreement between them.

Gay Lussac attempted to bring the atomic composition into agreement with the volumetric composition by assuming that, at the same temperature and pressure, the densities of gases, both simple and compound, are proportional to their empirically found combining weights or to simple multiples of them, but there were difficulties which he failed to explain.

Avogadro, in 1811, brought forward the hypothesis that equal volumes of all gases, measured at the same temperature and pressure, contain the same number of smallest particles or molecules. He saw, however, that the volumetric composition of gases could not be explained if it were assumed that the molecules of elementary gases were identical with the atoms; for, if that were so, it would follow that 2 atoms of hydrogen unite with 1 atom of oxygen to form 2 complex atoms of steam. This, however, would involve the subdivision of the atom of oxygen, which, by definition of the term "atom," is impossible.

To overcome this difficulty, Avogadro introduced the notion of two kinds of molecule, the *molécule integrante*, or smallest particle of an element or compound that exists in the free (gaseous) state, and the *molécule élémentaire*, *i.e.* the atom or smallest particle of an element capable of entering into combination. [The terms "molecule" and "atom" are now employed instead of integrant molecule and elementary molecule.] The molecule of a gaseous element need not, according to Avogadro, be identical with the atom, but may consist of two or more atoms united together.

Assuming that the molecules of hydrogen and oxygen are diatomic, it would follow from the volumetric composition that 2 diatomic molecules of hydrogen unite with 1 diatomic molecule of oxygen to form 2 molecules of steam, each consisting of 2 atoms of hydrogen and 1 atom of oxygen. The equation representing the synthesis of water would therefore be written—

$$2H_2 + O_2 = 2H_2O.$$

It might, however, equally well be assumed that the molecules of hydrogen and of oxygen are tetratomic, or, generally, that they each contain an even number of atoms, the equation being written—

$$2H_{2x} + O_{2y} = 2H_{2x}O_y$$

where x and y are any whole numbers.

The simplest assumption is, no doubt, the most probable; but, granting the correctness of Avogadro's hypothesis, the only points actually proved are that the number of atoms of hydrogen in the molecule of water is the same as in the molecule of gaseous hydrogen, and that the number of atoms of oxygen in the molecule of water is half as great as in the molecule of gaseous oxygen.

In order to find the values of x and y in the equation

$$2H_{2x} + O_{2y} = 2H_{2x}O_y$$

it is necessary to ascertain the actual number of atoms of hydrogen and oxygen either (*a*) in the molecule of water, or (*b*) in the molecules of hydrogen and oxygen respectively.

(*a*) By the action of the metal sodium on water, hydrogen is expelled, and a compound, sodium hydroxide, is formed which, for a given weight of oxygen, contains exactly half as much hydrogen as water does. There are many other ways in which the hydrogen in water may be replaced by other elements or groups of elements, and it is always found that either the whole or exactly one half of the hydrogen is so replaced. It may therefore be concluded that there are 2 atoms of hydrogen and 2 only in the molecule of water.

(*b*) The density of a gas, or the vapour density of a substance which is liquid or solid under ordinary conditions, is defined as the weight of it compared with that of the same volume of a standard gas, measured at the same temperature and pressure.

As already stated (p. 38), it is found best—for accurate work—to take oxygen as the standard gas and to call its density 16; but for the present purpose the slight error introduced by taking the density of hydrogen as unity is of no importance. Calling the gas or vapour A, and hydrogen H, the density d_A of A is equal to—

$$\frac{\text{weight of A}}{\text{weight of same volume of H at same temperature and pressure}}.$$

But the weight of a gas is equal to the number of its molecules, N, multiplied by the weight of a single molecule (the molecular weight) M.

Therefore $$d_A = \frac{N_A M_A}{N_H M_H}.$$

But by Avogadro's hypothesis $N_A = N_H$, therefore—

$$d_A = \frac{M_A}{M_H}$$

and $$M_H = \frac{M_A}{d_A}.$$

If, then, the values of M_A and d_A can be determined, that of M_H may be calculated.

The density of methane, compared with that of hydrogen, is 8 (approximately), and it is found that in 8 parts by weight of methane there are 6 parts of carbon and 2 of hydrogen. It is found that the hydrogen in methane can be replaced in 4 and only 4 equal stages by chlorine, the compounds known as methyl chloride, methylene chloride, chloroform, and carbon tetrachloride, respectively, being formed.

Thus $\frac{1}{4}$, $\frac{2}{4}$, $\frac{3}{4}$, or $\frac{4}{4}$ of the hydrogen may be replaced by chlorine, and it is found that one or other of these fractional amounts of hydrogen may also be replaced in methane by other elements, or by groups of elements. The most probable explanation is that the molecule of methane contains 4 atoms of hydrogen. Taking the atomic weight of hydrogen as unity, the weight of hydrogen in the molecule of methane must be 4, that of carbon $\frac{6 \times 4}{2} = 12$, and the molecular weight of methane $4 + 12 = 16$.

But $$M_H = \frac{M_A}{d_A} = \frac{16}{8} = 2.$$

The vapour density of acetic acid is variable at low temperatures, but at high temperatures and under moderate or low pressures it has the constant value 30.

In 30 parts by weight of acetic acid there are found to be 12 parts of carbon, 2 of hydrogen, and 16 of oxygen.

When acetic acid reacts with metallic oxides, hydroxides, or carbonates, one fourth of the hydrogen is always replaced by the metal, and when the acid is treated with chlorine $\frac{1}{4}$, $\frac{2}{4}$, or $\frac{3}{4}$ of the hydrogen is replaced by that element; it may therefore be concluded that there are 4 atoms of hydrogen in the molecule of acetic acid, and 4 parts by weight of hydrogen in the molecular weight of the acid.

Therefore the molecular weight, $M_A = \frac{30 \times 4}{2} = 60$.

But $$M_H = \frac{M_A}{d_A} = \frac{60}{30} = 2.$$

The vapour density of metallic mercury is 100, and it may be

proved by the methods which will be considered later that its atomic weight is 200.

The velocity of sound in mercury vapour was determined by Kundt and Warburg, and the ratio of the specific heat at constant pressure to that at constant volume was found to be 1·66. From this it follows (p. 188) that there is no increase of internal energy of oscillation or vibration of the parts of the molecule with rise of temperature, but only of the kinetic energy of rectilinear motion of the molecules as a whole; in other words, it follows that the molecules are monatomic. Therefore the molecular weight is equal to the atomic weight, or $M_A = 200$;

and $$M_H = \frac{M_A}{d_A} = \frac{200}{100} = 2.$$

By these different methods it is proved that the molecular weight of hydrogen = 2, and since the atomic weight = 1, there must be 2 atoms in the molecule.

Therefore in the equation

$$2H_x + O_y = 2H_xO_y$$

it follows that $x = 1$.

The replacement of oxygen in water or other compounds by hydrogen, chlorine, or other elements or groups of elements cannot be effected so easily as that of hydrogen, but the atomic weight of oxygen and, indirectly, the value of y may be ascertained in a different manner.

The value of M_H in the equation

$$d_A = \frac{M_A}{M_H}$$

having now been definitely established, that of M_A may be calculated for any gas or vapour if d_A has been determined; for

$$M_A = d_A \times 2.$$

A very large number of oxygen compounds are either gaseous or can be vaporized without decomposition. Their vapour densities have been determined, and their composition has been ascertained by analytical methods. From these data the weight of oxygen in the molecular weight of each compound has been calculated.

The atomic weight of an element may be defined as the smallest weight of that element which is present in the molecular weight of any of its compounds, and it is found that the smallest weight of

oxygen calculated in the manner just described is 16. Moreover, when the weight is greater, it is always a simple multiple of 16.

Inasmuch as the number of oxygen compounds examined is exceedingly large, it is highly improbable that one will in the future be discovered containing 8, 24, 40, or 56 parts by weight of oxygen, or, generally, any weight expressed by a number which is a simple multiple of 8, but not of 16. If such a compound were ever discovered, it would be necessary to adopt the value 8—or possibly 4—for the atomic weight of oxygen, but as matters stand, the evidence in favour of the value 16 may be regarded as conclusive. But the density of oxygen compared with that of hydrogen is found to be 16 (approximately); therefore the molecular weight of oxygen is 32, or twice the atomic weight, and there must be 2 atoms in the molecule.

It follows, therefore, that in the equation

$$2H_{2x} + O_{2y} = 2H_{2x}O_y$$

both x and $y = 1$, and the equation may be written in the simple form—

$$2H_2 + O_2 = 2H_2O.$$

Lastly, since 2 atoms of hydrogen unite with 1 atom of oxygen to form water, the ratio of the atomic weight of oxygen to its equivalent = 2. In other words, oxygen is said to be a divalent or dyad element, and as the equivalent of oxygen is now taken as 8 (exactly), the atomic weight of oxygen = 16 (exactly).

The vapour density of phosphorus, at temperatures not too far above its boiling point, is found to be 62 (approximately); the molecular weight of this element is therefore about 124.

If the molecule of phosphorus were monatomic, the atomic weight would be 124; if diatomic, $\frac{124}{2}$; or, generally, the atomic weight of phosphorus must be $\frac{124}{n}$, where n is a whole number. The majority of the phosphorus compounds may be divided into two classes: the equivalent of phosphorus derived from the compounds which include the most stable hydride and chloride is $10\cdot\dot{3}$; that derived from the higher chloride and the compounds related to it is 6·2. As the atomic weight is generally a simple multiple (rarely a submultiple) of the equivalent, it has most probably the value—

$$n' \times 10\cdot\dot{3} = n'' \times 6\cdot2$$

where n' and n'' are whole numbers.

Three numbers only, 31, 62, and 124, fulfil the condition that

$$\frac{124}{n} = 10{\cdot}3n' = 6{\cdot}2n''$$

n, n', and n'' having the values 4, 3, and 5; 2, 6, and 10; or 1, 12, and 20 respectively in the three cases.

A moderate number of volatile phosphorous compounds are known, and it is found that the smallest weight of phosphorus in the molecular weight of any of these compounds is 31, and that the other values are simple multiples of 31. There is thus fairly strong evidence in favour of this value for the atomic weight.

That the value is about 31 is found from the vapour densities of the element and of its compounds; the ratios of the atomic weight to the two equivalents must therefore be 3 and 5 respectively. The equivalents are determined accurately, and give the accurate value 31·04 for the atomic weight.

A very large number of gaseous or volatile carbon compounds are known; the weight of carbon in the molecular weights of these compounds is always either 12 or a simple multiple of 12. The atomic weight is therefore in all probability 12. In this case the vapour density has in nearly every case been determined only approximately, and the value 12 is only an approximate value.

The equivalent of carbon is 3, and the ratio of atomic weight to equivalent is therefore 4. The equivalent has been determined with accuracy, and the ratio (the quantivalence or valency) must be expressed by a whole number; therefore the accurate atomic weight is 3·00 × 4 = 12·00.

The densities of the two oxides of carbon have been determined with great care and accuracy, and the deviations from Boyle's law ascertained (p. 45). It is therefore possible to calculate the atomic weight accurately from the molecular weights of these compounds, and the values so obtained agree very well with those derived from the equivalent.

The Law of Dulong and Petit.—Dulong and Petit[1] in 1819 determined the specific heats of some of the metals, and observed that the product of the specific heat into the (most probable) atomic weight was practically the same, 6·4, in all cases. In other words, the atoms of these elements have nearly the same capacity for heat; and Dulong and Petit concluded that the relation might be regarded

[1] *Ann. Chim. Phys.*, ii. 10, 395 (1819).

as a general one for all elements. The limitations and extensions of this law are considered in Chapter XII. (p. 229); it will be sufficient here to mention that it may be safely employed for the calculation of the approximate atomic weight, if the element is solid and the specific heat has a low value. The specific heat of solid mercury is found to be 0·03136; hence the atomic weight $= \frac{6{\cdot}4}{0{\cdot}03136} = 204$ approximately. Mercury forms two series of salts, and the two equivalents, found by the accurate analysis of the mercurous and mercuric compounds, are 200·6 and 100·3 respectively. Mercury is therefore monovalent and divalent respectively in these compounds, and the atomic weight = 200·6 × 1 = 100·3 × 2 = 200·6 accurately.

Mitscherlich's Law of Isomorphism.—This law is based on observations of the crystalline form, and the behaviour on crystallization of analogous chemical substances. Mitscherlich [1] examined first the arsenates and phosphates of sodium, potassium, and ammonium, and by comparing the corresponding phosphates and arsenates of the same metal—the number of molecules of water of crystallization being the same for any two substances compared—he made out the following points:—

1. The form of the crystals, as shown by the measurement of their angles, is the same.

2. Each crystal deposited from a mixed solution contains both substances, and is of the same form as crystals obtained from a solution of either pure substance.

3. A crystal of one substance, placed in a saturated solution of the other, continues to grow by superposition of the second substance, the form of the crystal remaining unaltered.

Substances which have the same crystalline form and are capable of forming either *mixed* or *superposed* crystals, in the manner described, are said to be *isomorphous*.

It may be stated that, as a general rule, isomorphous substances have analogous chemical constitution; thus, if the chemical formula of one substance is known, and another substance is found to be isomorphous with it, it may be concluded that, in all probability, the formula of the second substance is analogous to that of the first.

The equivalent of gallium, taking that of oxygen as 8, is 23·3;

[1] *Ann. Chim. Phys.*, ii. 14, 172 (1820); 19, 350 (1821); 24, 264 (1823).

its atomic weight is therefore 23·3, 46·6, 69·9, 93·2, . . . according as the formula of the oxide is Ga_2O, GaO, Ga_2O_3, GaO_2 . . . The oxide is basic, and the sulphate forms with potassium sulphate a double salt, which, like the alums, separates from its aqueous solution in regular octahedra. Moreover, gallium potassium sulphate can form mixed crystals with other alums, and is therefore isomorphous with them. Since the formula of ordinary alum is $K_2SO_4,Al_2(SO_4)_3,24H_2O$, it follows that that of gallium alum is $K_2SO_4,Ga_2(SO_4)_3,24H_2O$; hence the formula of the sulphate must be $Ga_2(SO_4)_3$, and this would be derived from the oxide Ga_2O_3 just as $Al_2(SO_4)_3$, is obtained from Al_2O_3. Gallium is therefore trivalent, and its atomic weight is $23·3 \times 3 = 69·9$.

By these different methods it may be decided whether the equivalent itself or what multiple (or possibly submultiple) of it must be taken for the atomic weight. Further light on the question is frequently thrown by the periodic arrangement of the elements, which is described and discussed in Chapter VI.

As already mentioned, the gaseous elements helium, neon, argon, krypton, and xenon (and to these the gaseous emanation from radium may be added) appear to be incapable of entering into combination with each other or with other elements; they have, therefore, no equivalents, or may be said to have zero valency.

The densities of these gases, however, and hence their molecular weights, have been determined, and it has been found by Ramsay and Travers,[1] by determining the velocity of sound in them, that the ratio of the specific heat at constant pressure to that at constant volume is in each case about 1·6. It is, therefore, concluded that their molecules, like those of mercury, are monatomic, and that their atomic weights are identical with their molecular weights.

[1] *Proc. Roy. Soc.*, **67**, 329 (1901).

CHAPTER V.

DETERMINATION OF ATOMIC WEIGHTS (*continued*).

ACCURATE DETERMINATION OF ATOMIC WEIGHTS.

Experimental Errors.—Before describing the actual determinations of the atomic weights of some of the elements, it will be well to consider shortly the nature of the experimental errors that are met with.

No observer, however expert, can hope to attain absolute accuracy in any measurement, however simple. Suppose, for example, that the determination is that of the mass—expressed in grams—of a certain piece of metal, and that a number of trials are made with the same balance and the same set of weights. The values found will probably agree in every case to the fourth place of decimals, possibly to the fifth, but probably not to the sixth; the limit of accuracy depending partly on the expertness of the observer, partly on the sensibility of the balance, and partly on the actual mass of the piece of metal, for the sensibility of a balance diminishes as the load on it is increased. It is usual to take the arithmetical mean of the individual values as the final result, and an estimate of the accuracy of the determinations is afforded by the smallness of the *probable error*, which is calculated by the formula—

$$e = 0{\cdot}6745\sqrt{\frac{s}{n(n-1)}}$$

where n is the number of observations in the series, and s the sum of the squares of the variations of the individual values from the mean. One of the weights, however, might be faulty, and yet a large error, due to this cause, would not be eliminated or even diminished by increasing the number of observations, since the same weights would be employed in each case. Errors of this kind are termed *constant errors*, and are frequently difficult to deal with. In this particular case the best plan would be to make a very careful comparison of the weights used with a set of standard weights; but

the probable existence of the constant error might at any rate be discovered by making a number of determinations with a second set of weights. It is improbable that the two sets of weights would be faulty to the same extent, and, if the second result did not differ from the first by an amount greater than the calculated probable error, the final mean might be accepted with much greater confidence than either singly. On the other hand, if there was a marked difference between the two results, the existence of a constant error in either one or the other would be demonstrated.

In all scientific work constant errors of the kind just described should be excluded as far as possible by a preliminary careful examination, calibration, etc., of the apparatus to be employed.

Again, it must be remembered that if a body is weighed in air it will appear to be lighter than in a vacuum by the weight of air displaced, and in accurate work the correction from apparent to true weight should always be made, otherwise a (practically) constant error will be introduced.

In the determination of atomic weights constant errors may readily occur owing to the incompleteness of a chemical change, the occurrence of a subsidiary and perhaps unnoticed reaction, the partial solubility of a precipitate, the slight volatility of a solid, the occlusion of a gas in a solid, and so on; and it is always advisable to determine a given atomic weight by two or more quite different methods in which the same constant error is unlikely to occur.

A valuable discussion of the errors met with in atomic weight determinations is contained in a series of recent papers by Guye and his co-workers,[1] and by de Gramont.[2]

Owing to the possible existence of constant errors, it does not always follow that, of two results, the one with the smaller *probable error* is to be preferred to the other. For example, in 1891, E. W. Morley made a series of wonderfully concordant determinations of the relative volumes of H and O which unite together to form water. The measurements were made with the utmost care, and the method was varied to the extent that in some observations hydrogen and in others oxygen was in excess. The mean result was 2·00023 ± 0·000015. Morley, however, was led to suspect the existence of a constant error, and he afterwards redetermined the ratio of the volumes from the specific gravity of the mixed gases evolved by the

[1] *J. Chim. phys.*, **14**, 25, 55, 83, 95 and 204 (1916); **15**, 360 and 405 (1917).
[2] *Ibid.*, **14**, 336.

electrolysis of acidified water. The mean result obtained was 2·00274 ± 0·00005, and although the *probable error* was considerably greater, he adopted the second value in preference to the first, and, in fact, rejected the first altogether. The higher value is shown to be the more correct by the determinations carried out by Scott and by Burt and Edgar.

When several series of determinations have been made by the same method, or by different methods which are all believed to be free from constant errors, the *probable error* of the mean of each series must be taken into account in calculating the final mean. This is done by means of the following formula:—

$$M = \frac{\frac{A}{a^2} + \frac{B}{b^2} + \frac{C}{c^2} \quad \cdot \cdot}{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \quad \cdot}$$

where A, B, C . . . are the individual means, and a, b, c . . . their respective probable errors.

The probable error of the final mean is given by the formula—

$$c = \frac{1}{\sqrt{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \cdot \cdot \cdot}}.$$

For the calculation of the probable errors in other cases, Clarke's "Constants of Nature," pt. v., 1910, Introduction and p. 9, may be consulted.

Oxygen and Hydrogen.—It has been stated that the present practice is to adopt the value 16 for the atomic weight of oxygen; but until recent years the atomic weight of hydrogen was taken as unity, and, as many results are stated in this form in the original papers on the relative atomic weights of oxygen and hydrogen, it will be most convenient to consider the problem as that of the determination of the atomic weight of oxygen in terms of that of hydrogen taken as unity.

The atomic weights of other elements (including hydrogen) will afterwards be given in terms of that of oxygen taken as 16.

The Equivalent of Oxygen.—It has been shown that the formula for water is H_2O; if, therefore, the weight of oxygen that unites with 1 part by weight of hydrogen to form water can be accurately determined, the equivalent of oxygen so obtained must be multiplied by 2 to get the atomic weight.

This is the method which was first adopted, and, as it is more convenient to weigh liquids or solids than gases, an indirect method was employed. Hydrogen, carefully purified and dried, was passed over strongly heated copper oxide, and the water formed was collected and weighed. The loss of weight of the copper oxide gave the weight of oxygen, and the difference between the weights of water and oxygen gave that of the hydrogen.

Three determinations were made by this method by Dulong and Berzelius, with the final result for the atomic weight—

$$O = 16{\cdot}03 \pm 0{\cdot}057$$

or, reducing the weights to a vacuum—

$$O = 15{\cdot}894 \pm 0{\cdot}057.$$

The first accurate determinations, however, are those of Dumas,[1] carried out in 1819. Dumas made altogether nineteen experiments, the total weight of water formed being 945·439 grams, and the weight of oxygen 840·161 grams. The difference, 105·278, is the weight of hydrogen, and the atomic weight of oxygen = 15·9607 ± 0·0070.

[From a determination of the relative densities of oxygen and hydrogen, Regnault, in 1845, arrived at practically the same value, 15·963, and for many years 15·96 was taken to be the true atomic weight of oxygen.]

There are, however, several sources of error in the method employed by Dumas, the most important of which are the following:—

1. The dilute sulphuric acid employed for the preparation of the hydrogen contained a little dissolved air. Dumas himself introduced a small correction for this, but he does not explain how it was estimated.

2. It is difficult to expel the air completely from such a large and complicated apparatus as that employed by Dumas, but any oxygen present would unite with hydrogen and form an additional amount of water, and this would tend to make the calculated atomic weight of oxygen too low.

3. It was observed by Melsens that metallic copper occludes from 0·00003 to 0·00020 per cent. by weight of hydrogen. The loss of weight of the copper oxide would therefore be too small, and this would make the atomic weight of oxygen too low.

4. Dumas dried his hydrogen, before it reached the copper oxide, with sulphuric acid and phosphoric anhydride, but he used

[1] *Compt. rend.*, 14, 537 (1842).

only calcium chloride to absorb the aqueous vapour from the uncombined hydrogen, which was allowed to escape. There would thus be some loss of water, and this would raise the atomic weight of oxygen.

5. Dittmar and Henderson have shown that hydrogen, when passed through sulphuric acid, becomes slightly contaminated with sulphur dioxide.

6. Morley has found that hydrogen prepared from zinc always contains carbon compounds, which cannot be removed by absorption.

7. Copper oxide may contain occluded nitrogen or other impurities.

8. It has been stated by Dittmar[1] that Dumas neglected to correct the weights of water for the air displaced. If this is really the case, and the corrections to a vacuum are made, the atomic weight of oxygen would be reduced from 15·96 to 15·77, but it is impossible to estimate with any accuracy the effect of the other sources of error.

In 1842 Erdmann and Marchand[2] made two series of determinations by the same method. They employed a simpler form of apparatus, so that the air could be more easily expelled, and in the second series they passed the hydrogen over heated metallic copper to remove any oxygen, and dried it again before it reached the copper oxide. The first series, consisting of four experiments, gave the result—

$$O = 15{\cdot}939 \pm 0{\cdot}014$$

and the second, taking all five determinations—

$$O = 16{\cdot}005 \pm 0{\cdot}006.$$

Cooke and Richards,[3] in 1887, made a very careful series of syntheses of water, weighing the hydrogen and the water. About 5 litres of hydrogen were employed in each experiment, and three different methods were employed for its preparation. There were sixteen experiments in all, and the results were very concordant, the value, as stated by the authors, being—

$$O = 15{\cdot}953 \pm 0{\cdot}002o.$$

It was afterwards pointed out by Lord Rayleigh[4] that, owing to

[1] *Chem. News* (1890) p. 75. [2] *Journ. fur prakt. Chem.*, **26**, 461.
[3] *Proc. Amer. Acad.*, **23** 149; *Amer. Chem. Journ.*, **10**, 81.
[4] *Beiblätter*, **12**, 732 (1888).

the change in internal pressure and to the elasticity of the glass, the capacity of the globe when vacuous would be slightly smaller than when filled with hydrogen. The vacuous globe would therefore displace less air, and its apparent weight would be too great; hence the observed weight of hydrogen would be too low, and the calculated atomic weight of oxygen too high. This criticism was accepted by Cooke and Richards, and they subsequently gave the corrected value—[1]

$$O = 15{\cdot}869 \pm 0{\cdot}0020.$$

In order to avoid the necessity of weighing gaseous hydrogen, Keiser [2] absorbed this gas in palladium, and was thus able to weigh it in the solid state. The hydrogen, after expulsion from the palladium, was passed over heated copper oxide in the usual manner. Two preliminary sets of experiments gave the values O = 15·864 and 15·951.

In 1898 Keiser [3] published the results of a new series of determinations by an improved method, all the weighings being made with a single piece of apparatus. The vessel was divided into two compartments, one containing phosphorus pentoxide, the other palladium. Five weighings were required for each determination :— That of (*a*) the vessel containing phosphorus pentoxide and exhausted of air; (*b*) the vessel containing phosphorus pentoxide and palladium and exhausted of air; (*c*) the same after saturation of the palladium with hydrogen; (*d*) the same after introduction of oxygen and complete oxidation of the hydrogen; (*e*) the same after removal of the palladium. The difference (*c*) − (*b*) gave the weight of hydrogen; (*d*) − (*c*) the weight of oxygen; (*e*) − (*a*) the weight of water. The ratios O/H and H_2O/H could thus be calculated, and the atomic weight of oxygen calculated from each ratio.

The final value obtained was 15·8799 ± 0·0046.

Lord Rayleigh [4] employed a different method for the synthesis of water. The hydrogen and oxygen were weighed, but not the water, and combination was effected by passing sparks through the mixture. The apparatus consisted of two globes for the hydrogen and oxygen; a eudiometer, standing over mercury, in which the gases were mixed; and a second eudiometer, also standing over mercury, in which they were exploded. The gases were drawn out of the globes and into the

[1] *Amer. Chem. Journ.*, **10**, 191 (1888).
[2] *Ibid.*, **10**, 249 (1888).
[3] *Ibid.*, **20**, 733 (1898).
[4] *Proc. Roy. Soc.*, **45**, 425 (1889).

mixing chamber by means of a Sprengel pump; then, by a second pump, into the explosion chamber; and the mixed gases were made to combine in very small quantities at a time. The residual gas was found to consist almost entirely of oxygen, and contained only a minute amount of carbon dioxide and nitrogen, and the water formed was quite free from nitric acid.

The final value obtained by Lord Rayleigh was—

$$O = 15{\cdot}89 \pm 0{\cdot}000.$$

Noyes[1] reduced copper oxide with hydrogen and collected the water formed in a single apparatus, which was first exhausted and weighed. The part of the apparatus which contained the copper oxide was then heated, that in which the water was to be condensed was cooled, and hydrogen was passed in. The increase in weight gave the weight of hydrogen. The small quantity of nitrogen introduced with the hydrogen was then removed by means of a Sprengel pump, and measured. The water was completely removed by exhaustion, and the difference between the first and last weights gave the amount of oxygen. Finally, the reduced copper was re-oxidized, and the small quantity of water formed by oxidation of the occluded hydrogen was estimated.

The final value, corrected in 1908 for a constant error, was—

$$O = 15{\cdot}879 \pm 0{\cdot}0017.$$

In 1907 Noyes[2] improved his method by weighing the hydrogen in palladium. The first series was rejected owing to a constant error; the remaining four series, comprising twenty-five experiments, gave the final value—

$$O = 15{\cdot}8745 \pm 0{\cdot}00021.$$

In the second paper Noyes discusses all published determinations of the atomic weight of oxygen.

Syntheses of water by Dumas' method have been carried out by Dittmar and Henderson[3] and by Leduc,[4] great care being taken to avoid the errors to which reference has been made. The final values, as stated by the authors, are as follows:—

Dittmar and Henderson . .	$O = 15{\cdot}8677 \pm 0{\cdot}0046$
Leduc	$O = 15{\cdot}881 \pm 0{\cdot}013$

[1] *Amer. Chem. Journ.*, **11**, 153 (1889); **12**, 441 (1890).
[2] *Ibid.*, **29**, 1718 (1907); **30**, 4 (1908).
[3] *Proc. Roy. Phil. Soc. Glasgow*, **22**, 33 (1891).
[4] *Compt. rend.*, **115**, 41 (1892).

E. W. Morley[1] carried out a remarkably careful and accurate series of syntheses of water, the hydrogen—occluded in palladium—the oxygen, and the water being all weighed. The atomic weight of oxygen could be calculated from the relative weights (*a*) of hydrogen and oxygen, and (*b*) of hydrogen and water. The results obtained are as follows:—

(*a*) from 12 determinations, O = 15·8792 ± 0·00032
(*b*) „ 11 „ O = 15·8785 ± 0·00066.

Determinations of the atomic weight of oxygen by the synthesis of water have also been carried out by two different methods by Julius Thomsen,[2] with the following results:—

(1) O = 15·91 ± 0·0113
(2) O = 15·8690 ± 0·0022.

The whole of these results have been carefully discussed by F. W. Clarke,[3] who gives as the final result, taking into account the probable errors of each series—

O = 15·8779 ± 0·00016.

Clarke points out that this general mean lies between the values found by Noyes in 1907 and Morley in 1892. The mean of their two values is 15·876 ± 0·00017.

From the synthesis of water, then, the atomic weight of oxygen may be taken as 15·878 if H = 1.

Volumetric Composition of Water, and Densities of Oxygen and Hydrogen.—If oxygen and hydrogen behaved as perfect gases, there would, according to Avogadro's hypothesis, be the same number of molecules in equal volumes of them, measured at the same temperature and pressure; and the statement that 2 volumes of hydrogen unite with 1 volume of oxygen would be strictly true.

It has already been stated that both gases show slight deviations from Boyle's and Gay Lussac's laws; nevertheless, the relative weights of oxygen and hydrogen that combine together to form water may be ascertained if accurate determinations have been made of (1) the densities of each gas at, say, 0° C. and 760 mm. pressure; (2) the relative volumes of the combining gases, also measured at normal temperature and pressure.

[1] "Smithsonian Contributions to Knowledge," **54**, 3 (1910).
[2] *Berichte*, **8**, 928 (1870); *Zeitschr. anorg. Chem.*, **11**, 14 (1895).
[3] "Constants of Nature," pt. v., 3rd edition (1910).

The method of determining the density of a gas is described on p. 38, and a few of the most accurate results are given on p. 39.

For the weight of a litre of oxygen at 0° and 760 mm. at the latitude of Paris, the mean of the values obtained by Rayleigh, Morley, and Germann, 1·42904, may be taken, and for the weight of a litre of hydrogen, Morley's result, 0·08987.

The relative volumes of hydrogen and oxygen which combine to form water have been determined by Scott, Morley, and Burt and Edgar. Their experiments were carried out with extreme care and accuracy, and the mean ratio, 2·00282 volumes of hydrogen to 1 volume of oxygen at 0° and 760 mm., may be taken as correct.

Adopting the above-mentioned values, it may be stated that, at 0° and 760 mm. at the latitude of Paris, 2·00282 litres of hydrogen weighing 2·00282 × 0·08987 grams combine with 1 litre of oxygen weighing 1·42904 grams. The equivalent of oxygen is therefore $\frac{1{\cdot}42904}{2{\cdot}00282 \times 0{\cdot}08987} = 7{\cdot}9394$, and its atomic weight is 15·8788.

If Morley's values only were employed in the calculations, the result would be—

$$O = 15{\cdot}8794$$

which agrees extremely well with the atomic weight deduced from his synthesis of water.

Densities of Oxygen and Hydrogen.—If Avogadro's hypothesis were strictly applicable to oxygen and hydrogen, the molecular weights of these gases would be exactly proportional to their densities, determined at the same temperature and pressure. Since the molecules of both gases are diatomic, the atomic weights would be proportional to the densities; and if both the density and atomic weight of hydrogen are taken as unity, the atomic weight of oxygen would be numerically equal to its density. The method by which the observed density of a gas may be corrected to the density which it would have if it behaved as a perfect gas has already been considered (p. 44), and it has been pointed out that, adopting Morley's value for the density of oxygen, 15·9001, and Rayleigh's value for a_0 $\left(= \frac{1}{pv} \cdot \frac{d(pv)}{dp} \text{ at } 0°\right)$, − 0·00094 and + 0·00053 for oxygen and hydrogen respectively, the corrected density, and therefore the atomic weight, of oxygen is 15·88.

The correction of the observed to normal densities may be

made by a different method depending on the modified equation of state. It has been stated that the equation PV = RT is not strictly applicable to real gases, the deviations under high pressures being very great. Van der Walls (Chapter XI.) has proposed the modified equation—

$$\left(p + \frac{a}{v_2}\right)(v - b) = RT$$

where a and b are constants depending on the nature of the substance.

From this equation—

$$\frac{d(\pi\phi)}{d\pi} = \frac{1}{3}\left(1 - \frac{27}{8} \times \frac{1}{\theta}\right)$$

where ϕ, π, and θ are the *reduced* volume, pressure, and temperature respectively (p. 200). But D. Berthelot[1] has shown that much better results are given by the equation—

$$\frac{d(\pi\phi)}{d\pi} = \frac{1}{4}\left(1 - \frac{6}{\theta^2}\right)$$

and if the critical volume, pressure, and temperature of a gas are known, this equation may be conveniently employed.

D. Berthelot shows that the corrected densities obtained by this method agree extremely well with those given by the method described on p. 44.

According to Clarke[2] the best determinations of the atomic weight of oxygen, taking that of hydrogen as unity, lead to the value—

$$O = 15{\cdot}8762.$$

Hence, if the atomic weight of oxygen is taken as 16, that of hydrogen $= \frac{16}{15{\cdot}8762} = 1{\cdot}0078$. The International Commission have adopted the value—

$$H = 1{\cdot}008.$$

For details of the determinations of the atomic weights of the elements, larger works such as Ostwald's "Lehrbuch der Allgemeinen Chemie," F. W. Clarke's "Recalculation of the Atomic Weights," ["Constants of Nature," pt. v. (1910), Smithsonian Institution], or

[1] *Compt. rend.*, 144, 194 (1907); "Sur les Thermomètres à Gaz," p. 49 (1903).

[2] *Loc. cit.*

Meyer and Seubert's "Die Atomgewichte der Elemente," must be consulted, also Brauner, "Handbuch d. anorg. Chemie," vol. ii., pt. 1. (1908); and Richards, "Exp. Untersuchungen uber Atomgewichte," Voss (1908). It is impossible here to describe more than a few typical examples.

Among the most accurate of the earlier atomic weight determinations are those of Stas[1] (1813-1891), who took the utmost care in purifying the materials used and employed as many different methods as possible, introducing, wherever practicable, minor variations in the conditions of experiment or in the materials employed.

Silver.—A large number of atomic weights are referred directly or indirectly to that of silver, and it will therefore be useful to give an account of the methods employed for the determination of the atomic weight of this element.

Stas himself employed no fewer than five different methods, depending on reactions represented by the following equations:—

I.	(*a*) $2KClO_3 = 2KCl + 3O_2$,	giving the ratio KCl : O
	(*b*) $KCl + Ag(NO_3) = AgCl + K(NO_3)$,	„ „ KCl . Ag
	[The silver was weighed and then converted into nitrate	
II.	(*a*) $2AgClO_3 = 2AgCl + 3O_2$,	giving the ratio AgCl : O
	(*b*) $2Ag + Cl_2 = 2AgCl$,	„ „ AgCl : Ag
III.	(*a*) $2AgBrO_3 = 2AgBr + 3O_2$,	„ „ AgBr : O
	(*b*) $2Ag + Br_2 = 2AgBr$,	„ „ AgBr : Ag
IV.	(*a*) $2AgIO_3 = 2AgI + 3O_2$,	„ „ AgI : O
	(*b*) $2Ag + I_2 = 2AgI$,	„ „ AgI : Ag
V.	(*a*) $Ag_2SO_4 + H_2 = 2Ag + H_2SO_4$,	„ „ Ag_2SO_4 : Ag
	(*b*) $2Ag + S = Ag_2S$,	„ „ Ag_2S : Ag
	and from (*a*) and (*b*)	
	(*c*) $Ag_2SO_4 - Ag_2S = 4O$,	„ „ Ag_2S : O

The final value obtained by Stas for the atomic weight of silver was 107·93, and this value was adopted by the International Committee on atomic weights until the year 1909. In consequence, however, of Lord Rayleigh's determinations of the densities and compressibilities of nitrogen and oxygen in 1894 and 1904, it appeared probable that Stas's value for the atomic weight of nitrogen, depending indirectly on that of silver, was about 0·03 too high; and as the correctness of the lower value was confirmed by the work

[1] *Vide* "Œuvres Complètes," Bruxelles, 1894.

of Leduc, Gray, and Guye and his co-workers, the International Committee adopted the value N = 14·01 instead of 14·04 in 1907.

Guye had pointed out in 1905 that the atomic weight of silver ought probably to be reduced from 107·93 to 107·88, and in 1907 Richards and Forbes[1] carried out an extremely careful quantitative synthesis of silver nitrate, with the result that the weight of pure silver nitrate obtained from 100 parts of silver was 157·479 ± 0·0001. The same ratio had been determined by other experimenters, including Stas, but the accuracy of the work of Richards and Forbes was so much greater that in the calculation of the final mean, taking the probable errors into account, Clarke found that their value was reproduced without change.

Taking the atomic weight of nitrogen as 14·01, this ratio would give Ag = 107·883, whereas if N = 14·04, then Ag = 107·935.

In the same year Richards and Jones[2] converted weighed quantities of silver sulphate into silver chloride by the action of hydrochloric acid gas on the heated salt. They found that 100 parts by weight of silver sulphate gave 91·933 ± 0·0004 parts of silver chloride. From this result, if Ag = 107·93, then Cl = 35·473 and S = 32·113; but if Ag = 107·88, then Cl = 35·457 and S = 32·069. [The values now adopted by the International Committee are Cl = 35·46 and S = 32·06.]

It will be noticed that in these two methods the calculated atomic weight of silver depends on the values adopted for nitrogen and for chlorine and sulphur.

Again, pure silver may be dissolved in nitric acid, and from the nitrate the chloride, bromide, or iodide may be precipitated, and in this way the relative atomic weights of silver and one or other of the halogens may be ascertained.

In the methods employed by Stas, the relative atomic weights of silver and oxygen are ascertained, but only indirectly, two different chemical reactions being involved in each case. The experimental errors are thereby increased. If only silver oxide could be obtained in a state of purity it could be easily reduced to metallic silver by the action of heat, and the relative atomic weights of silver and oxygen could be directly determined, but, unfortunately, it has not been found possible to purify silver oxide satisfactorily.

Making use of the large number of ratios available, Clarke calculates no fewer than twenty-nine independent values for the

[1] *Journ. Amer. Chem. Soc.*, **29**, 808 (1907). [2] *Ibid.*, **29**, 286 (1907).

atomic weight of silver, the final value, taking the probable errors into account, being 107·880 ± 0·00029.

Of these ratios the one with the lowest probable error, and probably the most satisfactory one in all respects, is that of silver to silver nitrate, which, as already stated, leads to the result Ag = 107·883 if N = 14·01, or 107·935 if N = 14·04.

The accurate determination of the atomic weight of nitrogen is, for this and other reasons, of great importance, and may next be considered.

The specific gravities of nitrogen and oxygen found by Lord Rayleigh[1] in 1894, and by Leduc[2] in 1898, showed good agreement, but indicated that, unless the deviations from Boyle's law were considerable, the results were not in accordance with the accepted atomic weights of the two elements. Lord Rayleigh[3] afterwards, as a result of his researches on the compressibilities of gases under low pressures, showed how the theoretical densities and the atomic weights could be calculated from the observed densities, and gave as the atomic weight of nitrogen 14·009.

The theoretical researches of D. Berthelot have already been discussed, and it need only be stated that in 1898 he deduced the following molecular weights from the data obtained by Leduc and Sacerdote, Rayleigh, and Morley—

$$N_2 = 28{\cdot}013\,;\ N_2O = 44{\cdot}000.$$

D. Berthelot has[4] discussed the results obtained by various experimenters since that date, and from Rayleigh's determinations he finds—

$$N_2 = 28{\cdot}016\,;\ N_2O = 43{\cdot}999$$

while from other data he calculates the following values:—

$NH_3 = 17{\cdot}015$ (Jaquerod and Sheuer)
$NH_3 = 17{\cdot}021$ (Perman and Davies)
$NO = 30{\cdot}003$ (Gray).

The mean atomic weight of nitrogen deduced from these molecular weights would be 14·0011.

The question has been very fully considered by Guye,[5] who discusses the relative accuracy of the physico-chemical and the old

[1] *Proc. Roy. Soc.*, **55**, 340 (1894).
[2] *Recherches sur les Gas*, Paris (1898); *Compt. rend.*, **125**, 299 (1897).
[3] *Proc. Roy. Soc.*, **73**, 153 (1904). [4] *Compt. rend.*, **144**, 269 (1907).
[5] *Soc. chim. de Paris*, June (1905); also *Archives des Sciences physiques et naturelles*, IV, **27**, 557 (1909).

gravimetric methods, and concludes that the evidence is in favour of the former, and that the atomic weight of nitrogen is probably a very little lower than 14·01. He also gives the results of gravimetric and volumetric determinations of the composition of nitrous oxide, from which he deduces the atomic weights, N = 14·007 and 14·015 respectively.

The analysis of nitric oxide has also been carried out by Gray,[1] with the result—

$$N = 14{\cdot}010,$$

while from the densities of nitrogen and nitric oxide, Gray has obtained the values 14·008 and 14·006 respectively. The last result has been confirmed by Guye and Davila.

Lastly, a complete analysis of nitrosyl chloride has been carried out by Guye and Fluss,[2] the chlorine being absorbed by silver, the oxygen by copper, and the nitrogen by calcium. The values N = 14·006 and Cl = 35·468 were thus obtained. It is probable that the atomic weight of nitrogen is slightly lower than 14·01, the value adopted by the International Commission.

The atomic weight of chlorine is involved in the calculation of the atomic weights of many elements, and its exact determination is therefore of great importance. The comparison in this case has usually been with hydrogen, the oxides of chlorine being unstable substances. We have, however, the complete analysis of nitrosyl chloride to which reference has just been made.

The synthesis of hydrogen chloride has been investigated by several observers. Dixon and Edgar[3] weighed both hydrogen (in palladium) and chlorine (liquid), burned the hydrogen in the chlorine, and estimated the excess of chlorine volumetrically. They obtained the result Cl/H = 35·195 ± 0·0019.

Noyes and Weber[4] weighed the hydrogen in palladium, and passed the gas over heated potassium chloroplatinate, the loss of weight giving the weight of chlorine. The hydrogen chloride was also weighed. The two ratios obtained were – Cl/H = 35·1843 ± 0·0014 and HCl/H = 36·1835 ± 0·0013.

Edgar[5] burned the chlorine in the hydrogen and weighed both

[1] *Trans. Chem. Soc.*, **87**, 1601 (1905).
[2] *Journ. Chim. phys.*, **6**, 732 (1908).
[3] *Trans. Roy. Soc.*, **205**, 169 (1905).
[4] *Journ. Amer. Chem. Soc.*, **30**, 13 (1908).
[5] *Proc. Roy. Soc.*, **81**, 216 (1908).

these and the hydrogen chloride formed. The ratios obtained were – Cl/H = 35·194 ± 0·0008 and HCl/H = 36·193 ± 0·0009.

From these results Clarke calculates the general mean, Cl/H = 35·1911 ± 0·00049, or, if H = 1·0078, Cl = 35·4652 ± 0·0005.

The following determinations of the density of hydrogen chloride have been made :—

Guye and Ter Gazarian[1] obtained the value 1·6398 ± 0·00007 for the weight of the normal litre. Correcting for the deviation from Boyle's law by the method of critical constants, the molecular weight of HCl was found to be 36·4693, and, if H = 1·0078, Cl = 35·4615 ± 0·0015.

Scheuer[2] found the mean value 1·63941 for the weight of the normal litre, and from this, correcting as above, Cl = 35·4528 ± 0·0007.

Gray and Burt[3] have determined both the density and the compressibility of hydrogen chloride with the following results : Weight of the normal litre, 1·63915 ; α_0 = – 0·00748 ; hence the *limiting* density of HCl at 0° and 760 mm. = 1·62698, and the molecular weight of HCl

$$= \frac{S_{HCl}}{S_{O_2}} \times 32 = \frac{1{\cdot}62698}{1{\cdot}42762} \times 32 = 36{\cdot}469,$$

hence Cl = 36·469 – 1·008 = 35·461.

The volumetric composition of hydrogen chloride has also been very carefully determined by Gray and Burt, who found that the volume R of hydrogen derived from two volumes of hydrogen chloride at 0° and 760 mm. was 1·00790. Hence, taking H = 1·00779, the molecular weight of HCl =

$$1{\cdot}00779 \times \frac{1{\cdot}63915}{0{\cdot}089873} \times \frac{2}{1{\cdot}00790} = 36{\cdot}473$$

and Cl = 36·473 – 1·008 = 35·465.

To these results may be added the synthesis of nitrosyl chloride from nitric oxide and chlorine by Wourtzel[4] who obtained the value Cl = 35·460 if N = 14·008 ; also the synthesis of ammonium chloride from ammonia and hydrogen chloride by Baume and Perrot[5] who, taking N = 14·009, found Cl = 35·465.

The International Committee have adopted the value Cl = 35·46,

[1] *Compt. rend.*, **143**, 1233 (1906).
[2] *Ibid.*, **149**, 599 (1909).
[3] *Trans. Chem. Soc.*, **95**, 1633 (1909).
[4] *Compt. rend.*, **155**, 345 (1912).
[5] *Ibid.*, **155**, 461 (1912).

whilst Clarke, from all available data, calculates the value Cl = 35·4584 ± 0·0002.

It may be useful now to consider shortly the ratio Ag/Cl, which may be ascertained by direct combination of the two elements, by conversion of silver into silver nitrate and precipitation of silver chloride by addition of hydrochloric acid or a soluble chloride, or by reduction of silver chloride to metallic silver. There are also indirect determinations in which the two ratios RCl/Ag and RCl/AgCl have been obtained by the same investigator, but independently of each other. All these data have been considered by Clarke who, from twenty-three individual values, arrives at the result—Ag : Cl = 100 : 32·8606 ± 0·00031. From this, if Ag = 107·88, Cl = 36·450, a lower value than that adopted. It is true that later indirect determinations by Archibald, Richards and Willard, and Thorpe and Francis would give a somewhat higher value, 35·455, but a small discrepancy would still remain. It has been pointed out by Guye and Germann[1] and by de Gramont[2] that the most carefully purified specimens of silver still contain minute quantities of impurities.

The atomic weight of lead is of special interest on account of the existence of several isotopes of this metal with different atomic weights.[3] The various methods employed are described by Clarke, and it may be sufficient to state that that of Baxter and Wilson[4] is regarded as the most satisfactory and has been employed in the more recent investigations. The lead is converted into chloride which, after thorough purification, is fused in an atmosphere of gaseous hydrogen chloride. Silver nitrate is added to the aqueous solution of the lead salt to precipitate silver chloride, and the equivalent weight of silver or of silver chloride or both may be determined. Baxter and Wilson calculated both ratios and obtained the value Pb = 207·19. Richards and Lembert,[5] employing the same method, found Pb = 207·15; and Baxter and Grover[6] determined the atomic weight of ordinary lead obtained from eleven different sources, and obtained quite concordant results, the mean value being Pb = 207·21.

[1] *Journ. Chim. phys.*, **14**, 195 and 204 (1916). [2] *Ibid.*, p. 336.

[3] For an account of the parentage of these isotopes of lead, and the relation of the radio-elements to the periodic law, *vide* Soddy, *Annual Report of the Chemical Society* (1914), p. 262.

[4] *Journ. Amer. Chem. Soc.*, **30**, 187 (1908).

[5] *Ibid.*, **36**, 1329 (1914). [6] *Ibid.*, **37**, 1027 (1915).

Baxter and Thorwaldsen,[1] with the same samples of lead, determined the ratio $PbBr_2/AgBr$, from which they calculated the atomic weight, Pb = 207·19; and, finally, Richards and Wadsworth,[2] from the chlorides, obtained the value Pb = 207·183.

The value adopted by the International Committee is Pb = 207·20.

Reference has already been made (p. 4) to the atomic weights of the lead from radio-active minerals.

[1] *Journ. Amer. Chem. Soc.*, p. 1020. [2] *Ibid.*, **38**, 2613 (1916).

CHAPTER VI.

THE PERIODIC LAW.

CERTAIN simple relations have long been known to exist between the atomic weights of nearly related elements, such, for example, as the fact that the atomic weight of bromine is approximately equal to the mean of those of chlorine and iodine; but it was not until 1864 that attention was called by Newlands to the existence of a general relation between the properties of the elements and their atomic weights.

Newlands pointed out that if the elements are arranged in the order of the atomic weights a system of *octaves* is obtained, the first and last of any eight consecutive elements possessing similar properties; thus chlorine resembles fluorine, sulphur is closely related to oxygen, and so on. To this generalization Newlands gave the name of the law of "octaves".

At that time, however, there was much difference of opinion regarding the atomic weights of many of the elements, and the views of Newlands were not accepted.

A similar generalization was subsequently arrived at by Mendeléeff and by Lothar Meyer, and the question was studied by Carnelley and others. The generalization, commonly known as the "periodic law," may be expressed by the statement that *the properties of the elements are periodic functions of their atomic weights.*

PHYSICAL PROPERTIES OF THE ELEMENTS.

Atomic Volumes.—Lothar Meyer paid special attention to the physical properties of the elements, notably their specific gravities in the solid state; but he pointed out that the periodicity is seen more clearly by considering, instead of the specific gravities or specific volumes, the products of the specific volumes into the atomic weights, or the *atomic* volumes.

$$\text{Atomic volume} = \text{sp. vol.} \times \text{at. wt.} = \frac{\text{at. wt.}}{\text{sp. gr.}}.$$

In the following table are given the specific gravities and atomic

volumes of the elements in the solid state so far as they are known, and in a few cases the same constant for the elements in the liquid state at the ordinary boiling point or at some other temperature. The constants for the liquid state are enclosed in brackets. For the solid state the specific gravities would be somewhat higher and the atomic volumes lower. The atomic weights are taken from the International Table for 1917.

Element.	Symbol.	Atomic Weight.	Specific Gravity.	Atomic Volume.
Hydrogen	H	1·008	0·076	13·2
Helium	He	4·00	(0·154)[1]	26·0
Lithium	Li	6·94	0·594	11·7
Glucinum[2]	Gl	9·1	1·73	5·3
Boron	B	11·0	2·45	4·49
Carbon	C	12·05	1·57-3·5	7·6-3·4
Nitrogen	N	14·01	(1·026)[1]	(13·7)
Oxygen	O	16·0	(1·425)[1]	(11·2)
Fluorine	F	19·0	(1·14)[1]	(16·7)
Neon	Ne	20·2	—	—
Sodium	Na	23·00	0·974	23·6
Magnesium	Mg	24·32	1·713	14·0
Aluminium	Al	27·1	2·67	10·2
Silicon	Si	28·3	2·49	11·4
Phosphorus	P	31·04	1·83-2·34	16·9-13·3
Sulphur	S	32·06	1·96-2·05	16·4 15·6
Chlorine	Cl	35·46	(1·6)[1]	(22·2)
Argon	A	39·88	(1·42)[3]	(28·1)
Potassium	K	39·10	0·865	45·2
Calcium	Ca	40·07	1·578	25·4
Scandium	Sc	44·1	3·8	11·6
Titanium	Ti	48·1	4·5	10·7
Vanadium	V	51·0	5·5	9·3
Chromium	Cr	52·0	6·9	7·5
Manganese	Mn	54·93	7·4	7·4
Iron	Fe	55·84	7·9	7·1
Nickel	Ni	58·68	8·3	7·1
Cobalt	Co	58·97	8·9	6·6
Copper	Cu	63·57	8·9	7·1
Zinc	Zn	65·37	6·9	9·5
Gallium	Ga	69·9	5·95	11·7
Germanium	Ge	72·5	5·5	13·2
Arsenic	As	74·96	4·7-5·7	16·0-13·2
Selenium	Se	79·2	4·5-4·8	17·6-16·5
Bromine	Br	79·92	(3·19)[4]	(25·1)
Krypton	Kr	82·92	(2·15)[1]	(38·6)
Rubidium	Rb	85·45	1·52	56·0
Strontium	Sr	87·63	2·5	35·1
Yttrium	Y	88·7	—	—
Zirconium	Zr	90·6	6·4	14·2
Columbium[5]	Cb	93·1	7·06	13·2
Molybdenum	Mo	96·0	9·0	10·7

[1] Liquid at boiling point. [2] Or Beryllium. [3] Liquid at − 189°.
[4] Liquid at 0° C. [5] Or Niobium.

Element.	Symbol.	Atomic Weight.	Specific Gravity	Atomic Volume.
Ruthenium	Ru	101·7	12·1	8·4
Rhodium	Rh	102·9	12·1	8·5
Palladium	Pd	106·7	11·9	9·0
Silver	Ag	107·88	10·47	10·3
Cadmium	Cd	112·40	8·65	13·0
Indium	In	114·8	7·42	15·5
Tin	Sn	118·7	7·2	16·5
Antimony	Sb	120·2	6·8	17·7
Tellurium	Te	127·5	6·2	20·6
Iodine	I	126·92	4·95	25·6
Xenon	Xe	130·2	(3·5)[1]	(37·2)
Cæsium	Cs	132·81	1·88	70·6
Barium	Ba	137·37	3·75	36·7
Lanthanum	La	139·0	6·16	22·6
Cerium	Ce	140·25	7·0	20·0
Praseodymium	Pr	140·9	—	—
Neodymium	Nd	144·3	—	—
Samarium	Sm	150·4	—	—
Europium	Eu	152·0	—	—
Gadolinium	Gd	157·3	—	—
Terbium	Tb	159·2	—	—
Dysprosium	Dy	162·5	—	—
Holmium	Ho	163·5	—	—
Erbium	Er	167·7	—	—
Thulium	Tm	168·5	—	—
Ytterbium	Yb	173·5	—	—
Lutecium	Lu	175·0	—	—
Tantalum	Ta	181·5	16·6	10·9
Tungsten	W	184·0	18·7	9·8
Osmium	Os	190·9	22·5	8·5
Iridium	Ir	193·1	22·4	8·6
Platinum	Pt	195·2	21·5	9·1
Gold	Au	197·2	19·26	10·2
Mercury	Hg	200·6	14·2	14·1
Thallium	Tl	204·0	11·8	17·3
Lead	Pb	207·20	11·37	18·2
Bismuth	Bi	208·0	9·74	21·4
Niton[2]	Nt	222·4	—	—
Radium	Ra	226·0	—	—
Thorium	Th	232·4	12·2	19·0
Uranium	U	238·2	18·7	12·8

The atomic volumes are plotted against the atomic weights in Fig. 14. Starting with lithium, it will be seen that the atomic volumes fall to a minimum, boron and carbon (in the form of diamond) having lower values than any other known elements. Neglecting minor irregularities, the atomic volumes rise again until the first halogen, fluorine, is reached. The value for neon is not yet known, but sodium has a considerably higher atomic volume

[1] Liquid at boiling point.

[2] Or Radium emanation.

than fluorine or magnesium, the elements on either side of it. A second minimum is shown by aluminium, which is closely related to boron, silicon also having a low value; and a maximum again with the third alkali metal, potassium, the second halogen, chlorine,

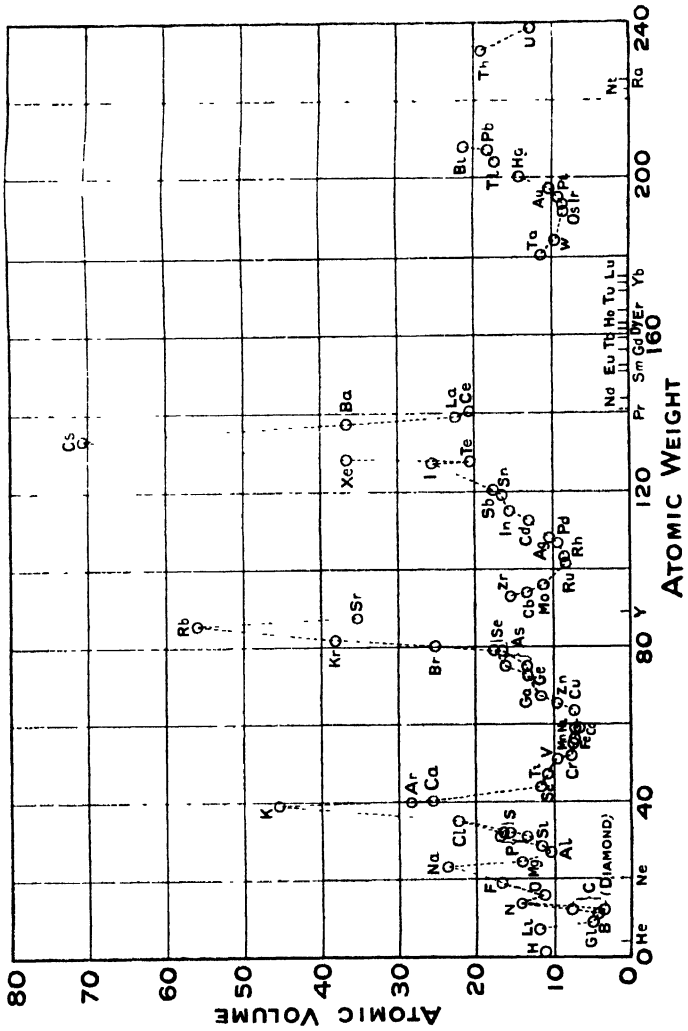


FIG. 14.

having a moderately high value. Scandium, the analogue of aluminium, has a low but not a minimum atomic volume, and before the next halogen, bromine, is reached, a large number of comparatively heavy elements are met with. The next maximum

occurs with rubidium, the fourth alkali metal, and the curve from this element to iodine, the fourth halogen, closely resembles that from potassium to bromine.

The fifth alkali metal, cæsium, has the highest observed atomic volume, and the next three elements, barium, lanthanum, and cerium, occupy positions on a curve similar to the corresponding portions of the two previous ones. After cerium, however, come a number of rare metals, the atomic volumes of which are as yet unknown, but it is certain that these elements are not analogues of those from vanadium to zirconium. The following ten elements, tantalum to bismuth, are closely allied to the ten from columbium to antimony, tantalum being related to columbium, tungsten to molybdenum, and so on, and the portions of the atomic-volume curve which include the two groups of elements show striking similarity. Of the four remaining elements of higher atomic weight, niton, or radium emanation, is probably allied to xenon, radium to barium, thorium to zirconium and uranium to molybdenum. The atomic volumes of niton and radium are not yet known.

The following points are clearly brought out by the diagram :—

1. The whole curve of atomic volumes is made up of a series of periods or waves. The summits are occupied by the alkali metals, the atomic weights of which, with their differences, are given below.

		Δ
Cs =	133	
		47·5
Rb =	85·5	
		46·5
K =	39	
		16
Na =	23	
		16
Li =	7	

There are thus two short periods: (1) between Li and Na, and (2) between Na and K; and two long periods: (3) between K and Rb, and (4) between Rb and Cs. The remainder of the atomic volume curve is either partly of a different form or incomplete. There seems no reason to anticipate that an alkali metal of atomic weight 170-180 will be discovered, but there appears to be the possibility of the existence of such a metal with an atomic weight a little lower than that of radium, say about 222, or 89 units higher than the atomic weight of Cs. The atomic volume of this metal, if it exists, should be very high.

2. The difference between the short and long periods is clearly

seen when the troughs of the waves are considered. The elements with minimum atomic volumes are boron (or carbon as diamond), aluminium, cobalt, ruthenium, and osmium. The atomic weights and their differences are as follows :—

		Δ
Os =	191	
		89
Ru =	102	
		43
Co =	59	
		32
Al =	27	
		16
B =	11	

These five elements do not, like the alkali metals, form a single group of allied elements, but belong to two widely different groups, boron and aluminium showing no chemical analogy to cobalt, ruthenium, and osmium.

Omitting the first two elements, hydrogen and helium, it appears that the others fall into two short periods or series, beginning with lithium and sodium respectively; two complete long series, with potassium and rubidium respectively as the first members; a third long series, starting with cæsium, followed in a regular manner by barium, lanthanum, and cerium, then interrupted by the intrusion, as it were, of a number of closely related rare elements, and followed again in a regular manner by the metals from tantalum to bismuth, but with no element corresponding to iodine yet known; and, lastly, a small portion of a fourth long series.

With regard to the third long series, it seems best to regard the elements Cs, Ba, La, Ce, Ta, W, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, as belonging to the same period, the rare metals coming between cerium and tantalum forming a special intermediate group.

When the periodic arrangement of the elements was discussed by Mendeléeff and by Lothar Meyer, not only the majority of the rare metals just referred to, but also gallium, scandium, and germanium, and the inert gases of the argon group, were unknown, but Lothar Meyer clearly recognized the existence of the short and long series.

Electro-chemical Character.—When a binary chemical compound, such as sodium chloride, undergoes electrolysis, one of the elements is liberated at the negative electrode, and is therefore said to be electro-positive; the other, termed the electro-negative element, is set free at the positive pole. The terms electro-positive and electro-negative are merely relative, thus sulphur is negative

with regard to sodium, but positive with regard to chlorine. In general, combination takes place most readily between elements of widely different electro-chemical character; thus the alkali metals, which are strongly positive, unite very readily with the halogens, which are strongly negative.

Again, under suitable conditions, a strongly electro-positive element will displace a weaker one from any of its compounds with a negative element. Thus magnesium will replace silicon when heated with the oxide silica, forming magnesia and silicon—

$$2Mg \text{ and } SiO_2 = Si + 2MgO.$$

So also, when a piece of copper is placed in a solution of silver nitrate, silver will be deposited and copper nitrate will be formed, showing that copper is more electro-positive than silver. Conversely, a strongly electro-negative element, such as chlorine, will displace a weaker one from a metallic compound, thus—

$$Cl_2 + 2\,KI = 2\,KCl + I_2.$$

By such considerations the elements may be arranged approximately in order as regards their electro-chemical character; and it is found that the alkali metals as a group are the most electro-positive elements, and the halogens the most electro-negative, while, of the individual members, cæsium is the most electro-positive alkali metal, and fluorine the most electro-negative halogen. Thus in these groups the elements become more positive or less negative as the atomic weights increase; and the same rule is followed by the elements in most of the other groups.

With regard to the elements of minimum atomic volume, however, it is found that, while aluminium is more electro-positive than boron or carbon, the order is reversed with the elements of higher atomic weight, cobalt and the allied metals iron and nickel being more electro-positive than ruthenium, rhodium, and palladium, and these metals more positive than osmium, iridium, and platinum. So, also, the electro-positive character becomes less marked with rise of atomic weight in the groups copper, silver, gold; and zinc, cadmium, mercury.

Leaving the inert gases out of consideration, it may be stated that in each of the two short series the elements become regularly less electro-positive or more electro-negative as the atomic weights rise, but in the long series the change is less regular. Taking, for example, the first long series, the metals potassium, calcium,

scandium, titanium are progressively less electro-positive, and the elements germanium, arsenic, selenium, bromine progressively more electro-negative, but the metal zinc is undoubtedly more electro-positive than vanadium. Similar changes are observed in the other long series.

TABLE OF HYDRIDES AND HALIDES.

Series.	Highest Hydrides.	Chlorides		Highest Fluorides or other Halides.
		Lowest.	Higher	
I. (partial) . .	—	HCl	—	HF
II. (short) . .	—	—	(Helium)	—
	LiH	LiCl	—	($LiICl_4$)
	—	$GlCl_2$	—	GlF_2
	BH_3	BCl_3	—	BF_3
	CH_4	CCl_4	—	CCl_4
	NH_3	NCl_3	—	NCl_3
	OH_2	O_7Cl_2	OCl_2	OCl_2
	FH	—	—	—
III. (short) . .	—	—	(Neon)	—
	NaH	NaCl	—	($NaBr_3$)
	—	$MgCl_2$	—	MgF_2
	—	$AlCl_3$	—	AlF_3
	SiH_4	Si_2Cl_6	$SiCl_4$	SiF_4
	PH_3	PCl_3	PCl_5	PF_5
	SH_2	S_2Cl_2	SCl_2, SCl_4	SF_6
	ClH	—	—	—
IV. (long) . .	—	—	(Argon)	—
	KH	KCl	—	($KICl_4$)
	CaH_2	$CaCl_2$	—	CaF_2
	—	$ScCl_3$	—	$ScCl_3$
	—	Ti_2Cl_4	Ti_2Cl_6, $TiCl_4$	TiF_4
	—	VCl_2	VCl_3, VCl_4	(VF_5)
	—	$CrCl_2$	$CrCl_3$	CrF_3
	—	$MnCl_2$	Mn_2Cl_6, ($MnCl_4$)	($MnCl_4$)
	—	$FeCl_2$	Fe_2Cl_6	Fe_2F_6
	—	$NiCl_2$	—	NiF_2
	—	$CoCl_2$	—	CoF_2
	(Cu_2H_2)	Cu_2Cl_2	$CuCl_2$	CuF_2
	—	$ZnCl_2$	—	ZnF_2
	—	$GaCl_2$	$GaCl_3$	$GaCl_3$
	—	$GeCl_4$	—	GeF_4
	AsH_3	$AsCl_3$	—	(AsF_5)
	SeH_2	Se_2Cl_2	$SeCl_4$	SeF_6
	BrH	—	—	—
V. (long) . .	—	—	(Krypton)	—
	RbH	RbCl	—	($RbICl_4$)
	SrH_2	$SrCl_2$	—	SrF_2
	—	YCl_3	—	YF_3
	—	$ZrCl_4$	—	ZrF_4
	—	$CbCl_3$	$CbCl_5$	CbF_5
	—	$MoCl_2$	$MoCl_3$, $MoCl_4$, $MoCl_5$	$MoCl_5$
	—	$RuCl_2$	Ru_2Cl_6, $RuCl_4$	$RuCl_4$

Series.	Highest Hydrides.	Chlorides.		Highest Fluorides or other Halides.
		Lowest.	Higher.	
V. long (*cont.*)	—	$RhCl_2$	Rh_2Cl_6	Rh_2Cl_6
	—	$PdCl_2$	$PdCl_4$	$PdCl_4$
	—	Ag_4Cl_2?	AgCl	AgF
	—	$CdCl_2$	—	CdF_2
	—	InCl	$InCl_2$, $InCl_3$	$InCl_3$
	—	$SnCl_2$	$SnCl_4$	SnF_4
	SbH_3	$SbCl_3$	$SbCl_5$	SbF_5
	TeH_2	$TeCl_2$	$TeCl_4$	TeF_6
	IH	ICl	ICl_3	IF_5
VI. (long and unique)	—	—	(Xenon)	—
	CsH	CsCl	—	$(CsICl_4)$
	BaH_2	$BaCl_2$	—	BaF_2
	—	$LaCl_3$	—	LaF_3
	—	$CeCl_3$	—	CeF_4
Intermediate elements.		$PrCl_3$	—	—
		$NdCl_3$	—	—
		$SmCl_3$	—	—
		$EuCl_3$	—	—
		$GdCl_3$	—	—
		$TbCl_3$	—	—
		$DyCl_3$	—	—
		$HoCl_3$	—	—
		$ErCl_3$	—	ErF_3
		$TuCl_3$	—	—
		$YbCl_3$	—	—
		$LuCl_3$	—	—
	—	$TaCl_5$	—	TaF_5
	—	WCl_2	WCl_4, WCl_5, WCl_6	WCl_6
	—	$OsCl_2$	$OsCl_4$	$OsCl_4$
	—	$IrCl_2$	Ir_2Cl_6, $IrCl_4$	$IrCl_4$
	—	$PtCl_2$	$PtCl_4$	$PtCl_4$
	—	AuCl	$AuCl_3$	$AuCl_3$
	—	Hg_2Cl_2	$HgCl_2$	HgF_2
	—	TlCl	$TlCl_3$	TlF_3
	—	$PbCl_2$	$PbCl_4$	$PbCl_4$
	—	Bi_2Cl_4	$BiCl_3$	BiF_3
VII. (incomplete)	—	—	(Niton)	—
	—	$RaCl_2$	—	$RaBr_2$
	—	$ThCl_4$	—	ThF_4
	—	UCl_3	UCl_4, UCl_5	UCl_5

Other Physical Properties.—Similar periodicity is to be observed if the melting points, the boiling points, or the magnetic powers of the elements, are considered, but the data are less complete and the results less striking.

Valency.—If the known hydrides are tabulated, the elements uniting with hydrogen being arranged in the order of their atomic weights, and when more than one hydride of a given element is known, that one being chosen which contains the relatively largest

amount of hydrogen, the periodicity of the formulæ becomes evident (Table, p. 88). But the number of known hydrogen compounds is not large, and it is useful to tabulate also the compounds of the elements with other monads, such as chlorine and fluorine; and when more than one chloride or fluoride is known, it is of interest to consider not only the compounds richest, but also those poorest, in the halogen. As regards the latter, it will be seen that the periodicity is, on the whole, similar to that in the case of the hydrides, but the number of known compounds is much larger, and there are many irregularities.

Starting with lithium, which is monovalent, and considering the hydrides, or, where these are unknown, the lowest chlorides, we have glucinum, divalent; boron, trivalent; carbon, tetravalent; nitrogen, trivalent; oxygen, divalent; fluorine, monovalent. Neon, the next element, is not known to combine with any other substance, and must be regarded for the present as having zero valency. After neon come monovalent sodium, divalent magnesium, trivalent aluminium, tetravalent silicon, trivalent phosphorus, divalent sulphur, and monovalent chlorine. The first series from lithium to fluorine shows striking similarity to the second from sodium to chlorine, and the first element lithium is chemically closely related to the *ninth*, sodium (neon was, of course, unknown to Newlands); the second, glucinum, to the tenth, magnesium; and so on.

Passing on from chlorine, the next element would be potassium, with atomic weight 39·15, followed by argon, 39·9. But argon is closely related to neon, forming no compounds, and potassium resembles sodium and lithium, not only in its monovalency, but in other respects, and to bring these two elements into their proper groups it is necessary to reverse their order and to take argon first. Following monovalent potassium, we have divalent calcium and trivalent scandium, but the valency of the elements from titanium to gallium is not generally shown by the formulæ of the lowest chlorides, and hydrides are unknown excepting that of copper. The remaining elements are germanium, tetravalent; arsenic, trivalent; selenium, divalent; bromine, monovalent.

In the next long group, also, the valency is only clearly defined in the case of the first four and the last three members.

It is quite evident, however, that in each group, whether short or long, the valency rises regularly at the beginning from monad to tetrad, and falls regularly at the end from triad or tetrad to monad.

A consideration of the highest halides (omitting the exceptional compounds of the alkali metals) leads to similar results as regards the first four members of each group, but a difference is observed with the later members.

Nitrogen and oxygen have so little affinity for the halogens that the group in which they occur need not be considered. But in the next group we have SiF_4, PF_5, SF_6, after AlF_3, so that the valency continues to rise.

In the first long group TiF_4 is followed by VF_5, and GeF_4 by AsF_5 and SeF_6; the two pentafluorides are, however, only known in a state of combination.

In the second long group the valency is more clearly defined, for in the first part of the group ZrF_4 is followed by CbF_5, and in the last part we have AgF, CdF_2, $InCl_3$, SnF_4, SbF_5, TeF_6, and finally IF_5.

There appears, then, to be a tendency for the valency to rise from monad to pentad or hexad, and for the order of valency to be the same for the last seven elements as for the first seven.

These points are, however, more clearly shown by considering the oxides; and it was chiefly on the valency of the elements, as shown by their hydrides, halides, and oxides that Mendeléeff based his periodic arrangement.

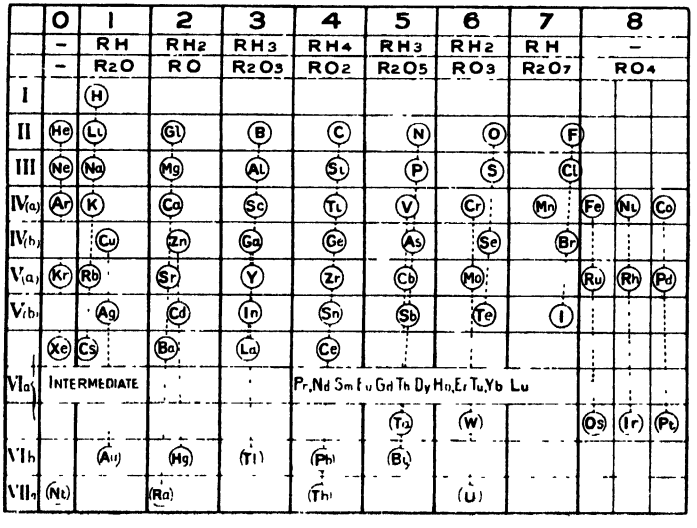
Lothar Meyer, on the other hand, considered more especially the physical properties of the elements, and he adopted a different arrangement. In both cases the elements were divided into groups and series. The groups were eight in number, and each group contained more or less closely related elements. In Mendeléeff's table (p. 92) the alkali metals, and copper, silver, and gold, are all placed in Group I., but sodium occurs in the odd series with the copper metals, the other alkali metals in the even series.

So also fluorine is separated from the other halogens, oxygen from sulphur, and so on.

In Lothar Meyer's table the alkali metals are brought together, fluorine is found with the other halogens, oxygen with the sulphur elements, and so with the other groups. This table is therefore generally preferred to that of Mendeléeff, and it is given in a slightly modified form on p. 92. The inert gases of the argon group were unknown when the first tables were constructed; they are now generally placed in a separate group, which is conveniently numbered 0, because these elements form no known compounds and cannot be said to have any valency.

Groups.	Series.						
		2	4	6	8	10	12
I.	—	Li	K	Rb	Cs	—	—
II.	—	Be	Ca	Sr	Ba	—	—
III.	—	B	(Sc)	Y	La	—	—
IV.	—	C	Ti	Zr	Ce	—	Th
V.	—	N	V	Nb	[Di]	Ta	—
VI.	—	O	Cr	Mo	—	W	U
VII.	—	F	Mn	—	—	—	—
VIII.	—	—	Fe	Ru	—	Os	—
	—	—	Ni	Rh	—	Ir	—
	—	—	Co	Pd	—	Pt	—
I.	H	Na	Cu	Ag	-	Au	—
II.	—	Mg	Zn	Cd	—	Hg	—
III.	—	Al	(Ga)	In	—	Tl	—
IV.	—	Si	(Ge)	Sn	—	Pb	—
V.	—	P	As	Sb	—	Bi	—
VI.	—	S	Se	Te		—	—
VII.	—	Cl	Br	I	—	—	—
	1	3	5	7	9	11	(13)

The electro-chemical character of the elements is roughly indicated by the position of the symbols in the spaces they occupy, the electro-positive elements being placed to the left of the spaces, and the electro-negative elements to the right. Thus the symbol for



cæsium is placed far to the left of its space, that for fluorin the right.

The Oxides.

The oxides may be divided into three classes: (*a*) basic oxides, such as lime, which unite with acids to form salts with elimination of water, thus—

$$CaO + 2HCl = CaCl_2 + H_2O,$$

(*b*) acid-forming oxides, which unite with water to form acids; for example—

$$SO_3 + H_2O = H_2SO_4,$$

(*c*) other oxides, including suboxides and peroxides. Of these, the suboxides are generally reducing agents, while the peroxides act as oxidizing agents.

Many of the elements form more than one oxide, one of them, manganese, as many as six. When such a series is formed, it is found that the oxides tend to become less basic or more acidic as the amount of oxygen increases, and several elements form both basic and acid-forming oxides. Thus, of the six oxides of manganese, two, MnO and Mn_2O_3, are basic; two others, MnO_3 and Mn_2O_7, are acid forming; and one, MnO_2, is classed as a peroxide, although, as it gives a very unstable tetrachloride when treated with cold hydrochloric acid, it might also be called a feebly basic oxide.

Manganese thus forms at least four groups of compounds, and the following are typical members of them:—

Manganous sulphate, $MnSO_4$,	derived	from	MnO
Manganic sulphate, $Mn_2(SO_4)_3$,	,,	,,	Mn_2O_3
Potassium manganate, K_2MnO_4,	,,	,,	MnO_3
Potassium permanganate, $KMnO_4$	,,	,,	Mn_2O_7

Manganese is found, in fact, to show relationship to one group of elements in the manganous compounds, to another in the manganic compounds, and so on.

The oxides of the elements are tabulated on p. 94, according to Lothar Meyer's arrangement (slightly modified), the formulæ for the basic oxides being printed in German characters, the acid-forming oxides in italics, and the other oxides in ordinary type. Some oxides have both basic and acid-forming properties, and in such cases the symbol for oxygen is printed in one type, and that for the associated element in the other.

Series.	Group. 0	1	2	3	4	5	6	7	8
I.	— —	H_2O H_2O_2	— —	— —	— —	— —	— —	— —	— —
II.	(He) — — — —	Li_2O — — — —	GlO — — — —	B_2O_3 — — — —	C_3O_2 CO CO_2 — —	N_2O NO N_2O_3 NO_2 N_2O_5	(O) — — — —	(F) — — — —	— — — — —
III.	(Ne) — — —	Na_2O Na_2O_2 — —	MgO — — —	Al_2O_3 — — —	SiO_2 — — —	P_4O P_4O_8 P_2O_4 P_2O_5	S_2O_3 SO_2 SO_3 S_2O_7	Cl_2O ClO_2 — Cl_2O_7	— — — —
IV. (*a*)	(Ar) — — — — —	K_2O K_2O_4 — — — —	CaO CaO_2 — — — —	Sr_2O_3 — — — — —	TiO Ti_2O_3 TiO_2 TiO_3 — —	V_2O V_2O_2 V_2O_3 V_2O_4 V_2O_5 —	(CrO) Cr_2O_3 CrO_3 — — —	MnO Mn_3O_4 Mn_2O_3 MnO_2 MnO_3 Mn_2O_7	FeO, NiO, CoO Fe_3O_4, Ni_2O_3, Co_3O_4 Fe_2O_3 Co_2O_3 — — —
IV. (*b*)	— — — —	Cu_4O Cu_2O CuO CuO_2	ZnO — — —	Ga_2O_3 — — —	GeO GeO_2 — —	As_4O_6 As_2O_5 — —	SeO_2 — — —	(Br) — — —	— — — —

V. (*a*)	(Kr)	Rb_2O	SrO	Y_2O_3	ZrO_2	Cb_2O_2	Mo_2O_3	—	RuO, RhO, (Pd_2O)
	—	—	—	—	ZrO_3	Cb_2O_4	MoO_2	—	Ru_2O_3, Rh_2O_3, PdO
	—	—	—	—	—	Cb_2O_5	MoO_3	—	RuO_2, RhO_2, PdO_2
	—	—	—	—	—	—	—	—	RuO_4
V. (*b*)	—	Ag_2O	CdO	InO	SnO	Sb_4O_5	TeO	I_2O_5	—
	—	Ag_2O_2	—	In_2O_3	SnO_2	Sb_2O_4	TeO_2	—	—
	—	—	—	—	—	Sb_2O_5	TeO_3	—	—
VI. (*a*)	(Xe)	($CsOH$)	BaO	La_2O_3	Ce_2O_3	—	—	—	—
	—	—	BaO_2	—	CeO_2	—	—	—	—
Inter-mediate	Pr_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tu_2O_3, Yb_2O_3, Lu_2O_3								
VI. (*a*) (*continued*)	—	—	—	—	—	Ta_2O_4	WO_2	—	OsO, Ir_2O_3, PtO_3
	—	—	—	—	—	Ta_2O_5	WO_3	—	Os_2O_3, IrO_2, PtO_4
	—	—	—	—	—	—	—	—	OsO_2, PtO_2
	—	—	—	—	—	—	—	—	OsO_3
	—	—	—	—	—	—	—	—	OsO_4
VI. (*b*)	—	Au_2O	Hg_2O	Tl_2O	Pb_2O	Bi_2O_2	—	—	—
	—	Au_2O_2	HgO	Tl_2O_3	PbO	Bi_2O_3	—	—	—
	—	Au_2O_3	—	—	Pb_3O_4	Bi_2O_4	—	—	—
	—	—	—	—	Pb_2O_3	Bi_2O_5	—	—	—
	—	—	—	—	PbO_2	—	—	—	—
VII. (*a*)	—	—	(Ra)	—	ThO_2	—	UO_2	—	—
	—	—	—	—	—	—	U_3O_8	—	—
	—	—	—	—	—	—	UO_3	—	—

Referring to this table, comparing it with the atomic volume diagram (Fig. 14) and the periodic table on p. 92,[1] and considering first the alkali metals, it is found that their characteristic oxides have the general formula M_2O; the oxides combine readily with water, forming soluble and strongly alkaline hydroxides, thus,

$$M_2O + H_2O = 2MOH.$$

There are also peroxides known.

Descending the atomic volume curves to the right, the elements (neglecting argon) which follow the alkali metals are glucinum, magnesium, calcium, strontium, barium, and to these may be added radium. Their characteristic oxides have the general formula MO; they are strongly basic, especially those of calcium, strontium, and barium, these elements being frequently known as the alkaline earth metals. The oxides are, however, less basic than those of the corresponding alkali metals, their affinity for water is less pronounced, and the hydroxides, $M(OH)_2$, are less soluble. Peroxides are also known.

Following the calcium group are the elements B, Al, Sc, Y, La. Their oxides have the general formula M_2O_3; that of boron is acid-forming; aluminium oxide is both basic and feebly acid-forming; the others are basic, but not nearly so strongly as the corresponding oxides of the metals of the previous group.

Next in order we have the elements C, Si, Ti, Zr, Ce, and it is probable that thorium also belongs to this group. The general formula of the characteristic oxides is MO_2. The first four of these oxides are acid-forming; the last two are basic.

Starting again from the alkali metals (excluding lithium and also the inert gases) and descending the curves to the left, the first elements met with are the halogens, F, Cl, Br, I.[2] These elements have little affinity for oxygen; indeed, the only stable oxide known is iodine pentoxide. It may be remarked, however, that the most stable oxyacid of chlorine is perchloric acid, $HClO_4$, a derivative of the anhydride Cl_2O_7, thus $Cl_2O_7 + H_2O = 2HClO_4$. Similarly the anhydride of periodic acid would have the formula I_2O_7. It may

[1] The student is strongly advised to make copies of the two tables and the atomic volume diagram. The general relationships between the elements can best be grasped by constant reference to them, and the study of inorganic chemistry is thus greatly facilitated.

[2] Tellurium has a slightly higher atomic weight, but a lower atomic volume than iodine.

therefore be permissible to take M_2O_7 as the general formula of the characteristic, or, at any rate, of the highest oxides of the group; and it will be noted that fluorine is the seventh element from lithium, and chlorine the seventh from sodium, in ascending order of atomic weights.

After the halogens come the elements of the oxygen group, O, S, Se, Te. The characteristic compounds of this group are the acids H_2SO_4, H_2SeO_4, H_2TeO_4, of which the corresponding anhydrides, SO_3 and TeO_3, are known. We may therefore take the general formula for the oxides as MO_3.

The nitrogen group of elements, N, P, As, and Sb, comes next, and bismuth, on account of its close chemical relationship to the others, may also be included. Each of these elements forms several oxides, the highest of which is the pentoxide M_2O_5. With the exception of Bi_2O_5, the pentoxides are acid-forming.

All the elements from lithium to fluorine and from sodium to chlorine are thus accounted for, but there remain the heavy metals between Ti and As, Zr and Sb, Ce and Bi respectively, and lastly the single metal uranium.

Descending the curves to the right, titanium is followed by vanadium and zirconium by columbium; after cerium come the series of rare metals from praseodymium to lutecium, and then the element tantalum. The three elements vanadium, columbium, and tantalum, in their chemical properties, show close relationship to nitrogen and phosphorus; thus the pentoxides V_2O_5, Nb_2O_5, and Ta_2O_5 are acid-forming. Vanadium, however, is more metallic in character than arsenic, although it has a lower atomic weight. The eight elements N, P, V, As, Cb, Sb, Ta, Bi may then be classed together in one large group, which may be subdivided into the two smaller groups, N, P, As, Sb, Bi, and V, Cb, Ta.

Following the vanadium elements, we have chromium, molybdenum, and tungsten, and to these may be added uranium. In their physical properties these elements differ completely from oxygen and sulphur; they are hard, lustrous metals of very high melting point, whereas sulphur and oxygen are typical non-metals. In a low state of oxidation their compounds show no resemblance to those of the elements of the sulphur group; but, on the other hand, they form oxides of the general formula MO_3, and some of these oxides unite with water to form acids, the others with alkalis to form salts, corresponding to sulphuric acid and the sulphates respectively. The

trioxides may therefore, like sulphur trioxide, be classed as acid-forming oxides. It is to be noted, also, that all these elements form oxychlorides of the general formula MO_2Cl_2. It appears, then, that in their highest state of oxidation, the elements Cr, Mo, W, and U are chemically related to the sulphur elements, and the eight elements form one large group consisting of two sub-groups, O, S, Se, Te and Cr, Mo, W, U.

The next element to chromium is manganese, a hard metal of high melting point. As already stated, manganese forms two basic oxides, MnO and Mn_2O_3, and these oxides and the compounds derived from them closely resemble the corresponding chromium compounds. The oxide MnO_3, an acid-forming oxide, also resembles CrO_3, but the highest oxide, Mn_2O_7, unites with water to form permanganic acid, which is closely analogous to perchloric acid. In its highest state of oxidation, then, manganese, the seventh element from potassium, is related to the halogens. No other metal resembling both manganese and the halogens is known.

The three metals, iron, nickel, and cobalt, which follow manganese, are closely allied to each other; they are similar in appearance, hardness, malleability and fusibility, and they all possess magnetic properties; they also exhibit close analogies in many of their compounds. In many respects they resemble manganese, and iron shows some relationship to chromium also. The lowest oxides have the general formula MO, and the corresponding sulphates of Mn, Fe, Ni, and Co form isomorphous double sulphates of the form $M_2'SO_4,M''SO_4,6H_2O$, in which M' may be potassium, rubidium, cæsium, or the group NH_4. All three metals form sesquioxides; of these Fe_2O_3 is basic, and the sulphate, like the corresponding sulphates of manganese and chromium, forms a double salt with potassium sulphate, crystallizing with twenty-four molecules of water. These double sulphates are isomorphous with ordinary alum, and are termed chrome alum, manganese alum, and iron alum respectively. Lastly, iron forms salts known as ferrates, such as K_2FeO_4 which are analogous to the manganates and chromates.

In the next long series of elements from rubidium to iodine there is a similar triplet consisting of ruthenium, rhodium, and palladium, and in the broken series from cæsium to bismuth, a third triplet, osmium, iridium, and platinum. These six metals are characterized by their high specific gravity, their infusibility and their chemical inactivity; they are not attacked by any single acid, but, with the ex-

ception of rhodium, are converted into tetrachlorides by the action of aqua regia, and the tetrachlorides unite with potassium chloride to form double chlorides of the form $K_2M^{IV}Cl_6$. It is noteworthy that ruthenium and osmium form easily fusible tetroxides, and that OsO_4 is volatile without decomposition. These are the only known cases of octavalency.

Following the three triplets are the metals copper, silver, and gold. These metals show relationships, on the one hand to the triplets which they follow, and on the other hand to the alkali metals. They are heavy metals of high melting point, not acted on by water, and not easily attacked by acids, gold being only dissolved by aqua regia. But silver is monovalent, and copper and gold form monochlorides in addition to the higher compounds; the oxide of silver is slightly soluble in water, giving an alkaline solution, and many of the silver salts are isomorphous with those of potassium.

The next in order are the metals zinc, cadmium, and mercury, and these elements show double relationship, on the one hand to copper, silver, and gold, and on the other hand to the alkaline earth metals. They are usually divalent, but mercury behaves as a monad in the mercurous compounds. These metals are more electro-positive than the corresponding elements of the copper group, less so than the alkaline earth metals. Many zinc and cadmium salts are isomorphous with those of magnesium, and some with those of manganese, iron, nickel, and cobalt. This is notably the case with the double sulphates isomorphous with ferrous ammonium sulphate, $(NH_4)_2SO_4,FeSO_4,6H_2O$. In this salt the ferrous iron may be replaced by Cr, Mn, Ni, Co, Cu, Mg, Zn, and Cd.

In the following groups are the metal gallium, indium, and thallium, which show the closest relationship to the elements of the aluminium group in both their physical and chemical properties. They are triads, but, in addition to the sesquioxides, indium and thallium form monoxides. It is noteworthy that thallous chloride shows close analogy to the chlorides of the alkali metals, and that thallous oxide, Tl_2O, unites with water, forming a soluble and strongly alkaline hydroxide, TlOH. Gallium and indium can replace aluminium in alum; thallium cannot do so, but it can replace potassium in the same compound.

There are lastly the tetrad metals, germanium, tin, and lead, which are very closely allied to the elements of the carbon group.

Utility of the Periodic Table.—In Mendeléeff's table, p. 92,

the symbols for scandium, gallium, and germanium are placed in brackets. These elements were unknown when the Russian chemist brought forward his periodic law, but he left blank spaces where they occur in order to bring the succeeding elements into their appropriate groups. Moreover, he predicted that these elements would eventually be discovered, and he gave a very full account of their chemical and physical properties, based on a consideration of those of the elements near them in the table. The elements, when discovered, were found to possess the properties described by Mendeléeff.

The existence of other unknown elements has similarly been predicted. For example, it was from a consideration of the position of argon and helium in the periodic table that Ramsay suspected the existence of similar inert gases, and these were afterwards discovered by Ramsay and Travers. One may also anticipate the ultimate discovery of a metal resembling manganese and showing some relationship to the halogens, with an atomic weight between those of molybdenum and ruthenium, and there is the possibility of the existence of a sixth alkali metal, a fifth halogen, a third metal of the manganese group between tungsten and osmium, and a higher homologue of tellurium.

The periodic table has been of great value in calling attention to doubtful atomic weights; thus glucinum (beryllium) was regarded by many chemists as a triad, and, its equivalent being 4·5, it was believed by them to have the atomic weight 13·5. But there would be no place for a triad element with this atomic weight in the table, whereas if the metal were divalent, its atomic weight would be 9, and it would fall naturally between lithium and boron. The question was finally decided by Nilson and Pettersson, who obtained the value 40 for the vapour density of the chloride. The molecular weight is therefore 80, and this agrees with the formula $GlCl_2$ (9 + 71 = 80), but not $GlCl_3$ (13·5 + 106·5 = 120).

It must, however, be admitted that potassium and argon, and tellurium and iodine, respectively, can only be brought into their proper groups by reversing the order of the well-determined atomic weights.

Since the discovery of radium in 1898 by M. and Mme. Curie, our conception of the nature of the atom has undergone fundamental alterations, and fresh light has been thrown on the periodic law. The well-established fact that radium suffers a slow process of disin-

tegration, attended by the expulsion of α and β-particles and the evolution of an immense amount of energy, rendered it necessary either to modify the definition of an element (p. 2) or to regard radium as a new kind of compound, different in its behaviour from all other known compounds in so far that it undergoes spontaneous disintegration at a perfectly definite rate, and that the rate cannot apparently be altered by any known chemical or physical agency. It is considered best to classify radium as an element, but, that being so, it is clear that the atom of this and of other similar elements, at any rate, cannot be regarded as a homogeneous indivisible particle of matter. Indeed it is now considered that an atom is a very complex body. The mass of the atom, in association with positive electricity—about 1 unit of charge per 2 units of mass—is considered to occupy a single central nucleus which, according to Rutherford, is of excessively small dimensions, the diameter being only one ten-thousandth of the atomic diameter. Around this nucleus a number of negative electrons, equal in value to the positive nuclear charge, are considered to circulate as an outer ring or shell.

The mass of this central positive charge, in terms of that carried by the hydrogen ion, is probably the same as the "atomic number," that is to say, the number of the place occupied by the element in the periodic table, that of hydrogen being 1, of helium 2, of lithium 3, and so on.

In any given stage of disintegration of an atom of a radio-active element either an α-particle—an atom of helium carrying two positive charges—or a β-particle—an "atom" of negative electricity—is expelled, and it is believed that the α-particles and probably also these β-particles have their origin in the nucleus. It is therefore now assumed that the positively charged nucleus of the atom contains some negative electrons—at least six in the case of uranium to account for the six β-rays expelled in the course of the disintegration. These negative electrons are to be distinguished from those in the outer shell.

When an α-particle is expelled there is a loss of 4 units in the atomic weight and, according to Soddy,[1] the new element occupies the next place but one in the periodic table in the direction of diminishing group number and diminishing atomic mass. On the other hand, when a β-particle is expelled, there is no appreciable

[1] "Chemistry of the Radio-elements," p. 30 (1911).

loss of weight, but the element moves one place in the periodic table in the opposite direction.[1]

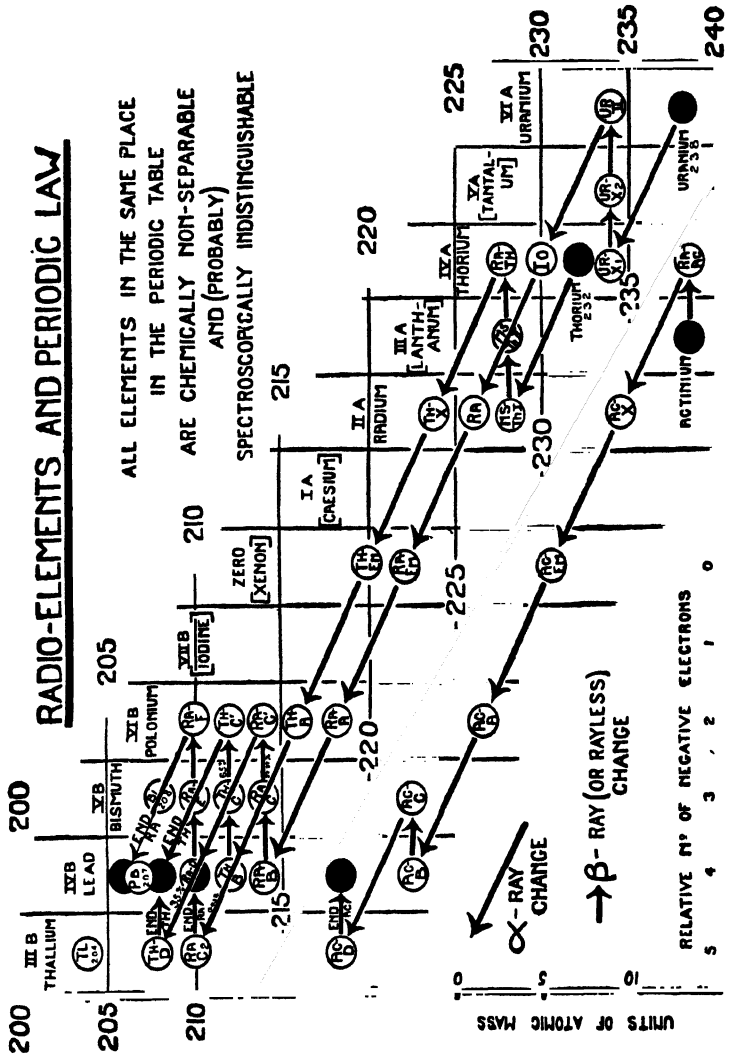


FIG. 15.

The generalization is illustrated in the chart (Fig. 15) reproduced by kind permission from a block illustrating "The Radio-elements

[1] Russell, *Chem. News*, **107**, 49 (1913); Fajans, *Physik. Zeitschr.*, **14**, 131 and 136 (1913); Soddy, *Chem. News*, **107**, 97 (1913).

and the Periodic Law" ["The Chemistry of the Radio-elements," pt. ii., p. 3, by F. Soddy (1916), Longmans, Green & Co.].

Whenever, by the expulsion of α or β-rays, two or more elements come to occupy the same place in the periodic table, they are non-separable from one another and are, so far as is known, identical in chemical character, although they may differ in atomic weight and specific gravity. For example, the case of uranium (at. wt. 238) may be considered. By the expulsion of an α-particle from an atom of this element it is converted into uranium X_1 (at. wt. 234) which is an isotope of radio-actinium, thorium, ionium, and radio-thorium, the atomic weights of the four isotopes ranging from 228 to 234. An atom of uranium X_1 loses a β-particle and is converted into uranium X_2 which, by loss of another β-particle, becomes uranium II, isotopic with uranium itself, but with the atomic weight 234. Uranium is in the sixth group (series VII. *a*) of the periodic table (p. 92), uranium X_1 in group 4, uranium X_2 in group 5, and uranium II in group 6 again. By loss of an α-particle uranium II gives rise to ionium (at. wt. 230), and from this, by further loss of an α-particle, radium (at. wt. 226) is produced. Ionium is in the fourth group (series VII. *a*) and radium, the homologue of barium, in the second. The radium atom now loses an α-particle and gives rise to radium emanation or niton (at. wt. 222) which belongs to the group of inert monatomic gases occupying the zero group. The atom of emanation, losing an α-particle, forms radium A (at. wt. 218), and this, by a similar change, is converted into radium B, an isotope of lead with atomic weight 214. Radium A is in group 6 (series VI. *b*) and radium B in group 4. Radium B is now converted successively into radium C and radium C_1 by loss of β-particles, radium C being in group 5 and radium C_1 in group 6. Another α-particle is now lost, and radium D, an isotope of lead with atomic weight 210, is formed. Radium D, like radium B, loses β-particles with formation of radium E (group 5) and radium F (group 6). Finally, radium F loses an α-particle and gives rise to radium G, which is the lead of atomic weight 206 found in uranium minerals.

The time occupied by these changes varies enormously, thus for one half of a given quantity of radium to be converted into the emanation, a period of 2500 years would be required, whilst for the conversion of half the total quantity of radium A into radium B, 4·3 minutes are sufficient.

It is now regarded as proved that, so long as the net charge of

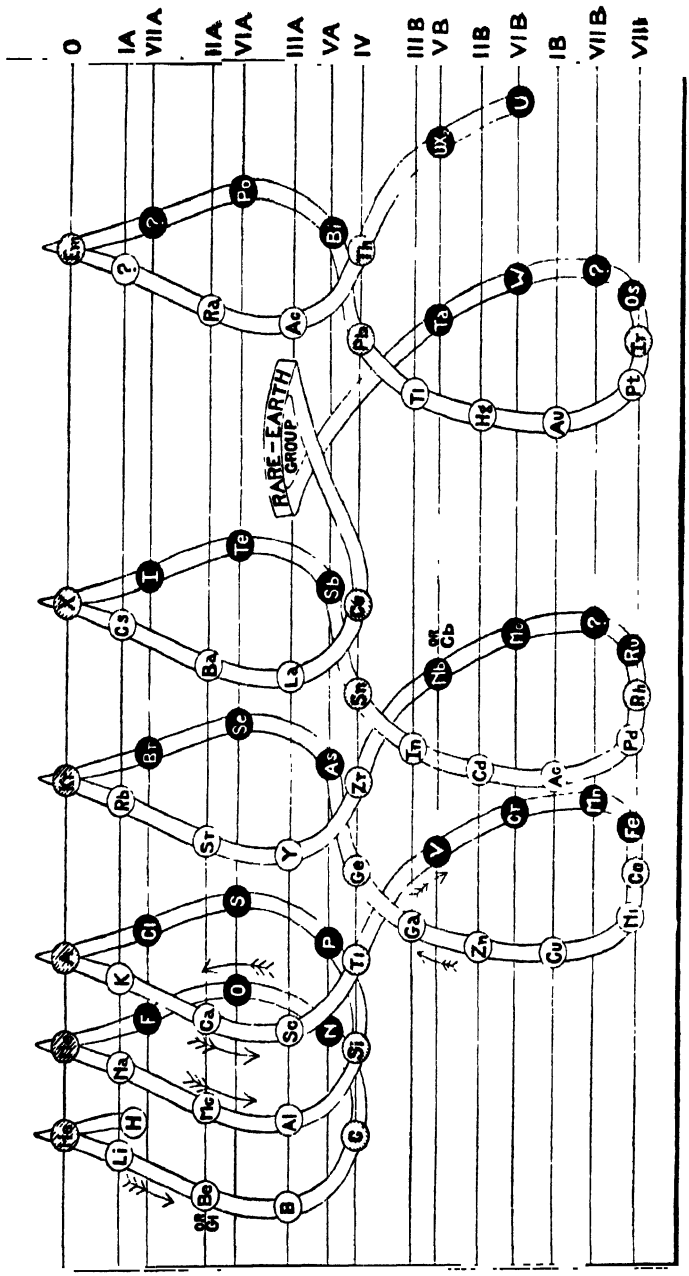

HELICAL REPRESENTATION OF PERIODIC LAW.
0
IA
VIIA
IIA
VIA
IIIA
VA
IV
IIIB
VB
IIB
VIB
IB
VIIB
VIII
RARE-EARTH GROUP
Nb or Cb
Be or Gl

Fig. 16.

the nucleus of the atom is the same, the element will show the definite chemical and physico-chemical character associated with one or other of the ninety-two places in the periodic table, quite independently of the nature and constitution of the nucleus. But the same net charge of the nucleus may result from different absolute numbers of positive and negative charges, in which case atoms of identical chemical character will show different atomic masses, the mass being primarily a function, although, in all probability, not a simple additive function of the number of positive charges present. For example, the expulsion in any order of an α-particle, carrying two positive charges, and of two β-particles, each carrying one negative charge, from the nucleus leaves the net nuclear charge and the chemical properties unchanged, although the atomic mass has been lowered by 4 units by the expulsion of the α-particle. Again, when the series branches (*vide* thorium C, Fig. 15), as, for example, when some of the atoms expel first an α and then a β-particle, whilst others expel first a β and then an α-particle, both the net and gross nuclear charges of the resulting product are identical; but although the chemical characters, spectra, and atomic masses are alike the atoms are not the same, and if the process of disintegration proceeded further, the difference would be revealed in the manner and rate of the subsequent transformation.[1]

A very clear and useful modification of the periodic table has been suggested by Soddy; it is reproduced in Fig. 16 from "The Chemistry of the Radio-elements," pt. ii., p. 11 (1916) (Longmans, Green & Co.).[2]

[1] Soddy, "Annual Reports on the Progress of Chemistry, 1916," p. 245.

[2] For further suggestions regarding the periodic arrangement of the elements, *vide* Rydberg, *Journ. Chim. phys.*, **12**, 585 (1914), and Harkins and Hall, *Journ. Amer. Chem. Soc.*, **38**, 169 (1916).

CHAPTER VII.

THE DISSOCIATION OF GASES AND VAPOURS.

THE earliest experiments on the dissociation or reversible decomposition by heat of compounds which are stable at ordinary temperatures were made by Deville in 1858.[1]

Deville studied chiefly the commoner gaseous compounds which require a very high temperature to bring about their decomposition. Recognizing the fact that if left in contact with each other the constituents would recombine, partially at any rate, on cooling, he devised various methods of separating the gases at the high temperature. For example, Deville[2] was able to demonstrate the dissociation of water vapour at temperatures from 1100° to 1300° C. by passing the steam through a porous tube placed in a wider porcelain tube through which a current of carbon dioxide was passed. The tubes were heated in a furnace, and measurable quantities of hydrogen and oxygen were found in the carbon dioxide, although the vapour density of water appeared to be normal at 1157°.

When electric sparks are passed through a gas, the temperature in the immediate neighbourhood of the sparks is exceedingly high, but the temperature gradient is very steep, and as recombination of the products of dissociation can only take place within definite limits of temperature, it may easily happen that they cool below the lower limit before they have an opportunity of recombining. Thus it is well known that ammonia gas may be decomposed by the passage of sparks through it, but it is found that the decomposition is never quite complete, and it was noticed by Morren,[3] and, later, by other observers, that when sparks are passed through a mixture of nitrogen and hydrogen a very small amount of ammonia is formed. Moreover, by placing some acid over the mercury in the eudiometer tube which contained the mixed gases, the ammonia was absorbed, or by cooling the tube in liquid air it was condensed,[4] and it was thus

[1] *Compt. rend.*, **45**, 821 (1857).
[2] *Ibid.*, **56**, 195 (1863). [3] *Ibid.*, **52**, 527 (1861).
[4] Briner and Mettler, *Compt. rend.* (March, 1907).

found possible to bring about the combination of a considerable amount of nitrogen and hydrogen. In all probability the diatomic molecules of nitrogen and hydrogen are dissociated at the high temperature of the sparks, and, on cooling, the atoms recombine for the most part to form gaseous nitrogen and hydrogen, but also to a small extent to form ammonia. When the molecules of ammonia reach the high-temperature region they are at once decomposed again, and a state of equilibrium is soon reached in which the number of molecules of ammonia formed and decomposed in unit time is equal. But if some of the ammonia is absorbed or condensed, the amount left falls below that required for equilibrium, and a fresh quantity must be formed to take the place of that removed. Thus the amount of ammonia formed in unit time exceeds that decomposed, and a large quantity of the mixed gases may be slowly caused to combine. Deville imitated the conditions of the spark by employing a glazed porcelain or metal inner tube and passing a current of cold water through it, and was thus able to demonstrate the dissociation of carbon monoxide into carbon dioxide and carbon. A further improvement was effected by making a narrow slit in the inner tube and diminishing the internal pressure, so that gas from the outer tube passed slowly into the water. In this way the dissociation of sulphur dioxide, hydrogen chloride, and carbon dioxide was clearly demonstrated.

Abnormal Vapour Densities.—According to the rule that the molecular weight of a substance is numerically equal to twice its vapour density (compared with that of oxygen taken as 16), the vapour density of ammonium chloride should be either

$$\frac{14 + 4 + 35{\cdot}4}{2} = 26{\cdot}7$$

if the molecules of gas are simple, or $n \times 26{\cdot}7$ if they are complex, n being the number of simple NH_4Cl molecules united together. Deville and Troost,[1] however, determined the vapour density of ammonium chloride at 350° and at 1040°, and obtained the values 14·6 and 14·45. Deville considered that the vapour of ammonium chloride did not follow the ordinary laws relating to gases, but Pebal[2] showed that when a piece of the salt is placed in a tube on one side of a plug of asbestos (Fig. 17) and heated strongly, an excess of ammonia passes through the asbestos, leaving excess of hydrogen

[1] *Annalen*, **123**, 199 (1862). [2] *Ibid.*, **123**, 199 (1862).

chloride on the other side. The separation was shown by passing air through the tubes and over moistened litmus paper. The vapour from the ammonium chloride must therefore have contained free ammonia and free hydrochloric acid; in other words, dissociation must have occurred.

Deville considered that dissociation was caused by contact of the heated vapour with the asbestos, but Than[1] showed that the same result was obtained when a porous diaphragm of ammonium chloride was employed in place of the asbestos. Deville[2] brought about the admixture of ammonia gas and hydrogen chloride in a vessel heated by the vapour of boiling mercury, and observed that an air thermometer placed by the side of the other vessel indicated a rise of temperature; but Than[3] showed that when the two gases were mixed together at 350°, no contraction or expansion took place.

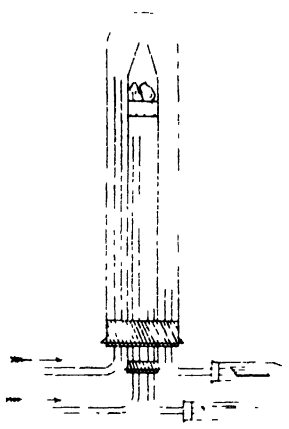


FIG. 17.

The discrepancy between the two last-named results may perhaps be explained by the fact that the pressure in Than's experiment was lower than in Deville's, and that dissociation is complete at the lower pressure, but not quite at the higher. At any rate, such a discrepancy might well be observed at 280°, for at this temperature the vapour density of ammonium chloride was found by Ramsay and Young[4] to be 13·3 under a pressure of 88·4 mm., but 15·2 under a pressure of 135 mm.

The vapour density of tertiary amyl bromide, formed by the combination of amylene with hydrogen bromide, was found by Wurtz[5] to be normal up to about 60° above its boiling point under atmospheric pressure; the density then diminished with rise of temperature, slowly at first, then more rapidly, and finally more slowly again until it became constant at half the original value.

Phosphorus pentachloride has been the subject of much controversy and of many experiments. Cahours[6] observed that the

[1] *Annalen*, **131**, 138 (1864).
[2] *Compt. rend.*, **56**, 729 (1863).
[3] *Annalen*, **131**, 129 (1864).
[4] *Phil. Trans.*, **177**, pt. i., 99 (1886).
[5] *Compt. rend.*, **60**, 728 (1865).
[6] *Ann. Chim. Phys.* (3), **20**, 373 (1847).

vapour density of this substance diminishes with rise of temperature, becoming constant, however, above 300°, with a value half as great as that calculated for the formula PCl_5.

Deville[1] called attention to the fact that the vapour has the peculiar colour of chlorine, and that the depth of colour increases as the temperature rises. He pointed out that the phenomena could be best explained by the assumption that the pentachloride undergoes dissociation into the trichloride and chlorine.

The correctness of the explanation was confirmed by Wanklyn and Robinson,[2] who, by the simple arrangement shown in Fig. 18, effected a partial separation of the components of phosphorus pentachloride and also of sulphuric acid without the aid of a porous diaphragm. Sulphuric acid or phosphorus pentachloride was heated in the bulb A, and a current of air was passed through B. The residue in A was found to contain an excess of SO_3 and of PCl_3 respectively.

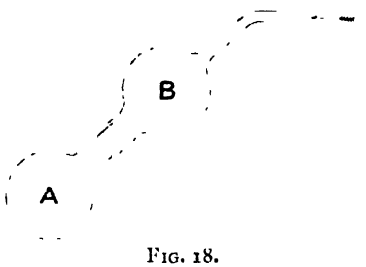


FIG. 18.

Wurtz[3] also made the important discovery that in presence of an excess of phosphorus trichloride the pentachloride is more stable, and by determining the vapour densities of mixtures of the two chlorides in known proportions he was able to show that the dissociation of the pentachloride could be entirely prevented by employing a sufficiently large excess of the trichloride.

The dissociation of hydrogen iodide and the combination of hydrogen and iodine have been very thoroughly studied by Lemoine ("Études sur les équilibres chimiques," p. 72 [1881]), who showed that, under any given conditions of temperature and pressure, the final state of equilibrium ($H_2 + I_2 \rightleftarrows 2HI$) is the same, whether the change that takes place is the partial combination of equivalent quantities of hydrogen and iodine or the partial dissociation of hydrogen iodide (Fig. 19).

Lemoine observed that the rate of change is much greater at high than at low temperatures; thus, starting with hydrogen and iodine, he found that at 440° equilibrium was attained in about an hour, at 350° after several days, and at 260° only after several

[1] *Compt. rend.*, **62**, 1158 (1866). [2] *Annalen*, **127**, 110 (1873).
[3] *Compt. rend.*, **76**, 601 (1873).

months. The rate of combination was also increased by raising the pressure. More rapid combination was also brought about by the presence of spongy platinum, but in this case the amount of combination when equilibrium was established was not increased.

The influence of temperature and of pressure on the amount of dissociation or combination was carefully studied, and it was found—the experiments being always continued until equilibrium was finally attained—that the amount of dissociation was increased, or the amount of combination diminished, (*a*) by rise of temperature under constant pressure, (*b*) by diminution of pressure at constant temperature. Similar results have more recently been obtained by Bodenstein.[1]

Lastly, it was found by Lemoine that the stability of hydrogen iodide is increased by the presence of an excess of either component.

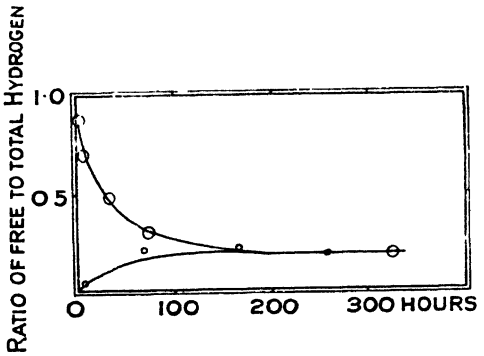


FIG. 19.

Thus at 440° and under a pressure of 0·9 atmos., the following results were obtained :—

Composition of mixture.	Ratio of combined to total iodine.
1 equivalent H + 1 equivalent I	0·74
2 equivalents H + 1 „ I	0·84
3 „ H + 1 „ I	0·87
4 „ H + 1 „ I	0·88

The effect of alteration of temperature and of pressure on the vapour density of iodine has been thoroughly investigated by Meier and Crafts,[2] who give their results in the form of a diagram (Fig. 20).

[1] *Ber.*, **26**, 2603 (1893); *Zeit. physik. Chem.*, **22**, 1 (1897).
[2] *Compt. rend.*, **92**, 39 (1881).

It will be seen that at constant pressure the vapour density remains constant at 8·8 (air = 1) up to about 700°, then diminishes, slowly at first, afterwards more rapidly, and finally slowly until, at the lowest pressure at any rate, it again becomes constant at 4·4. At constant temperature (between, say, 700° and 1500°) the vapour density is diminished by lowering the pressure. These results are precisely such as are obtained with a substance which undergoes dissociation, and as the higher density corresponds to the formula I_2

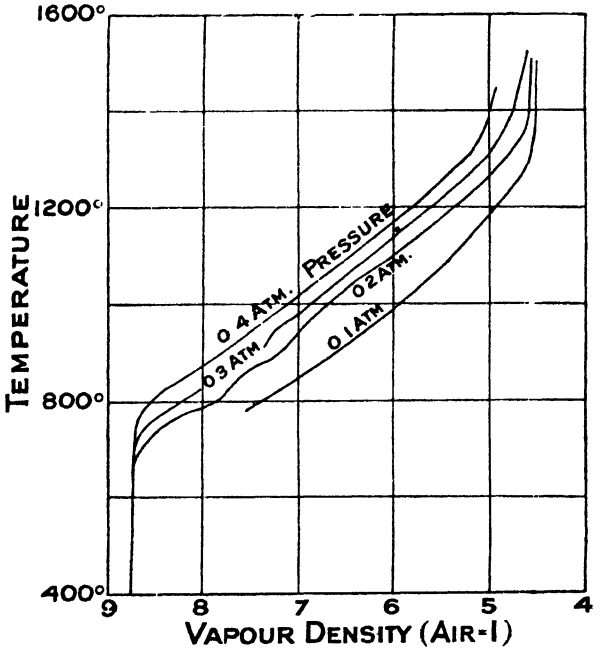


FIG. 20.

and the lower density to the formula I, it is assumed that the changes are represented by the equation $I_2 \rightleftarrows I + I$.

Similar results have been obtained by Deville and Troost [1] and by E. and L. Natanson [2] with nitrogen peroxide, and by Ramsay and Young [3] with acetic acid, and in all probability dissociation takes place in these cases in accordance with the equations—

$$N_2O_4 \rightleftarrows 2NO_2$$
$$(C_2H_4O_2)_2 \rightleftarrows 2C_2H_4O_2.$$

[1] *Compt. rend.*, **64**, 237 (1867). [2] *Wied. Ann.*, **27**, 606 (1886).
[3] *Trans. Chem. Soc.*, **49**, 790 (1886).

The dissociation of iodine, nitrogen peroxide, and acetic acid differs from that of hydrogen iodide in two respects: (1) the final state of equilibrium is reached with great rapidity; (2) the products of dissociation are alike, thus $I + I$, $NO_2 + NO_2$, whereas with hydrogen iodide they are different, $H_2 + I_2$. For this reason it is, of course, impossible to have an excess of either component.

In the case of nitrogen peroxide the change of density is accompanied by a change of colour. Thus, at a low temperature, say $-20°$ C., nitrogen peroxide is colourless, or nearly so; at 0° C. the colour is yellow, and as the temperature rises it changes to orange, orange red, and finally red-brown, reaching its greatest intensity at 140°, the temperature at which the change from N_2O_4 to $2NO_2$ is complete. If the temperature is raised still higher the intensity of the colour again diminishes, slowly at first, then rapidly, and at last slowly again, and at about 600° the gas is quite colourless. On cooling, the colour reappears, and becomes most intense again at 140°.

This further change has been investigated by Richardson,[1] who showed that the NO_2 molecules are dissociated into molecules of nitric oxide and oxygen, thus—

$$2NO_2 \rightleftarrows 2NO + O_2.$$

In this case two molecules of the peroxide give three molecules of the mixed gases, and the densities are in the ratio of 3 : 2.

The dissociation of nitrogen peroxide and of sulphuric acid has been investigated by Bodenstein and Katayama,[2] who made use of a spiral silica manometer of the aneroid type, similar to that devised by Johnson.[3] The temperature range for sulphuric acid was from 325° to 477°, and for nitrogen peroxide 20° to 701°. A similar method was employed by Preuner [4] in an investigation of the dissociation at high temperatures of hydrogen sulphide and the vapours of sulphur, selenium, arsenic, and phosphorus.

It has been shown, chiefly by H. B. Baker and his co-workers, that many chemical changes will not take place in absence of moisture, and that several compounds which, under ordinary conditions, dissociate when vaporized, become far more stable when very thoroughly

[1] *Trans. Chem. Soc.*, 51, 397 (1887).

[2] *Zeit. Elektrochem.*, 15, 244 (1902).

[3] *Zeit. physik. Chem.*, 61, 4, 457 (1908).

[4] *Zeit. anorg. Chem.*, 55, 279 (1907), *Zeit. physik. Chem.*, 68, 129 (1909); *ibid.*, 81, 129 (1912).

dried. For example, nitrous anhydride when prepared in the ordinary manner is an indigo-blue liquid at, say, – 20°. On warming the liquid the colour becomes duller, and ebullition takes place freely at about 4° with complete dissociation into nitric oxide and nitrogen peroxide. H. B. Baker and M. Baker [1] have shown, however, that when very carefully dried, it can be vaporized without decomposition. The boiling point of the dried anhydride is 42·5° or 43°, and vapour densities as high as 62 were observed, that calculated for N_2O_3 being 38 and for N_4O_{10}, 76. Moreover, after five years' contact with phosphoric anhydride, the liquid retained its bright blue colour at the ordinary temperature.

Nitrogen peroxide was also evidently rendered far more stable by thorough drying, for while the boiling point of the freshly prepared peroxide is 22°, that of the carefully dried liquid was higher than 69°, but the quantity available was insufficient to admit of an exact determination.

Again, Baker [2] finds that ammonium chloride, when thoroughly dried, vaporizes without decomposition. Johnson [3] states that the vapour pressure of the dry stable substance is identical with that of the salt when sufficiently moist to dissociate.

[1] *Trans. Chem. Soc.*, **91**, 1862 (1907); **101**, 2339 (1912).
[2] *Ibid.*, **65**, 611 (1894). [3] *Zeit. physik. Chem.*, **61**, 45 (1908).

CHAPTER VIII.

THE PROPERTIES OF LIQUIDS.

Liquefaction.—The relations between the temperature, pressure, and volume of carbon dioxide were first carefully studied by Andrews,[1] who illustrated his results by means of the diagram which is reproduced in Fig. 21, pressures being measured as ordinates, and volumes as abscissæ.

Consider first the gas under the conditions of temperature, pressure, and volume represented by A. When the volume is diminished by compression at the constant temperature 13·1°, the pressure rises steadily until it reaches a definite value, indicated, together with the corresponding volume, by the point B. It then ceases to rise, but the volume continues to diminish, and liquefaction gradually takes place. The volume of vapour diminishes rapidly, while that of the liquid formed by its condensation increases slowly, until the whole of the vapour is converted into liquid. The change of volume is indicated by the horizontal line BC, the pressure being constant. Afterwards, as shown by the line CD, the pressure increases rapidly, while the volume of liquid diminishes very slowly.

At 21·5° the changes are similar to those at 13·1°, but the constant pressure under which liquefaction occurs is higher, the volume of gas is smaller when liquefaction begins, and the volume of liquid is greater when it is complete. The liquid is also more compressible.

At 31·1° the curve is continuous, and is not quite horizontal in any part of its course. At this temperature no separation of liquid is seen to occur. At 32·5° the flattening of the curve is less marked; it is still noticeable at 35·5°, but at 48·1° it is too slight to be seen in the diagram.

Andrews showed that above a certain temperature, which he called the critical temperature, ordinary liquefaction cannot occur. Under low pressures the carbon dioxide is certainly gaseous; under very high pressures it possesses some of the properties of a liquid, but

[1] *Phil. Trans.*, pt. ii., p. 575 (1869).

the passage from the one state to the other, if it can be said to occur at all, is continuous. He gives this temperature as 30·92°.

The dotted lines in the upper left-hand side of the diagram show what the position of the isothermals for 48·1°, 31·1°, and 13·1°, respectively, would be if the behaviour of carbon dioxide, as regards Boyle's and Gay Lussac's laws, were similar to that of air.

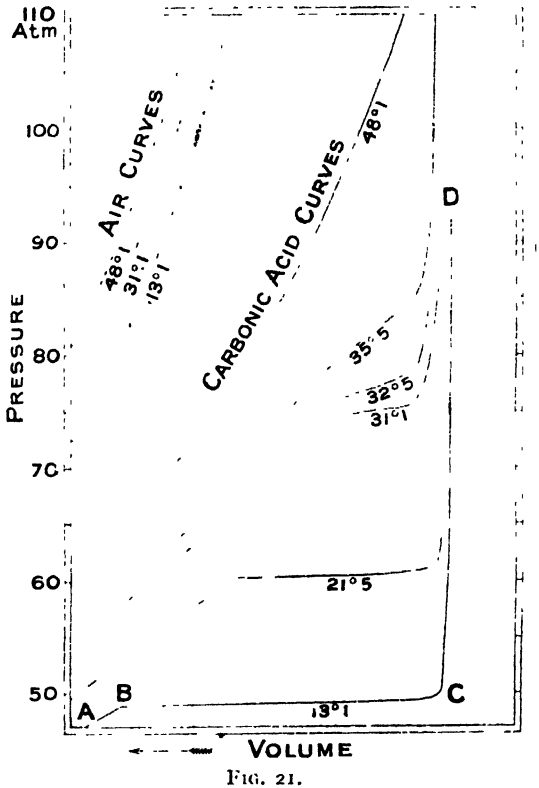


FIG. 21.

Vapour Pressure.—Below 30·92° there is, for any given temperature t, a definite pressure p—the vapour pressure—under which liquefaction of carbon dioxide occurs; a definite volume (for a given mass of carbon dioxide) v_V—the volume of saturated vapour—at which liquefaction commences; and a definite volume v_L—that of the condensed liquid—at which it is complete. If at the same temperature t, starting with compressed liquid, the process is reversed, evaporation begins when the pressure falls to p, the volume of liquid being v_L, and is complete when the volume is v_V.

In Fig. 7, p. 22, where the values of pv observed by Amagat are plotted against the pressures, the process of liquefaction is also illustrated, the vertical portions of the isothermals at and below 30° indicating constancy of pressure with change of pv between definite limits.

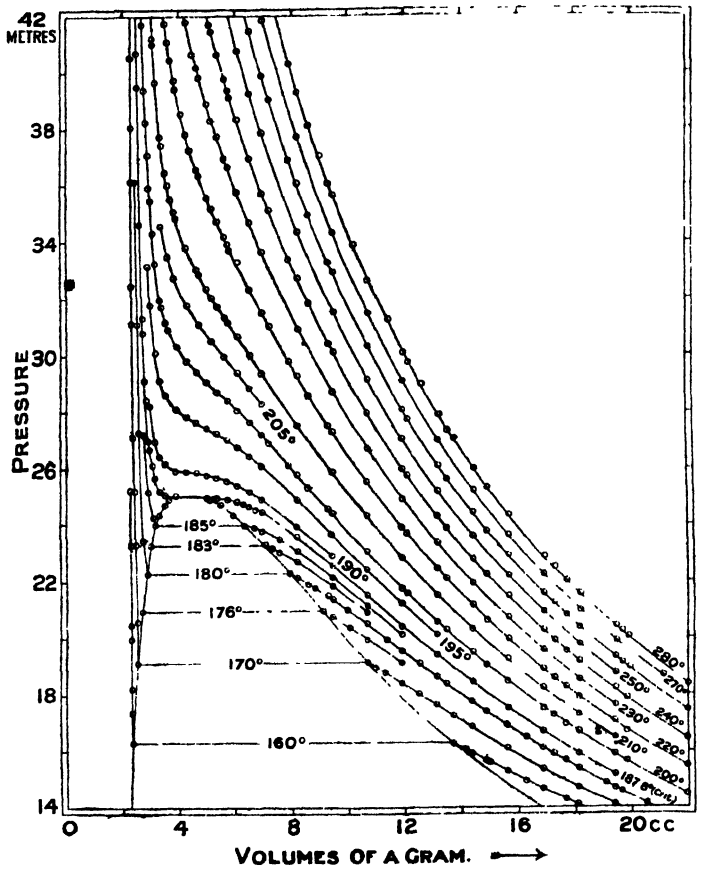


FIG. 22.

In the "Andrews" diagram it will be noticed that the 13·1° isothermal between B and C is not perfectly horizontal, but that it slopes very gently upwards and is rounded off at C, and these peculiarities are even more noticeable at 21·5°. The corresponding portions of the isothermals (0° to 30°) in Amagat's diagram are made perfectly vertical, and in Fig. 22, in which the volumes of a gram of isopentane are mapped against the pressures, the experimental

observations being represented by small circles, it will be seen that there is no sign whatever of a rise of pressure during the process of liquefaction. The gradual change in the form of the isothermals is also more fully shown than in Andrews's diagram for carbon dioxide. Andrews explained this slight rise and final rounding off of the isothermals by the fact that he was unable to remove the last traces of air from his carbon dioxide. During the process of liquefaction the greater part of this air remained undissolved, the pressure rising slowly owing to its gradual compression, and it was only by raising the pressure considerably that the last bubble of air could be got into solution. Amagat succeeded in obtaining practically pure carbon dioxide, and the rise of pressure during condensation was in his case negligible.

The critical point of pure carbon dioxide, as observed by Amagat, is 31·35°.

The vapour pressures of carbon dioxide and the volumes of saturated vapour and liquid observed by Amagat at a few temperatures are given below.

Temperature	Vapour Pressure in Atmospheres.	Volumes of a Gram of	
		Liquid.	Saturated Vapour.
0°	34·3	1·094	10·4
10	41·2	1·168	7·52
20	56·3	1·305	5·26
30	70·7	1·672	2·99
31·25	72·8	2·012	2·37

It will be seen that the vapour pressure of carbon dioxide increases more and more rapidly with rise of temperature, and a similar dependence of vapour pressure on temperature is observed with all liquids. At a given temperature, however, the vapour pressures of different substances may differ widely, as will be seen from the following table :—

	Vapour pressure at 0° in mm.
Carbon dioxide	26070·0
SO_2	1165·0
Ethyl ether	184·9
Water	4·6
Mercury	0·0002

It has been stated that Andrews explained the rise of pressure

which he observed during the condensation of carbon dioxide by the presence of a very small amount of air in the gas. He stated his belief that if the carbon dioxide had been quite pure, no such rise of pressure would have been observed. The opinion expressed by Andrews has generally been accepted as correct, but some experimenters, notably Battelli, have observed a similar rise of pressure during the condensation of vapours, and have refused to admit that the rise could be due to the presence of air or other impurity, or to experimental error. They believe, on the contrary, that the vapour pressure depends on the relative volumes of liquid and vapour.

It has been shown, however,[1] that it is only when great care is taken to ensure absence of air or other impurities, and when other errors are very carefully avoided, that trustworthy results can be obtained. The various sources of error are discussed, and it is shown that their influence is greater (*a*) at high temperatures than at low ones, and (*b*) during condensation than during evaporation. Under the best conditions the vapour pressure was found to be quite independent of the volume. For example, in 152 determinations of the vapour pressures of various hydrocarbons at temperatures up to 180°, instead of a fall in pressure being observed during partial evaporation of the liquid, there was on the average an apparent rise of 0·001 per cent., due, no doubt, to slight errors of experiment. In 493 determinations of the vapour pressures of twenty-one different stable substances at all temperatures (up to 310° in one case), the mean fall in pressure during partial evaporation was only 0·037 per cent., which is quite within the limits of probable experimental error.

Moreover, if Battelli's contention were correct, it would, of course, make no difference in what manner the alteration in the relative volumes of vapour and liquid was brought about, whether by condensation, by evaporation, or by removal of part of the liquid or vapour. For example, imagine a barometer tube of the form shown in Fig. 23. Let there be a short column of a pure liquid over the mercury, but below the stopcock, the whole space above the mercury containing nothing but the pure liquid and its vapour; and let the temperature be kept constant by means of a suitable bath. Let the height of the mercury be first read with the stopcock open, when the volume of vapour is very large relatively to that of the liquid. Then let the stopcock be closed, so as to shut off the bulb. The volume

[1] Young, *Journ. de Chim. phys.*, 4, 425 (1906).

of vapour will now be relatively small, and, according to Battelli, the vapour pressure should therefore be higher. A depression of the mercury should in that case be observed. Thus by alternately opening and shutting the stopcock, the mercury would alternately rise and fall, and work might be done; moreover, this work would bear no relation to the energy, if any, expended in opening and shutting the stopcock. It may safely be stated that such a result would not be obtained, and that the vapour pressure of a pure substance at constant temperature is independent of the relative volumes of liquid and vapour.

All pure stable substances behave alike in so far that the vapour

Fig. 23.

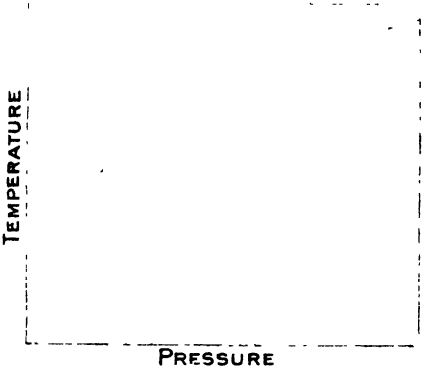


Fig. 24.

pressure increases more and more rapidly with rise of temperature. If the pressures are plotted against the temperatures, a curve like that in Fig. 24 is obtained. The upper limit of this curve is the critical point; the lower limit would be the freezing point of the liquid if this, like the melting point of a solid, were a fixed point; in practice, however, most substances may remain liquid several degrees, some substances many degrees, below their freezing points if carefully cooled, and the vapour pressures of liquids in this unstable or *metastable* condition may be determined.

Many attempts have been made to discover a general relation between temperature and vapour pressure. The formulæ which have been proposed are discussed in the volume on Thermodynamics, and it will be sufficient here to point out that, for purposes of

calculation and interpolation, it is frequently convenient to employ an empirical formula such as that suggested by Biot—

$$\log p = a + ba^t + c\beta^t.$$

The constants a, b, c, a, and β may best be calculated from the observed—or graphically smoothed—vapour pressures at five equidistant temperatures, and the pressures at any intermediate temperatures may then be calculated by means of the formula. Such empirical formulæ cannot, however, as a rule, be safely employed for purposes of extrapolation far beyond the limits between which the actual experiments extend.[1]

It is frequently requisite to ascertain the rate of increase of vapour pressure with rise of temperature, $\frac{dp}{dt}$. This might be done graphically by drawing a tangent to the curve (Fig. 24) at the required temperature, but it is better, when great accuracy is desired, to calculate the pressure by means of Biot's formula 0·1° above and 0·1° below the required temperature, when $5\,(p_{t+0.1} - p_{t-0.1}) = \frac{dp}{dt}$.

But the values of $\frac{dp}{dt}$ may be calculated with the greatest accuracy by means of the formula—

$$\frac{dp}{dt} = 5{\cdot}3019p(b\,.\log a\,.\,a^t + c\,.\log\beta\,.\,\beta^t).$$

It has been pointed out by J. E. Mills (*loc. cit.*) that in the neighbourhood of the critical point there is a slight change in the trend of the vapour-pressure curve which cannot be reproduced by Biot's formula. This change is so slight that the difference between the actual pressures and those given by the formula are not of serious importance, but, on the other hand, the difference between the real and calculated values of $\frac{dp}{dt}$ may be considerable.

Mills, however, has pointed out that the value of $\frac{dp}{dt}$ at the critical temperature may be arrived at independently of the vapour pressures at lower temperatures, and he has made the remarkable observation[2] that at this temperature $\frac{dp}{dt} = \frac{2R}{V_c}$, where R is the ordinary gas con-

[1] J. E. Mills, *Journ. Phys Chem.*, **9**, 402 (1905).
[2] *Cf.* Dieterici, *Ann. d. Physik*, **12**, 144 (1903).

stant in the formula for a perfect gas, $PV = RT$, and V_c is the critical molecular volume. That is to say, at the critical temperature the value of $\frac{dp}{dt}$ is exactly twice what it would be for the substance as a perfect gas occupying the same volume.

Determination of Vapour Pressure.—The vapour pressures of a liquid at temperatures below its ordinary boiling point may be determined by placing a little of the liquid in a barometer tube so that it rests on the surface of the mercury (Fig. 25). Some of the liquid at once evaporates, and the pressure exerted by the vapour causes the mercury to fall a certain distance which depends on the temperature and on the liquid introduced. If a second barometer tube be placed in the same trough of mercury, the difference between the heights of the two columns of mercury—each of them corrected to 0 C.—is proportional to the vapour pressure, and it is usual to express this pressure directly in millimetres—or centimetres—of mercury.

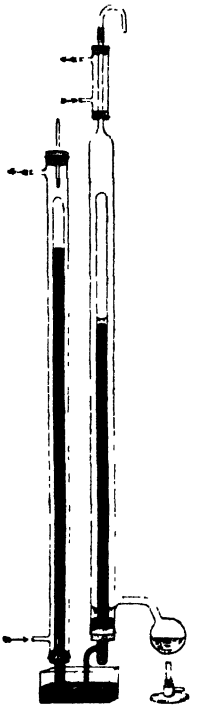


FIG. 25.

To obtain an accurate result it is obvious that the liquid must be pure, and also that air must not be introduced with it. But it is probable that all liquids are capable of dissolving a small amount of air, and this dissolved air can only be removed by boiling. Also in filling a barometer tube the mercury must be boiled, so as to remove not only the dissolved gas, but also that adhering to the walls of the tube.

For the determination of vapour pressure, a tube of the form shown in the diagrams (Figs. 25 and 26) may be employed. It is first held with the open end upwards, and nearly filled with mercury, and it is then connected with an air-pump and exhausted. The mercury is then heated with a Bunsen burner until it boils freely, beginning at the bottom of the tube so as to drive bubbles of gas gradually up the tube. After this process is complete, the tube is disconnected from the pump, and about a cubic centimetre of the pure liquid is introduced. The tube is again exhausted, and the

liquid is boiled gently for some time to expel all dissolved air, and, while still boiling, mercury is admitted, the tube being placed in such a position that the liquid rises into the closed end of the tube near the junction. Disconnecting from the pump, the tube, the open end of which is closed by a finger, is inverted in such a manner that the liquid flows past the mercury to the other end, and the tube is then placed in the trough of mercury, and the finger removed. If air has been satisfactorily removed, the liquid should remain adhering to the top of the tube and to the mercury until the tube has been heated or vigorously tapped.

The tube may conveniently be heated to a constant known temperature by means of the jacketing apparatus shown in Figs. 25 and 11. By reducing the pressure in the jacketing apparatus the temperature of the vapour may be lowered, and thus a series of readings of vapour pressure at different temperatures may be taken with a single liquid in the bulb.

Fig. 26.

For the determination of vapour pressure at temperatures higher than the ordinary boiling point, an apparatus similar in principle to that employed by Andrews in his researches on carbon dioxide is the most suitable.

The apparatus, which may also be employed for the determination of the specific volumes of liquids and saturated vapours, and of the compressibilities of liquids, vapours, or gases, is shown in Fig. 27. It consists of a long wrought-iron or steel tube, with three shorter tubes at right angles to it. The long tube is securely fixed in a horizontal position, the branches being vertical. One end of the horizontal tube is closed, the other end is fitted with a thick steel ring A and perforated screw B, through both of which passes a steel plunger C. The space between the ring and the screw serves as a stuffing box to prevent leakage. It may be filled with the wick of a common tallow candle from which most of the outer part of the tallow has been removed, and which may be wound round the plunger before the screw is inserted. The other extremity of the plunger is cut as a screw, and passes through the nut D, which is rigidly fixed to the same stand as the iron tube. The screw can be turned by means of the circular handle E, and the capacity of the iron vessel thus increased or diminished. Each of the vertical branches, like the horizontal tube, is provided with a steel ring and perforated screw, and through each screw and ring passes a thick-walled

glass tube of about 1·5 mm. internal diameter, kept in position by an enlargement which presses against a leather washer fitting the bottom of the screw. Each stuffing box contains, instead of a candle-wick, a well-greased, perforated, cylindrical india-rubber stopper, which rests on a greased leather washer fitting the upper side of the steel ring. The glass tubes are closed above, but

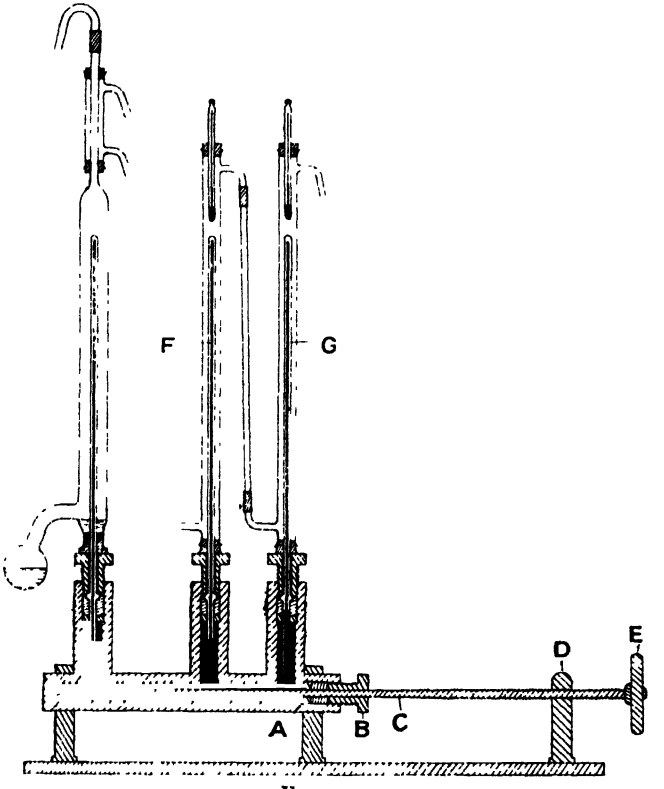


FIG. 27.

open below; they are all graduated in millimetres and carefully calibrated; two of them serve as air manometers. The internal diameter of one of them, F, which serves for the measurement of moderate pressures, is the same throughout; that of the lower end of the other, G, which is intended for high pressures, is much greater, so that this tube is provided with a reservoir of relatively great capacity. The third or "experimental" tube contains the liquid under investigation, and is usually similar to the simpler manometer.

The iron apparatus is filled with pure mercury when the plunger is drawn out as far as possible, and the manometers, containing dry air free from carbon dioxide, are then inserted. The manometers are kept at a known and nearly constant temperature by a current of cold water.

If the total capacity v_0 of a manometer were known, and also the absolute temperature T_0 and pressure p_0 of the air when the manometer was inserted in the iron apparatus, the pressure corresponding to any reading of the volume and temperature of the air—correcting for the deviations from Boyle's law—would be given by the formula—

$$\frac{pv}{T} = \frac{p_0 v_0}{T_0}$$

$$\text{or } p = \frac{p_0 v_0}{T_0} \times \frac{T}{v}$$

$$= \frac{T}{v} c.$$

But in practice it is better to ascertain the constant c for the low

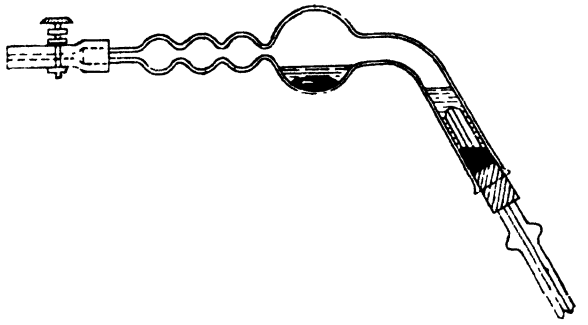


FIG. 28.

pressure manometer by comparison with a direct column of mercury in a very long tube placed temporarily in the third side tube. This side tube may then be closed by a glass rod, and the constant for the high-pressure manometer ascertained by taking readings simultaneously on both manometers.

It is absolutely necessary that the liquid in the experimental tube should be pure and free from air. The tube is filled in the following manner: A little pure dry mercury is first placed in the bulb apparatus (Fig. 28), and while the pure liquid is being distilled—over phosphoric anhydride, if possible—the distillate is collected directly in the bulb. The experimental tube is then placed in the bulb

apparatus in the manner shown in the diagram. The bulb apparatus and tube are exhausted by a pump, the clip is closed, and the apparatus removed from the pump.

By alternately warming and cooling the experimental tube some liquid is caused to flow into it, and this liquid is vigorously boiled away. The process is repeated several times to remove all air from the tube. Liquid is then allowed to enter until it nearly fills the tube, and it is then carefully boiled away from above downwards until the required amount is left. The tube is then tilted up so that mercury enters and completely fills the remainder of the tube. The mercury should give a clear metallic sound on meeting the liquid, and condensation of the vapour should be instantaneous, otherwise air has not been completely removed. The tube is then allowed to cool, and is inserted in the iron apparatus, great care being taken to prevent the entry of air at the moment that the open end of the tube is plunged under the mercury.

The experimental tube is heated in the same manner as the barometer tube (Fig. 25), and readings of pressure—preferably with the liquid and vapour occupying a series of different volumes at each temperature—are taken.

The pressure, calculated by the formula $p = c\frac{T}{v}$, must be corrected (1) for the difference in level of the mercury in the experimental tube and manometer, (2) for the pressure of the column of unvaporized liquid, (3) for the expansion of the heated column of mercury, (4) if necessary, for capillarity, (5) for the deviation of air (in the manometer) from Boyle's law, as determined by Amagat.

No correction for the vapour pressure of mercury should be applied, because evaporation through a long column of liquid is an exceedingly slow process.

If, when the volume is reduced, the last bubble of vapour cannot be condensed without noticeable rise of pressure, it may safely be concluded that air has not been completely removed. In that case the results must be rejected, and the experimental tube taken down, emptied, cleaned, dried, and refilled, and the determinations repeated.

More accurate results are obtained by taking readings at a series of increasing than of diminishing volumes.

For substances such as carbon tetrachloride, which attack mercury at high temperatures, the experimental tube may be modified

in such a manner that the mercury is not heated.[1] The method of calculation is, however, more troublesome.

The Boiling Point of a Pure Liquid.—Consider a sealed tube containing a pure liquid and its vapour, but no air or other gas. If the whole tube is at a temperature t, the vapour of the liquid will exert a definite pressure p. If the tube be heated to a higher temperature t', evaporation will take place until the vapour pressure has risen to p', that corresponding to the new temperature. If air were present in the tube, evaporation would take place more slowly, because time would be required for the vapour to diffuse through the air, but eventually the partial pressures of the vapour would be p and p', respectively, at the two temperatures, while the total gaseous pressure in the tube would be greater on account of the air.

Consider next an open, long-necked flask containing a pure liquid heated below by a flame. The temperature will rise and evaporation will take place, so that the partial pressure of the vapour in the flask will increase, while that of the air will diminish, the total pressure remaining equal to that of the atmosphere. Some of the vapour, coming in contact with the cool walls of the vessel, will give up heat and be condensed again, and thus the walls will be warmed. As the temperature continues to rise evaporation will increase, until at last the liquid will boil and vapour will be evolved with great rapidity. In a vessel of this form the vapour from the boiling liquid will drive the air before it, diffusion being too slow to enable air from outside to enter the flask, and the upper surface of the liquid will eventually be in contact with its vapour only.

When the liquid boils, the pressure of the vapour in the flask is equal to that of the atmosphere outside, but the term "boiling point" is somewhat ambiguous, for it is not the temperature reached by the liquid when ebullition takes place, nor that of the freely boiling liquid. In order that a bubble may be formed at the bottom of the liquid, where the heat is applied, it is clear that in addition to the pressure of the vapour in the flask, that of the column of liquid must be overcome. Also the cohesion of the liquid and its adhesion to the walls of the vessel must be overcome, and if the vessel be clean and smooth, and the liquid free from dissolved air, a bubble may not form until the temperature has risen very considerably—in other words, until the liquid has become considerably *superheated*. When a bubble is at last formed it may expand with explosive

[1] Young, *Trans. Chem. Soc.*, 59, 911 (1891).

rapidity, and there will be a sudden burst of vapour; at the same time the temperature will suddenly fall towards the point at which it would remain stationary if ebullition were to take place regularly and freely. Failing the formation of fresh bubbles, the temperature will rise again until explosive ebullition again takes place. The liquid in this state is said to boil with *bumping*. Clearly, then, its temperature does not depend on the pressure only, but also on the facility with which bubbles are formed.

The vapour which escapes from a superheated liquid may itself be superheated at first, but as it rises and gives up heat to the walls of the vessel, its temperature falls until condensation begins to take place. Now, the temperature of condensation—except in special circumstances and in absence of liquid—is found to depend only on the pressure, and to be identical with what in the language of science is termed the *boiling point*.

In practice, therefore, the boiling point is measured, not by placing a thermometer in the liquid, but in the vapour well above it. When, however, the liquid bumps violently, the rush of superheated vapour may be so great that the temperature does not fall to the condensing point before reaching the thermometer, and the temperature is then observed to fluctuate more or less violently.

In order to prevent a liquid from bumping, bits of platinum wire, small tetrahedra of silver or platinum, or small pieces of porous material, such as fragments of pumice stone or of a broken clay pipe, may be placed in the liquid, or a very slow current of air may be passed into it through a capillary tube. If, however, the latter method is adopted, an error is necessarily introduced, for the true boiling point of a liquid depends on the pressure of its vapour, and not necessarily on the total gaseous pressure to which it is exposed. If an indifferent gas—that is to say, a gas which has no chemical action on the liquid—is present, the total pressure remains the same, but the pressure of the vapour is reduced, and the boiling point must therefore be lower.

That this is really the case may easily be proved by a simple experiment. An air-bath, provided with a regulator for admission of air and with two holes for the insertion of thermometers, is heated to about 200°, the temperature being registered by a thermometer. The second thermometer is fitted with a grooved cork, so that when placed in the bath a passage may be left for escape of air or steam; its bulb is well covered with cotton-wool, and is immersed in

boiling water. The thermometer is transferred as rapidly as possible from the boiling water to the heated bath, when the temperature is seen to fall very quickly from about 100° to 60° or 70°. If the air regulator be now closed the temperature will slowly rise, but will fall again when more air is admitted. Finally, if steam be passed rapidly into the bath the temperature will rise to nearly 100°, but will fall again if the current of steam be stopped. From these changes it is clear that the temperature of the water on the cotton-wool does not depend on that of the bath, nor on the atmospheric pressure, but on the relative amount of aqueous vapour in the air in contact with the water—that is to say, on the partial pressure of the steam.

In the case of the wet and dry bulb hygrometer, the reason why the temperature of the wet bulb usually falls below that of the dry bulb, is that the boiling point of water under a pressure equal to the partial pressure of the moisture in the air is lower than the actual temperature of the air as registered by the dry bulb. This is usually expressed by saying that the air is not saturated with moisture.

When a drop of water is placed on a red-hot piece of platinum foil and assumes the spheroidal state, its temperature is found not to rise to 100°, and the reason for this may be that the drop of water is not surrounded by pure steam, but by a mixture of steam and air.

Again, if a large flat dish, such as a frying-pan, be nearly filled with water and strongly heated from below, it is not easy to make the water boil, because air from the sides readily mixes with the steam, and so reduces its partial pressure considerably below the atmospheric pressure.

From what has been stated it is evident that the "boiling point" of a liquid can under no conditions be the temperature at which the liquid "boils," or is in a state of ebullition, because a bubble must be formed below the surface, and, even if ebullition takes place with perfect freedom, the pressure on the vapour in the bubble must be greater than that of the atmosphere. On the other hand, the boiling point of a liquid may be determined by reading its temperature, when the conditions are such that the liquid cannot boil in the ordinary sense of the word. The necessary conditions are that the liquid shall have a perfectly free surface for evaporation, and that the heat shall be applied from outside the free surface. A method based on these considerations, and devised by Ramsay and Young,[1]

[1] *Phil. Trans.*, 175, 37 (1884).

is specially suitable for the determination of boiling points under greatly reduced pressures, and it is under very low pressures that bumping is most liable to occur when a liquid is boiled in the ordinary way.

The apparatus (Fig. 29) consists of a wide vertical glass tube A, closed below, to which a side tube B is fused near the top. The side tube is connected with a bulb C, which may be cooled by water or a freezing mixture, and from the bulb passes a second tube D,

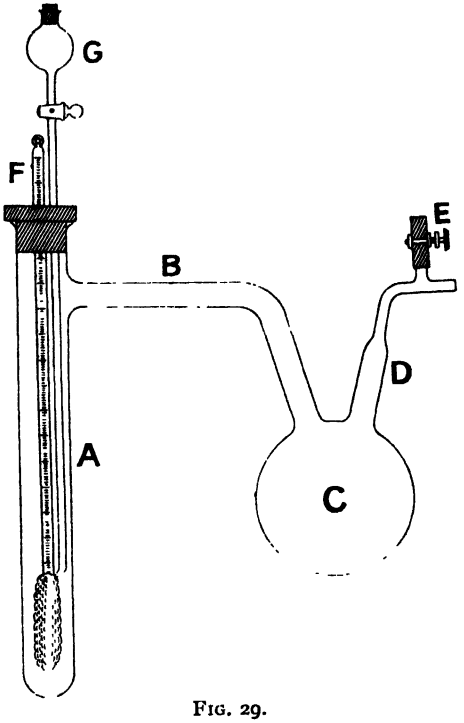


FIG. 29.

which is connected with an air-pump and gauge to measure the internal pressure. A small tube, closed by an india-rubber tube and clip E, serves to admit air into the apparatus. The vertical tube is closed above by an india-rubber stopper perforated with two holes, through one of which passes a thermometer F, and through the other a glass tube provided with a stopcock and reservoir G, above. The bulb of the thermometer is covered with cotton-wool, and the lower extremity of the glass tube is drawn out and bent round so that the narrow end just touches the cotton-wool.

The liquid to be investigated is placed in the reservoir, and the apparatus is exhausted. A little liquid is then admitted so as to moisten the cotton-wool. The condensing bulb is then cooled, and the vertical tube is heated by means of a water or oil-bath, which should always be kept at a temperature at least 20° higher than that registered by the thermometer.

The liquid on the cotton-wool evaporates rapidly and displaces the air in the lower part of the vertical tube, so that the remaining liquid is soon surrounded by vapour quite free from air. Under these conditions the liquid soon reaches its true boiling point, but it cannot become superheated since evaporation takes place with perfect freedom, and, of course, ebullition is impossible. The temperature and pressure are read, and a small quantity of air is then admitted to raise the pressure, when the temperature rises at once, and soon becomes constant again at the boiling point under the higher pressure. Or, of course, the pressure may be reduced by pumping, when the temperature falls. Fresh quantities of liquid are added from time to time in small quantities from the reservoir. A large number of readings can thus be taken in an hour or two, and the reduction of pressure can be carried to any desired extent.

For pressures above about 500 mm. the boiling points are best determined in the ordinary way, the thermometer being placed in the vapour and not in the liquid. This method was employed by Regnault for the determination of boiling points under very high pressures, closed iron vessels being substituted for the ordinary glass apparatus. Errors due to bumping or to superheating of the vapour when the quantity of liquid is very small may be almost completely obviated by covering the bulb of the thermometer with a very little cotton-wool, so as to keep it always moist. The whole of the mercury—not only in the bulb, but also in the stem of the thermometer—should be heated by the vapour so as to avoid the somewhat uncertain correction for the cool portion.

Definition of the Term "Boiling Point".—The scientific term *boiling point* may be defined as the highest temperature attainable by a liquid under a given pressure of its own vapour, when evaporating with a perfectly free surface, and when the heat reaches the surface from without. It is identical with the condensing point of the pure vapour in contact with liquid under the same pressure.

If the boiling points of a pure liquid are determined under a series of pressures, and the temperatures are plotted against the

pressures, a curve is obtained which is identical with the vapour-pressure curve for the same substance. In other words, the vapour pressures or boiling points of a liquid may be determined either by the *statical* methods described under the heading "Vapour pressure," or by the *dynamical* methods described under the heading "Boiling point". That the vapour pressure of a pure liquid at a given temperature is equal to the pressure under which the liquid boils at that temperature (or, more correctly, under which the vapour from the boiling liquid has that temperature) may readily be demonstrated by means of the apparatus (Fig. 25) employed for the determination of vapour pressures. If some of the same liquid be placed in the barometer tube and in the bulb of the jacketing apparatus, it will be found that when the liquid is boiling under any pressure, the heated barometer and the gauge—correcting, of course, for the difference in temperature of the mercury columns—register the same pressure.

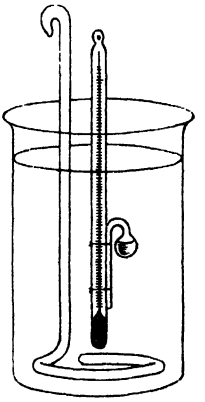


FIG. 30.

When the quantity of liquid available is small, the method of determining boiling points devised by Alex. Smith and A. W. C. Menzies[1] may be recommended. The arrangement is similar to that usually employed for the determination of melting points, but in place of the capillary tube closed at the bottom a tube from 3 to 4 cm. long, and not less than 1 mm. in width, with a small bulb at the closed end, is attached to the thermometer in the manner shown in Fig. 30. The bulb contains the liquid (or solid) under investigation, and the beaker may contain water, a strong solution of calcium chloride, sulphuric acid, melted paraffin wax, or, for temperatures above 220°, a eutectic mixture of potassium and sodium nitrates containing 45 per cent. of the potassium salt. The tube is attached to the thermometer with thread or asbestos cord, wire being apt to cause breakage.

The bath is heated and, when the boiling point of the substance is approached, is stirred vigorously. At first a few bubbles of air are expelled, but when the boiling point is reached the air remaining in the bulb is rapidly displaced by vapour which itself escapes rapidly and, if not soluble in the bath liquid, rises to the surface in bubbles.

[1] *Journ. Amer. Chem. Soc.*, **32**, 897, 905, 907 and 1448 (1910).

On removing the flame, a fall in temperature of a fraction of a degree interrupts the stream of bubbles sharply, and a re-elevation to the previous temperature restores it. The reading is taken when, with very slowly falling temperature, accompanied by vigorous stirring, the stream of bubbles ceases, and the process of slow heating and cooling is repeated until the readings become constant.

If the substance is soluble in the bath liquid the bubbles will not rise to the surface and are not so readily seen. In this case the temperature is taken when, on slow cooling, the bath liquid has ascended the capillary to a predetermined point.

The chief correction required is for the pressure of the column of bath liquid above the open end of the capillary or above the point to which the bath liquid is allowed to rise in the capillary as the case may be, and a table of specific gravities of four bath liquids at a series of temperatures is given in the original paper. Precautions for special accuracy and other small corrections are also fully discussed.

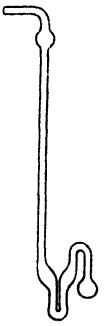


FIG. 31.

The method may be conveniently employed for the determination of the boiling points of liquids or the volatilizing points of solids under reduced pressures.

The same authors also describe a very convenient method for the determination of the vapour pressures of liquids and solids.[1] The apparatus, which is termed an isoteniscope, is shown in Fig. 31. The liquid or fusible solid to be investigated is placed in the small spherical bulb, about 20 mm. in diameter, and the U-tube, about 30 to 35 mm. in height, which acts as a gauge, contains a sufficient amount of the same liquid. [For the sake of compactness the spherical bulb is placed behind the U-tube and not in the same plane as shown in the diagram.] By suitable reduction of pressure any air between the U-tube and the bulb and also any air dissolved in the liquid is caused to bubble through the liquid in the U-tube, and this process may be carried on until the air is completely removed. The pressure is then adjusted until the liquid stands at the same height in the two limbs of the U-tube. The apparatus is very simple and effective, and the use of mercury, with the difficult correction for its vapour pressure, is avoided.

When the vapour pressure of a non-fusing solid is to be determined, the solid is introduced into the bulb before this is fused to

[1] *Journ. Amer. Chem. Soc.*, **32**, 1412 and 1541 (1910); **36**, 1363 (1914).

the U-tube, and a suitable liquid is placed in the U-tube. For moderate temperatures, mercury or melted paraffin wax may be used, and, for higher temperatures, fusible alloys or molten salts or mixtures of salts. Very vigorous stirring of the bath in which the isoteniscope is immersed is essential, and a suitable stirring arrangement is described. A platinum resistance thermometer is recommended for the measurement of temperature.

Relations between the Boiling Points of Different Substances.—When the boiling points of certain closely related substances—such as chlorobenzene and bromobenzene, ethyl bromide and ethyl iodide, or methyl acetate and ethyl acetate—are compared together under equal pressures,[1] the following simple relation is found to hold good. If T_A and T_B are the boiling points, on the absolute scale of temperature, of the two substances under a pressure p, and T_A' and T_B' their boiling points under another pressure p'—

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} = \text{constant.}$$

This relation, expressed in the form $t' = r + qt$, where t and t' are the boiling points (on the centigrade scale) of two liquids under the same pressure, and r and q are constants, had been brought forward by Duhring[2] as applicable to all liquids. In ordinary cases, however, the actual relation is less simple, and may be expressed by the equation—

$$R' = R + c\,(t' - t)$$

where R is the ratio of the absolute temperatures of the two substances corresponding to any vapour pressure, the same for both; R′ is the ratio at any other pressure, again the same for both; c is a constant; and t' and t are the temperatures of one of the substances corresponding to the two vapour pressures. If the values of R′ are plotted against the temperature differences, $t' - t$, a straight line is therefore obtained (Ramsay and Young, *loc. cit.*).

Strictly speaking, the equation should be expressed in the form—

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + c(T_A' - T_A)$$

and Porter[3] has shown that this relation can be derived from Bertrand's vapour-pressure formula—

[1] Young, *Brit. Ass. Rep.*, *Aberdeen* (1885); Ramsay and Young, *Phil. Mag.*, (5) **20**, 515 (1885); **21**, 33, **22**, 37 (1886).

[2] "Neue Grundgesetze zur rationellen Physik und Chemie," p. 70. Leipzig (1878).

[3] *Phil. Mag.* (June, 1907), p. 724; *cf.* S. A. Moss, *Phys. Rev.*, **25**, 453 (1907).

$$p = G\left(\frac{T - a}{T}\right)^n$$

if n has the same value for different substances.

But since c is very small, the equation may usually be written—

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + c(T_B' - T_B)$$

without sensible error, the value of c being, of course, different in the two cases; and it is in this form that it has most frequently been employed (Fig. 32).

The constant $c = 0$ for the closely related substances referred to above; in the comparison of ten esters the highest value of c was found to be 0·000048, but for widely different substances it may be higher, for example, 0·000141 for methyl acetate and benzene, and 0·0006845 for sulphur and carbon bisulphide.

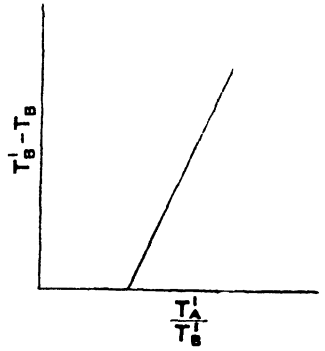


FIG. 32.

The formula is applicable from the lowest pressures to the critical point, and is of considerable utility in two respects: (1) If the boiling points of a pure substance are known through a wide range of pressure, those of a second substance may be ascertained for any pressure between the same limits if the constant c has been calculated from determinations at a few pressures sufficiently far apart. Thus $T_A' = T_B' \left\{\frac{T_A}{T_B} + c(T_B' - T_B)\right\}$. (2) If, on plotting the ratios $\frac{T_A'}{T_B'}$ against the temperature differences $(T_B' - T_B)$ for a standard substance B, a straight line is not obtained—that is to say, if c is not a constant—it may be concluded either that the experimental results are inaccurate (for example, Regnault's determinations of the vapour pressures of mercury at low temperatures), or that the substance A behaves abnormally, most probably that it undergoes dissociation on heating, as indicated by the changes in vapour density in such cases as those of nitrogen peroxide or acetic acid, or that there is molecular association in the liquid state. Now, it is found that the values of c for substances such as water, the alcohols, and the oxy-acids, which contain a hydroxyl group, are not quite constant, and, moreover,

that these substances exhibit many other peculiarities in their physical properties, and the conclusion is generally adopted that their molecules in the liquid state are more or less associated.

In many cases water has been taken as a standard substance in the comparison of boiling points, and while little objection can be taken to this procedure so long as the range of pressure over which the comparison is made is small, it would be better, if possible, to choose a substance of normal behaviour as a standard, and in no case should the comparison over a very wide range of pressure be made with water.

Surface Tension.—There can be no doubt that just as there is a force of attraction, known as gravitation, between large masses of matter, so there is a force of attraction between molecules, though physicists have not been able to arrive at a definite conclusion with regard to the laws which govern it.

Each molecule in the interior of a liquid is, no doubt, attracted by those around it, the attraction diminishing rapidly as the distance increases. Since the molecules must be regarded as evenly distributed in the liquid, the attractive force—neglecting the gravitational attraction of the earth—must be equal in all directions, so that there is no tendency for any molecule to be drawn more strongly in one direction than another.

Under ordinary conditions, however, a molecule on the surface is in close proximity to closely packed molecules in the liquid, while there are relatively very few molecules in the vapour outside. The surface molecule, then, is attracted equally in all directions along the surface and towards the interior of the liquid, but not to any appreciable extent outwards, and the resultant attractive force is therefore inwards and at right angles to the surface.

There is thus a tendency for the molecules to be drawn from the surface to the interior, and, consequently, for the surface to become as small as possible. The surface therefore acts like an extended elastic film, tending to contract.

Of all possible configurations, the spherical is that in which the ratio of surface area to volume is smallest; and when a quantity of liquid is not acted on by any external force except that of gravity, it tends to take the spherical form. This is seen in the case of a falling drop of rain, a drop of oil immersed in water, or of water in oil, and—with slight distortion—a small globule of mercury resting on a table or plate of glass.

The force acting along the surface and tending to diminish it is known as the "surface tension" (Thomas Young, 1804). It is usually denoted by the symbol γ, and is expressed as the force acting at right angles to a line 1 cm. long on the surface.

Let *abc* (Fig. 33) be a section through a solid plate placed perpendicularly to the surface of a liquid and partially immersed in it, the plate having previously been moistened by the liquid. The surface of the liquid, originally *abd*, tends to become smaller and assumes the form $a\beta d$, some of the liquid being raised against the force of gravity. There is equilibrium when the mass m of liquid raised along the wall of length $l = \gamma l$.

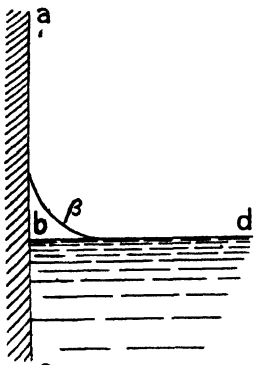


FIG. 33.

In practice a cylindrical wall or tube is usually employed, and if r is the internal radius of the tube, $l = 2\pi r$, and the elevating force $= 2\pi r\gamma$. The mass of liquid raised, $m = \pi r^2 hs$, where h is the height of the liquid in the tube above that outside, and s is the specific gravity of the liquid.

$$\text{Therefore } 2\pi r\gamma = \pi r^2 hs$$

$$\text{and } \gamma = \frac{hrs}{2}.$$

The surface tension depends on the nature of the liquid and on its temperature; it diminishes with rise of temperature, and vanishes at the critical point.

Thomas Tate,[1] in 1864, as the result of his experiments with water, announced the following laws:—

1. Other things being the same, the weight of a drop of liquid (falling from a tube) is proportional to the diameter of the tube in which it is formed.

2. The weight of the drop is in proportion to the weight which would be raised in that tube by capillary action. [In other words, the weight of the falling drop is proportional to the surface tension.]

3. The weight of a drop of liquid, other things being the same, is diminished by an augmentation of temperature.

The experimental work carried out during the succeeding forty

[1] *Phil. Mag.* [iv.], **27**, 176 (1864).

years seemed to indicate that the first two of Tate's laws could not be regarded as more than first approximations.[1]

In 1908 J. L. R. Morgan and R. Stevenson[2] published the results of a careful preliminary investigation of the subject, and Morgan and his assistants continued the work during the next seven years and published their results in a series of eighteen papers.[3] The apparatus finally employed is described in vol. 33, pp. 351-357, and the necessary precautions are fully explained in the same paper. By means of this apparatus, the weight of any number of drops of liquid falling from any sharp-edged capillary dropping-tip, at any temperature below 90°, with no loss from evaporation, can be accurately determined.

It was proved that under certain definite conditions the drop-weights of liquids falling from any one dropping-tip are proportional to their surface tensions at the same temperature. It was found that, for general purposes, tips from 4·5 to 5·5 mm. in diameter are the only ones which can be relied upon to give satisfactory results. Within these limits the drop-weights of the great majority of liquids are directly proportional to the diameter of the tip. As might be expected, the weight of the falling drop of any given liquid, under otherwise similar conditions, diminishes with rise of temperature.

A useful résumé and criticism of the researches on the measurement of surface tension by the falling-drop method has recently been published by Perrot.[4]

The exact relation of surface tension to temperature is of great theoretical interest, and is fully considered in Chapter XVII.

Heat of Vaporization.—The amount of heat required to convert 1 gram of a liquid at its boiling point under any given pressure into saturated vapour at the same temperature is called the *heat of vaporization.*

The volume of vapour is greater than that of the liquid, and therefore work must be done (1) in increasing the volume against the constant pressure, (2) in overcoming the mutual attraction of the molecules, which diminishes as the distance between them increases.

[1] Guye and Perrot, *Arch. Scien. phys. et nat.* [iv.], **11**, 225 (1901); **15**, 312 (1903).

[2] *Journ. Amer. Chem. Soc.*, **30**, 360 (1908).

[3] *Ibid.*, vols. **33**, **35**, and **37**, notably **33**, 349 and 643 (1911), and a résumé of the conditions necessary for success, **37**, 1461 (1915).

[4] *Journ. de Chim. phys.*, **15**, 164 (1917).

In the case of a substance which undergoes dissociation on conversion into vapour, work is also required to overcome the chemical attraction, but it is assumed that the molecules of an ordinary substance undergo no change during vaporization.

The external work done in expansion is measured as the product of the pressure into the change of volume. If a gram-molecule of a liquid, at its boiling point (on the absolute scale) T under the pressure p, and occupying the volume V_L, were converted into saturated vapour occupying the volume V_v under the same pressure, the external work would be equal to $p(V_v - V_L)$. If p is very small the volume V_v will be very great as compared with V_L, and the external work will therefore not differ sensibly from pV_v. Finally, if the vapour under such pressures as p and at such temperatures as T behaved as a perfect gas, the formula $PV = RT$ would be applicable to it.

In other words, the external work done by the evaporation of a gram-molecule of the liquid would equal RT. It would be independent of the nature of the substance, and, for a given liquid, would be proportional to the absolute temperature.

These conditions are in reality never strictly fulfilled, and as the temperature rises the value of V_L increases while that of V_v falls, so that $V_v - V_L$ differs more and more widely from V_v. Moreover, the density of the saturated vapour becomes considerably greater than that calculated for a perfect gas.

On the whole, therefore, the external work divided by the absolute temperature does not remain constant, but diminishes as the temperature rises.

The work required to overcome molecular attraction depends on the nature of the substance, and, since $V_v - V_L$ diminishes with rise of temperature and vanishes at the critical point, it is evident that the internal work also decreases and finally vanishes.

The heat of vaporization is the equivalent of the total work, external and internal, done in vaporizing a gram of liquid. It is found to depend on the nature of the substance, and in the case of *normal*[1] substances it diminishes with rise of temperature and vanishes at the critical point.

[1] The term *normal* is applied to substances which do not show such peculiarities in their physical properties as those exhibited by water, the alcohols, or fatty acids. It is probable that with normal substances there is no molecular association in either the liquid or gaseous state.

An important relation, based on the second law of thermodynamics, and established independently by Clausius and Clapeyron, may be expressed by the equation—

$$L = \frac{T}{J} \times \frac{dp}{dt}(v_v - v_l)$$

where L is the heat of vaporization, T is the absolute temperature, J is the mechanical equivalent of heat, $\frac{dp}{dt}$ is the rate of increase of vapour pressure per degree, and v_v and v_l are the volumes of saturated vapour and liquid. The relation is really a special case of a wider and quite general law; its truth has been proved in many instances in which all the data have been determined experimentally. From the equation it is clear that if either L or $v_v - v_L$ vanishes at the critical point, the other must vanish also.

Determination of the Heat of Vaporization.—The heat of vaporization of a liquid may either be determined experimentally or it may be calculated by means of the formula—

$$L = \frac{T}{J} \times \frac{dp}{dt}(v_v - v_l)$$

if the values of $\frac{dp}{dt}$ and $v_v - v$ are known at the absolute temperature T. The latter method has been very frequently employed, especially at high temperatures, at which the direct determination is attended with great difficulties.

The earliest experimental determination of the heat of vaporization of water was made by Black; but the method he employed was not capable of giving accurate results. Afterwards, at Black's suggestion, Irvine, and later Watt, employed the method of condensation in a calorimeter,[1] the steam from a boiler being passed into a calorimeter, and the rise of temperature and weight of water formed by condensation being ascertained; and Watt obtained the value 533 calories at 100°. The researches of Regnault were far more complete; he employed the same method, but worked with very large quantities and with a much more elaborate apparatus, and he investigated the various sources of error with great care. He also made determinations over a wide range of temperature, not only for water, but for a number of other substances. For water Regnault obtained the values 606·5 at 0°, 536·5 at 100°, and 464·3 at 200°.

[1] *Vide* Preston's "Theory of Heat" for a full account of the earlier experiments.

The chief error to be guarded against is the loss or gain of heat by the calorimeter, which may be caused by radiation, convection, or conduction while the experiment is proceeding.

Every object in a room is constantly losing heat by radiation, and gaining heat by absorbing that radiated from surrounding objects. A calorimeter should therefore be constructed in such a manner as to reduce this interchange of heat to a minimum, and it should not be in contact with a good conductor.

Bearing in mind that a brightly polished metallic surface radiates and absorbs heat badly, that air is a bad conductor, although convection currents take place freely in it, and that glass and ebonite are bad conductors, the principle on which the apparatus in general use is based may be readily understood.

A known quantity of water is placed in the calorimeter A, Fig. 34, made of brightly polished silver. The outer metallic vessel B contains water or other badly conducting material, such as felt or cotton-wool. Contact between the metallic walls of the two vessels is prevented by the conical buttons of ebonite C, C, and conduction from one wall to the other must be exceedingly slow through air or ebonite. The calorimeter also is perfectly shielded from draughts, and the temperature changes are so slow that convection currents are hardly appreciable.

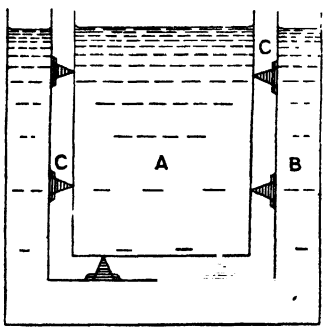


FIG. 34.

A still better form of calorimeter is, however, afforded by the silvered vacuum vessels devised by Dewar for the storage of liquid air. In these, conduction between the inner and outer vessel can only take place through the glass connecting them at the top, convection currents are entirely absent, and radiation is reduced to a minimum. The vacuum vessel may be further protected by wrapping felt or cotton-wool round it, or placing it in an outer vessel, as in the case of the ordinary calorimeter (B, Fig. 34). Under the best conditions, however, some interchange of heat takes place, and there must be some loss of heat by evaporation of water from the calorimeter. The rate of change of temperature must therefore be measured before and after the experiment, and from the data so

obtained the change of temperature during the actual experiment, due to other causes than the condensation of vapour, can be estimated.

The liquid under investigation is heated in a flask or boiler near the calorimeter, the vapour being conveyed to the condenser by a tube which slopes upwards, so that any liquid formed in it by condensation may return to the boiler. The connecting tube should be protected by non-conducting material, or may be heated externally by vapour from the boiler.

The calorimeter must obviously be protected by a screen from the heat radiated from the boiler, but it is impossible entirely to prevent the transference of heat from the hot connecting tube to the calorimeter by conduction. The amount of heat thus gained should be estimated, if possible, by a blank experiment.

The water in the calorimeter must be thoroughly stirred, for two reasons: firstly, warm water is lighter than cold and tends to rise to the surface; secondly, water is a very bad conductor of heat.

Not only the water itself, but the calorimeter, the stirrer, the thermometer, and the condenser, and the receptacle for the liquid formed by condensation receive heat, and the weight of water which has the same capacity for heat as these various parts of the apparatus must be estimated once for all, and is termed the *water equivalent* of the calorimeter.

Calling the actual weight of water m', the water equivalent m'', the observed initial and final temperatures of the water t_1 and t_2, the final temperature after all corrections t_2', and the mean specific heat of water between t_1 and t_2 c', the amount of heat received by the calorimeter is—

$$(m' + m'')c'(t_2' - t_1).$$

The vapour, on reaching the calorimeter, condenses, and the temperature of the liquid formed by condensation falls from the condensing point t to the final temperature t_2. Calling the weight of vapour condensed m, and the mean specific heat of the liquid between t and t_2 c, the heat given up to the calorimeter is $m\mathrm{L} + mc(t - t_2)$. Therefore—

$$m\mathrm{L} = (m' + m'')c'(t_2' - t_1) - mc(t - t_2).$$

A separate determination of the specific heat of the liquid is required. In Regnault's experiments the condensed liquid was not retained in a receptacle in the calorimeter, but was collected in a

separate vessel placed below it. The final temperature of the liquid was therefore t_1 at the beginning of the experiment, but t_2 at the end. The mean final temperature may be taken as $\frac{t_1 + t_2}{2} = t_m$, and the expression $mc(t - t_2)$ becomes $mc(t - t_m)$.

The apparatus employed by Regnault is cumbrous, and can only be employed for liquids which are obtainable in large quantities.

Berthelot[1] employed as boiler a glass pear-shaped flask (A, Fig. 35) with a wide vertical delivery tube passing centrally through the bottom of the flask. The liquid was heated by a ring-shaped burner B. Very much smaller quantities of liquid could be used, and the duration of the experiment was reduced to from 2 to 4 minutes, exclusive of the time required to determine the radiation correction. Berthelot obtained the value 536·2 for the heat of vaporization of water at 100°.

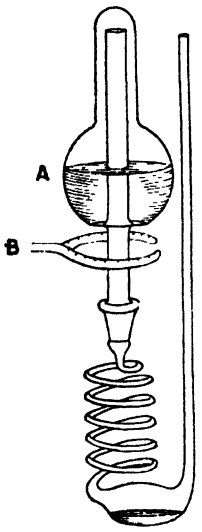


FIG. 35.

Many determinations by the ordinary method have been made by Andrews,[2] Brix,[3] Favre and Silbermann,[4] Louguinine,[5] and others. Special precautions are described by Richards and Matthews[6] who obtained the value 538·1 cal.

Various other methods or modifications of those described have been devised. Among the more important are the following:—

The substance is distilled from a vessel placed in the calorimeter itself, the heat being supplied by the water or ice in the calorimeter. This method, which is only suitable for volatile substances, has been employed by Regnault, also by Chappius,[7] Mathias,[8] Jahn,[9] Griffiths and Marshall,[10]

[1] *Compt. rend.*, **85**, 647 (1877); *Journ. de Phys.*, **6**, 337 (1877).
[2] *Quarterly Journ. Chem. Soc.*, **1**, 27 (1847).
[3] *Pogg. Ann.*, **55**, 341 (1842).
[4] *Compt. rend.*, **39**, 729 (1854); *Ann. Chim. Phys.* (3), **37** (1853); *ibid.* (5), **1**, 225 (1874).
[5] *Ann. Chim. Phys.* (7), **7**, 251 (1896).
[6] *Amer. Acad. Proc.*, **46**, 511 (1911).
[7] *Ann. Chim. Phys.* (6), **15**, 498 (1888).
[8] *Ibid.* (6), **21**, 69 (1890); and *Journ. de Phys.* (Nov. 1905).
[9] *Zeit. physik. Chem.*, **11**, 788 (1893).
[10] *Phil. Mag.*, **41**, 1 (1896).

Fletcher and Tyrer,[1] and others. Mathias made an important investigation of the heats of vaporization of carbon dioxide, and of sulphur dioxide and nitrous oxide. He kept the temperature of his calorimeter constant, and at the same time measured the heat absorbed by carefully adding concentrated sulphuric acid. Griffiths and Marshall, who made an exceedingly careful determination of the heat of vaporization of benzene, obtained the same results by passing a measured current of electricity through a coil of platinum wire in the calorimeter.

An electrically heated platinum wire has been used as a source of heat in the still by Ramsay and Marshall,[2] Kahlenberg,[3] Shearer,[4] J. C. Brown,[5] Estreicher,[6] and others Ramsay and Marshall and Brown kept the liquids at their boiling points by heating them with a jacket of their own vapour. Ramsay and Marshall's method was a comparative one, pure benzene being taken as the standard substance. The other experimenters calculated the heat directly or indirectly from the current.

A quite different method was employed by Dewar,[7] and by Behn,[8] for liquefied gases. They dropped pieces of metal of known weight and specific heat into the liquid, and measured the volume of gas evolved.

Joly's steam calorimeter has been employed with good results by Wirtz.[9]

A special electrical method, suitable for very high temperatures, is described by Wehnelt and Musceleanu;[10] the results appear to be very satisfactory.

The experiments of Mathias on the heats of vaporization of carbon dioxide are of great interest, for they extended from 6·65° to 31·16°, or almost to the critical temperature. The carbon dioxide contained 0·75 per cent. of air, which would cause the critical temperature to be rather lower than the true value 31·35°. The formula deduced by Mathias from his results, $L^2 = 118{\cdot}485\ (31 - t) - 0{\cdot}4707\ (31 - t)$,[2] gives L = 0 at 31°. The experiments may be

[1] *Trans. Chem. Soc.*, **103**, 517 (1913).
[2] *Phil. Mag.*, **41**, 38 (1896).
[3] *Journ. Phys. Chem.*, **5**, 215 and 284 (1901).
[4] *Phys. Rev.*, **17**, 469 (1903). [5] *Trans. Chem. Soc.*, **83**, 987 (1903).
[6] *Zeit. physik. Chem.*, **49**, 597 (1904); *Acad. Sci. Cracovie, Bull.* **7a**, 345 (1910).
[7] *Chem. News*, **71**, 192 (1895). [8] *Drude's Ann.*, **1**, 270 (1900).
[9] *Wied. Ann.*, **40**, 438 (1890). [10] *Deutsch. Phys. Gesell.*, **14**, 1032 (1912).

taken to prove that the heat of vaporization does really become zero at the critical point.

J. E. Mills[1] has calculated the heats of vaporization of a large number of substances, chiefly those investigated by Young, over a wide range of temperature, generally from 0° to the critical point, by means of the formula—

$$L = \frac{T}{J} \times (v_s - v_l) \frac{dp}{dt},$$

and has shown that the formula—

$$\frac{L - E_1}{\sqrt[3]{s_L} - \sqrt[3]{s_s}} = \text{constant } (\mu')$$

(where L is the heat of vaporization, E_1 is the heat equivalent to the external work, and therefore $L - E_1$ is the internal heat of vaporization; s_l and s_s are the densities of liquid and saturated vapour respectively) holds, with a few doubtful exceptions, for all the stable substances at all temperatures.

Thirty-one substances were examined; of these, water, three alcohols, and acetic acid are known to behave abnormally in many respects, and the accuracy of the measurements of three others is not altogether satisfactory. The remaining twenty-three substances, excluding determinations within 10° of the critical temperature, afforded 378 values of μ'; of these 349 were within 2 per cent. of the mean values of μ' adopted, and only 3 showed divergences greater than 5 per cent. The 29 divergences greater than 2 per cent. occurred where the measurements were likely to be least accurate.

The formula $\frac{L - E_1}{\sqrt[3]{s_L} - \sqrt[3]{s_v}}$ was based on the assumptions that—

1. The molecules are evenly distributed.

2. The number of molecules does not change during vaporization.

3. No energy is spent in intra-molecular work; in other words, the molecules are stable.

4. The attraction does not vary with the temperature.

5. The molecular attraction varies inversely as the square of the distance.

[1] *Journ. Phys. Chem.*, **6**, 209 (1902); **8**, 383 and 593 (1904); **9**, 402 (1905); **10**, 1 (1906); *cf.* Appleby and Chapman, *Trans. Chem. Soc.*, **105**, 734 (1914); and Sutton, *Phil. Mag.*, **29**, 593 (1915).

Mills concludes that if the first four assumptions are valid the fifth must be accepted, and that the law of molecular attraction is similar to that of gravitation as far as the variation of the force with the distance is concerned.

The Law of Despretz.—It was pointed out by Despretz[1] that the ratio $\frac{L}{v_V - v_L}$ is approximately the same for different substances at their boiling points under the same pressure. But under atmospheric pressure v_L is very small relatively to v_V, and may be neglected. The statement may therefore be made that $\frac{L}{v_V}$ is approximately a constant.

But the volume $v_V = \frac{22{\cdot}4}{M} \cdot \frac{T}{273}$ litres under atmospheric pressure (where M is the molecular weight).

$$\therefore v_V = c\frac{T}{M}$$

therefore, from the law of Despretz—

$$\frac{ML}{T} = \text{constant.}$$

This law was discovered independently by Pictet in 1876 (reference unknown), Ramsay in 1877,[2] and by Trouton in 1884,[3] and is generally known as Trouton's law. It has been the subject of numerous investigations, and the conclusion generally stated is that it is not true for widely different substances, but that it generally holds for the members of any group of closely related bodies.

The following are a few values of $\frac{ML}{T}$:—

Hydrocarbons	20 to 21
Hg, Cd, Zn, Bi[4]	19·36 to 20·20
Esters	about 21
P, PCl_3, CO_2, H_2S, CS_2 . . .	21·2 to 21·4
S, $SiCl_4$, Hg	21·6 to 22
Br_2, HI	23
NH_3	23·6
Water and alcohols . . .	about 26

[1] *Ann. Chim. Phys.*, **24**, 323 (1823). [2] Philosoph. Soc. of Glasgow.
[3] *Phil. Mag.*, **18**, 54.
[4] Van Aubel, *Compt. rend.*, **156**, 456 (1913).

From the equation $\frac{L}{v_V - v_L} = \frac{dp}{dt} \cdot \frac{T}{J}$ it follows that if $\frac{L}{v_V - v_L}$ = constant for different substances at their boiling points under equal pressures, $\frac{dp}{dt} \cdot T$ must also be constant. The values of $\frac{dp}{dt} \cdot T$ were calculated by Young in 1884 for a number of substances at a series of equal pressures, and the conclusions are given in the *Brit. Ass. Rep.*, 1885.

The whole subject was discussed by Ramsay and Young in 1885 and 1886.[1] It is pointed out (1) that closely related substances have in many cases the same value of $\frac{dp}{dt} \cdot T$ (*e.g.* chlorobenzene and bromobenzene, or ethyl chloride and ethyl bromide); (2) that the values for substances which are not closely related, other than those which dissociate when heated, or which contain a hydroxyl group, show differences amounting generally to less than 10 per cent., but in extreme cases reaching even 15 per cent. (*e.g.* carbon disulphide and aniline); (3) that if the comparison for any two such substances is made at a series of pressures extending over a wide range, the ratio of the values of $\frac{dp}{dt} \cdot T$ is practically independent of the pressure; (4) that if one of the two substances undergoes dissociation (*e.g.* nitrogen peroxide) or contains a hydroxyl group (*e.g.* water or an alcohol or fatty acid), the values of $\frac{dp}{dt} \cdot T$ may differ by more than 60 per cent. (*e.g.* ammonium carbamate and carbon disulphide); (5) that in such cases the ratio of the values of $\frac{dp}{dt} \cdot T$ may not remain constant at different pressures.

These points are illustrated in the following table, which contains the values of $\frac{dp}{dt} \cdot T$ at a few of the pressures at which the comparisons were made :—

[1] *Phil. Mag.* (5), **20**, 515; **21**, 135.

VALUES OF $\frac{dp}{dt} \times T$.

Pressure in mm.	CS_2	C_6H_5Cl.	C_2H_5Br.	Ether.	Aniline	Ethyl Alcohol.	N_2O_4.	Ammonium Carbamate.
50	676	—	715	—	750	853	—	1087
100	1,280	—	1,364	1,304	1481	1,642	1331	2102
200	2,373	2,528	2,438	2,531	2788	3,155	3030	3938
300	3,430	3,536	3,513	3,598	4014	4,541	4304	5870
500	5,417	5,520	5,654	5,612	6231	7,197	6939	—
1000	10,100	10,290	10,371	10,513	—	13,827	—	—
2000	18,470	19,141	18,848	19,787	—	25,179	—	—
5000	41,130	41,702	41,306	43,374	—	56,460	—	—

They are more clearly seen by taking the value for carbon disulphide as unity at each pressure.

REDUCED VALUES OF $\frac{dp}{dt} \times T$, TAKING THAT FOR CS_2 AS UNITY AT EACH PRESSURE.

Pressure in mm	CS_2.	C_6H_5Cl.	C_2H_5Br.	Ether.	Aniline.	Ethyl Alcohol.	N_2O_4	Ammonium Carbamate
50	1·000	—	1·058	—	1·110	1·262	—	1·609
100	1·000	—	1·066	1·019	1·157	1·283	1·043	1·643
200	1·000	1·065	1·027	1·066	1·175	1·329	1·277	1·659
300	1·000	1·031	1·024	1·049	1·165	1·324	1·255	1·711
500	1·000	1·019	1·044	1·036	1·150	1·329	1·281	—
1000	1·000	1·019	1·027	1·041	—	1·369	—	—
2000	1·000	1·037	1·021	1·072	—	1·364	—	—
5000	1·000	1·014	1·004	1·053	—	1·373	—	—
Mean of all values	1·000	1·032	1·032	1·049	1·152	1·336	1·219	1·667

The values of $\frac{dp}{dt}$ were mostly determined graphically by drawing tangents to the vapour-pressure curves, and individual errors as high as 2 per cent. are not improbable. The probable errors in the mean value are of course very much smaller.

Correction of Boiling Point to Normal Pressure.—It is frequently required to compare the boiling points of different substances, either that of a liquid under investigation with the known boiling point of the pure substance in order to identify it, or to obtain information as to its purity; or it may be desired to compare the boiling points of a series of homologous or isomeric compounds.

A satisfactory comparison can only be made if the pressure is the same in all cases, and, as it is usually most convenient to determine the boiling point under the actual atmospheric pressure, the temperature must be corrected for the difference between the actual pressure and the normal pressure of 760 mm.

The temperature correction, Δt, to be added to the observed boiling point t, the barometric pressure being p, is—

$$\Delta t = c(760 - p)\,(273 + t)$$

where $c = \frac{dt}{dp} \times \frac{1}{T}$.

For ordinary substances the mean value of c is about 0·00012. It is, however, considerably higher for some of the liquefied gases; for example, about 0·000145 for oxygen and nitrogen. On the other hand it is much lower, about 0·00010, for the alcohols and water.

The values of c for a large number of substances are given in Young's "Fractional Distillation," p. 15; also *Trans. Chem. Soc.*, **81**, 777 (1902). A smaller list had previously been published by Crafts.[1]

[1] *Berichte*, **20**, 709 (1887).

CHAPTER IX.

THE PROPERTIES OF LIQUIDS (*continued*).

The Densities and Specific Volumes of Liquids.—If the density of a liquid is merely required to be known at 0° or at about the ordinary temperature, it may be determined by means of the specific-gravity bottle or the Sprengel tube, preferably of the modified form devised by Perkin.[1] The capacity of the vessel at 0° is deduced from the weight of water it contains at that temperature. With the ordinary specific-gravity bottle the actual determinations must be made at a temperature higher than that of the room, and corrections must be made for the expansion of water and glass. The Perkin-Sprengel tube (Fig. 36) has the great advantage that it may be filled at 0° and afterwards weighed at a higher temperature.

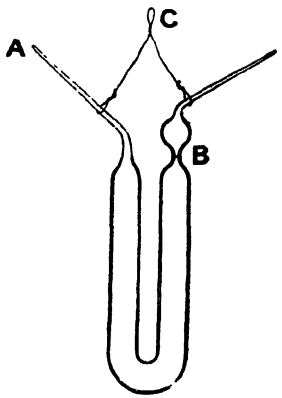


FIG. 36.

The tube must contain liquid at 0° from the end A to the etched mark B, any excess being removed by tilting the tube and touching A with a piece of filter-paper. When the tube is replaced in a vertical position some of the liquid flows back into the little bulb, and when expansion takes place with rise of temperature—small with water, which contracts up to 4°, but considerable with some substances—the liquid passes into the bulb.

The determination is first made with water to find the capacity of the tube, and afterwards with the liquid under investigation, either at 0° or with the tube immersed in water of known temperature. Diffusion of vapour through the narrow tubes is so slow that no appreciable loss even of volatile liquids occurs during the determination. The specific-gravity tube may be suspended from the balance

[1] *Trans. Chem. Soc.*, 45, 444 (1884).

beam by the looped platinum wire C. All weighings must be corrected for the buoyancy of the air.

The density $s = \frac{m}{v}$, where m is the corrected weight of liquid, and v is the capacity of the vessel from A to B at the temperature of experiment.

If the densities are required at a series of temperatures not extending above the boiling point of the liquid under atmospheric pressure, a cylindrical bulb sealed to a long graduated tube of narrow bore is usually employed. The bulb and tube are calibrated, and the freshly distilled liquid is run in until it fills the bulb and part of the tube. The liquid is weighed, and readings of the volume are taken at different temperatures. Accurate determinations of the specific volumes and expansions of liquids up to their boiling points have been made by Kopp, Pierre, Thorpe, Elsasser, Gartenmeister, Zander, and others.

For temperatures above the boiling point an apparatus such as that of Andrews must be employed, on account of the increased pressure. The volume of a liquid at a given temperature and under a pressure equal to the vapour pressure is termed the *orthobaric* volume.[1] At temperatures below the ordinary boiling point the compressibility is so slight that the determinations may be made without sensible error under atmospheric pressure. Above the boiling point the pressure should be made as nearly as possible equal to the vapour pressure. No difficulty is experienced until the temperature reaches about 0·85 of the critical temperature (calculated on the absolute scale), because a small alteration in pressure has no sensible effect on the volume. At higher temperatures the liquid becomes so compressible that it is necessary to make the pressure exactly equal to the vapour pressure. To do this, however, is difficult, because at these relatively very high temperatures ebullition takes place very easily even when the liquid is quite free from air. If, when the vapour is all condensed, the pressure is reduced even slightly below the vapour pressure, ebullition at once takes place, and the pressure must be raised again to condense the vapour formed. If, on the other hand, the pressure is even slightly too high, the observed volume of liquid will be appreciably less than the orthobaric volume.

In order to obtain the greatest possible accuracy, it is best to

[1] Ramsay and Young, *Phil. Trans.*, **177**, pt. i., 135 (1886).

adopt a method which has been employed with some differences in detail by Mathias,[1] Amagat,[2] and Young.[3]

Starting with the vapour completely condensed, the volume is increased until a little vapour has been formed; when the temperature is quite constant, readings of the volumes of liquid and saturated vapour are taken. The volume is again increased, and after the temperature has become constant the volumes of liquid and vapour are again read. The process is continued so as to obtain four or more readings of the two volumes. Each time that the total volume is increased some of the liquid evaporates, so that the volume of liquid diminishes and that of the saturated vapour increases. Calling the first and third volumes of liquid v_L' and v_L''' and the corresponding volumes of saturated vapour v_V' and v_V''', the ratio R of the specific volume of saturated vapour to that of liquid is given by the equation—

$$R = \frac{v_V''' - v_V'}{v_L' - v_L'''} = \frac{v_V'''' - v_V''}{v_L'' - v_L''''}$$

In this way two independent values of R are obtained, and the mean may be taken as correct.

The volume of liquid, if all the vapour were condensed, would be—

$$v_L = v_1' + \frac{v_V'}{R} = v_L'' + \frac{v_V''}{R} \quad \cdots$$

so that there are four independent values of the othobaric volume of liquid. Finally, if m is the weight of substance in the tube, the orthobaric volume of a gram of liquid $= v_L = \frac{v_L}{m}$.

The volume of a gram of saturated vapour v_V may be calculated from the same data, for $v_V = Rv_L$.

If the two values of R and the four values of v_1, respectively, are not concordant, evidence is afforded either that the liquid contains air or some other impurity, or that there is some other source of error which requires investigation. If, on the other hand, the vapour pressure has been found to be independent of the relative volumes of liquid and of vapour, and concordant values of R and of v_L have been obtained, there is strong evidence that the liquid is pure, and

[1] *Ann. de Toulouse*, 1891. [2] *Compt. rend.*, **114**, 1093 (1892).
[3] *Trans. Chem. Soc.*, **59**, 908 (1891); Young and Thomas, **63**, 1199 (1893).

that the various details of the experiment—method of heating and of reading the volumes, calibration of the tubes, and so on—are satisfactory.

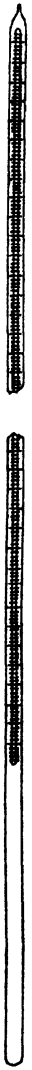


FIG. 37.

There are many liquids which attack mercury either at all temperatures or when heated, and the specific volumes of such substances cannot be determined by the method just described.

The difficulty has been overcome by Young[1] by the employment of a graduated and calibrated sealed tube (Fig. 37), containing only the pure liquid and its vapour.

When the temperature of such a tube is raised, the volume of liquids tends, on the one hand, to increase owing to expansion, but, on the other hand, to diminish owing to evaporation into the space above.

Let m be the weight of substance (liquid and vapour) in the tube, v_L the observed volume of liquid, and v_V that of the saturated vapour at the temperature t. If the weight of substance had been 1 gram, and the capacity of the tube $\frac{v_L + v_V}{m}$, the volumes of liquid and saturated vapour would have been $\frac{v_L}{m}$ and $\frac{v_V}{m}$ respectively, say $\mathbf{v}_L$ and $\mathbf{v}_V$. Let R be the ratio of the specific volume of saturated vapour to that of liquid, and v_L the true volume of a gram of liquid at t; then—

$$R = \frac{\mathbf{v}_V}{\mathbf{v}_L - \mathbf{v}_L}$$

but neither R nor v_L are known.

Let a second tube, similar to the first, but containing a relatively smaller amount m' of substance, be heated to the same temperature t. Calling the observed volumes of liquid and saturated vapour v_L' and v_V', the reduced volumes for 1 gram of substance and a tube of capacity $\frac{v_L' + v_V'}{m'}$ would be $\frac{v_L'}{m'}$ and $\frac{v_V'}{m'}$ respectively, say $\mathbf{v}_L'$ and $\mathbf{v}_V'$.

From the second determination—

[1] *Trans. Chem. Soc.*, **59**, 37, 126, 929 (1891); *Proc. Phys. Soc.*, **13**, 617 (1895).

$$R = \frac{v_v'}{v_L - v_L'}$$

$$\therefore \frac{v_v}{v_L - v_L} = \frac{v_v'}{v_L - v_L'},$$

$$\text{and } v_L = \frac{v_L v_v' - v_L' v_v}{v_v' - v_v}$$

R can then be calculated, and the volume of a gram of saturated vapour = Rv_L.

The method of constructing and filling the tube is described in the *Trans. Chem. Soc.*, **59**, 37 (1891) and in the *Sci. Proc. Roy. Dublin Soc.*, **12** (N.S.), 374 (1910), also a method of heating by which the volumes of liquid and saturated vapour may be determined with a single tube. The calculation in that case is different, and the experimental difficulties are much greater. The simplified method of heating the tube is described in the *Proc. Phys. Soc.*, **13**, 617 (1895); also *Zeit. physik. Chem.*, **29**, 193 (1899) and *Sci. Proc. Roy. Dublin Soc.*, *loc. cit.*

At low temperatures the orthobaric volumes of a gram of liquid increase slowly with rise of temperature, but at higher temperatures the rate of increase becomes greater, and it is very great near the critical point. For purposes of calculation the formula

$$v_t = v_0(1 + at + bt^2 + ct^3 \ldots)$$

is usually employed, the number of terms depending partly on the range of temperature and partly on the accuracy required (v_0 = the volume at the lowest temperature $t_0°$, and $t = t° - t_0°$).

At low or moderate temperatures the relation between density and temperature may, according to Mendeléeff,[1] be expressed by the simple formula—

$$s_t = s_0 (1 - kt).$$

This equation is discussed on p. 159.

Expressed as volumes, the equation is—

$$v_t = \frac{v_0}{1 - kt}$$

$$\text{or } v_t = v_0(1 + kt + k^2t^2 + k^3t^3 \ldots).$$

Volumes of Saturated Vapour.—The methods of determining the volumes of saturated vapour by means of the modified Andrews apparatus and by the sealed-tube method have already been

[1] *Ann. Chim. Phys.* (6), **2**, 271 (1884).

described. It is much more difficult to obtain accurate determinations of the volume of saturated vapour than of liquid, and when both have been determined with the Andrews apparatus it is frequently advisable to employ the sealed-tube method for the saturated vapours only. In this case only one tube is required for a given range of temperature, for in the equation—

$$R = \frac{v_v}{v_L - v_l}$$

the values of v_l obtained with the Andrews apparatus may be taken as correct. There are thus two partially independent values of the specific volume of saturated vapour at each temperature.

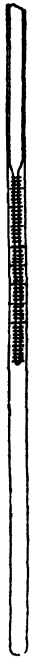


Fig. 38.

In order to calculate R by either method, it is necessary to measure a relatively large volume of saturated vapour and a relatively small volume of liquid. Moreover, the determination of the volume of liquid involves two readings. The lower the temperature the greater is the value of R and the smaller the difference between the two volumes of liquid; the greater, therefore, is the influence of errors of reading. With the Andrews apparatus the method can only be employed at temperatures above about 0·85 of the critical temperature (absolute scale), but the sealed-tube method can be made available for lower temperatures by greatly increasing the internal diameter of the middle portion of the tube, so as to greatly increase the volume of saturated vapour, while keeping the extremities of the tube narrow where the volume of liquid is read (Fig. 38).

For larger volumes of saturated vapour it is best to read the point of intersection of the isothermal (Fig. 22) with the horizontal line of constant vapour pressure.

If the volumes of a gram of liquid and saturated vapour are plotted against the temperature, a closed curve is obtained, as ACB, Fig. 39, where the observed results for normal pentane are given. The summit of the curve C indicates the critical temperature and the critical volume.

Law of Cailletet and Mathias.—When the densities of liquid and saturated vapour are plotted against the temperatures, the closed

curve takes the form ACB, in Fig. 40. It was pointed out by Cailletet and Mathias[1] that the means of the densities of any sub-

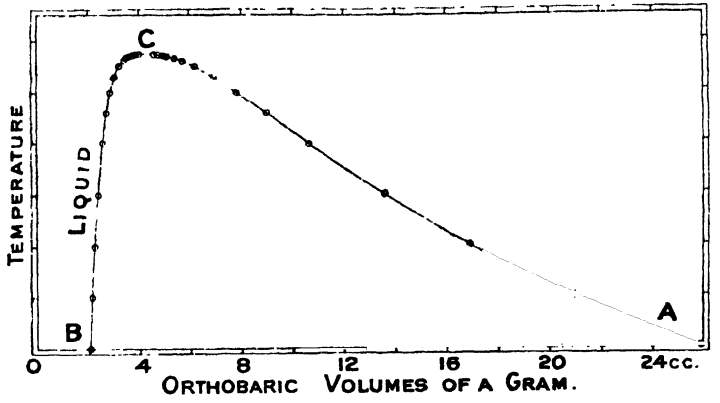


FIG. 39.

stance in the state of liquid and saturated vapour, when plotted against the temperature, fall on a straight line (DC, Fig. 40).

The law of Cailletet and Mathias was confirmed by Amagat

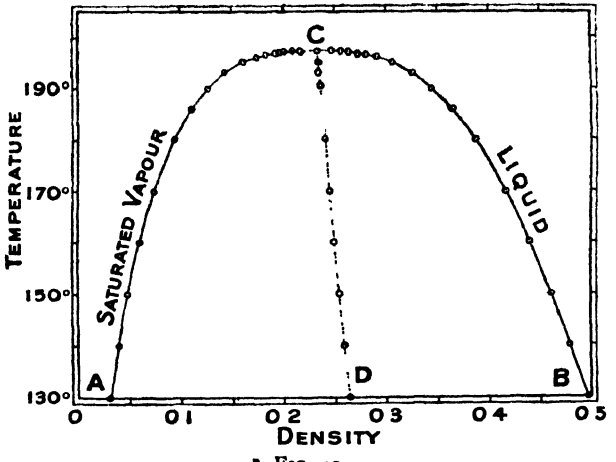


FIG. 40.

in the case of carbon dioxide within the limits of experimental error, and has been fully discussed by Young.[2]

In the case of normal pentane the law was found to hold with perfect accuracy from 0° to the critical temperature 197·2°, as will

[1] *Compt. rend.*, **102**, 1202 (1886); **104**, 1563 (1887).

[2] *Phil. Mag.*, **50**, 291 (1900).

be seen from the diagram and from the table below, where the observed mean densities are compared with those calculated from the equation

$$s_t = s_0 + at$$

where $s_0 = 0{\cdot}3231$, $a = -0{\cdot}00046$, and $t = t^\circ$ C.

Temperature.	s_L.	s_V.	Mean.	Calculated.	$\Delta \times 10^4$.
0°	0·6454	0·0008	0·3231	0·3231	0
30	0·6165	0·0025	0·3095	0·3093	− 2
50	0·5957	0·0046	0·3001	0·3001	0
70	0·5739	0·0079	0·2909	0·2909	0
90	0·5503	0·0129	0·2816	0·2817	+ 1
110	0·5248	0·0203	0·2725	0 2725	0
130	0·4957	0·0310	0·2634	0·2633	− 1
150	0·4604	0·0476	0·2540	0·2541	+ 1
170	0·4162	0·0735	0·2448	0·2449	+ 1
180	0·3867	0·0935	0·2401	0·2403	+ 2
190	0·3445	0·1269	0·2357	0·2357	0
195	0·3065	0·1609	0·2337	0·2334	− 3
197	0·2640	0·2005	0·2323	0·2325	+ 2
197·1	0·2560	0·2090	0·2326	0·2324	− 2
197·15	0·2472	0·2168	0·2320	0·2324	+ 4

With other substances, however, excepting perhaps normal hexane, there was found to be very slight curvature of the diameter, so slight in most cases that until the whole of the data were carefully examined it was attributed to error of experiment. For ordinary purposes of calculation over a moderate range of temperature the formula $s_t = s_0 + at$ may, in fact, be employed, but when great accuracy is required, or when extrapolation is necessary, the formula $s_t = s_0 + at + \beta t^2$ must be used. The experimental data are then reproduced with great exactitude, except in the case of the alcohols, which show marked deviation from the simple law.

At the upper extremity of the diameter, where it intersects the closed curve, the densities of liquid and saturated vapour are equal; the temperature is the critical temperature, and the density may therefore be termed the critical density; its reciprocal is the critical volume of a gram.

If determinations of the two kinds of density have been made at a series of high temperatures, extending to within 10° or 20° of the critical temperature, a straight line drawn to pass as evenly as possible through the points representing the mean densities would give the critical density with very fair accuracy, but if the curvature

is at all marked the same straight line would not give the true mean densities at low temperatures, as will be seen from Fig. 41*a*, in which the mean densities for normal octane are given. Conversely, a straight line drawn through the points representing the mean densities at low temperatures would not give the true critical density (Fig. 41*b*). In either case the formula $s_t = s_0 + at + \beta t^2$ would have to be used, and the extrapolation should not be carried too far.

The lower limit of the diameter would be the freezing point of the substance, if it were not possible to cool a liquid below that temperature without solidification taking place. This process is, however, possible to some extent with all substances, and may be carried very far with some, as, for example, glycerol. If cooling without solidification could be carried on down to the absolute zero of temperature, the liquid would be deprived of all heat and the molecules would be at rest, and, as pointed out by D. Berthelot, it may be supposed that they would be as close together as they could be brought by any possible process. If, then, the diameter were correctly extrapolated to the absolute zero point, its lower extremity would give the mean density of liquid and saturated vapour at that temperature. But the density of saturated vapour diminishes rapidly with fall of temperature, and becomes negligible not very far below the ordinary boiling point.

At these low temperatures, therefore, the mean density of liquid and saturated vapour is equal to half the density of the liquid. The density of the liquid at the absolute zero would therefore be twice the mean density given by the extremity of the diameter, and the reciprocal of the density of the liquid would be the volume of a gram. This may be regarded as the actual volume occupied by the molecules themselves in 1 gram of the substance, and D. Berthelot has calculated these minimum volumes for a number of substances on the assumption that the diameter is straight.

In the case of normal pentane there is no appreciable curvature between 0° C. and the critical temperature; but Timmermans [1] has determined the densities of a number of pure liquids at temperatures from about 15° to their freezing points, six of which are lower than − 90°. In every case, even that of normal pentane, there was slight curvature of the diameter, but the whole of the observed data for that substance, from − 130·8° to + 197·15°, may be represented very

[1] *Sci. Proc. Roy. Dublin Soc.*, 13 (N.S.) 310 (1912).

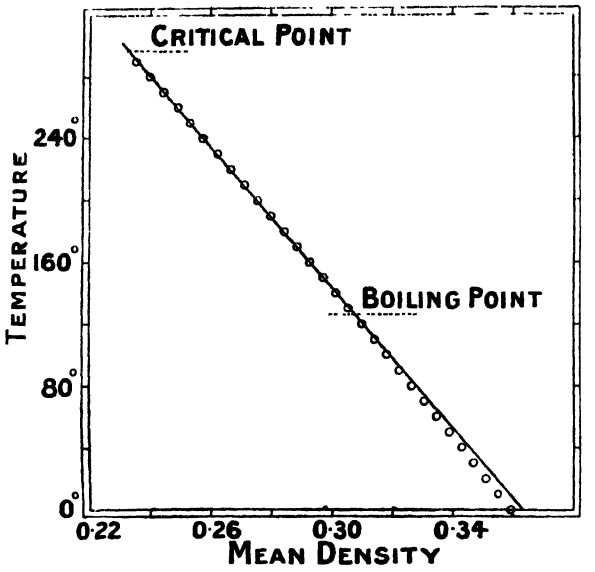


FIG. 41*a*.

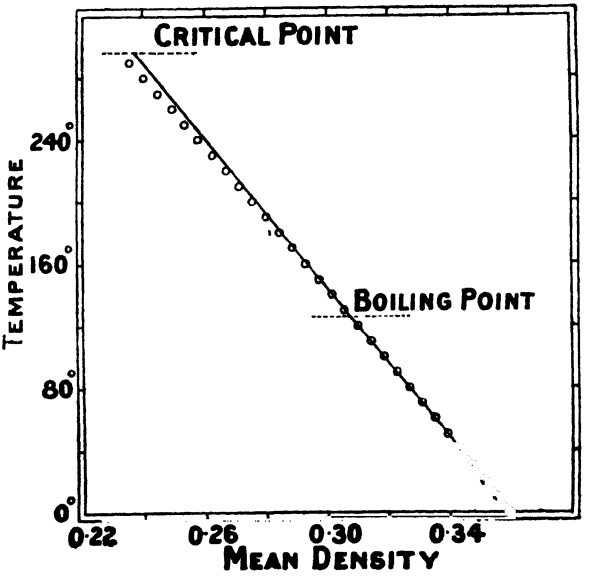


FIG. 41*b*.

well by the formula $s_t = 0{\cdot}44402 - 0{\cdot}0_343413\ T - 0{\cdot}0_73477\ T^2$, where s is the mean density and T is the absolute temperature. The greatest individual difference between the calculated and observed mean density over the whole range of 328° is only just over 0·2 per cent.

The accurate experiments of Thorpe[1] on some liquids of high boiling point appear to indicate that there is very slight curvature in those cases also at temperatures at which the density of saturated vapour may be neglected.

The law of Cailletet and Mathias has the same form as that of Mendeléeff, which relates to liquids only, for a is always negative; and since the density of saturated vapour becomes negligible at low temperatures, the two laws become identical, except in so far that the s_t in Mendeléeff's formula refers to the actual density of the liquid, and in that of Cailletet and Mathias to half the density.

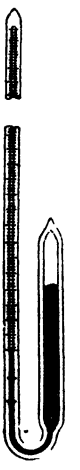


FIG. 42.

THE CRITICAL POINT.

It was observed by Cagniard de la Tour, in 1822,[2] that when a sufficient, but not too great, quantity of liquid was gradually heated in a sealed tube it became more mobile, and at a certain temperature, depending on the liquid, it was converted into a perfectly transparent vapour. On allowing the tube to cool, a very thick cloud was first formed, and the liquid then reappeared.

By employing a sealed tube of the form shown in Fig. 42, Cagniard de la Tour was able to make an approximate determination of the pressure at which this change occurred. He thus obtained the following results:—

	Temperature.	Pressure.
Ether . .	175° C.	38 atmos.
CS_2 . .	258°	71 „

The phenomena were carefully studied by Andrews, and described in his great memoirs on the continuity of the gaseous and liquid states of matter.[3] Andrews observed that when carbon dioxide was

[1] *Trans. Chem. Soc.*, 37, 141 (1880).

[2] *Ann. Chim. Phys.* (2), 21, 127 and 178; 22, 410.

[3] Miller's "Chemical Physics," 1863; *Phil. Trans.*, 1869, pt. ii., 575; Royal Institution Lectures, 1871; *Phil. Trans.*, 1876, pt. ii., 421.

partially liquefied by pressure alone, and the temperature was then gradually raised to 31°, "the surface of demarcation between the liquid and the gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout the entire mass." Andrews called the temperature at which these phenomena were observed the *critical point.*

In the apparatus employed by Andrews, or the modified form of it described on p. 122 (Fig. 27), the volume of the substance under investigation can be altered at will, and may be adjusted so that the critical phenomena can be seen under the best conditions.

If, on the other hand, a sealed tube be employed, the quantity of liquid introduced must be within certain not very wide limits, for the following reasons: When a tube containing only a pure stable liquid and its vapour is heated, the liquid expands, but at the same time part of it is converted into vapour. The volume of liquid, therefore, on the one hand tends to increase on account of the expansion, but on the other hand tends to diminish on account of evaporation. If the quantity of liquid in the tube is small to begin with, the diminution in volume due to evaporation will, at high temperatures at any rate, be greater than the increase due to expansion, and the level of the surface of separation of liquid and vapour will fall until the whole of the liquid is converted into vapour. No visible change then occurs when the temperature is further raised.

If the quantity of liquid at low temperatures is large, the gain by expansion will be greater than the loss by evaporation, and the volume will increase until the liquid completely fills the tube. If the temperature be still allowed to rise, the pressure will increase enormously, and the tube will in all probability burst. In neither case will the critical phenomena be seen.

But if the quantity of liquid is neither too small nor too great, the surface of contact will not reach either the bottom or the top of the tube, and it will be seen that the meniscus, which at low temperatures is concave (except in the case of liquids such as mercury which do not wet the glass, when it is convex), becomes flatter at high temperatures, slowly at first, but more rapidly as the critical point is approached. The meniscus finally becomes quite flat and less distinct, and then disappears, its place being taken by a broad band

of mist. At a slightly higher temperature the mist disappears, and the substance becomes homogeneous throughout. On allowing the tube to cool very slowly, the mist reappears, and then the meniscus. The range of temperature over which the change takes place, from the flat but quite visible meniscus to the broad band of mist, is so small that it should be quite possible to determine the critical temperature with an error of not more than 0·1°.

The mist or opalescence in fluids at and near the critical temperature has been carefully observed by Travers and Usher.[1] If the temperature of a sealed tube containing a pure liquid and its vapour is very slowly raised to and then above the critical point of the liquid, the following phenomena may be observed:—

1. If the surface of separation of liquid and vapour vanishes at the critical point near the bottom of the tube (in other words, if the quantity of substance is small), then at a slightly lower temperature the space below the surface becomes opalescent, appearing brownish by transmitted light, and whitish by reflected light. The nearer the surface is to the bottom of the tube, the more intense is the opalescence. When the surface vanishes the opalescence becomes gradually diffused through the whole tube, and this result may be attained at once by stirring the contents of the tube by means of an iron stirrer operated by a magnet outside the tube.

2. If the surface vanishes near the top of the tube the opalescence appears above the surface, and the nearer the surface is to the top of the tube, the more intense is the opalescence.

3. If the surface remains stationary, or nearly so, and is near the middle of the tube, while the temperature rises to the critical point, the fluid appears slightly and evenly opalescent throughout its entire length. In all cases the even distribution of the opalescence after the surface has vanished may be produced at once by stirring the contents of the tube.

In the case of sulphur dioxide the opalescence was first visible at 0·1° below the temperature at which the surface vanished; it attained a maximum at about 0·05° above it, and completely disappeared at a temperature 0·1° higher. With ether the effects persisted over about 2°. Travers and Usher made a few experiments in which the volume of the fluid could be altered; and they point out that when the surface remains stationary near the middle of the

[1] *Proc. Roy. Soc.*, **78A**, 247 (1906).

tube before disappearing, and the temperature is within the range over which the opalescence is visible, and when the volume is increased or decreased so slowly that the temperature is not lowered or raised appreciably, opalescence appears below or above the surface itself or the point at which it vanished, and its intensity is inversely proportional to the space it occupies. In other words, the phenomena described under (1) and (2) can be produced in this way.

Travers and Usher conclude that the opalescence is always visible in that phase[1] which is diminishing in volume, but experiments carried out by Young (*ibid.*, p. 262) in a modified Andrews apparatus at the critical temperature, while in complete agreement with those of Travers and Usher so far as comparison is possible, seem to indicate that the position of maximum opalescence depends rather on the mean specific volume of the fluid than on the alteration of either "phase," because when the volume was reduced from that at which opalescence was first visible to that at which it finally disappeared, the opalescence first appeared at the bottom of the tube (that is to say, just above the mercury), and as the volume diminished it spread upwards. When the critical volume was reached the opalescence was pretty evenly distributed, though densest about the middle, and when the volume was small the opalescence was confined to the top of the tube. The point cannot be definitely decided without further experiments.

From Young's experiments it appears that the limits of volume between which opalescence is visible at the critical temperature are nearly the same for the four paraffins (isopentane and normal pentane, hexane, and octane) examined, being about 1·17 or 1·18 to about 0·87 or 0·88, taking the critical volume as unity in each case.[2]

The temperature at which the liquid-vapour surface vanishes can be determined with great precision by means of the modified Andrews apparatus, because while the temperature of the vapour surrounding the experimental tube is kept constant, that of the sub-

[1] Employing the term "phase" not only for liquid and vapour, but also for the fluid above or below the level at which the surface disappeared, although it is believed that the fluid is really homogeneous at and above the critical temperature.

[2] *Vide* K. Onnes and Keesom, *Comm. Phys. Lab., Leiden*, **104** *b* (1908), and F. B. Young, *Phil. Mag.*, **20**, 793 (1910).

stance under investigation may be temporarily lowered or raised to a minute extent by increasing or diminishing the volume suddenly but slightly. The substance may be regarded as being at its critical temperature when no surface is visible so long as the temperature remains quite steady, but when a surface becomes visible for a moment on suddenly increasing the volume to a slight extent. Under favourable conditions it should be possible to determine the critical temperature by this method to within 0·05°, and in many cases determinations of the critical temperatures of different specimens of a compound have differed from each other by less than 0·05°.

For example, three specimens of isopentane were examined, the first, A, obtained from Kahlbaum, who prepared it from amyl alcohol; the second, B, separated from American petroleum; and the third, C, prepared by reduction of amyl iodide. The specimen A was heated in the vapours of both aniline and quinoline, the specimens B and C in the vapour of aniline only. With aniline vapour as the jacket the observed critical temperatures of the three specimens were between 187·75° and 187·8°, but the actual pressures (reduced to 0° C.) under which the aniline was boiling were only recorded in the case of specimens A and B. The read pressures were as follows:—

Specimen.	Pressure (aniline).	Pressure (quinoline).
B	827·8	—
A	827·45	216·55
A	827·45	216·6
A (small quantity)	828·35	216·85
Mean	827·76	216·67
Maximum difference from mean	0·59	0·18
Corresponding temperature difference	0·028°	0·030°

Again, in three determinations of the critical temperature of normal pentane, one with a sealed tube and two with the modified Andrews apparatus, the pressures under which the quinoline boiled were 281·1, 281·35, and 281·2 mm. respectively. The maximum difference from the mean pressure is 0·13 mm., and the corresponding temperature difference 0·017°.

Various other methods of determining the critical temperature of a substance have been devised, and are fully described by Mathias ("Le Point Critique des Corps Purs").

The question whether, for a given substance, the highest temperature at which a liquid-vapour surface is visible depends, on the one hand, on the mean specific volume of the substance, or, on the other hand, on the direction of the change of temperature, whether slowly rising or slowly falling, has given rise to much controversy.

Battelli, Zambiasi, Galitzine, de Heen, and others have obtained very discordant results. De Heen[1] found in the case of ether that the greater was the mean density s [$= \frac{m}{v}$, where m is the weight of ether, v the capacity of the tube] the higher was the temperature t_c at which the surface disappeared. Differences of 1° or 2° were observed, but it may be pointed out that the critical temperatures observed by De Heen differ widely in some cases from those of other experimenters.[2] Battelli,[3] on the other hand, finds—at any rate when s is either greater or not much less than the critical density—that t_c falls as s increases. But there were two series of determinations for both alcohol and ether carried out at different times, and the differences between two values of t_c observed at different times for the same value of s are in some cases greater than the maximum differences between the values of t_c observed at the same time for different values of s.

Zambiasi[4] arrives at the conclusion that t_c rises as s decreases, the maximum temperature being reached when $s = s_c$, the critical density; but Mathias[5] shows that Zambiasi's results, if correct, indicate that t_c continues to rise when s falls below s_c. The total observed variation was 0·5°. Hannay[6] found that for some liquids t_c was independent of s, while for others a variation was noticed. He attributed this variation to the presence of impurities.

Galitzine,[7] experimenting with ether, found that t_c was independent of s, but that t_c', the temperature at which the meniscus reappeared on cooling, was somewhat lower than t_c, and that there was an indication of a slight rise of t_c' with increase of s.

Travers and Usher (*loc. cit.*) state definitely that they found the Cagniard de la Tour temperature to be independent of s, and their experiments indicate that $t_c = t_c'$.

[1] *Bull. de l'Acad. roy. de Belgique*, **24**, 96 (1892).
[2] In the case of methyl acetate the error actually amounts to about 45°.
[3] *Nuovo Cimento*, III. **33**, 22 (1892).
[4] *Atti d. R. Acc. dei Lincei*, V. **1**, 423 (1892).
[5] "Le Point Critique des Corps Purs," p. 34.
[6] *Proc. Roy. Soc.*, **30**, 484 (1880). [7] *Wied. Ann.*, **50**, 521 (1893).

Young, in his determinations of the critical constants of numerous carefully purified substances, has found that t_c is independent of s, and that $t_c = t_c'$, or at least that the differences are within the limits of experimental error.

Even as regards the results of de Heen and Battelli, the statement may be made that the observed differences, although larger, are within the limits of the larger experimental errors, and the evidence, on the whole, is therefore in favour of the conclusion that, in the case of a pure substance free from air, the Cagniard de la Tour temperature is independent of the mean density and of the direction of the change of temperature.

The Critical Pressure.—The critical pressure may be best determined experimentally by means of the modified Andrews apparatus.

The determination is carried out in the same manner as that of the vapour pressures of the liquid at lower temperatures. The critical isothermal is so nearly horizontal in the immediate neighbourhood of the critical volume that there is no difficulty in ascertaining the critical pressure if a series of readings are taken over a range which includes the critical volume.

The critical pressure is altered by the presence of air or other impurities to even a greater extent than the critical temperature, and it is absolutely necessary that the utmost care be taken to purify the liquid under investigation and to remove all traces of dissolved air from it. The observed critical pressures of two specimens of a substance should not differ by 0·2 per cent.

If the critical temperature is very high so that the vapour pressure of mercury is considerable, or if the substance attacks mercury at a high temperature, the modified form of experimental tube referred to on p. 125 may be employed; or if the critical pressure only, and not the temperature, is to be measured, the method of Altschul[1] may be employed. The apparatus required is similar in principle to that of Andrews, but the experimental tube is fixed in a nearly horizontal position. A small portion only of the liquid in it is heated by a small Bunsen flame, a sheet of metal being interposed between the flame and the glass tube. When the liquid boils there is a meniscus on each side of the vapour, and the pressure is so arranged that the two liquid surfaces are near each other. The

[1] *Zeit. physik. Chem.*, **11**, 577 (1893); also Guye and Mallet, *Arch. de Genève*, [4], 13 (1902).

temperature is slowly raised, and the pressure is first read when the surfaces vanish, and again when they reappear on slow cooling. Guye and Mallet have always found the two pressures to be identical, provided that the substance investigated was pure and stable, and a further proof is thus afforded that the temperature at which the meniscus disappears is the same as that at which it reappears.

The Critical Volume.—Owing to the extreme compressibility of matter at and near its critical point, it is impossible to read the critical volume accurately on the critical isothermal in the pressure-volume diagram.

For the same reason it is impossible, by any method yet devised, to make a direct experimental determination of the critical volume (or density) with sufficient accuracy. It is indeed impossible, as pointed out by Gouy,[1] for the whole of the fluid in a tube to be in the critical state, because, although the temperature may be the same throughout, the pressure must vary slightly at different levels; that at the bottom of a tube being greater than at the top by $\frac{s \cdot h}{13{\cdot}6}$ mm. of mercury, where s is the mean density of the fluid, h the height of the column, and 13·6 is the density of mercury. In a cylindrical tube the value of $\frac{s \cdot h}{13{\cdot}6}$ is, of course, independent of the temperature, since h varies inversely as s, and it may be determined once for all at any low temperature for which s and h have been determined.

But at the critical temperature, when the volume is not very different from the critical volume, a very small alteration in pressure makes a marked difference in the density. Gouy has calculated that in a tube of 10 cms. height, containing pure carbon dioxide heated uniformly to its critical temperature, there may be a difference of 6 per cent. between the densities at top and bottom. The variation is greatest at the level where the pressure is exactly the critical pressure, a difference in height of 0·5 mm. being sufficient to produce a difference of 1 per cent. in density, and a difference in height of 0·004 mm. a difference of 0·2 per cent. in density.

Strictly speaking, below the critical temperature it is only immediately above and below the surface of separation that the vapour and liquid respectively have their true (orthobaric) densities. At a higher level the vapour is not quite saturated, and at a lower level the liquid is slightly compressed, but it is only in the neighbourhood

[1] *Compt. rend.*, **115**, 720 (1892).

of the critical temperature that either vapour or liquid is so compressible that the variation in density at different levels is considerable.

When the temperature of a vertical tube containing a pure liquid and its vapour is very slowly raised until the critical point of the substance is reached, the meniscus, if it does not reach the top or bottom of the tube at a lower temperature (p. 160), becomes flat, then indistinct, and finally vanishes. It is evidently at the level where the meniscus vanishes that the density is the true critical density, and it is also at this level that the opalescence is most marked. Above this level the density is lower; below, it is higher. If the meniscus vanishes near the top of the tube, the mean density will be considerably higher than the critical density; if near the bottom of the tube, the mean density will be considerably lower. It follows that the critical phenomena can be observed even when the mean density of the fluid is considerably higher or lower than the critical density; in other words, the quantity of liquid in a sealed tube may vary within moderate limits.

To put the matter in another way: the condition as regards pressure and volume of a fluid enclosed in a long vertical tube and exhibiting the critical phenomena, is not represented by the point on the critical isothermal which coincides with the summit of the liquid-vapour surface, but by a length along the isothermal which includes this point. If the tube, while its temperature remained constant, were moved into a horizontal position, the variation in pressure and in specific volume would diminish and the length of isothermal represented would be greatly shortened. In a tube of narrow bore held in a horizontal position the mean density would require to be very nearly equal to the critical density for the critical point to be included in the isothermal, and if the meniscus disappeared near the top or bottom of the tube when vertical, it may be concluded that no part of the fluid would be in the critical state when it was horizontal.

If the mean density of the fluid in a tube is equal to the critical density, the meniscus will vanish at about the middle of the tube on slowly raising the temperature to the critical point, and an approximate determination of the critical volume might be made with the modified Andrews apparatus by adjusting the plunger so that the volumes of liquid and saturated vapour immediately below the critical temperature were equal.

The critical temperature of normal pentane is 197·2°, and four readings of the volume of vapour and of the total volume were taken by Young at each of a series of temperatures. Thus at 197·0°, calling the total volume v, and the volume of vapour v_v, the following values of $\frac{v_v}{v}$ and v were obtained:—

$\frac{v_v}{v}$ . . .	0·1363	0·3286	0·5079	0·6732
v . . .	0·4271	0·4483	0·4694	0·4905

Plotting $\frac{v_v}{v}$ against v, the value of v corresponding to $\frac{v_v}{v} = 0{\cdot}5$ is found to be 0·4686 c.c., and this divided by the weight of substance, 0·10922 gram, gives 4·290 as the critical volume of a gram, v_c, the value found by the more accurate method of Cailletet and Mathias being 4·268. The values found in a similar manner at other temperatures very near the critical point are—

Temperature .	196·9	197·1	197·15
v_c . . .	4·282	4·284	4·286 mean 4·285

The method could not, however, be employed for temperatures far below the critical point; thus at 170° the calculated value of v_c would be 4·091.

F. B. Young [1] considers that the observed differences in density are greater than can be accounted for by the action of gravity and attributes them in great measure to minute temperature differences.

The curve enclosing the liquid-vapour surface in (*a*) the pressure-volume (Fig. 22), (*b*) the temperature-volume (Fig. 39), (*c*) the pressure-density, and (*d*) the temperature-density (Fig. 40) diagram, is in each case of such a form that while the critical pressure or temperature can be read with considerable accuracy, neither the critical volume nor the critical density can be estimated with any approach to exactness.

As already mentioned, however, it was stated by Cailletet and Mathias that the mean densities of liquid and saturated vapour, when plotted against the temperature, fall on a straight line, and although there is in reality, as a rule, very slight curvature of the diameter, yet their method affords by far the most accurate method of determining the critical density.

[1] *Phil. Mag.*, **20**, 793 (1910).

To obtain the best results the curvature should be taken into account, and the critical density calculated from the formula $s_t = s_0 + a(t_c - t_0) + \beta(t_c - t_0)^2$.

In the table on the following page the critical and a few other constants are given for a number of substances.

Relation between Critical Temperature and Boiling Point.—The question whether any simple relation exists between the boiling points under normal pressure and the critical temperatures of different substances seems to have been first discussed by Pawlewski,[1] who arrived at the conclusion that the difference between the two temperatures was the same for all substances, and he gave a list of seventeen esters for which the observed differences varied only between 181·2° and 182·9°; but in a later list of twenty-four widely different substances the differences varied between 150·1° and 210·0°.

That the rule is not even roughly applicable to all substances may, however, be seen from the following table, in which the temperatures are given on the absolute scale:—

	Critical Temperature = T_c.	Boiling Point = T_b.	Difference, $T_c - T_b$.	Ratio, $\frac{T_c}{T_b}$.
	Degrees.	Degrees.	Degrees.	
Hydrogen .	35	20	15	1·75
Oxygen . .	154	90·5	63·5	1·70
Methane . .	191	108·3	82·7	1·76
Octane . .	569·2	398·8	170·4	1·43
Benzene . .	561·5	353·2	208·3	1·63
Water . .	633	373	260	1·59

It would, indeed, as will be seen from the table, be more correct to state that the critical temperatures are roughly proportional to the boiling-points. This rough proportionality, to which attention was directed by Guldberg,[2] may, in fact, be occasionally useful in obtaining an idea of the critical point of a substance, especially if the following points are borne in mind:—

1. In any homologous series the ratios $\frac{T_c}{T_b}$ diminish—though usually at a decreasing rate—with rise of molecular weight.

[1] *Berichte*, **15**, 460 and 2460 (1882); **16**, 2633 (1883).
[2] *Zeit. physik. Chem.*, **5**, 371 (1890).

Name.	Specific Gravity at 0°.	Boiling Point at 760 mm.	Critical Temperature.	Critical Pressure.	Critical Density.	$\frac{^{c}c}{S_c}$
		Degrees.	Degrees.	Millimetres.		
Carbon tetrachloride	1·63255	76·75	283·15	34,180	·5576	3·680
Hexamethylene	0·79675	80·9	280·0	30,280	·2735	3·706
Isopentane	0·63930	27·95	187·8	25,020	·2343	3·735
Di-isopropyl	0·67948	58·1	227·35	23,360	·2411	3·741
Stannic chloride	2·27875	114·1	318·7	28,080	·7419	3·740
Benzene	0·90006	80·2	288·5	36,395	·3045	3·755
Normal pentane	0·64539	36·2	197·2	25,100	·2323	3·766
Iodobenzene	1·86059	188·45	448·0	(33,910)	·5814	3·780
Chlorobenzene	1·12786	132·0	359·2	33,926	·3654	3·776
Fluorobenzene	1·04653	85·2	286·55	33,910	·3541	3·796
Bromobenzene	1·52182	156·0	397·0	(33,910)	·4853	3·809
Di-isobutyl	0·71021	109·2	276·8	18,660	·2366	3·810
Ether	0·73620	34·6	193·8	27,060	·2625	3·813
Normal hexane	0·67696	68·95	234·8	22,510	·2344	3·831
Normal heptane	0·70048	98·4	266·85	20,430	·2341	3·854
Methyl isobutyrate	0·91131	92·3	267·55	25,740	·3012	3·866
Normal octane	0·71848	125·8	296·2	18,730	·2327	3·865
Propyl formate	0·92868	80·9	264·85	30.460	·3093	3·869
Ethyl formate	0·94802	54·3	235·3	35,535	·3232	3·895
Methyl propionate	0·93871	79·7	257·4	30,030	·3124	3·909
Methyl butyrate	0·92006	102·75	281·3	26,055	·3002	3·903
Ethyl propionate	0·91240	99·0	272·9	25,217	·2965	3·923
Methyl formate	1·00319	31·9	214·0	45,030	·3489	3·922
Propyl acetate	0·91016	101·55	276·2	25,227	·2957	3·934
Methyl acetate	0·95932	57·1	233·7	35,212	·3252	3·943
Ethyl acetate	0·92436	77·15	250·1	28,880	·3077	3·949
Propyl alcohol	0·81930	97·2	263·7	38,120	·2734	3·998
Ethyl alcohol	0·80625	78·3	243·1	47,850	·2755	4·026
Methyl alcohol	0·81000	64·7	240·0	59,660	·2722	4·559
Acetic acid	1·06970	118·5	321·6	43,400	·3506	4·992

Critical density not calculated from formula, but read from curve constructed graphically.

2. The ratios are generally nearly the same for the members of a group of closely related (not homologous) substances.

3. In the case of isomeric substances the ratios for iso-compounds are higher than for normal, and for di-iso-compounds they are still higher.

Homologues.	$\frac{T_c}{T_b}$	Isomers.	$\frac{T_c}{T_b}$	Closely Related Substances.	$\frac{T_c}{T_b}$
Methane	1·764	Isobutane	1·566	Fluorobenzene	1·562
Ethane	1·694	n-butane	1·555	Chlorobenzene	1·563
Propane	1·616	Isopentane	1·531	Silicon tetra-chloride	1·513
n-butane	1·555	n-pentane	1·520	Stannic chloride	1·529
n-pentane	1·520	Isopropyl benzene	1·492	Germanium tetra-chloride	1·532
n-hexane	1·485	Propyl benzene	1·485	Chlorine	1·749
n-heptane	1·454	Di-isopropyl	1·511	Bromine	1·734
n-octane	1·427	n-hexane	1·485	Iodine	1·716
n-nonane		Di-isobutyl	1·443	Argon	1·791
n-decane	1·402	n-octane	1·427	Krypton	1·735
Methyl formate	1·597	Methyl isobutyrate	1·480	Xenon	1·756
,, acetate	1·535	,, butyrate	1·475		
,, propionate	1·504				
,, butyrate	1·475				

Thorpe and Rücker's Relation.—Thorpe and Rucker[1] have proposed the following formula, by which the critical temperature of a substance may be approximately calculated from the densities of the liquid at two temperatures not necessarily higher than the ordinary boiling point:—

$$T_c = \frac{T_2 s_1 - T_1 s_2}{A(s_1 - s_2)}$$

where T_1 and T_2 are the two absolute temperatures, s_1 and s_2 the corresponding densities, and A is a constant which the authors take to be 1·995.

Calculating the values of A for twenty-four substances for which the required data are accurately known, and taking the melting point of ice and the boiling point of the substance under normal pressure in each case, values were obtained ranging from 1·926 for ethyl propionate to 2·030 for fluorobenzene and chlorobenzene. The mean value is 1·974, and it is only in few cases that the difference from this value exceeds 2 per cent.

Walden[2] has brought forward the following relations: Men-

[1] *Trans. Chem. Soc.*, **45**, 135 (1884).
[2] *Zeit. physik. Chem.*, **65**, 129 (1908).

deléeff's formula $s_t = s_o(1 - kt)$ may be written $v_t = \frac{v_o}{1 - kt}$, where k is the coefficient of expansion. Walden states that k is approximately inversely proportional to the critical temperature for a considerable number of normal liquids, and he gives the equation— $k = \frac{0{\cdot}34}{t_c}$. Taking $k_o = \frac{v_2 - v_1}{v_2T_2 - v_1T_1}$, where T_1 and T_2 are absolute temperatures, he also states that $k_o = \frac{0{\cdot}49}{T_c}$ and shows that the relation holds approximately for nine liquids with boiling points ranging from 77° to 535° abs.

Walden further states that for many normal liquids the coefficients of expansion k are inversely proportional to γ, the surface tensions, and that $k = \frac{0{\cdot}032}{\gamma}$ approximately; also that the coefficients of expansion are roughly proportional to the compressibilities.

Guye[1] discusses the various relations said to exist between the critical temperatures, boiling points, and coefficients of expansion of liquids.

Kendall[2] derives the following expressions, which are found to agree with Young's experimental results over the ordinary range of temperature :—

1. $L = k(T_c - T)^n$, where L is the heat of vaporization, T and T_c the absolute temperature and absolute critical temperature respectively, k is a constant characteristic of each particular liquid, and $n = 0{\cdot}386$ for all normal liquids.

2. $\sqrt[3]{s_L} - \sqrt[3]{s_c} = k_1(T_c - T)^{\frac{1}{3}}$, where s_L is the density of the liquid at T°, s_c the critical density, and k_1 a constant depending on the liquid. Also $\sqrt[3]{s_c} - \sqrt[3]{s_v} = k_2(T_c - T)^{\frac{1}{3}}$, where s_v is the density of the saturated vapour at T°, and k_2 a constant for any particular substance.

3. $L = 0{\cdot}00003183\,3\,p(v_V - v_L) + k_1\mu(T_c - T)^{\frac{1}{3}} + k_2\mu(T_c - T)^{\frac{1}{3}}$, where p is the vapour pressure, v_V and v_L the volumes of a gram of saturated vapour and liquid respectively, and μ a constant for any particular compound.

[1] *Trans. Faraday Soc.*, **7**, 119 (1911).

[2] *Medd. K. Vet. Nobelinstitut*, **2**, 1 (1913), *vide Science Abstracts*, No. 1009 (1914).

CHAPTER X.

THE KINETIC THEORY OF GASES.

It was first pointed out by Bernoulli, in 1740, that the pressure of a gas is due to the impact of the molecules against the body on which the pressure is exerted. The theory was greatly extended and advanced by J. J. Waterston, but, unfortunately, his paper, which was read before the Royal Society in 1845, was not then published, and was entirely forgotten. It was found by Lord Rayleigh in the archives of the society, and was published in 1892.[1]

Meanwhile the theory was independently developed by Krœnig in 1856, and Clausius in 1857, and has been further extended by Clausius, Maxwell, Boltzmann, Van der Waals and others.

The molecules of a gas are considered to be extremely minute, but still of finite dimensions. The volume actually taken up by the molecules of a gas under ordinary conditions of temperature and pressure is very small compared with the total volume of the gas. The molecules are, therefore, relatively to their size, very far apart, and it is assumed that they exert no appreciable attraction on each other. When they approach each other they are regarded as behaving like perfectly elastic bodies.

Consider the path of an individual molecule in a quantity of gas kept at constant temperature and pressure. As it is not acted on by any forces (other than gravity, which need not be considered), the molecule will move with uniform velocity in a straight line until it collides[2] with another molecule. It will rebound from this in a new direction and with a different velocity, with which it will move uniformly until a second collision occurs. Thus the direction and velocity will change after each collision, but the velocities will vary about a definite mean value. The "free path" also will vary from

[1] *Phil. Trans.*, **183**, 1 (1892).

[2] It is not necessary to assume that actual contact between the molecules takes place; the assumption is that the effects are the same as if the two molecules were perfectly elastic, and came into collision.

collision to collision, but under constant conditions of temperature and pressure its mean value will remain constant.

The mean kinetic energy of rectilinear motion of a single molecule $= \frac{1}{2}mu^2$, where m is the mass of the molecule, and u its mean velocity. But besides the kinetic energy of rectilinear motion, the molecule may possess internal energy, due to rotation or oscillation of the atoms composing it. It is believed that the internal energy also varies about a definite mean value.

Boyle's Law.—The pressure which the gas exerts on the walls of the vessel containing it is caused by the impact of the molecules against the sides, and it is clear that, under otherwise similar conditions, the pressure will be proportional to the number of impacts in unit time, which, in their turn, will be proportional to the number of molecules in unit volume; that is to say, to the density of the gas. The pressure will therefore vary directly as the density or inversely as the volume occupied by a given mass of the gas. Boyle's law, therefore, follows at once from the kinetic theory.

In order to calculate the pressure, consider the gas in a cube of unit volume, each surface and each side being therefore equal to unity. Let m be the mass of a molecule, and N the number of molecules in the unit volume; then $m\mathrm{N} = s$, where s is the density, or mass of gas in unit volume.

The pressure depends in two ways on the velocity of the molecules, for not only the force of the impacts, but also the number of them in unit time is proportional to the velocity. A molecule which collides vertically with a wall of the cube rebounds with the same velocity as before, but in exactly the opposite direction, and, as the original momentum is mu, the change of momentum is $2mu$.

The number of impacts in unit time on the whole surface is proportional to the total number of molecules, N, and to the velocity u, and is equal to $\mathrm{N}u$. But as there are six walls, the number of impacts on a single wall $= \frac{1}{6}\mathrm{N}u$, and the pressure, p, on one wall, that is to say, on unit area, is—

$$2mu \times \tfrac{1}{6}\mathrm{N}u = \tfrac{1}{3}m\mathrm{N}u$$
$$= \tfrac{1}{3}su^2.$$

Take the case of hydrogen gas at 0° C. and 760 mm. pressure. The mass of 1 c.c. = 0·0000899 gram, and the pressure on 1 sq. cm. = 1033 grams, or 1033 × 981 dynes. Therefore, since—

$$u^2 = \frac{3p}{s}$$

$$u = \sqrt{\frac{3p}{s}} = \sqrt{\frac{3 \times 1033 \times 981}{0{\cdot}0000899}}$$

$$= 184{,}000 \text{ cms. per second.}$$

The molecules of hydrogen at 0° C. therefore move at the mean rate of 1·84 kilometres per second; and those of any other gas, the density of which at 0° C. and 760 mm. is s', move at the rate of $1{\cdot}84\sqrt{\frac{s}{s'}}$ kilometres per second; or if d is the density of the second gas, taking that of hydrogen at the same temperature and pressure as equal to unity, the molecular velocity at 0° $= \frac{1{\cdot}84}{\sqrt{d}}$ kilometres per second.

The mean velocity of the molecules is independent of the pressure, but it increases with rise of temperature. It is found experimentally that the pressure of a gas at constant volume is directly proportional to the absolute temperature; but the pressure is proportional to u^2, and therefore to $\frac{1}{2}mu^2$; therefore, the mean kinetic energy of rectilinear motion of the molecules is directly proportional to the absolute temperature.

Avogadro's Hypothesis.—If two different gases are compared at the same temperature and pressure, $p = \frac{1}{3}m_1N_1u_1^2 = \frac{1}{3}m_2N_2u_2^2$, where m_1 and m_2 are the masses of the molecules of the two gases respectively, and N_1 and N_2 the number of molecules in unit volume.

But when two gases at the same (high) temperature and (low) pressure are mixed together, the change of pressure or temperature which occurs is so slight that it may be assumed that no change whatever would take place in the case of *perfect* gases. It may therefore be concluded that the kinetic energy of the molecules of different gases at the same temperature is equal, and that—

$$\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2.$$

But since $\frac{1}{3}m_1N_1u_1^2 = \frac{1}{3}m_2N_2u_2^2$, it follows that $N_1 = N_2$.

Avogadro's hypothesis, therefore, receives very strong support from the kinetic theory of gases.

Ratio of the Specific Heats at Constant Pressure and Constant Volume.—The heat energy of a gram-molecule of a gas is given by the kinetic energy of rectilinear motion of the molecules

plus the internal energy of the molecules. Let e be the increase of internal energy per unit rise of temperature, and C_v the molecular heat at constant volume; then—

$$C_v = \frac{1}{J}\left(\frac{1}{2} \times \frac{mu^2}{T} + e\right)$$

where J is the mechanical equivalent of heat,

and the molecular heat at constant pressure $= C_p$

$$= \frac{1}{J}\left(\frac{1}{2} \times \frac{mu^2}{T} + e + \frac{1}{3} \times \frac{mu^2}{T}\right)$$

the latter term being due to the work done in expansion against external pressure.

The ratio of the specific heats $= \frac{C_p}{C_v} = \gamma$

$$= \frac{\frac{5}{6} \times \frac{mu^2}{T} + e}{\frac{1}{2} \times \frac{mu^2}{T} + e}.$$

If $e = 0$, then $\gamma = \frac{5}{3} \times 2 = 1{\cdot}66\dot{6}$; but if e has a finite value, γ must be less than 1·66, and the higher the value of e, the more closely will γ approach to unity.

If the molecules of a gas consist of single atoms, it may be concluded that there is no internal energy, and that $e = 0$.

Kundt and Warburg, employing a modification of Kundt's apparatus, found that $\gamma = 1{\cdot}66$ for mercury vapour,[1] and Ramsay and Travers have obtained values approximating closely to 1·6 for the inert gases of the argon family; it is therefore believed that the molecules of these gases are monatomic.

For oxygen the value 1·404 has been obtained, and for nitrogen 1·410, and as it is practically certain that the molecules of these gases, like those of hydrogen, are diatomic, it may be concluded that the normal values of γ for gases which consist of diatomic molecules is 1·40 to 1·41.

Determinations of γ have been made for a number of other gases and vapours, and the data obtained clearly indicate that as the complexity of the molecules increases, the value of γ approaches more closely to unity. Thus for ethyl ether, $C_4H_{10}O$, values of γ from 1·03 to 1·06 have been obtained.

[1] *Vide* p. 59.

Mean Free Path.—According to Clausius the mean free path L is given by the equation—

$$L = \frac{\lambda^3}{\frac{1}{\sqrt{2}}\pi l^2}$$

where λ is the mean distance from centre to centre of two molecules regarded as spherical, so that λ^3 is the size of cube that would contain one molecule, or the space inhabited by one molecule; and l is the distance between the centres of two molecules when in the position of closest contact—for example, at the moment of collision.

The question was examined by Maxwell, who in 1860 determined the values of L for some gases from their internal friction. Independent values of L were subsequently obtained by Maxwell and Clausius from the conductivities of gases for heat, and by Maxwell and Stefan from their rates of diffusion.

O. E. Meyer has given the following values of L for a number of gases at 20° C. and 760 mm.

	L
Hydrogen . . .	18·5 millionths of a mm.
Methane	8·5 ,, ,,
Carbon monoxide . .	9·8 ,, ,,
,, dioxide . . .	6·8 ,, ,,
Ammonia	7·4 ,, ,,
Ethylene	5·8 ,, ,,
Methyl ether . . .	4·2 ,, ,,

The Dissociation of Gases.

Maxwell's Law of Velocities.—It has been pointed out that the velocity of any individual molecule in a mass of gas at constant temperature changes after each collision with other molecules, although its mean velocity, calculated for a sufficient number of free paths, remains constant. It is clear, therefore, that the molecules cannot all be moving at the same rate, and if, at a given moment, the velocity of every molecule of the gas could be determined, and if the molecules were grouped according to their velocities, say—

$(u - n), \ldots (u - 2), (u - 1), (u), (u + 1), (u + 2), \ldots (u + n)$

metres per second, where u includes all velocities from $(u - \frac{1}{2})$ to $(u + \frac{1}{2})$ and so on, a great many molecules would be found with

velocity u, a smaller number with velocities $(u - 1)$ and $(u + 1)$, a still smaller number with velocities $(u - 2)$ and $(u + 2)$, and so on. In fact, if the number of molecules in each group were plotted against the velocities, a curve of the form shown in Fig. 43 would be obtained.

The distribution of velocities would be similar to that of a set of observations of a constant quantity, according to their (+ or −) deviations from the true value; or of the bullet-marks in and round the bull's-eye on a target fired at (on a still day) by a good marksman, the marks outside the bull's-eye being counted to left and right of the centre of the target.

Now, since the absolute temperature of a gas is proportional to the mean square of the velocities of the molecules, it may be inferred that the individual molecules are not all at the mean temperature, but that there are many molecules at temperatures near the mean

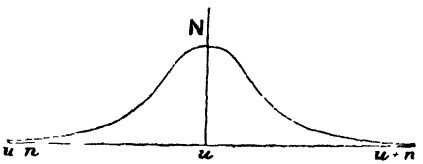


FIG. 43.

and few at temperatures far above or far below the mean. The distribution of temperatures would, in fact, be of the same nature as that of velocities.

Take the case of a gas, such as nitrogen peroxide or iodine, which dissociates into like molecules when heated, and consider what happens to a single molecule. The attraction between the component parts of the molecule tends to keep them together, while, on the other hand, the vibration or oscillation of the parts tends to drive them asunder. As the temperature rises, the oscillation increases until the attraction between the components is no longer able to hold them together, and dissociation then takes place. If the internal energy, like the kinetic energy of rectilinear motion, is directly proportional to the absolute temperature, there must be a definite temperature, which may be called the true temperature of dissociation, T_D, at which the single molecule dissociates.

The same reasoning would apply to any other single molecule, and if all the molecules were at the same temperature, it may be

concluded that the gas would suffer no dissociation until the temperature T_D was reached, but that at that temperature complete dissociation would take place. There would therefore be an abrupt change of density at T_D.

If, however, when the mean temperature of the gas is considerably lower than T_D, a few molecules reach that temperature, they will undergo dissociation, and the components will intermingle with the other molecules. But as the velocities, and therefore the temperatures, of the individual molecules are constantly changing, some or all of the component molecules will soon cool below T_D, and when they happen to come in contact with each other, recombination will take place.

Meanwhile other molecules will have dissociated, and for a time the number of molecules dissociated in unit time will be greater than the number re-formed; but as the number of component molecules increases, the chances of recombination become greater, and eventually a state of equilibrium will be established, dissociation being balanced by recombination.

Suppose now that the temperature is raised until it reaches T_D. There will then be as many molecules with temperatures above as below T_D, and it may be concluded that when equilibrium is established one-half the total number of molecules will be dissociated. At a still higher temperature the number of molecules dissociated will increase, but it is only when the mean temperature is far higher than T_D that there can be complete dissociation.

On allowing the temperature to fall again, gradual recombination will take place, the composition of the gas at any constant temperature depending solely on that temperature, and not on previous conditions. It follows that the curve representing the relation between the percentage number of molecules dissociated and the temperature will have the general form indicated in Fig. 44, and this conclusion is borne out by the experimental evidence.

When nitrogen peroxide is undergoing dissociation, only two kinds of molecule, N_2O_4 and NO_2, can be present at temperatures below that at which the NO_2 begins to dissociate; but by the dissociation of phosphorus pentachloride the unlike molecules PCl_3 and Cl_2 are formed. There may therefore be three kinds of molecule present in the gas, PCl_5, PCl_3, and Cl_2. The chances of recombination are smaller in this case than with nitrogen peroxide, because while any two molecules of NO_2 may reunite, it is only when a

molecule of PCl_3 comes in contact with a molecule of Cl_2 that recombination can occur.

But whenever a compound dissociates into unlike components the chances of recombination of either component may evidently be increased by introducing a larger number of molecules of the other component, and this without increasing the chances of decomposition. Thus in the case of phosphorus pentachloride, the greater the number of PCl_3 molecules the greater the chance of a chlorine molecule meeting a PCl_3 molecule at a temperature below T_D. In other words, by increasing the quantity of either component, the stability of the compound is apparently increased. Experimental

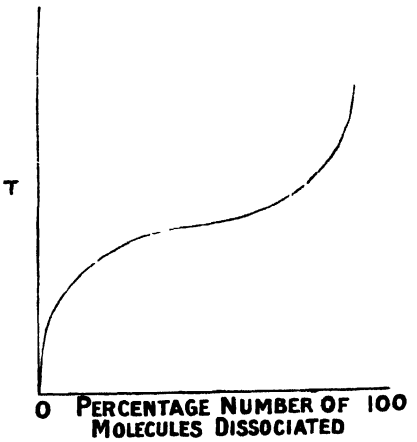


FIG. 44.

evidence of the correctness of this conclusion has already been adduced (pp. 109 and 110).

Calculation of the Percentage Number of Molecules Dissociated.—If a molecule, when dissociated, forms n simpler molecules, then, when dissociation of the gas is complete, the volume of unit mass will become n times as great, and the vapour density will be $\frac{D}{n}$, where D is the density of the undissociated gas.

Let d be the observed vapour density of a substance which, at the temperature of experiment, has undergone partial dissociation, and of every 100 complex molecules suppose that x have dissociated, giving nx simpler molecules. There will therefore be $100 - x + nx$ or $100 + (n - 1).x$ molecules altogether. But the density is in-

versely proportional to the volume, and therefore to the number of molecules, and—

$$\frac{D}{d} = \frac{100 + (n-1)x}{100}$$

therefore

$$x = \frac{100(D-d)}{(n-1)d}$$

and when $n = 2$

$$x = \frac{100(D-d)}{d}$$

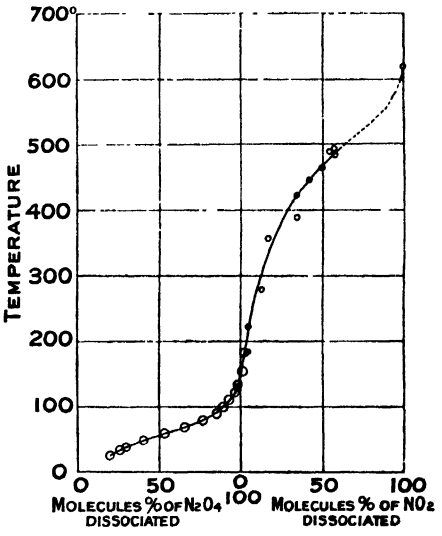


FIG. 45.

In the diagram (Fig. 45) the double dissociation $N_2O_4 = 2NO_2$, where $n = 2$, and $2NO_2 = 2NO + O_2$, where $n = \frac{3}{2}$, is represented, the data for the first stage in the dissociation having been obtained by Deville and Troost,[1] and for the second stage by Richardson.[2] The pressure is that of the atmosphere. In no case has the whole course of dissociation been satisfactorily observed, but this diagram shows the middle and upper parts of the first curve, and the lower and middle parts of the second curve, very satisfactorily.

It is, of course, quite probable that at 140° there may be a very few molecules of NO_2 dissociated, and at 150° a few molecules of N_2O_4 remaining.

[1] *Compt. rend.*, **64**, 237 (1867). [2] *Trans. Chem. Soc.*, **51**, 397 (1887).

Deville and Troost.			Richardson.		
Temperature.	Vapour Density.	Molecules per cent. of N_2O_4 Dissociated.	Temperature.	Vapour Density.	Molecules per cent. of NO_2 Dissociated.
Degrees.			Degrees.		
26·7	38·3	20·1	130·0	23·26	97·8 [2]
35·4	36·5	26·0			
39·8	35·5	29·6			
49·6	32·8	40·3	184·0	22·45	4·33
60·2	30·0	53·3	184·1	22·35	5·80
70·0	27·7	66·0	222·1	22·52	4·17
80·6	26·0	77·0	222·5	22·40	5·26
90·0	24·8	85·4	278·4	21·53	13·57
100·1	24·3	89·5	279·2	21·59	13·10
111·3	23·8	93·2	358·0	21·19	17·09
121·5	23·4	96·6	390·0	19·57	35·05
135·0	23·1	99·2	423·2	19·63	34·48
			447·0	18·98	43·28
			448·2	19·20	40·63
154·0	22·8	1·76 [1]	466·3	18·37	50·40
183·2	22·7	2·64	485·4	17·84	57·84
			490·0	18·04	55·00
			494·4	17·98	55·84
			494·4	17·78	58·71
			619·5	15·30	100·00

It has been stated (p. 17) that for a perfect gas at constant volume the pressure varies directly as the absolute temperature; in other words, the isochors are straight lines radiating from the zero of pressure and absolute temperature. Ordinary gases and vapours under moderate or low pressures show only slight deviations from this law. In the diagram (Fig. 46*a*) the theoretical isochors for isopentane representing 4000, 2000, and 1000 c.c. per gram respectively, are indicated by dotted straight lines, and actual observations (or rather points read from the isotherms constructed from actual observations) by circles, and it will be seen that the deviations for 4000 c.c. are too small to be recognizable on so small a diagram. With a substance which undergoes dissociation, however, the case is quite different.[3]

Consider, for example, such a substance as nitrogen peroxide, the molecules of which are believed to correspond to the formula N_2O_4 at low temperatures, and to the formula NO_2 at high temperatures

[1] Molecules per cent. of NO_2 dissociated.

[2] „ „ N_2O_4 „

[3] Ramsay and Young, *Phil. Mag.* (V.), **24**, 196 (1887).

(140° under normal pressure). Theoretical isochors may be constructed on the assumption that the gas does not dissociate, and that the formula is (*a*) NO_2, (*b*) N_2O_4.

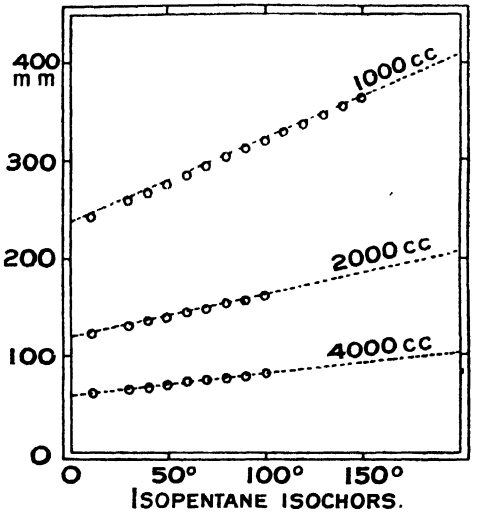


FIG. 46*a*.

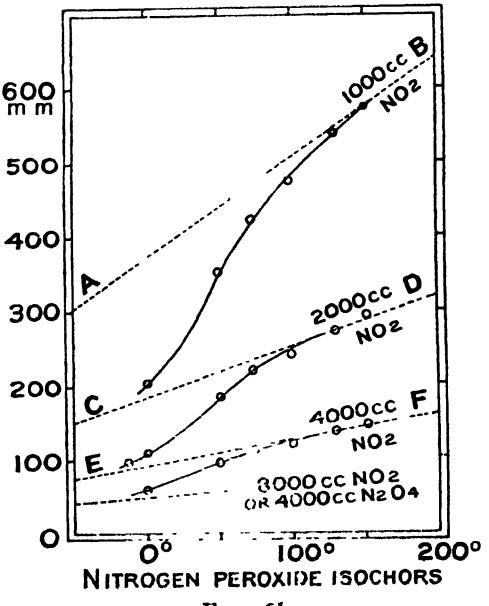


FIG. 46*b*.

In Fig. 46*b* the straight line AB is the theoretical isochor for 1000 c.c. of NO_2 per gram, and the line CD for 2000 c.c. of NO_2 per gram. But the number of molecules in 1 gram of N_2O_4 would be only half as great as in 1 gram of NO_2, therefore the theoretical volume of a gram would be only half as great. The isochor CD, therefore, represents not only 2000 c.c. of NO_2 per gram, but also 1000 c.c. of N_2O_4 per gram. Similarly the isochor EF represents 4000 c.c. NO_2, and also 2000 c.c. N_2O_4. If, then, when the temperature falls, the NO_2 molecules gradually unite to form N_2O_4 molecules, the isochor representing 1000 c.c. of the real gas, nitrogen peroxide, should start—at the higher temperature—on the theoretical isochor AB, and descend gradually to the isochor CD. The circles representing observations by E. and L. Natanson indicate clearly that the change does proceed in this manner, although the experiments could not be carried quite far enough to show the complete passage from one theoretical isochor to the other.

The experiments of Ramsay and Young on acetic acid lead to quite similar results, and confirmation is thus afforded of the conclusion that the changes of vapour density in these cases are really due to dissociation. The actual data for isopentane and nitrogen peroxide are given in the following table:—

Isopentane.				Nitrogen Peroxide.			
Volume in c.c. per gram.	4000	2000	1000	Volume in c.c. per gram.	4000	2000	1000
Temperature	Pressures.			Temperature.	Pressures.		
Degrees.				Degrees.			
10·75	—	—	241·5	− 12·6	—	97·0	—
11·0	61·3	121·8	—	0	58·5	110·0	204·2
30·0	65·3	130·1	258·5	49·7	96·2	183·7	353·0
40·0	67·7	134·8	267·0	73·7	112·5	220·0	422·5
50·0	69·8	139·2	275·0	99·8	121·2	241·0	473·5
60·0	71·8	143·1	284·5	129·9	136·0	271·3	540·0
70·0	74·2	147·5	293·5	151·4	146·3	294·0	573·5
80·0	76·2	151·8	302·0	—	—	—	—
90·0	78·5	156·6	311·0	—	—	—	—
100·0	80·4	160·7	319·5	—	—	—	—
110·0	—	—	328·5	—	—	—	—
120·0		—	327·0	—	—	—	—
130·0	—	—	346·0	—	—	—	—
140·0	—	—	355·0	—	—	—	—
150·0	—	—	363·5	—	—	—	—

CHAPTER XI.

THE KINETIC THEORY OF GASES (*continued*).

Gases under High Pressures.—It has been stated that the laws of Boyle, Gay Lussac, and Avogadro are only strictly applicable to *perfect* gases. The deviations from these laws are very small in the case of real gases under very low pressures, but they increase as the pressure is raised, and are very great when the gases are highly compressed.

It is believed, however, that the kinetic energy of rectilinear motion of the molecules is directly proportional to the absolute temperature under all conditions.

It is important to ascertain, if possible, what modifications must be made in the kinetic theory in order to explain the observed deviations, and a great step towards the solution of the problem was made in 1883 by Van der Waals.[1]

In the kinetic theory of gases, the pressure, due to the bombardment of the walls of a vessel by the molecules of gas, is calculated on the assumption (1) that the actual volume occupied by the molecules themselves is inappreciable compared with the total volume of the gas, and (2) that the molecules exert no appreciable attraction on each other. Both these assumptions are admissible when a gas is greatly rarefied, but they cease to be so when the molecules, by compression of the gas, are brought much closer together. The influence of both these factors must be taken into account in modifying the formula—

$$PV = RT.$$

Consider two perfectly elastic spherical balls, A and B, moving from end to end of a table with vertical walls. It is clear that the free path of the larger ball A is as much shorter than that of the smaller one B as the diameter of A is greater than that of B; and if both balls were moving at the same uniform rate backwards and

[1] "Continuitat der gasförmigen und flussigen Zustandes."

forwards, the number of collisions in unit time against the sides of the table would be greater in the case of the large ball than of the small one.

So, also, the molecules, if they are of finite size, must have shorter free paths than they would have if they were mere mathematical points; the number of impacts in unit time, and therefore the pressure, must also be greater. So long as the mean free path is exceedingly long compared with the diameter of a molecule, the error introduced by disregarding the actual size of the molecule is unimportant, but a correction is necessary in the case of compressed gases, and, in very accurate work, even in the case of gases under moderate pressures.

According to Van der Waals, the ratio of the corrected to the uncorrected pressure $= \frac{v}{v - b}$, where b represents four times the actual volume, v_m, of the molecules. O. E. Meyer, however, arrives at the conclusion that $b = 4\sqrt{2}v_m$.

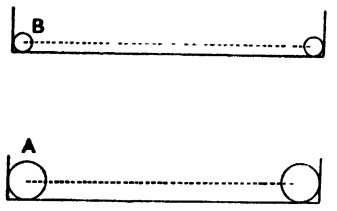


FIG. 47.

On the other hand Van Laar[1] believes that b is the actual volume occupied by the molecules. Richards[2] shows that for carbon dioxide at 1·15° above the critical temperature, b is nearly constant until by compression the critical volume is reached, but that it then diminishes rapidly; for this and other reasons he concludes that the molecules themselves are compressible.

Again, when the molecules are very close together, it can hardly be doubted that there is a force of attraction between them. In 1854 Joule and Thomson showed experimentally that strongly compressed gases (with the exception of hydrogen), when allowed to expand without overcoming external pressure, become distinctly cooler. It follows, therefore, that work must be done against the molecular attraction. In other words, there is in gases a force of cohesion which increases with the density. There are many reasons for believing that the attractive force is very great when the molecules are close together, but that it diminishes rapidly as the distance increases. J. E. Mills (p. 144) has brought forward strong evidence in favour

[1] *Proc. K. Akad. Wet. Amsterdam*, **16**, 808; **17**, 451 (1914).
[2] *Journ. Amer. Chem. Soc.*, **36**, 617 (1914).

of the view that the force, like that of gravity, varies inversely as the square of the distance, but it has generally been considered that the distance must be raised to a higher power.

It has been suggested by Lord Rayleigh that there are two forces acting between molecules, one of attraction, the other of repulsion, and that the force of repulsion varies inversely as a higher power of the distance than that of attraction. In that case the resultant force simulates a single force varying inversely as the (approximate) square of the distance.

A molecule in the interior of a mass of gas is not attracted in any one direction more than another, since it is surrounded by evenly distributed molecules attracting it equally in all directions. A molecule on the surface of the gas, however, is attracted towards the interior. The force of its impacts against the walls of the vessel, and consequently the pressure of the gas, is therefore diminished.

Consider a portion of the surface layer of gas. The force with which each molecule is attracted inwards must be proportional to the number of molecules attracting it, that is to say, to the density of the gas. But the force must also be proportional to the number of molecules in the portion of surface layer considered, or, again, to the density of the gas. Van der Waals concludes that the attraction is proportional to the square of the density, or inversely proportional to the square of the volume of unit mass of the gas.

If p' is the pressure calculated from the volume by the formula $p'(v - b) = \mathrm{RT}$, and p the observed pressure, then—

$$p' - p = \frac{a}{v^2} = k$$

where a is a constant depending on the molecular attraction, and k may be termed the molecular pressure.

The equation $\mathrm{P}v = \mathrm{RT}$ therefore becomes, according to Van der Waals—

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT}$$

where p and v are the observed pressure and volume respectively, and R is the gas constant (p. 46); and it should, if correct, be applicable to liquids as well as gases.

The general behaviour of a gas, when compressed at constant temperature, is very well expressed by the equation of Van der Waals.

When the volume is very large, the factors $\frac{a}{v^2}$ and b have no appreciable influence, and the equation becomes simply $pv = RT$. But as the volume diminishes, the attractive force between the molecules comes, as a rule, first into play, and the product pv, instead of remaining constant, becomes smaller. When, however, the pressure is very great, the factor b ceases to be negligible, and its influence increases more rapidly than that of $\frac{a}{v^2}$. The product pv therefore reaches a minimum, and afterwards increases, until eventually it becomes much greater than at low pressures.

The ratio of the molecular pressure $\frac{a}{v^2}$ to the actual pressure, however, diminishes with rise of temperature, and at relatively very high temperatures it has always less influence than b. The product pv, therefore, does not diminish at all with rise of pressure, but shows a slow increase from the first. This is the case with hydrogen at 0° C., and with nitrogen at 100° (pp. 21 and 32).

For ethylene Baynes has calculated the constants—

$$\left(p + \frac{0{\cdot}00786}{v^2}\right)(v - 0{\cdot}0024) = 0{\cdot}0037(272{\cdot}5 + t)$$

where t is the centigrade temperature.

Calling $pv = 1000$ for $p = 1$ at 20° C., the values of pv calculated from the formula are compared with those observed by Amagat in the following table:—

p	pv	
	Observed.	Calculated.
1·c	1000	1000
31·6	914	895
72·9	416	387
110·5	454	446
176·0	643	642
282·2	941	940
398·7	1248	1254

Making $(272{\cdot}5 + t) = 1000$, the following values of pv are given by the equation, making again $pv = 1000$ for $p = 1$:—

p	pv (calculated).
1·0	1000·0
3·7	1000·2
37·1	1003·2
408·2	1103·0

According to the formula, at this high temperature the values of pv would rise slowly with increase of pressure.

It is assumed by Van der Waals that the molecules of an ordinary substance undergo no alteration during the process of liquefaction, and his equation is intended to apply only to such substances. When molecular association takes place, as with acetic acid, nitrogen peroxide, and probably water and the alcohols, the relation between temperature, pressure, and volume must necessarily become much more complex.

The equation $\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT}$, if v remains constant, takes the form—

$$(p + c)c' = \mathrm{RT}$$

$$\text{or } p + c = \frac{\mathrm{R}}{c'} \times \mathrm{T}$$

$$\text{or } p = k\mathrm{T} - c$$

where c and c' are constants, and $k = \frac{\mathrm{R}}{c'}$.

The pressure is thus a linear function of the temperature when the volume of a given mass of the substance remains constant; in other words, the isochors are straight. They do not, however, start from zero pressure, but the pressure corresponding to 0° abs. is negative. This relation was first observed experimentally by Amagat[1] in the case of substances in the gaseous state, and by Ramsay and Young[2] in the case of gaseous and liquid ether. Barus[3] has shown that for some liquids it holds up to pressures of about 1000 atmos., but that there are marked deviations at higher pressures. The later experiments of Amagat[4] on carbon dioxide and ethylene and of Young on isopentane[5] and normal pentane,[6]

[1] *Compt. rend.*, **94**, 847 (1882). [2] *Phil. Mag.* (V.), **23**, 435 (1887).
[3] *Ibid.* (V.), **30**, 358 (1890).
[4] *Ann. Chim. Physik.*, Series VI., vol. **29** (1893).
[5] *Proc. Phys. Soc.*, **13**, 602 (1895); *Zeit. physik. Chem.*, **29**, 193 (1899).
[6] Rose-Innes and Young, *Phil. Mag.* (V.), **48**, 213 (1899).

indicate that the relation is very nearly, but not quite, true. In the case of the pentanes the isochors corresponding approximately to their critical volumes are straight, but those on either side are slightly curved. At very large volumes, however, no curvature could be detected.

The constants a and b in the equation of Van der Waals may be calculated from experimental results in the gaseous and liquid states; and from these constants the pressures may be calculated at temperatures below the critical point, and at volumes greater than the orthobaric volumes of liquid and smaller than the orthobaric volumes of saturated vapour.

Or, from a number of isothermals, the pressures and temperatures at a series of constant volumes may be read off, and the values of the constants k and c in the formula $p = kT - c$ may be calculated for each volume. By extrapolation the pressures at other temperatures may be determined for the same series of volumes.

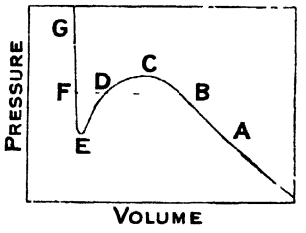


FIG. 48.

Whichever plan is adopted, the calculated isothermals show a continuous rise of pressure with diminution of volume above the critical temperature; but at any temperature below the critical point the pressure rises to a maximum (C, Fig. 48), then falls to a minimum (E), and finally rises again. If the conditions represented by these theoretical isothermals could be realized in practice, there should be a continuous passage from the gaseous to the liquid state, the substance remaining homogeneous throughout. Moreover, at sufficiently low temperatures the minimum pressure should be negative. Under ordinary conditions, when the unsaturated vapour is compressed, the pressure rises to B, remains constant during liquefaction, and then rises again, the isotherm taking the course ABFG. Conversely, when the pressure on the liquid is lowered, ebullition takes place when the point F is reached, and continues at constant pressure until evaporation is complete, when the pressure again falls.

If, however, the liquid is very pure, and free from dissolved air, and if the walls of the vessel are very smooth, the pressure may be lowered far below F before ebullition commences. For example; some methyl formate (B.P. 31·9°) was heated to 80° in the experi-

mental tube in a modified Andrews apparatus, the whole of the vapour being at first condensed. The pressure was then lowered below 800 mm. without ebullition taking place. The vapour pressure of methyl formate at 80° is 3500 mm., so that the pressure was reduced to less than a fourth of the vapour pressure. In other words, the methyl formate at 80° and under a pressure of less than 800 mm. was more than 45° above its boiling point under that pressure. Ebullition finally took place with explosive violence.

Again, Worthington[1] has shown that when a sealed tube nearly full of a pure liquid free from air is gently warmed, until the liquid, by expansion, completely fills the tube, a bubble of vapour will not be formed on cooling until a very large negative pressure is reached; and in some experiments the thick-walled tube actually collapsed, owing to the enormous tension.

It has also been shown by Aitken[2] that when a vapour is very carefully freed from dust-particles, its temperature may be lowered many degrees below the condensing point before liquefaction takes place; and there can be no doubt that the same effect could be produced by raising the pressure at constant temperature.

It has therefore been proved that part of the continuous isothermal from F towards E, and from B towards C, may be realized experimentally.

From E to C there would be an increase in volume, attended by a rise in pressure; and there can be little doubt that such a change, if it could be brought about, would take place with explosive rapidity.

It has been stated that when a vapour is compressed under ordinary conditions, liquefaction begins when the point B on the isothermal is reached, and that the pressure remains constant until all the vapour is condensed. The external work done during the process is equal to the product of the (constant) pressure into the change of volume, $p(v_v - v_l)$. It is therefore represented by the rectangle BFHK (Fig. 49).

If the change from B to F were to take place without separation into the liquid and vapour phases, that is to say, along the continuous isothermal BCDEF, the work done would be the same as before since the initial and final states are the same. It has been pointed out by Clausius that the work in that case is represented by the irregular

[1] *Phil. Trans.*, 183 A, 355 (1892).
[2] *Trans. Roy. Scott. Soc. of Arts*, vol. 9

figure BCDEFHK, and that, since the areas of the two figures are necessarily equal, the area of the portion BDC above the rectangle must be equal to that of the portion DFE within the rectangle.

If, then, the continuous isothermal be constructed in the manner described, by calculation from data at higher temperatures, and if a horizontal line be drawn in such a position that the areas BDC and DFE are equal, the pressure represented by this horizontal line should be equal to the observed vapour pressure. This equality was found by Ramsay and Young (*loc. cit.*) to hold good in the case of

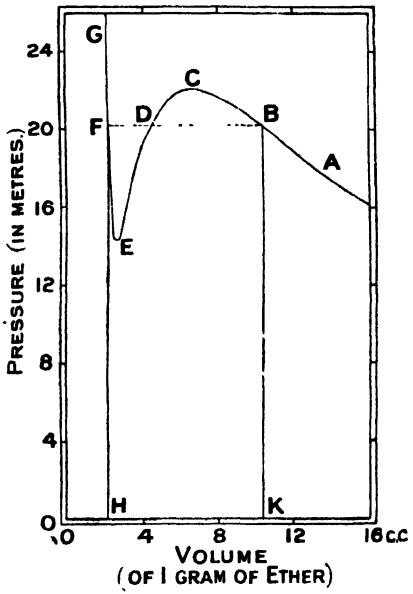


FIG. 49.

ether at temperatures from 150° to the critical point 193·8°, with a maximum error of only 1·08 per cent. (at 150°).

The calculated and observed pressures are given in the table on opposite page.

At all temperatures above the critical point the pressure rises continuously with diminution of volume; but below the critical point there is on each continuous isothermal a maximum and a minimum pressure corresponding to the points C and E (Figs. 48 and 49), the difference between the two pressures increasing rapidly as the temperature falls, and the minimum pressures being negative,

in the case of ether, below about 160°, or only about 34° below the critical temperature.

Temperature.	Vapour Pressures.	
	Calculated.	Observed.
Degrees.		
192	26,350	26,331
190	25,554	25,513
185	23,703	23,693
175	20,259	20,230
160	15,900	15,778
150	13,405	13,262

There may, therefore, be constructed two pressure-temperature curves, in addition to the ordinary curve of vapour pressures, and these three curves, which are widely divergent at low temperatures, should meet at the critical point. Or from the read pressures the constants for a formula such as that of Biot may be determined, and the pressures at other temperatures may be calculated from the formulæ. The read and calculated pressures for ether are given in the table.

Temperature	Ordinary Vapour Pressures.		Superior Curve Pressures.		Inferior Curve Pressures.	
	Read[1]	Calculated.	Read.	Calculated.	Read.	Calculated.
Degrees.						
150	13,405	13,084	17,380	17,437	− 10,400	− 10,185
160	15,900	15,900	19,090	19,090	− 20	− 100
175	20,259	20,259	22,100	22,100	+ 14,060	+ 14,060
185	23,703	23,678	24,510	24,549	21,660	21,704
190	25,554	25,556	25,870	25,935	24,960	24,900
192	26,350	26,341	26,490	26,523	26,125	26,065
193	—	26,739	—	26,826	—	26,624
193·83	—	27,075	—	27,077	—	27,077

The critical temperature and pressure calculated in this way are 193·83° and 27,076 mm. respectively, the observed values being 193·8° and 27,060 mm.

Isochors.—If the pressures corresponding to a series of definite volumes are read from the isothermals constructed from the experimental data, and if these pressures are plotted against the absolute

[1] For equal areas.

temperatures, straight or very slightly curved lines may be drawn to pass through the points corresponding to each volume. The isochors so constructed are shown in Fig. 50. They start from the vapour-pressure curve, those for large volumes being below and to the right of the curve, and those for small volumes above and to the left of it. If *straight* lines are drawn to pass as evenly as possible through the points and produced downwards, a diagram of the form shown in Fig. 51 is obtained. The vapour-pressure curve is indicated by dotted lines, and it will be seen that two other curves are formed, one of them, ABC, to which the large-volume isochors are

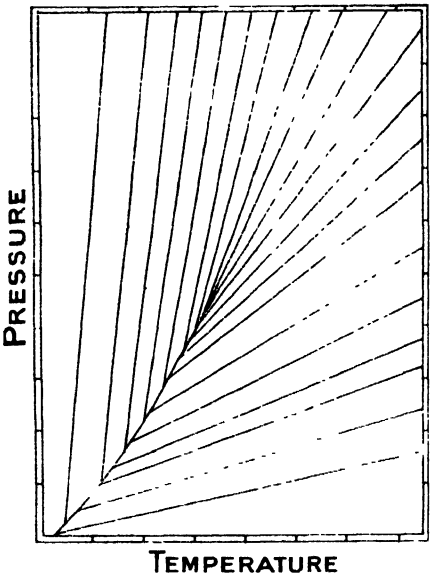


FIG. 50.

tangential, starting from the zero of temperature and pressure and terminating at C; the other, EDC, to which the small-volume isochors are tangential, also terminating at C, but starting from an exceedingly large negative pressure.

It will be observed that outside the surface enclosed by the two curves, and above the line of zero pressure, the isochors never cut each other; in other words, only a single isochor passes through any given point in this region. Outside the surface, but below the line of zero pressure, there are no isochors.

Three isochors may pass through any point within the surface and above the line of zero pressure, but only two isochors below the

zero line. Lastly, one isochor may be tangential to any point on either curve, and above the zero line a second isochor may pass through the point, but not below the zero line.

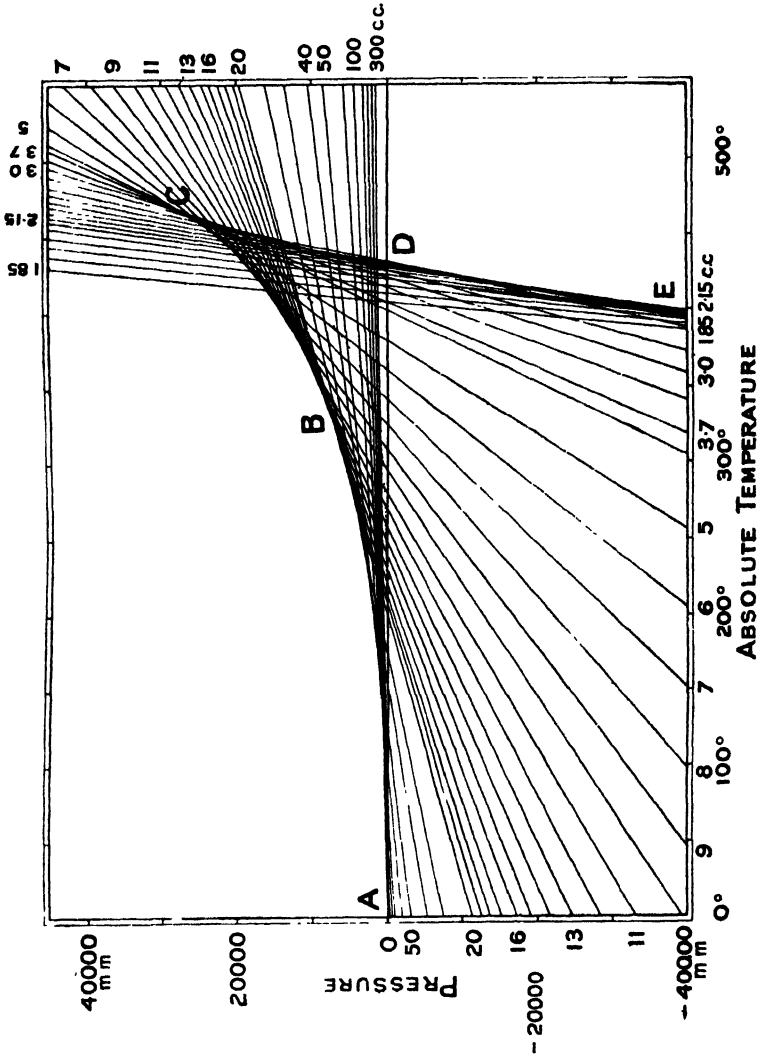


FIG. 51.

In other words, there are three volumes corresponding to the pressure and temperature represented by any point within the surface ADCB; two volumes corresponding to the pressure and temperature

represented by any point within the surface ADE, or on the curves ABC and DC; one volume only for any point outside the curvilinear triangle ADC and above the zero line, or on the curve DE.

Turning to the pressure-volume diagram for ether (Fig. 52), it will be seen that at a temperature higher than the critical point there is only one volume corresponding to any pressure. At lower

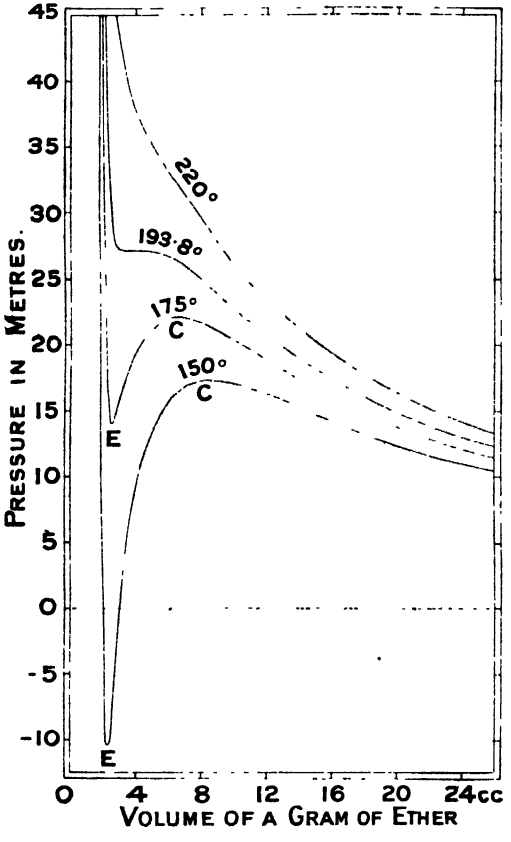


FIG. 52.

temperatures on each continuous isothermal, between the limits of pressure corresponding to the points C and E, there are three volumes for each pressure, provided that the minimum pressure is positive; but where the pressures are negative there can be only two volumes for each pressure. At the pressures corresponding to the point C there are only two volumes, and at that corresponding to E there are two volumes if the pressure is positive, but one only if it is negative.

A comparison of the isochoral and isothermal diagrams makes it clear that the curve ABC in the former is the curve of maximum pressures, and EDC that of minimum pressures. These two curves and the ordinary vapour curve meet at C, which is the critical point. This point is the summit of the curvilinear triangle ACD, and the only isochor which passes through it is that corresponding to the critical volume. The isochors for large volumes cut the curve CD, and those for smaller volumes the curve AC.

The direction and position of an isochor are defined by the equation $p = kT - c$, where $k = \frac{dp}{dT}$; it is the tangent of the angle which the isochor makes with the horizontal line of zero pressure. The constant c is the (negative) pressure corresponding to the absolute zero of temperature, for $p = -c$ when $T = 0$.

It has been pointed out by J. E. Mills [1] that the value of k for the critical isochor is the same as that of $\frac{dp}{dt}$ on the vapour-pressure curve at the critical temperature; in other words, the critical isochor forms a tangent to the vapour-pressure curve at the critical temperature. It is true that the values of $\frac{dp}{dt}$ given by Biot's formula are considerably lower than those of k; but Mills has shown that Biot's formula does not give good results near the critical point. On the other hand, the values of dp calculated from his formula

$$\frac{dp}{dt} = \frac{124{,}860}{Mv} = \frac{2R}{V}$$

(where M is the molecular weight, and R is the usual gas constant) agree very well with those of k, as will be seen from the table below.

Substance	Critical volume of a gram.	$\frac{dp}{dt}$		k
		from Biot.	from $\frac{124{,}860}{Mv}$.	
Ether . . .	3·814	391·6 [2]	441·9	436·0
Isopentane . .	4·268	367·8	405·7	401 to 411
n-pentane . .	4·305	364·8	402·3	406·7

[1] *Journ. Phys. Chem.*, 9, 402 (1905).

[2] It may be pointed out that the constants for Biot's formula, with only three constants ($\log p = a + ba^t$), employed for calculating the vapour pressures of

Calculation of Critical Constants from Van der Waals' Formula.—The equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

when $p = 1$, $v = 1$, and $T = 273$, takes the form—

$$(1 + a)(1 - b) = R \times 273$$

therefore

$$R = \frac{(1 + a)(1 - b)}{273}.$$

Substituting for R in the original equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = (1 + a)(1 - b) \times \frac{T}{273}$$

from which—

$$v^3 - \left\{b + \frac{(1 + a)(1 - b) \times T}{p \times 273}\right\}v^2 + \frac{a}{p} \times v - \frac{ab}{p} = 0.$$

This being an equation of the third degree for v if p is constant, there are three roots, of which either one or all three may be real.

There is one particular value of T for which there is only one real root—that is to say, only one volume—for all values of p except one; but for this particular pressure there are three real roots, all of which are equal. This temperature is the critical temperature, T_c; the pressure p_c, at which there are three equal roots, is the critical pressure; and the volume v_c is the critical volume.

For all temperatures higher than T_c there is only one real root, whatever the pressure; in other words, the pressure rises continuously with diminution of volume. At any temperature lower than T_c there is only one real root below a certain pressure $p_{min.}$ and above another pressure $p_{max.}$, but at all pressures between these limits there are three real roots. At these two pressures two of the three roots are equal, but at all intermediate pressures they are all different; that is to say, at temperatures lower than T_c the pressure rises with diminution of the volume until $p_{max.}$ is reached. It then falls to $p_{min.}$, and finally rises again continuously. The continuous isothermals are thus given by the equation.

ether from 150° to the critical point (Ramsay and Young, *loc. cit.*), give $\frac{dp}{dt} = 405$ at the critical point, a decidedly higher value than that given by the larger formula employed for the whole range of temperature.

The values of the critical constants derived from the equation are—

$$v_c = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8}{27} \times \frac{a}{1 + a} \times \frac{273}{b(1 - b)}.$$

The constants a and b in Van der Waals' equation may be calculated either from the observed pressures and volumes at a series of temperatures, or from the observed critical constants. In the latter case, however, it is found that the isothermals are not very satisfactorily reproduced by the equation—

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

On the other hand, if a and b are calculated by means of the isothermals, the critical constants are not given by them with sufficient accuracy.

It is evident, then, that the equation of state proposed by Van der Waals, although it reproduces the general form of the isothermals quite satisfactorily, does not accurately represent the complete relations between temperature, pressure, and volume for both gases and liquids. Numerous attempts have been made to modify the formula in such a manner that it shall accurately reproduce the whole of the experimental data. The subject has been discussed and alternative formulæ proposed by many mathematicians and physicists, among whom the following may be mentioned:—Clausius,[1] Reinganum,[2] Dieterici,[3] Tait,[4] Rose-Innes,[5] Amagat,[6] Kamerlingh Onnes,[7] D. Berthelot,[8] Haigh,[9] Leduc,[10] Van Laar,[11] Schames,[12] Traube,[13]

[1] *Wied. Ann.*, **9**, 348 (1880).

[2] "Dissertation" (Göttingen, 1899); *Annalen der Physik* (4), **6**, 533 (1901).

[3] *Ann. Phys. Chem.*, **69**, 685 (1899); *Annalen der Physik* (4), **5**, 51 (1901); **12**, 144 (1903); **35**, 220 (1911).

[4] *Trans. Roy. Soc. Edin.*, **36**, pt. ii., 257 (1891).

[5] *Phil. Mag.*, **44**, 80 (1897); **45**, 105 (1898); **47**, 353 (1899); **48**, 213 (1899).

[6] *Compt. rend.*, **118**, 566 (1894); **120**, 489 and 580 (1895).

[7] *Comm. Phys. Lab. Leiden*, No. 71 (1901); No. 128 (1912).

[8] "Sur les Thermomètres à Gaz" (1903), pp. 45-49.

[9] *Phil. Mag.*, **16**, 201 (1908).

[10] *Compt. rend.*, **148**, 1670 (1909).

[11] *Konink. Akad. Wet. Amsterdam*, **14**, 278, 428, 563, 711 (1911-1912); **16**, 808, 924, 1047; **17**, 451, 606 (1914); **18**, 1220; **19**, 2 (1916).

[12] *Deutsch. Phys. Gesell.*, **15**, 1017 (1913); **16**, 518 (1914).

[13] *Ibid.*, **16**, 1219 (1914).

Petzalski,[1] Dalton,[2] Richards,[3] Bouty,[4] Davis,[5] v. Kaufmann,[6] Schimank,[7] MacDougall,[8] and Kam.[9]

For a full account of this subject the following memoirs may be consulted: "Die Zustands-gleichung der Gase und Flussigkeiten und die Kontinuitats-theorie," by J. P. Kuenen (Vieweg, 1907), "Die Zustands-gleichung," by H. Kamerlingh Onnes, and W. H. Keesom, *Comm. Phys. Lab. Leiden*, vol. ii., suppl. No. 23 (1912).

The Reduced Equation of State.—Van der Waals has deduced the following generalizations from his equation. If the pressures are reckoned as fractions of the critical pressure—

$$\pi = \frac{p}{p_c}$$

the volumes as fractions of the critical volume—

$$\phi = \frac{v}{v_c}$$

and the temperatures as fractions of the critical temperature—

$$\theta = \frac{T}{T_c}$$

the equation takes the following form :—

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$$

which is independent of the nature of the substance considered, provided that molecular association or dissociation does not take place.

The values π, ϕ, and θ are called by Van der Waals the reduced pressure, volume, and temperature respectively. When the reduced pressures of any two substances are equal, that is to say, when $\frac{p}{p_c} = \frac{p'}{p_c'}$, the actual pressures p and p' are termed *corresponding* pressures; so also the volumes of liquid v_L and v_L', and of saturated vapour v_V and v_V', are termed corresponding volumes when

[1] *Compt. rend.*, **157**, 113 (1913).
[2] *Trans. Roy. Soc. of S. Africa*, **4**, 123 (1914).
[3] *Journ. Amer. Chem. Soc.*, **36**, 617 (1914).
[4] *Journ. de Phys.*, **4**, 601 (1914).
[5] *Phys. Rev.*, **6**, 59 (1915).
[6] *Phil. Mag.*, **29**, 146 (1915).
[7] *Phys. Zeits.*, **17**, 393 (1916).
[8] *Journ. Amer. Chem. Soc.*, **38**, 528 (1916).
[9] *Phil. Mag.*, **31**, 22 (1916).

$\frac{v_L}{v_c} = \frac{v_L'}{v_c'}$ and $\frac{v_V}{v_c} = \frac{v_V'}{v_c'}$, respectively; and the absolute temperatures are termed corresponding temperatures when $\frac{T}{T_c} = \frac{T'}{T_c'}$.

The two substances are defined by Van der Waals as being in *corresponding* states when their pressures are proportional to their critical pressures, their volumes to their critical volumes, and their temperatures to their critical temperatures; in other words, when their reduced pressures, volumes, and temperatures, respectively, are equal.

Van der Waals deduced the following exceedingly important generalization regarding corresponding states from his reduced equation: When the absolute temperatures of two substances are proportional to their absolute critical temperatures, their vapour pressures will be proportional to their critical pressures, and their orthobaric[1] volumes, both as liquid and vapour, to their critical volumes. The generalizations regarding corresponding temperatures, pressures, and volumes are not dependent on the particular form of the fundamental equation of state, but would follow from any modified equation which, like that of Van der Waals, is reducible, as regards volume, to one of the third degree. The fact, therefore, that the original equation of state requires modification, does not preclude the possibility that the generalizations may be strictly true, and it is necessary to investigate them independently of the equation itself.

The question most easily decided is whether the vapour pressures of two substances at corresponding temperatures are corresponding pressures. The experimental data which have been obtained leave no doubt that this generalization is only strictly true in the case of certain closely related substances, such as chlorobenzene and fluorobenzene, or propyl acetate and ethyl propionate, and the critical pressures of the related substances are in both cases equal, so that corresponding pressures are equal pressures. The generalization is also very nearly true for some, but not nearly all closely related substances which have different critical pressures. Thus, as will be seen from the table (p. 202), it is nearly true for methyl acetate and propyl formate, but not for methyl acetate and propyl acetate, and it is far from true for normal pentane and normal octane. It is in some cases very nearly true, in others very far from true, for substances which have no close chemical relationship; compare, for example,

[1] *Vide* p. 150.

Reduced Temperature . . .		0·5170	0·6400	0·7334	0·8464	0·9288
Critical Pressure.	Substance	Ratio of Vapour Pressure to Critical Pressure.				
mm.						
33,910	Fluorobenzene .	0·00147	0·02241	0·08847	0·2949	0·5898
33,910	Chlorobenzene .	0·00149	0·02252	0·08744	0·2956	0·5938
25,210	Propyl acetate .	0·00059	0·01404	0·06613	0·2583	0·5558
25,210	Ethyl propionate .	0·00059	0·01407	0·06697	0·2585	0·5573
35,180	Methyl acetate .	0·00093	0·01765	0·07598	0·2765	0·5757
30,440	Propyl formate .	0·00094	0·01799	0·07791	0·2801	0·5772
25,100	Normal pentane .	0·00154	0·02256	0·08888	0·2960	0·5933
18,730	Normal octane .	0·00060	0·01406	0·06645	0·2567	0·5537
34,180	Carbon tetrachloride	0·00203	0·02681	0·09801	0·3088	0·6022

on the one hand normal octane and propyl acetate or normal pentane and chlorobenzene, and on the other hand carbon tetrachloride and normal octane.

If this first generalization were strictly true, it would make no difference whether the volumes were compared at corresponding temperatures or at the boiling points of the substances under corresponding pressures. Inasmuch, however, as the generalization is only an approximate one, it is necessary to find which method of comparing the volumes gives the better results. A preliminary investigation[1] showed that the agreement is better at corresponding pressures than at corresponding temperatures, and the former method of comparison will therefore be adopted. In the following table are given the ratios (1) of the boiling points to the critical temperatures, $\frac{T}{T_c}$, (2) of the orthobaric volumes of liquid to the critical volumes, $\frac{v_L}{v_c}$, (3) of the orthobaric volumes of vapour to the critical volumes, $\frac{v_V}{v_c}$, for thirty substances at the same reduced pressure, 0·08846.

If the critical temperatures and pressures are known, but not the critical volumes, it is still possible to test the validity of the generalizations regarding corresponding volumes by means of the data at lower temperatures. For the generalization requires that $\frac{v_L}{v_c} = \frac{v_L'}{v_c'}$, at corresponding pressures, and therefore that $\frac{v_L}{v_L'} = \frac{v_c}{v_c'} = \text{const.}$

[1] Young, *Phil. Mag.* (V.), **33**, 153 (1892).

Now, in the case of fluorobenzene and chlorobenzene the critical pressures are equal, so that $\frac{p_c}{p_c'} = 1$, and it is found that the ratios of the volumes of chlorobenzene to those of fluorobenzene at equal pressures are very nearly constant from the lowest pressures to the

RATIO OF PRESSURE TO CRITICAL PRESSURE = 0·08846.

Substance	$\frac{T}{T_c}$.	$\frac{v_I}{v_c}$.	$\frac{v_V}{v_c}$.
1. Haxamethylene . .	0·7277	0·4090	27·7
2. Benzene . . .	0·7282	0·4065	28·3
3. Isopentane . . .	0·7292	0·4085	27·7
4. Di-isopropyl . . .	0·7329	0·4093	28·4
5. Normal pentane . .	0·7331	0·4061	28·4
6. ,, hexane . .	0·7406	0·4055	29·1
7. ,, heptane . .	0·7483	0·4029	29·5
8. Di-isobutyl . . .	0·7498	0·4046	28·2
9. Normal octane . .	0·7544	0·4006	29·35
10. Fluorobenzene . .	0·7334	0·4067	28·4
11. Chlorobenzene . .	0·7345	0·4028 [2]	28·5
12. Bromobenzene . .	0·7343 [1]	0·4024 [2]	28·3
13. Iodobenzene . . .	0·7337 [1]	0·4020 [2]	28·3
14. Carbon tetrachloride .	0·7251	0·4078	27·45
15. Stannic chloride . .	0·7357	0·4031	28·15
16. Ether	0·7380	0·4030	28·3
17. Methyl formate . .	0·7348	0·4001	29·3
18. Ethyl ,, . .	0·7385	0·4003	29·6
19. Propyl ,, . .	0·7430	0·4008	29·4
20. Methyl acetate . .	0·7445	0·3989	30·15
21. ,, propionate . .	0·7485	0·4008	29·6
22. ,, isobutyrate .	0·7502	0·4014	29·15
23. Ethyl acetate . .	0·7504	0·4001	30·25
24. Methyl butyrate . .	0·7522	0·4004	29·5
25. Ethyl propionate . .	0·7540	0·3989	30·0
26. Propyl acetate . .	0·7541	0·3985	30·35
27. Acetic acid . . .	0·7624	0·4100	25·4
28. Methyl alcohol . .	0·7734	0·3973 [3]	34·35
29. Propyl ,, . .	0·7736	0·4002 [3]	30·85
30. Ethyl ,, . .	0·7794	0·4061 [3]	32·15

[1] Critical temperatures and pressures not directly determined.

[2] Values of v_c only approximate. Ratios of volumes to those of fluorobenzene at corresponding pressures very constant so far as experiments extend (*Phil. Mag.* (V.), **33**, 153 (1892)).

[3] Values of v_c only approximate, owing to marked curvature of "diameter" (Cailletet and Mathias).

highest at which accurate determinations were made. The ratios of the volumes of bromobenzene and of iodobenzene respectively to those of fluorobenzene at equal pressures are practically constant, and it may be assumed with great probability that their critical pressures are also equal to that of fluorobenzene. It is, therefore, most probable that the generalizations of Van der Waals hold accurately for this group of closely related substances, although the ratio $\frac{v'_1}{v'_c}$ for fluorobenzene at the reduced pressure 0.08846 given in the table is higher than those for the other halogen derivatives of benzene. In the case of ethyl propionate and propyl acetate the agreement is quite satisfactory whichever method of comparison is adopted. The ratios $\frac{v'_1}{v'_c}$ also show no greater differences in either case than may be attributed to errors of experiment.

Considering the ratios $\frac{T}{T_c}$ as a whole, it is clear that they are not quite constant for a homologous series of organic compounds, but tend to rise with increase of molecular weight. Again, the ratios for iso-compounds are uniformly lower than for isomeric normal compounds, and those for di-iso-compounds are lower still. The ratio for acetic acid is higher than for any of the preceding substances, and those for the alcohols are much higher.

The ratios $\frac{v'_L}{v'_c}$ show much smaller variations than those of $\frac{T}{T_c}$, especially in the case of the esters, but it is evident that among homologous hydrocarbons they diminish with increase of molecular weight, and that among isomers the ratios for iso-compounds are higher than for normal, and those for di-iso-compounds higher than for either. The ratio for acetic acid is high; those for the alcohols are irregular, but that for methyl alcohol is decidedly low, taking into account its small molecular weight.

The ratios $\frac{v'_v}{v'_c}$ follow as a rule the same order as the temperature ratios. For homologues they rise with increase of molecular weight, and for isomers, iso- and di-iso-compounds have low values. Among the esters the variations are small and irregular, but the ratio for acetic acid is very low, and for methyl alcohol very high, the other alcohols also having high ratios.

The wide variations observable in the ratios for acetic acid and

the alcohols may probably be explained as follows: It is known from determinations of the vapour density of acetic acid that in the state of vapour many of the molecules of this substance are associated, the simple molecules probably uniting in pairs, thus $2C_2H_4O_2 = (C_2H_4O_2)_2$, and that the relative number of complex molecules increases with fall of temperature. The amount of association will then be greater at a low temperature than at the critical point. The diminution in specific volume due to this cause will also be greater; hence the ratio $\frac{v_v}{v_l}$ will be low.

In the case of the alcohols there is no molecular association in the state of vapour at low temperatures, but there is strong evidence —to which reference will be made later (pp. 330, 339)—that in the liquid state there is a high degree of association, particularly with methyl alcohol, that the amount of association diminishes with rise of temperature, but that there is still a moderate degree of association at the critical point. At this point, then, there will be a diminution in volume, due to association, but not with the vapours at low temperatures; hence v_v may be regarded as normal, while v_l is low; hence $\frac{v_v}{v_l}$ will be high.

The effect of association on the volume of a liquid is very much less marked than on that of a gas, and it is not to be expected that the variations in the $\frac{v_l}{v_c}$ ratios should be very striking. If, however, the amount of association is very much greater at a low temperature than at the critical point, one would expect the ratio $\frac{v_L}{v_c}$ to be somewhat low, and this appears to be the case with methyl alcohol. Since, however, the critical volumes of the alcohols, and perhaps also of acetic acid, cannot be determined with great accuracy, it is not safe to attach much importance to small variations in their volume ratios.

As regards the temperature ratios, it may be pointed out that with the alcohols, in the conversion of liquid into vapour, work must be done not only in increasing the volume and in overcoming ordinary molecular attraction, but also in dissociating the complex molecules (if the assumption of molecular association is correct), and it is therefore reasonable to conclude that the liquid must be raised to a higher temperature than would otherwise be necessary. Hence, as the amount of association is greater at low temperatures than at

the critical point, the temperature ratios $\frac{T}{T_c}$ may be expected to be high. In the case of acetic acid the molecules of vapour are associated, though probably to a smaller extent than those of the liquid; hence the rise of temperature due to this cause is relatively smaller than with the alcohols, and the ratio $\frac{T}{T_c}$ is lower.

Van der Waals' equation of state and the generalizations deduced from it are based on the assumption that the molecules undergo no change when the temperature, pressure, or state of aggregation of a substance is altered; they are, therefore, not applicable to such compounds as acetic acid and the alcohols, and the fact that the $\frac{T}{T_c}$ and $\frac{v}{v_c}$ ratios for these substances differ so widely from those observed in other cases, cannot be used as evidence against the validity of the generalizations. There is, however, no known reason for assuming that molecular association occurs in the case of the hydrocarbons, and yet it cannot be questioned that the ratios are dependent to some extent on molecular weight and constitution.

With the esters the dependence of the ratios on molecular weight is somewhat less marked than with the hydrocarbons. A possible explanation of this fact is that there is slight molecular association in the liquid state, and still less at the critical point, the amount of association diminishing in this homologous series, as it does in that of the alcohols and of the fatty acids, as the molecular weight increases. Thus the $\frac{T}{T_c}$ and $\frac{v_v}{v_c}$ ratios would be somewhat higher, and the $\frac{v_l}{v_c}$ ratio somewhat lower for methyl formate, as compared with those for methyl butyrate and its isomers, than if there were no association.

If the generalizations of Van der Waals were strictly true, the following simple laws should follow from them:—[1]

1*a*. *At corresponding pressures the values of* $\frac{pV_v}{T}$ *should be the same for all substances.*

[1] Young, *Phil. Mag.*, **30**, 423 (1890); **37**, 1 (1894); *Trans. Chem. Soc.*, **59**, 125 (1891); Amagat, *Compt. rend.*, **156**, 271 and 843 (1913).

1*b*. *At corresponding pressures the values of* $\frac{pV_L}{T}$ *should be the same for all substances.*

1*c*. *At their critical points the values of* $\frac{p_cV_c}{T_c}$ *should be the same for all substances.*

For it is known that the saturated vapours of most substances behave more and more like perfect gases as the temperature falls, and at a sufficiently low temperature the molecular volume of the saturated vapour of a substance A will be given almost exactly by the formula—

$$V_v = 22{\cdot}4 \times \frac{T}{273} \times \frac{760}{p}$$

where T is the absolute temperature, and p the vapour pressure at that temperature; and that of another substance B by the formula—

$$V_v' = 22{\cdot}4 \times \frac{T'}{273} \times \frac{760}{p'}.$$

$$\text{Hence } \frac{V_v}{V_v'} = \frac{T}{T'} \times \frac{p'}{p}$$

$$\text{or } \frac{pV_v}{T} = \frac{p'V_v'}{T'}.$$

But if p and p' are corresponding pressures, T and T' should be corresponding temperatures, and V_v and V_v' corresponding volumes. Hence the relation should be true at any other corresponding pressure, and therefore at the critical pressures, or—

$$\frac{p_cV_c}{T_c} = \frac{p_c'V_c'}{T_c'}.$$

Again, if this relation were true for the two substances at their critical points, it should be true for the liquids at any corresponding pressures,

$$\text{or } \frac{pV_L}{T} = \frac{p'V_L'}{T'}.$$

When the critical pressures of the two substances are equal, the relations take the simple form $\frac{T}{T'} = \frac{V_v}{V_v'} = \frac{V_L}{V_L'}$ at equal pressures. Thus for $\pi = 0{\cdot}08846$ the ratios for propyl acetate and ethyl propionate are $\frac{T}{T'} = 1{\cdot}006$; $\frac{V_v}{V_v'} = 1{\cdot}015$; and $\frac{V_L}{V_L'} = 1{\cdot}002$. And at all pressures—

	$\frac{T}{T'}$	$\frac{V_V}{V_{V'}}$	$\frac{V_L}{V_{L'}}$
C_6H_5Cl/C_6H_5F . . .	1·1309	1·1246	1·137
C_6H_5Br/C_6H_5F . . .	1·1976	1·1802	1·189
C_6H_5I/C_6H_5F . . .	1·2885	1·2772	1·282
C_6H_5Br/C_6H_5Cl . . .	1·0590	1·0494	1·046
C_6H_5I/C_6H_5Cl . . .	1·1394	1·1357	1·128
C_6H_5I/C_6H_5Br . . .	1·0759	1·0822	1·078

2a. The ratio of the actual density of the saturated vapour to the theoretical density (calculated for the perfect gas) should be the same for all substances under corresponding pressures.

For the actual density—

$$s_v = \frac{1}{v_v} = \frac{M}{V_v}$$

where v_v is the volume of a gram and V_v the molecular volume; and the theoretical density—

$$S = \frac{M}{22{\cdot}41 \times \frac{T}{273} \times \frac{760}{p}}.$$

$$\text{Therefore } \frac{s_v}{S} = \frac{22{\cdot}41 \times T \times 760}{273 \times p \times V_v} = c \times \frac{T}{pV_v}.$$

But if $\frac{pV_v}{T}$ is the same for different substances at corresponding pressures, $\frac{s_v}{S}$ must also be the same (*vide* table, p. 211).

And if $\frac{s_v}{S}$ is the same for all substances at corresponding pressures, then—

2b. The ratio of the actual density at the critical point to the theoretical density (for a perfect gas), $\frac{s_c}{S_c}$, should be the same for all substances.

Graphical Representation of the Generalizations.—If in a diagram showing any relation between temperature, pressure and volume the reduced values are plotted instead of the actual ones, the diagram should be identical for all substances. Take, for example, the relation between the orthobaric volumes of liquid or of saturated vapour and the temperature. In Fig. 53 the actual orthobaric volumes of carbon tetrachloride, normal pentane, and normal octane

are plotted against the actual temperatures, and in Fig. 54 the reduced volumes against the reduced temperatures. The reduced volumes of carbon tetrachloride are indicated by small circles, those

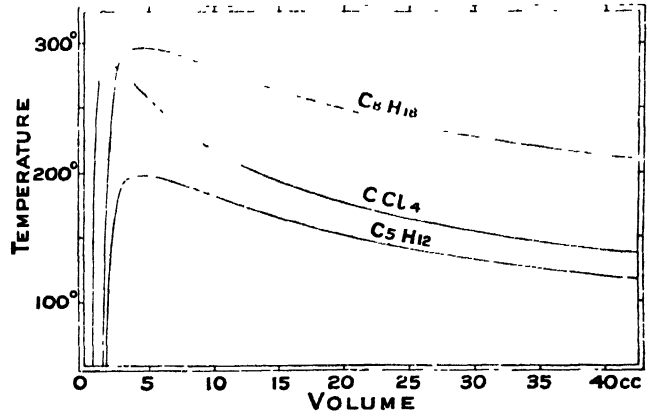


FIG. 53.

of normal octane by large circles, and the single curve for the volumes of liquid up to the critical temperature is drawn through the points representing n-pentane, which are not shown. For the liquid state

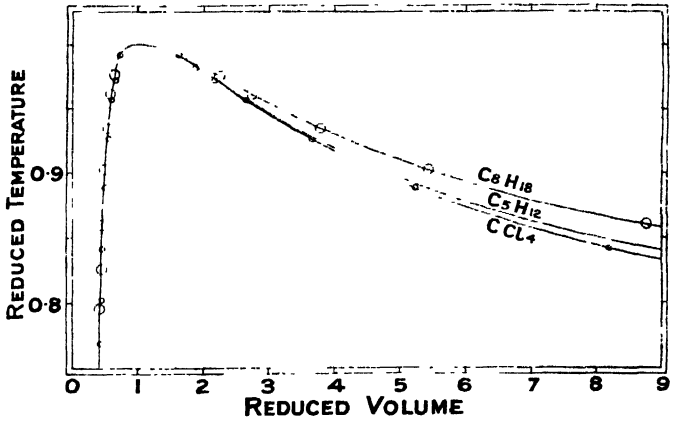


FIG. 54.

the deviations of the reduced volumes of carbon tetrachloride and n-octane are too small to be clearly seen on this diagram, although they are outside the limits of experimental error. The divergence of the three vapour curves is, however, very noticeable. On the

other hand, it may be mentioned that of the thirty substances examined by the author all except four, methyl, ethyl, and propyl alcohol, and propyl acetate, would give curves lying between those relating to carbon tetrachloride and normal octane, and the curve for propyl acetate is only slightly above that for normal octane. There is little doubt, however, that the curves for the so-called permanent gases would be lower, and for the higher paraffins higher, than those for CCl_4 and C_8H_{18} respectively.

Similarly, if the generalizations were strictly true, the ratios of the densities of liquid and of saturated vapour to the critical densities, when plotted against the reduced temperatures, should give coincident curves, and the diameters of these closed curves should also be coincident.

In other words, if the generalizations of Van der Waals were strictly true, and the mean densities of liquid and saturated vapour were accurately represented by the formula

$$s = A + at,$$

it would follow (3) that $\frac{a'T_c}{s_c}$ must be the same for all substances.[1]

It has been shown, however,[2] that for most substances the diameter is slightly curved, but can be accurately represented by the formula—

$$s = A + at + \beta t^2$$

where a is always negative, and β may be either positive or negative; and it is remarkable that there is a general relation between the values of $\frac{s_c}{S_t}$, $\frac{a'T_c}{s_t}$, and β, as will be seen from the following table. The substances are divided into groups of closely related compounds, the members of each group being arranged, as in the table on p. 203, in ascending order of the values of $\frac{T}{T_c}$ at the reduced pressure 0·08846. The order would not have been very different if it had been based on the values of $\frac{s_c}{S_c}$, $\frac{a'T_c}{s_c}$, or β.

The ratios $\frac{pV_v}{T}$ and $\frac{s_v}{S}$ are less accurate than most of the others,

[1] Mathias, *Ann. Fac. Sci. de Toulouse* (1892); Young, *Phil. Mag.* (V.), **34**, 506 (1892); *Trans. Chem. Soc.*, **63**, 1254 (1893).

[2] Young, *Phil. Mag.* (V.), **50**, 291 (1900).

on account of the relatively large experimental errors involved in the determination of the volumes of saturated vapour at moderate or low temperatures, and the variations in the case of the non-associating substances are hardly greater than the experimental errors.

The ratios $\frac{pV_1}{T}$ are much more accurate, and the variations are considerably greater, the ratio falling from 843·3 for hexamethylene to 738·5 for propyl acetate, or, taking only the hydrocarbons, to 755·7 for normal octane.

At reduced pressure 0·08846.	$\frac{pV_V}{T}$.	$\frac{pV_L}{T}$.	$\frac{s_V}{S}$.	$\frac{s_c}{S_c}$.	$\frac{-\alpha T_c}{s_c}$.	$\beta \times 10^{10}$.
1. Hexamethylene . .	56,400	843·3	1·100	3·706	0·882	+ 791
2. Benzene . . .	56,900	818·1	1·090	3·755	0·928	+ 693
3. Isopentane . . .	55,900	824·9	1·100	3·735	0·892	+ 463
4. Di-isopropyl . .	57,000	820·4	1·090	3·741	0·899	+ 413
5. Normal pentane . .	56,500	809·0	1·100	3·766	0·931	0
6. ,, hexane . .	56,400	786·1	1·105	3·831	0·967	0
7. ,, heptane . .	56,200	767·9	1·105	3·854	1·013	− 621
8. Di-isobutyl . . .	54,100	779·0	1·150	3·810	1·005	− 592
9. Normal octane . .	55,300	755·7	1·130	3·865	1·075	− 960
10. Fluorobenzene . .	56,100	804·3	1·105	3·796	0·927	+ 293
11. Chlorobenzene . .	56,600	798·7	1·100	3·776	0·949	− 509
12. Bromobenzene . .	55,700	791·8	1·115	3·809	0·953	− 725
13. Iodobenzene . .	56,100	797·5	1·105	3·780	0·956	− 519
14. Carbon tetrachloride .	56,600	841·4	1·100	3·680	0·899	+ 1480
15. Stannic chloride . .	56,200	803·9	1·105	3·740	0·991	+ 977
16. Ether	55,400	788·7	1·120	3·813	0·974	− 475
17. Methyl formate . .	56,000	764·2	1·110	3·922	0·997	− 665
18. Ethyl ,, . .	56,600	766·9	1·095	3·895	1·021	− 694
19. Propyl ,, . .	56,200	766·7	1·105	3·869	1·025	− 459
20. Methyl acetate . .	56,500	746·9	1·100	3·943	1·049	− 1467
21. ,, propionate .	55,700	753·9	1·115	3·909	1·055	− 729
22. ,, isobutyrate .	55,300	761·9	1·125	3·866	1·045	− 689
23. Ethyl acetate . .	56,200	743·1	1·105	3·949	1·061	− 764
24. Methyl butyrate . .	55,200	748·8	1·125	3·903	1·074	− 906
25. Ethyl propionate . .	55,800	741·8	1·115	3·923	1·090	− 784
26. Propyl acetate . .	56,300	738·5	1·105	3·934	1·088	− 1124
27. Acetic acid . . .	36,800	592·9	1·690	4·992	0·994	− 1191
28. Methyl alcohol . .	53,700	621·0	1·155	4·559	—	—
29. Propyl ,, . .	54,900	711·8	1·130	3·998	—	—
30. Ethyl ,, . .	56,300	711·9	1·105	4·026	—	—

Data are now available which allow of the calculation of $\frac{s_c}{S_c}$ and $\frac{-\alpha T_c}{s_c}$ for some gaseous substances.

	$\frac{s_c}{S_c}$.	$\frac{-\alpha T_c}{s_c}$.
Helium [1]	3·13	—
Argon [1].	3·424	0·744
Xenon [2].	3·60	0·766
Nitrogen [1]	3·421	0·792
Oxygen [1]	3·419	—
Carbondioxide . . .	3·59	—

It is noticeable that helium, the first of the group of monatomic inert gases, with a critical temperature only a few degrees above the absolute zero, has by far the lowest value of $\frac{s_c}{S_c}$, although considerably higher than that, 2·6, originally given by Van der Waals as the normal value.

The other gases have values of $\frac{s_c}{S_c}$ lower than any found for the liquids in the preceding table. The values of $\frac{-\alpha T_c}{s_c}$ are also lower than any in the table.

It may be stated that, in general, at equal reduced pressures the ratios $\frac{v_L}{v_c}$, $\frac{pV_v}{T}$, and $\frac{s_v}{S}$ show slight variations among non-associating substances, but that the variations are considerably greater for the ratios $\frac{T}{T_c}$, $\frac{v_v}{v_c}$, and $\frac{pV_L}{T}$.

The ratios $\frac{s_c}{S_c}$ are obviously dependent to some extent on molecular weight in the case of homologues, and on constitution in the case of isomers, the variations being in the same direction as $\frac{T}{T_c}$ and $\frac{v_v}{v_c}$.

[1] K. Onnes and co-workers, *Comm.*, 124*b*, 131*a*, 133*c*, 145*b*, 145*c* (1912-1915).
[2] Patterson, Cripps, and Whytlaw-Gray, *Proc. Roy. Soc.*, **86**, 579 (1912).

The rise in the values of $\frac{aT_c}{s_c}$ and the fall in those of β are very marked.

As regards the associating substances, the ratios for acetic acid are in most cases widely different from those for normal substances, and the differences are very marked also in the case of methyl alcohol, but less so with ethyl and propyl alcohols, and the generalizations are evidently not applicable to these substances.

Characteristic States of Matter.—Van der Waals considers that all stable non-associating substances are under strictly comparable conditions at their critical points, and D. Berthelot[1] has shown that there are other conditions of matter which are equally characteristic, and that, if the true equation of state is such that a reduced equation, applicable to all substances, can be derived from it, the temperatures peculiar to these conditions can be expressed in terms of the critical temperatures.

Assuming, in the first place, the correctness of Van der Waals' equation, $\left(p + \frac{a}{v_2}\right)(v - b) = RT$, the reduced equation may be written—

$$\left(\pi + \frac{3}{\phi^2}\right)\left(\phi - \frac{1}{3}\right) = \frac{8}{3}\theta.$$

1. *Deviation from Boyle's Law.*—According to this law, $\frac{d(pv)}{dp} = 0$ at constant temperature, therefore the value of the real coefficient is equal to the deviation from the law.

For low pressure the reduced equation takes the form $\frac{d(\pi\phi)}{d\pi} = \frac{1}{3}\left(1 - \frac{27}{8} \times \frac{1}{\theta}\right)$.

For $\theta = 0$, $\frac{d(\pi\phi)}{d\pi} = -\infty$.

(i.) For $\theta_1 = \frac{27}{8} = 3{\cdot}375$, $\frac{d(\pi\phi)}{d\pi} = 0$, or the gas follows Boyle's law.

For $\theta > \frac{27}{8}$, $\frac{d(\pi\phi)}{d\pi}$ becomes positive, and tends towards the limit $\frac{1}{3}$.

2. *Deviation from Avogadro's Law.*—

[1] "Sur les Thermomètres à Gaz," pp. 14 *et seq.*

Reduced equation, $\frac{1}{\pi\phi} \times \frac{d(\pi\phi)}{d\pi} = \frac{1}{8\theta}\left(1 - \frac{27}{8} \times \frac{1}{\theta}\right)$ for low pressures.

For $\theta = 0$, the coefficient $= -\infty$.

(ii.) For $\theta_1 = \frac{27}{8} = 3{\cdot}375$, the coefficient $= 0$.

For higher temperatures the coefficient becomes positive, reaches a maximum at $\theta_2 = 6{\cdot}750$; decreases, passes through a point of inflection at $\theta_3 = 10{\cdot}125$, and finally tends to zero.

3. *Deviation from Gay Lussac's Law.*—

Reduced equation,

$$1 - {}_a\theta = \frac{1}{8\theta}\left(1 - \frac{27}{4} \times \frac{1}{\theta}\right)d\pi,$$

where ${}_a = \frac{1}{\phi} \times \frac{d\phi}{d\theta}$, just as $\alpha = \frac{1}{v} \times \frac{dv}{dT}$; and $\alpha T = {}_a\theta$. For a gas which follows Gay Lussac's law, $1 - \alpha T = 0$.

For low temperatures $\alpha > \frac{1}{T}$.

(iii.) For $\theta_2 = 6{\cdot}75$, $\alpha = \frac{1}{T}$; and the gas follows Gay Lussac's law under low pressures. The deviation then becomes positive, reaches a maximum at $\theta_4 = 13{\cdot}5$, shows a point of inflection for $\theta_6 = 20{\cdot}250$, then diminishes, and tends towards zero.

Deviation from the Law of Charles.—The coefficient of increase of pressure at constant volume is $\beta = \frac{1}{p} \times \frac{dp}{dT}$, and for a perfect gas, $\beta T - 1 = 0$.

In reduced co-ordinates, let ${}_b = \frac{1}{\pi} \times \frac{d\pi}{d\theta}$;

$$\text{then } \beta T - 1 = \frac{RT}{p(v - b)} - 1.$$

It is convenient to take densities instead of pressures as abscissæ. Calling $\rho = \frac{v_c}{v} = \frac{1}{\phi}$, the deviation from Charles' law under a very low density, $d\rho$, is—

$${}_b\theta - 1 = \frac{d\rho}{3}$$

or the deviation from Charles' law is independent of the temperature; in other words, the isochors are straight, and the constant-volume thermometer gives correct readings. If Van der Waals' equation

were correct, this proposition should also be true for compressed gases and for liquids.

Deviation from Joule's Law.—According to this law, which is not strictly true, the internal energy of a given mass of gas is independent of its volume. The deviation is due simply to molecular attraction, and is expressed by the equation—

$$\frac{Jc_v}{R} \times \frac{\delta\Theta}{\delta\pi} = \frac{27}{64} \times \frac{1}{\theta}$$

where J is the mechanical equivalent of heat, and $\delta\Theta = \frac{\delta T}{T_c}$. For a gas under low pressure, $\frac{R}{J} = c_p - c_v$; and the equation may be written—

$$\frac{1}{\frac{c_p}{c_v} - 1} \times \frac{\delta\Theta}{\delta\rho} = \frac{9}{8}$$

which indicates that there must always be a cooling effect, due to this attraction, when a gas expands into a vacuous space, and that the cooling effect tends towards zero as the temperature rises.

Joule-Thomson Effect.—The variation in temperature, $\delta\theta$, accompanying the expansion of a gas through a porous diaphragm is due to two phenomena: the cooling, $\delta\Theta$, due to internal work, and the cooling or heating, $\Delta\theta$, due to the external work which results from the difference $p_1v_1 - p_0v_0$ between the pressures p_1 and p_0.

Consider the expansion from a very feeble pressure, $\delta\pi$, to zero pressure. The cooling due to internal work is given by the expression—

$$\frac{1}{\frac{c_p}{c_v} - 1} \times \frac{\delta\Theta}{\delta\rho} = \frac{9}{8}$$

and the heat change due to external work by the formula—

$$\frac{Jc_p}{R} \times \frac{\Delta\theta}{\delta\pi} = \frac{1}{8}\left(1 - \frac{27}{8} \times \frac{1}{\theta}\right).$$

(iv.) For $\theta = \frac{27}{8}$ there is no heat change due to external work on expansion; for lower temperatures there is a cooling effect, for higher temperatures a heating effect.

The resultant Joule-Thomson effect is given by the formula—

$$\frac{Jc_p}{R} \times \frac{\delta\theta}{\delta\pi} = \frac{1}{8}\left(1 - \frac{27}{4} \times \frac{1}{\theta}\right).$$

(v.) For $\theta = \frac{27}{4}$, the temperature at which the gas follows Gay Lussac's law, the heating and cooling effects compensate each other, and there is no heat change. At lower temperatures there is a cooling effect, at higher temperatures a heating effect. This is the case, for example, with hydrogen at 0° C.

The conclusions arrived at by D. Berthelot[1] are clearly indicated by the diagram (Fig. 55).

It will be seen that at the reduced temperature 3·375 the gas would follow the laws of Boyle and Avogadro, and that there would be no thermal effect due to external work on expansion. At the reduced temperature 6·750 the gas would follow Gay Lussac's law, and there would be no Joule-Thomson thermal effect.

The five reduced temperatures to which special reference has been made are the following:—

$$\theta_1 = 3{\cdot}375\,;\ \theta_2 = 2\theta_1 = 6{\cdot}750\,;\ \theta_3 = 3\theta_1 = 10{\cdot}125\,;$$
$$\theta_4 = 4\theta_1 = 13{\cdot}5\,;\ \theta_6 = 6\theta_1 = 20{\cdot}25$$

The modified equation of state proposed by Clausius—

$$\left(p + \frac{a}{Tv^2}\right)(v - b) = RT$$

leads to similar results, but the five reduced temperatures would have the values—

$$\theta_1' = \sqrt{\tfrac{27}{8}} = 1{\cdot}837 = \frac{\theta_2'}{\sqrt{3}} = \frac{\theta_3'}{\sqrt{6}} = \frac{\theta_4'}{\sqrt{9}} = \frac{\theta_6'}{\sqrt{18}}.$$

If this formula were correct, the isochors would not be quite straight, and the constant-volume thermometer would not give quite correct readings.

D. Berthelot points out that if the values of $\frac{d(\pi\phi)}{d\pi}$, calculated from the equation of Van der Waals, are plotted against $\tau \left(= \frac{T_c}{T}\right)$, a straight line is obtained, whereas those derived from the equation of Clausius give a parabola. In both cases the limiting value for $\tau = 0$ is $\frac{1}{3}$.

The experimental data for any one substance are not sufficiently complete to decide the question whether a straight line or parabola

[1] *Loc. cit.*, p. 25.

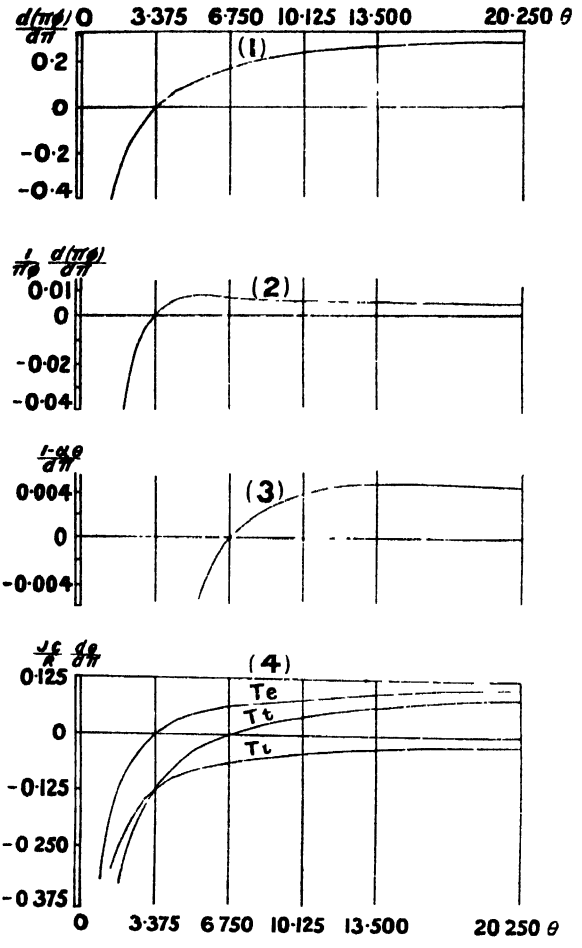


FIG. 55.—Diagrams of the deviations from the laws relating to perfect gases which would be observed in the case of gases under low pressures if the formula of Van der Waals were applicable to them.

Diagram 1.—Deviation from Boyle's law.

Diagram 2.— ,, ,, Avogadro's (Ampère's) law.

Diagram 3.— ,, ,, Gay Lussac's law.

Diagram 4.—Thermal effects produced during expansion.

Curve T_e.—Thermal effect due to external work, resulting from variation in value of PV.

Curve T_i.—Thermal effect due to internal work.

Curve T_t.—Joule-Thomson effect.

is correct, but Berthelot has collected all the available data for hydrogen, nitrogen, carbon monoxide, air, oxygen, nitric oxide, methane, and carbon dioxide, and calculated the values of $\frac{d(\pi\phi)}{d\pi}$ from them. These values, plotted against τ, fall satisfactorily on a parabola, which, however, is quite distinct from that derived from Clausius' equation. Moreover, the limiting value is not $\frac{1}{3}$, but $\frac{1}{4}$, and the value for $\tau = 1$ is 1·25. Inasmuch, however, as the law of corresponding states is not strictly true, the deviations from the curve cannot be entirely attributed to errors of experiment.

The points representing the values of $\frac{d(\pi\phi)}{d\pi}$, when plotted against τ^2 instead of τ, fall satisfactorily on a straight line, and the very simple expression

$$\frac{d(\pi\phi)}{d\pi} = \tfrac{1}{4}(1 - 6\tau^2)$$

is thus obtained.

The limiting value 0·25 represents the co-volume in reduced co-ordinates, and Berthelot points out that he had previously arrived at the same value, 0·25, by calculating the densities of liquids at the absolute zero of temperature by the method of Cailletet and Mathias;[1] he concludes that, as the same value has been obtained from data relating to matter on the one hand in its highest state of rarefaction, and on the other hand in its highest state of condensation, the co-volume must be regarded as an absolute constant.

It has been observed experimentally by Young[2] that the ratio of the actual to the theoretical density at the critical point $\frac{S_c}{S}$ is not $\frac{8}{3}$, as required by Van der Waals' equation, but that in a large number of cases it is between 3·7 and 3·9 (p. 211), the mean value for nine hydrocarbons being 3·783. For carbon tetrachloride the value is 3·674, and for carbon dioxide it is 3·6, according to the measurements of Amagat. D. Berthelot points out that for oxygen and nitrogen it is probably about 3·5 (observed, 3·42). For the ordinary gases Berthelot adopts the value 3·55, or $\frac{32}{9}$.

For low pressures the equation of Clausius takes the form—

$$pv = \mathrm{RT}\left\{1 + \frac{1}{v}\left(b + \frac{a}{\mathrm{RT}^2}\right)\right\}$$

but in place of the values—

[1] *Compt. rend.* (March 12, 1900). [2] *Phil. Mag.* (V.), **50**, 291 (1900).

$$b = \frac{v_c}{3} \qquad a = 3p_c v_c^2 T_c \qquad R = \frac{8}{3} \times \frac{p_c v_c}{T_c}$$

Berthelot adopts the following, based on experimental data:—

$$a = \frac{16}{3} p_c v_c^2 T_c \qquad R = \frac{32}{9} \times \frac{p_c v_c}{T_c} \qquad b = \frac{v_c}{4}$$

or $$a = \frac{27}{64} R^2 \times \frac{T_c^3}{p_c}.$$

From this equation with the new constants the five reduced temperatures are—

$$\theta_1'' = \sqrt{6} = 2{\cdot}45 = \frac{\theta_2''}{\sqrt{3}} = \frac{\theta_3''}{\sqrt{6}} = \frac{\theta_4''}{3} = \frac{\theta_5''}{3\sqrt{2}}.$$

Thus the deviations from the laws of Boyle and Avogadro vanish at the reduced temperature $\theta_1 = 2{\cdot}45$, and the deviations from the law of Gay Lussac and also the Joule-Thomson effect vanish at $\theta_2 = 4{\cdot}24$.

It is found that nitrogen obeys Boyle's law at about 52° C.; or $\theta = 2{\cdot}56$, and that air does so at about 54° C., or $\theta = 2{\cdot}46$.

Olszewski[1] finds the inversion temperature (Joule-Thomson effect) for hydrogen to be − 80·5° C., or 192·5 abs., which, taking the critical temperature of hydrogen to be 33° abs., would give the ratio 5·8. On the other hand, he has[2] found, on allowing air and nitrogen to expand from various high pressures to that of the atmosphere at different temperatures, that the inversion temperature falls as the initial pressure diminishes.

The experimental results obtained by Olszewski have, however, been criticized by Dickson[3] and by Dalton,[4] according to whom the inversion temperature falls with increasing initial pressure. The question has been discussed and the experimental data examined by Porter.[5]

Modifications of the Generalizations of Van der Waals.—No reduced formula can be strictly applicable to all substances, for it has been shown that the generalizations of Van der Waals are only approximately true in most cases.

It was suggested by M^me^ K. Meyer, in 1898,[6] that the reason why the generalizations of Van der Waals are in most cases not strictly accurate, is that the temperatures and volumes are in each

[1] *Bull. Acad. Crac.* (1901), p. 453. [2] *Ibid.* (1906), p. 792.
[3] *Phil. Mag.*, **15**, 126 (1908).
[4] *Comm. Phys. Lab. Leiden*, Nos. **109** *a* and *c* (1909).
[5] *Phil. Mag.*, **19**, 888 (1910). [6] *Zeit. physik. Chem.*, **32**, 1 (1900).

case reckoned from zero. On the assumption that each substance has its own special minimum temperature and minimum volume—pressures, however, being always reckoned from zero—a very much better agreement between the ratios may be obtained.

The reduced temperatures, volumes, and pressures on this assumption will be—

$$\theta' = \frac{T - T_{min.}}{T_c - T_{min.}} \qquad \phi' = \frac{v' - v_{min.}}{v_c - v_{min.}} \qquad \pi = \frac{p}{p_c}$$

and the modified generalizations may be stated thus—

1. At corresponding pressures the ratio $\frac{T - T_{min.}}{T_c - T_{min.}}$ is the same for all substances, where T is the boiling point, and $T_{min.}$ the minimum temperature, both on the absolute scale.

2. At corresponding pressures the ratio $\frac{v'_V - v_{min.}}{v_c - v_{min.}}$ is the same for all substances, and so also is the ratio $\frac{v_L - v_{min.}}{v_c - v_{min.}}$ where v_V and v_L are the orthobaric volumes of saturated vapour and of liquid, and $v_{min.}$ is the minimum volume.

Mme. Meyer took $T_{min.} = 0$ and $v_{min.} = 0$ arbitrarily for fluorobenzene, and calculated the values of these constants for other substances. On then calculating the modified ratios, the agreement was found to be very much more satisfactory than is the case with the original ratios.

The question has been further discussed by D. Berthelot,[1] who suggests that the volumes to be compared should be the observed volumes diminished by the co-volume; that the co-volume may be taken as the volume which the substance would occupy at its special zero of temperature; and that this minimum volume may be calculated by the method of Cailletet and Mathias.

If the minimum temperature of fluorobenzene be taken arbitrarily as 0° abs., those of some of the substances would be lower than the absolute zero, which of course is impossible; thus CCl_4 – 17·26° and CS_2 – 40·2. D. Berthelot takes the value of $T_{min.}$ for fluorobenzene to be 56°, and has calculated the following values of $T_{min.}$ and $v_{min.}$ (where $v_{min.}$ is the minimum volume for 1 gram of substance):—

[1] *Compt. rend.* (July, 1900). See also Brillouin (*Journ. de Physique* (VI.), **2**, 117 (1893)), and Raveau (*ibid.*, **6**, 433 (1897)); Timmermans, *Sci. Proc. Roy. Dublin Soc.*, **13** (N.S.), 367 (1912).

	$v_{min.}$	$T_{min.}$	Theor. vol. at temp. $T_c - T_{min.}$ and pres p_c. $\frac{v_c - v_{min.}}{}$
Benzene . . .	0·892	46·6	4·73
Fluorobenzene .	0·767	56·0	4·69
Chlorobenzene .	0·734	61·0	4·67
Bromobenzene .	0·554	69·0	4·68
Iodobenzene . .	0·459	72·0	4·65
Carbon tetrachloride	0·490	40·0	4·70
Ether . . .	1·019	51·4	4·64
Carbon dioxide .	0·599	21·0	4·66
Normal pentane .	1·171	46·0	4·67
Isopentane . .	1·179	43·3	4·68

It has been shown that if the generalizations of Van der Waals were correct, the ratio of the actual to the theoretical density at the critical point, or, in other words, the ratio of the theoretical volume (for a perfect gas at the temperature T_c and the pressure p_c) to the actual critical volume should be a constant for all substances.

D. Berthelot proposes the following modified law. There exists a constant ratio between the theoretical volume occupied by unit mass of a fluid under the pressure p_c and at the temperature $T_c - T_{min.}$, and the difference $v_c - v_{min.}$ between the actual critical volume and the minimum volume. The numerical value of this ratio is about 4·68 (see table above).

With the above values of $T_{min.}$ and $v_{min.}$ the ratios $\frac{T - T_{min.}}{T_c - T_{min.}}$ and $\frac{v - v_{min.}}{v_c - v_{min.}}$ for different substances at corresponding pressures show good agreement.

CHAPTER XII.

PROPERTIES OF SOLIDS.

WHEN a liquid is cooled below its freezing point, or when a gas, under sufficiently reduced pressure, is cooled below its condensing point, the substance assumes the solid state.

The internal friction of solid substances is much greater than that of liquids, and a much greater expenditure of work is required to alter their form. Moreover, when the form of a solid is forcibly altered—but not beyond a certain amount—the particles are put into a state of strain, so that the system acquires potential energy. When the force causing the strain ceases to act, the solid reverts to its original form: it is said to be elastic as regards shape. Some solids, such as tempered steel or india-rubber, are extremely elastic; others, such as lead or antimony, only to a very slight extent.

Solids vary also very greatly in their hardness, malleability, tenacity, and other properties.

Their compressibility is exceedingly slight, much less, even, than that of liquids.

Melting Points of Solids.—When a pure solid substance is heated, it melts, as a rule, at a definite temperature. The melting point depends on the nature of the substance, but was thought, until 1849, to be independent of the external pressure. It was shown, however, by James Thomson, that the melting point of ice should, theoretically, be slightly lowered by raising the pressure, and he calculated the rate of change of temperature per unit rise of pressure by means of the formula—

$$\frac{L'}{v_L - v_s} = \frac{T}{J} \times \frac{dp'}{dT} \text{ or } \frac{dT}{dp'} = \frac{T}{J} \times \frac{(v_L - v_s)}{L'}$$

where L' is the heat of fusion, v_L and v_s the volumes of a gram of liquid and solid respectively, J the mechanical equivalent of heat, T the melting point on the absolute scale of temperature, and $\frac{dT}{dp'}$ rate of change of temperature per unit rise of pressure.

Since T, J, and L′ are always positive, it follows that $\frac{dT}{dp'}$ will be either positive or negative, according as v_L is greater or less than v_s.

Most solid substances expand on fusion, and v_l is therefore generally greater than v_s. The melting point in these cases should be raised by increasing the pressure. Ice, however, contracts on fusion; v_s is therefore greater than v_l, and the melting point should fall when the pressure is raised.

In the case of ice, T = 273, v_l = 0·00100 (litre), v_s = 0·00109, L′ = 79·6 calories = $\frac{79·6}{24·17}$ litre atmospheres.

$$\therefore \frac{dT}{dp'} = -0·0075^{\circ} \text{ per atmos.}$$

This value of $\frac{dT}{dp'}$, calculated by James Thomson, agrees well

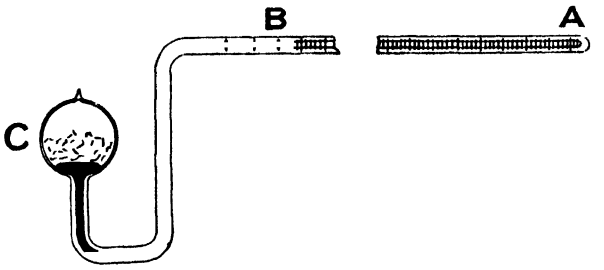


FIG. 56.

with that found experimentally by Sir William Thomson[1] in 1850, and it has subsequently been confirmed by Dewar, Goosens, and other observers.

The most striking case of a positive value of $\frac{dT}{dp'}$ yet observed is that of carbon tetrachloride, the melting point of which has been found by Amagat[2] to rise from −19·5° to +19·5° on increasing the pressure from 210 to 1160 atmos., so that $\frac{dT}{dp'}$ = +0·04° per atmos.

The rise in the melting point of acetic acid caused by increasing the pressure was measured by de Visser[3] by means of the simple apparatus shown in Fig. 56.

A thick-walled bulb C is fused to a long piece of capillary tubing,

[1] *Phil. Mag.*, **37**, 123 (1850). [2] *Compt. rend.*, **105**, 165 (1887).
[3] *Zeit. physik. Chem.*, **9**, 767 (1892).

which is bent three times at right angles, as shown in the diagram. The tube is sealed at A, and the horizontal portion is graduated and calibrated. The tube from A to B contains air, the volume of which at a known temperature and pressure has been measured. From B to C there is mercury, and the bulb contains acetic acid, which should be partly fused at its ordinary melting point, 16·6°; that is to say, when the pressure of the air in the tube is about 1 atmosphere. On raising the temperature of the bulb slightly, some of the solid melts; expansion takes place on fusion, and the air is compressed. Fusion goes on, and the pressure rises until equilibrium is established. On raising the temperature again, more of the solid melts until the pressure reaches the maximum corresponding to the new temperature. In this way a series of readings of temperature and pressure may be taken. The value of $\frac{dT}{dp}$, 0·02435° per atmos., ascertained in this way by de Visser, agrees very well with that calculated by the formula of Clapeyron, 0·0242°.

According to Damien,[1] the effect of pressure on the melting point of a solid may in general be expressed by the formula—

$$t = t_0 + a(p - 1) - b(p - 1)^2$$

where t_0 is the melting point under atmospheric pressure, and t the melting point under pressure p.

The constant b was found to be negative in every case investigated, and if the formula holds up to sufficiently high pressures, the melting point must reach a maximum, and then diminish with further rise of pressure. Such a maximum was actually observed in the case of naphthylamine, the melting point of which rises from 49·750° under atmospheric pressure to 50·543° under a pressure of 81 atmos., and falls again to 49·646° when the pressure is further raised to 173 atmos.

Vapour Pressures of Solids.—A solid substance, like a liquid, gives off vapour, and the vapour pressure, like that of a liquid, depends on the temperature. It is, however, in many cases too small to be measured.

The term *volatilization* may conveniently be applied to the vaporization of a solid, and the term *sublimation* to the double process of volatilization and condensation, just as the term *distillation* is

[1] *Compt. rend.*, **112**, 785 (1891).

applied in the case of a liquid to the double process of vaporization and condensation.

The vapour pressure of a solid, if high enough, may be measured by the statical method, some of the solid being placed over the mercury in a barometer tube. The curve representing the relation between vapour pressure and temperature is of the same form for solids as for liquids.

The Triple Point.—The vapour pressures of both ice and water were very carefully determined by Regnault,[1] and he was inclined to attribute the small differences observed to errors of experiment; but James Thomson,[2] in 1851, arrived at the conclusion, based on theoretical grounds, that at the melting point the vapour pressures of ice and water should be identical, but that at any lower temperature the vapour of water should be higher than that of ice. In fact, the curves representing (*a*) the vapour pressures of water, AC, Fig. 57, (*b*) the vapour pressures of ice, BA, and (*c*) the pressures under which ice melts at different temperatures, AD, should intersect at a point A, which he called the triple point. The same conclusion was arrived at independently by Kirchhoff in 1858.[3] A careful examination of Regnault's results showed that the vapour pressures of ice observed by him were in fact slightly lower than those of water at the same temperature, except at the melting point.

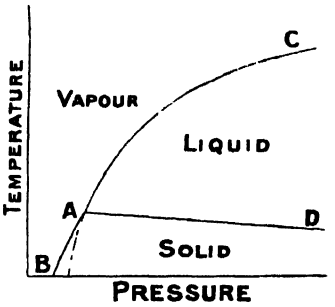


FIG. 57.

Volatilizing Points.—In the year 1880, Carnelley[4] observed that ice, when exposed to exceedingly low pressures, could not be melted by the application of heat, but that rapid volatilization, without fusion, took place. It was thought at first that the temperature of the ice rose above 0°, but it was suggested by Young[5] that if the ice did not really become hot, the curve representing the vapour pressures of ice at different temperatures might also represent the volatilizing points of ice under different pressures.

[1] *Ann. Chim. Phys.* [3], **11**, 273 (1844); "Relation des Expériences" (Paris, 1847), pp. 465-633.

[2] *Trans. Roy. Soc. Edin.* (1851). [3] *Pogg. Ann.*, **103**, 206 (1858).

[4] *Chem. News*, **42**, 130 and 313 (1880), **43**, 19 (1881).

[5] *Nature*, **24**, 239 (1881); cf. Pettersson, *ibid.*, p. 167.

In 1883 and 1884 Ramsay and Young[1] proved experimentally (*a*) that the volatilizing points of ice and other vaporizible solids depend on the pressure; (*b*) that the same curve represents the volatilizing points and the vapour pressures of a given solid; and (*c*) that the curve for ice agrees with that based on the formulæ employed by James Thomson. Experimental confirmation of the correctness of James Thomson's conclusions was obtained by Fischer[2] in 1886 in the case of ice, and by Ferche[3] in 1891 in that of benzene by the statical method.

The value of $\frac{dp''}{dT}$ for a volatilizing solid was calculated by James Thomson in the following manner:—

The heat of volatilization of a solid is given by the equation,

$$L'' = (v_v - v_s)\frac{T}{J} \times \frac{dp''}{dT},$$

where v_v and v_s are the volumes of a gram of vapour and solid respectively, and $\frac{dp''}{dT}$ is the rate of increase of the vapour pressure of the solid per unit rise in temperature. Since the vapour pressure is usually very low, the volume v_v is very large relatively to v_s, and the equation may be written—

$$L'' = v_v \times \frac{T}{J} \times \frac{dp''}{dT}.$$

At the melting point the heat of volatilization must be equal to the sum of the heat of fusion, L', and the heat of vaporization, L, or—

$$L'' = L' + L \text{ and } L' = L'' - L.$$

$$\text{But } L = v_v \times \frac{T}{J} \times \frac{dp}{dT},$$

$$\therefore L' = v_v \times \frac{T}{J} \times \left(\frac{dp''}{dT} - \frac{dp}{dT}\right),$$

$$\therefore \frac{dp''}{dT} = \frac{dp}{dT} + \frac{L'J}{Tv_v}.$$

But L' has always a positive value; therefore $\frac{dp''}{dT}$ is always greater than $\frac{dp}{dT}$.

[1] *Phil. Trans.*, **175**, 37 and 461 (1884); *Phil. Mag.* [V.], **23**, 61 (1887).
[2] *Wied. Ann.*, **28**, 400 (1886). [3] *Ibid.*, **44**, 265 (1891).

If the values of L', v_v, T, and $\frac{dp}{dT}$ are known, that of $\frac{dp''}{dT}$ may be calculated.

Taking the values for benzene found or adopted by Ferche, L' = 30·18 calories; v_v = 6243 c.c.; T = 273 + 5·4; $\frac{dp}{dt}$ = 1·931 mm. per degree; and J = 42,000 gram-cms.; and since a pressure of 1 mm. of mercury = 1·359 grams per square centimetre—

$$\frac{dp''}{dT} = 1{\cdot}931 + \frac{30{\cdot}18 \times 42{,}400}{278{\cdot}4 \times 6243} \times \frac{1}{1{\cdot}359}$$
$$= 2{\cdot}473.$$

The mean value of $\frac{dp''}{dT}$ observed by Ferche was 2·455, which agrees very well with that calculated.

The Crystalline Form.—When a substance passes from the liquid or gaseous to the solid state, or when it separates in the solid state from its solution in any solvent, it tends to assume a definite crystalline form. When the change of state occurs very rapidly, or when the substance is formed as a solid by a chemical change which takes place almost instantaneously, crystals may not be formed at all, and the substance is then said to be amphorous, or they may be very small. As a general rule, the slower the change of state or the chemical change, the larger and more regular are the crystals.

The *crystalline form* of a given chemical substance is usually constant, whatever the conditions under which the solid state is assumed, but at the same time the number and shape of the plane surfaces, or *faces*, may vary considerably. Careful examination of different crystals of the substance shows, however, that there is a symmetry in the arrangement of the faces which is common to all of them.

There are, however, some substances, such as sulphur or calcium carbonate, which may assume either of two totally different crystalline forms; and such substances are said to be dimorphous. A few substances, for example, titanium dioxide, occur in three distinct crystalline forms, and are said to be trimorphous.

The faces of every crystal may be referred to certain imaginary straight lines or axes within the crystal. Every crystal may be regarded as belonging to one or other of six systems, the Regular,

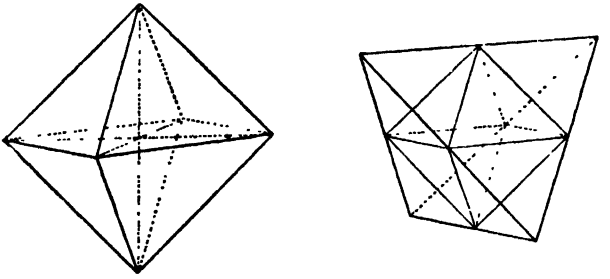
the Hexagonal, the Quadratic, the Rhombic, the Monoclinic, or the Asymmetric, and in each system the crystallographical axes are so chosen that the different forms may be most simply expressed by reference to them.

I. In the regular system there are three equal axes, each of them perpendicular to the plane of the other two.

II. In the hexagonal system there is one principal axis perpendicular to three others, which are equal and in the same plane, and cut each other at an angle of 60°.

III. In the quadratic system there are three axes, all at right angles to each other. Two of the axes are equal in length, the third or principal axis is either longer or shorter than the others.

IV. In the rhombic system there are three axes at right angles to each other, but all of them unequal.



Figs. 58, 59.

V. In the monoclinic system there are three unequal axes, of which one is perpendicular to the plane of the other two which are oblique.

VI. In the asymmetric system there are three unequal and oblique axes.

There are various forms of crystals belonging to each system; these may be fixed or invariable, as the cube, the regular octahedron, or the dodecahedron in the first system, or they may be variable.

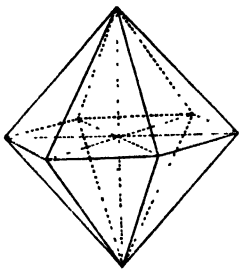
Again, the forms are said to be holohedral when all the faces are developed, or hemihedral when half of them are suppressed. Thus the form of the regular octahedron (Fig. 58) is holohedral, that of the tetrahedron (Fig. 59), derived from it by the suppression of alternate faces and the development of the others, is hemihedral. Again, both the dihexagonal pyramid and the rhombohedron (Figs. 60 and 61) belong to the hexagonal system, but the form of the first is holohedral, that of the second hemihedral.

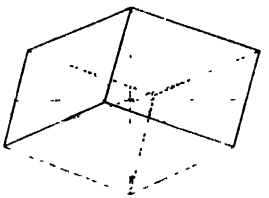
A chemical substance may sometimes be identified by a study of its crystalline form, or by an examination of the optical or other properties of the crystals.

An important relation has been shown by Barlow and Pope[1] to exist between the crystalline form and the valency of many chemical substances. This relation is dealt with in the volume on "Chemical Constitution and Physical Properties," by S. Smiles; and some of the optical properties of crystals are referred to in the volume on "Stereochemistry," by A. W. Stewart. Important relations have been discovered between chemical constitution and crystalline form.

Specific Heats of Solids.—It was noticed by Dulong and Petit[2] in 1819, that the following simple relation appeared to exist between the specific heats of the different solid elements and their most probable atomic weights:—

Specific heat × *atomic weight* = *constant.*





FIGS. 60, 61.

This constant, which is termed the *atomic heat*, is approximately 6·4. The relation may be simply expressed by the statement that all atoms have the same capacity for heat.

It is true that great doubt was felt regarding the atomic weights of some of the elements, but, as the relation was found to hold in many cases in which the atomic weights were firmly established, Dulong and Petit felt justified in stating the relation as a general law.

The specific heat was usually determined by measuring the amount of heat given up to a water or ice calorimeter by a weighed quantity of the solid on cooling from 100° C. to the temperature of the calorimeter.

It was found that the specific heats of certain elements, notably

[1] *Trans. Chem. Soc.*, **89**, 1675 (1906).
[2] *Ann. Chim. Phys.*, **10**, 395 (1819).

carbon, silicon, and boron, when multiplied by the accepted atomic weights, gave numbers very much lower than 6·4.

The subject was investigated by Weber,[1] who observed that at ordinary temperatures the specific heats of the diamond and graphite differed widely from each other, but that, as the temperature was raised, the specific heats increased, rapidly at first, then more and more slowly, until they became almost constant at about 600°. At this temperature, also, the specific heats of the two allotropic modifications of carbon are nearly equal, and the atomic heat, taking the atomic weight of carbon as 12, is 5·5, whereas at − 50° the atomic heat of the diamond was found to be only 0·76, and of graphite 1·37.

The specific heats[2] of the diamond and graphite are given in the following table:—

Temperature.	Specific Heat of Diamond.	Temperature.	Specific Heat of Graphite.
Degrees.		Degrees.	
− 50	0·0635	− 50	0·1138
+ 10	0·1128	+ 10	0·1604
85	0·1765	61	0·1990
250	0·3026	201	0·2966
606	0·4408	250	0·3250
985	0·4589	641	0·4454
		978	0·4670

Similar results were obtained by Weber with boron and silicon, and by Nilson and Pettersson[3] with beryllium (glucinum). In all these cases the specific heat rises rapidly with the temperature, but eventually becomes practically constant, boron at about 600°, silicon at about 200°, and glucinum probably at about 300°.

In other cases, also, the specific heat has not been found to be quite constant, and recent researches by Tilden, Harker, Bernini, and others indicate that the variations are larger than had previously been supposed. Tilden[4] arrives at the conclusion that there is no

[1] *Pogg. Ann.*, **154**, 367 (1875).

[2] Weber did not measure his high temperatures directly, but deduced them from the amount of heat given up by platinum when cooled through the same range of temperature. The specific heat of platinum has been redetermined by Magnus from 0° to 900°, and Weber's results have been recalculated. *Ann. d. Physik*, **48**, 983 (1915).

[3] *Berichte*, **13**, 1451 (1880); *vide* also L. Meyer, *ibid.*, p. 1780.

[4] *Trans. Chem. Soc.*, **87**, 551 (1905).

one condition or set of conditions under which the law of Dulong and Petit is true for all the elements. He considers it best for practical purposes to take the mean specific heat of metals between 0° and 100° C., recognizing the fact that carbon, boron, silicon, and glucinum must be regarded as exceptional.

In 1831 Neumann,[1] studying the specific heats of solid compounds, concluded that, for chemically similar substances, the product of the specific heat, c, into the *formula weight*, F, is constant. The term "formula weight" is employed in preference to "molecular weight," because the actual molecular formulæ of solids are as yet unknown. For example, it is uncertain whether the true molecular formula of calcium sulphate is $CaSO_4$ or $(CaSO_4)_n$, where n is a whole number greater than unity, but the formula is provisionally written in its simplest form, and the formula weight of calcium sulphate is therefore—

$$40 + 32 + 64 = 136.$$

Garnier[2] in 1852, and later Cannizzaro,[3] arrived at the conclusion that Neumann's law might be extended to dissimilar compounds, and that the *formula heat* divided by the number of atoms, N, in the formula is a constant for all solid substances; or—

$$\frac{F \cdot c}{N} = \text{constant.}$$

The whole subject was fully discussed and the published data collected and tabulated by Kopp,[4] who showed that very frequently the formula heat of a solid compound was equal to the sum of the atomic heats of the component atoms, but that the generalization of Garnier and Cannizzaro is not universally applicable, discordant results being obtained in the case of compounds which contain any of the five gaseous elements, hydrogen, fluorine, chlorine, nitrogen, and oxygen.

Tilden[5] has shown that the specific heats of solid compounds and alloys show variations with temperature very similar to those exhibited by the elements composing them. Thus the specific heat of aluminium increases far more rapidly than that of silver with rise of temperature; a silver aluminium alloy rich in silver behaves very much like

[1] *Pogg. Ann.*, **23**, 1 (1831). [2] *Compt. rend.*, **35**, 278; **37**, 130.
[3] *Il Nuovo Cimento*, **7**, 321; *Bull. Soc. Chim.* (1863), p. 171.
[4] *Wied. Ann.*, Suppl., **3**, 1 and 289 (1864).
[5] *Phil. Trans.*, A., **203**, 139 (1904).

pure silver, while an alloy rich in aluminium shows the characteristic behaviour of that metal.

In general, the molecular or formula heat of a compound or alloy was not found to differ greatly from the sum of the atomic heats, at the same temperature, of the solid elements composing it, taking, of course, the composition into account.

E. H. Griffiths and E. Griffiths[1] propose the formula $c = 4{\cdot}80.4 \times A^{-0{\cdot}95}$ in place of that of Dulong and Petit, $c = 6{\cdot}4/A$, as agreeing better with the observed results, but carbon, boron, and some other elements are still found to be anomalous.

Gruneisen[2] states that the ratio of the coefficient of expansion of a metal to its specific heat is nearly independent of the temperature through an observed range of from 500 to 1200 degrees.

The specific heats of nickel and iron have been found by Lecher[3] to show remarkable variation at high temperatures. Nickel shows a maximum at 350°, 50 per cent. higher than at the ordinary temperature, and iron a maximum at 700°, no less than three times as high as at the ordinary temperature.

In recent years researches have been carried out on the specific heats of elements and compounds at very high temperatures by Corbino[4] and others, and at low and very low temperatures by many observers.[5] Richards and Jackson have determined the mean specific heats of a considerable number of solid elements between the temperature of liquid air and that of the room, and find that, with the exception of those of the elements of lowest atomic weights, they conform approximately to the law of Dulong and Petit. On the other hand, Nernst concludes that at very low temperatures the actual specific heats approach zero or, at any rate, become very small, and the re-

[1] *Phil. Trans.*, A., **213**, 119 (1913); **214**, 319 (1914).

[2] *Ann. d. Physik*, **26**, 211 (1908); **33**, 65 (1910); *Deutsch. Phys. Gesell.*, **13**, 426 (1911).

[3] *Akad. Wiss. Wien, Sitz. Ber.*, **117**, 111 (1908).

[4] *Accad. Lincei. Atti.*, **22**, 430 (1913).

[5] Richards and Jackson, *Zeit. physik. Chem.*, **70**, 14 (1910); Nernst, *Preuss. Akad. Wiss. Berlin* (1910), p. 262; (1911), pp. 306 and 494; (1914), p. 355: Lindemann, *ibid.* (1911), pp. 316 and 494; Nernst, *Ann. d. Physik*, **36**, 395 (1911); Koref, *ibid.*, p. 49; Estreicher and Staniewski, *Acad. Sci. Cracovie*, **8a**, 834 (1912); Eucken and Schwers, *Deutsch. Phys. Gesell.*, **15**, 578 (1913); Dewar, *Proc. Roy. Soc.*, **89**, 158 (1913); Keesom and Onnes, *Comm. Phys. Lab. Leiden*, Nos. 143 and 147*a* (1915); 149*a* (1916); Onnes and Holst, *ibid.*, 142*c* (1914); Ewald, *Ann. d. Physik*, **44**, 1213 (1914).

sults obtained by other observers, notably Dewar and Kamerlingh Onnes, lead to the same conclusion.

Dewar has determined the specific heats of fifty-three elements at temperatures between the boiling points of hydrogen and nitrogen, and shows that when the atomic heats are plotted against the atomic weights, a periodic curve is obtained which closely resembles Lothar Meyer's atomic volume curve. He considers that if the specific heats were taken between the boiling points of helium and hydrogen, the atomic heats would be very small and nearly constant.

A few determinations at the temperature of liquid helium have actually been carried out by Kamerlingh Onnes and his co-workers. Onnes and Holst find that the specific heat of mercury is 0·00142 between 4·26° and 6·48° (absolute), and 0 000534 between 2·93° and 3·97°. Again, Keesom and Onnes find that the atomic heat of solid nitrogen varies from 1·60 at 15·27° abs. to 5·48 at 61·68° abs., that of liquid nitrogen rising from 6·48 at 63·95° to 6·87 at 76·49° abs.

CHAPTER XIII.

MIXTURES.

1. Mixed Gases—Diffusion.—All gases which do not act chemically on each other possess the property of infinite miscibility.

When two gases are brought into actual contact with each other, or when they are separated only by a porous diaphragm, diffusion takes place and goes on until a homogeneous mixture of the two gases is obtained.

Thus if a jar of air, in which there is a strip of filter paper moistened with a solution of potassium iodide and starch, reaching from top to bottom of the jar, is inverted over a jar of chlorine, the diffusion of the chlorine into the upper jar is rendered evident by the changes of colour. A blue colour is at first developed owing to liberation of iodine and formation of iodide of starch, and this extends rapidly upwards long before the greenish-yellow colour of the chlorine is itself visible. As the amount of chlorine increases, chloride of iodine is formed, and the blue colour disappears again. The bleaching begins below and spreads slowly upwards, but eventually the whole strip of paper becomes colourless or yellow.

The experiment proves that a small amount of the heavier gas penetrates the lighter gas above it very rapidly, but that a considerable time elapses before the process of diffusion is complete.

The diffusion of different gases through porous diaphragms was studied by Thos. Graham,[1] who showed that the rates of diffusion are inversely proportional to the square roots of the densities of the gases. Thus the relative densities of hydrogen, steam, and oxygen at the same temperature and pressure are $1 : 9 : 16$, and the rates of diffusion are $1 : 1/3 : 1/4 = 12 : 4 : 3$.

This result is in accordance with the kinetic theory of gases, for the kinetic energy of rectilinear motion of the molecules of two gases is the same if the gases are at the same temperature; or—

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

[1] *Phil. Mag.*, **2**, 175 (1833).

If $m_1 = 16$, and $m_2 = 1$, then—

$$16u_1^2 = u_2^2$$

and $$u_1 = \frac{u_2}{4}$$

That is to say, the mean velocity of the heavier molecules is one-fourth of that of the lighter ones.

Since the molecular weights of gases are proportional to their densities, if the relative rates of diffusion of two gases and the molecular weight of one of them are known, the molecular weight of the other may be calculated. This method was adopted for the determination of the molecular weight of ozone. In the cases, however, of the emanations from radium, thorium, and actinium, the molecular weights (or atomic weights, the molecules of these gases being monatomic) calculated from the rates of diffusion are far too low, the actual atomic weights being nearly three times as great. On the other hand, Debierne [1] found that Bunsen's method of determining the densities of gases by measuring their rates of escape through a minute orifice was applicable to mixtures; and by this method he obtained the value 220 for the molecular (atomic) weight of radium emanation, the true value being 222. In a similar manner Mlle. Leslie [2] obtained values of 200 to 210 for thorium emanation.

A commonly occurring case of direct diffusion is that in which a volatile liquid is brought into contact with a gas free, or partly free, from the vapour of the liquid, as, for example, when water comes into contact with dry air. Consider the case of an inverted cylindrical jar of dry air standing over water at constant temperature. The vapour pressure of water at ordinary temperatures is very much lower than the atmospheric pressure, and if diffusion did not occur the air would act like a piston, and evaporation would be impossible. Diffusion, however, goes on, and as the vapour first formed passes into the air above it, a fresh supply is constantly being received from below by the evaporation of the water. The process continues until the partial pressure of the aqueous vapour is equal to the vapour pressure of the water. In such a case the rate of diffusion depends on the pressure of the air, the free paths of the water molecules diminishing as the pressure of the air increases. When the vapour molecules, as in this case, are lighter than those of the gas, the

[1] *Compt. rend.*, **150**, 1740 (1910). [2] *Ibid.*, **153**, 328 (1911).

process of mixing may be accelerated by the formation of convection currents.

An experiment may be mentioned in which the liquid was mercury and the gas isopentane far above its critical temperature. The isopentane gas was contained in a long tube sealed above and closed below by a column of mercury. The internal diameter of the tube was about 1·5 mm., the length of the column of gas 320 mm.; the pressure of the gas was 876 mm., and the temperature of both gas and mercury 280° C. The vapour pressure of mercury at this temperature is 158 mm. The progress of the diffusion was indicated by the rise of total pressure, which, since that of the isopentane was constant, was due to the increase in the partial pressure of the mercury vapour. The pressure rose very rapidly at first, then more and more slowly, and only became constant after about four hours. In a second experiment, in which the conditions were precisely similar, except that the pressure of the isopentane gas was 2622 mm., the process was much slower, and the pressure was still rising slowly after six hours. When, in a third experiment, the pressure of the isopentane was 6056 mm., the rate of increase was slow even at first, and the pressure was far from constant after five hours, indeed the rate had not diminished to any great extent during the last two hours, and it was evident that the maximum pressure would not have been attained until after many hours additional heating.

Dalton's Law of Partial Pressures.—When two or more gases, each of them occupying the volume v, and exerting pressures $p_1, p_2 \ldots$, are mixed together at constant temperature, the volume of the mixture being v, the pressure p exerted by the mixture is equal to the sum of the original pressures $p_1 + p_2 + \ldots$ and the *partial* pressures of the gases in the mixture $p_1', p_2' \ldots$, are equal to the original pressures $p_1, p_2 \ldots$

This law, like the others already considered, is only strictly applicable to perfect gases. According to Leduc[1] it would be more correct to state the law, as applicable to ordinary gases, in the following form. "The volume occupied by a mixture of gases is equal to the sum of the volumes which the component gases would separately occupy at the same temperature and under the same pressure as the mixture."

Thus the composition of atmospheric air, free from moisture and carbon dioxide, may be calculated with sufficient accuracy from the

[1] *Compt. rend.*, **123**, 805 (1896); Jan., 1·98.

densities of oxygen, "atmospheric" nitrogen[1] and air if compared at the same temperature and pressure, but not if compared at the same temperature and volume. The first calculation gives 23·21 per cent. by weight of oxygen, the second 23·33 per cent. by weight, the direct determinations of Leduc for air at Paris giving values between 23·18 and 23·23 per cent., mean 23·20.

D. Berthelot and Sacerdote[2] show that when two gases, originally at the same pressure, are mixed in such a manner that the temperature and the total volume remain unaltered, the pressure of the mixture may be calculated if the coefficients of deviation from Boyle's Law, $A_0^{p_1} = \left(\frac{p_0 v_0}{p_1 v_1} - 1\right) \times \frac{1}{p_1 - p_0}$, between the common pressure p_1 and zero pressure p_0 are known for the mixture and for each of the two gases. There is found to be usually a very slight increase of pressure on admixture, hardly measurable except in the case of the more condensible gases. Thus for a mixture of SO_2 and CO_2 the increase of pressure, Δp, was found to be 1·36 mm.; calculated 1·52. For atmospheric air the calculated increase is only 0·01 mm., so that Leduc's law is confirmed for this mixture.

Just as the pressure of a mixture of gases may be calculated with but slight error from those of its components, so also other physical properties of mixtures, the refractive power, the power of absorbing light, the specific heat, the solubility in liquids, and so on, may be predicted.

When two gases at the same temperature and pressure are allowed to diffuse into each other, no evolution or absorption of heat is observed, and the total energy therefore remains unaltered. This statement, however, is only strictly applicable to perfect gases; it is very nearly true for ordinary gases under low pressures, but not when the pressure is high.

Mixed Liquids.

The molecules of a liquid are much closer together than those of a gas under ordinary pressures, and the attractive forces between their molecules cannot be left out of account. Consider a mixture of two liquids, A and B. The properties of the mixture will be

[1] The term "atmospheric nitrogen" is conveniently employed to denote the mixture of nitrogen with argon and its associated gases, which is obtained in the ordinary manner from air.

[2] *Compt. rend.*, March and May, 1899.

affected (*a*) by the attraction of the like molecules—those of A for each other, and those of B for each other—and (*b*) by the mutual attraction of the molecules of A and B.

If the attraction of the unlike molecules is relatively very slight indeed, it may be expected that the liquids will be non-miscible, or nearly so, as in the case of benzene and water, or mercury and either benzene or water.

If the attraction between the unlike molecules is greater than in the cases just considered, but still relatively small, miscibility within limits may be expected, as, for example, with aniline and water or ether and water. In such cases there is frequently slight expansion and slight absorption of heat on admixture. Comparing together various pairs of liquids, as the mutual attraction of the unlike molecules increases relatively to that of the like molecules, the following changes may be expected: (*a*) increasing and finally infinite miscibility; (*b*) slight expansion, diminishing to zero and followed by increasing contraction; (*c*) diminishing absorption of heat changing to increasing heat evolution. These changes do not, in many cases, run strictly *pari passu*, and among liquids which are miscible in all proportions it is not unusual to find a small amount of contraction attended by slight absorption of heat, as, for example, when a little water is added to normal propyl alcohol; but when certain compounds which are chemically closely related are mixed together, there is neither any appreciable change of volume nor any measurable evolution or absorption of heat. For such substances it is probable that the different molecular attractions, A for A, B for B, and A for B, are very nearly equal, and that the relation suggested by Galitzine[1] and by D. Berthelot,[2] namely, that $a_{A \cdot B} = \sqrt{a_A . a_B}$ holds good [where $a_{A \cdot B}$ represents the attraction of the unlike molecules, and a_A and a_B the respective attractions of the like molecules].

It would appear, then, that there are two very simple cases—

1. That in which the attraction of the unlike molecules is so slight that the liquids are practically non-miscible. In this case there can, naturally, be no heat or volume change when the liquids are brought together, but the vaporization of such pairs of liquids must be considered.

2. That of two infinitely miscible and closely related liquids which show no heat or volume change on admixture.

In the latter case the properties of a mixture can be accurately

[1] *Wied. Ann.*, 41, 770 (1890). [2] *Compt. rend.*, 126, 1703 (1898).

calculated from those of the components, and the term "additive" has been applied by Ostwald to such properties.

Density and Specific Volume of Mixtures.—Let v be the volume of the mixture, and v_A and v_B the volumes of the components; v, v_A and v_B the corresponding specific volumes (volumes of a gram); and m_A and m_B the weights of the components.

Then $v = v(m_A + m_B)$, $v_A = v_A m_A$, $v_B = v_B m_B$

And if $v = v_A + v_B$

$$v = \frac{v_A m_A + v_B m_B}{m_A + m_B}$$

and the density $s = \frac{1}{v}$.

The changes in volume observed on mixing various pairs of liquids are given in the following table, together with the (uncorrected) temperature changes, which show the direction and give a rough indication of the magnitude of the corresponding heat changes. The substances were mixed in equimolecular proportions, except in the four cases marked with an asterisk in which the molecular percentage of water was 40.

Substances.		Changes on Admixture	
A	B	Volume per Cent.	Temperature.
Bromobenzene .	Chlorobenzene .	0	0°
Ethyl propionate .	Ethyl acetate .	+ 0·015	− 0·02
,, benzene . .	Toluene . .	− 0·034	+ 0·05
n-Octane . . .	n-Hexane . .	− 0·053	+ 0·06
Ethyl alcohol . .	Methyl alcohol .	+ 0·004	− 0·10
Toluene . . .	Benzene . . .	+ 0·161	− 0·45
Ethylene dichloride .	,, . . .	+ 0·34	− 0·35
Benzene . . .	Carbon tetrachloride	− 0·13	− 0·69
Toluene . . .	,, ,,	− 0·07	+ 0·25
Ethyl acetate .	,, ,,	+ 0·03	+ 0·55
Chlorobenzene .	,, ,,	− 0·12	− 0·4
Benzene . . .	n-Hexane . .	+ 0·52	− 4·7
Carbon disulphide .	Methylal .	+ 1·22	− 6·5
Acetone . . .	Carbon disulphide .	+ 1·21	− 9·85
Chloroform . .	Acetone . . .	− 0·23	+ 12·4
Water * .	Methyl alcohol .	− 2·98	+ 7·85
,, * .	Ethyl ,, .	− 2·56	+ 2·95
,, * .	Propyl ,, .	− 1·42	− 1·15
Isobutyl alcohol * .	Water . . .	− 0·90	− 3·15
Benzene . . .	Methyl alcohol .	− 0·01	− 3·8
,, . . .	Ethyl ,, .	0	− 4·2
Propyl alcohol . .	Benzene . . .	+ 0·05	− 4·65
Isobutyl ,, . .	,, . . .	+ 0·16	− 6·35
Isoamyl ,, . .	,, . . .	+ 0·23	− 5·25

It will be seen that with closely related substances the changes are very small, in other cases they are usually but not invariably much larger. There are five cases in which contraction is accompanied by a fall in temperature and one in which a very slight expansion is attended by a rise in temperature.

Specific Heat.—The specific heat of a mixture may be approximately calculated from the specific heats of the components.

Let c be the specific heat of the mixture, and c_A and c_B the specific heats of the components, the weights of which are m_A and m_B.

$$\text{Then } c = \frac{c_A m_A + c_B m_B}{m_A + m_B}$$

Here, again, the differences between the observed and calculated specific heats are very small in some cases, but may be very considerable, as, for example, with ethyl alcohol and water, a pair of substances which also show large volume and temperature changes on admixture. For equal weights of these liquids the observed specific heat is more than 11 per cent. higher than that calculated.

Specific Refractive Power.—The specific refractive power, R, of a mixture may be calculated in a precisely similar manner—

$$R = \frac{R_A m_A + R_B m_B}{m_A + m_B} \text{ (approximately).}$$

For R any of the proposed formulæ may be employed. For example, $\frac{\mu - 1}{s}$ (Landolt, Gladstone and Dale), where μ is the refractive index for a given wave-length, and s the density; or $\frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{1}{s}$ (Lorentz and Lorenz). The latter formula generally gives the better results.

Other properties of mixtures may be deduced with more or less accuracy from those of the components, as, for example, the power of absorbing light, rotation of the plane of polarization, and so on. It is evident that if, in any case, the property were strictly additive, it would not only be possible to calculate its value for the mixture from those of its components; but if the value for only one component were known, that for the mixture might be determined, and the value for the other component calculated by means of the formula.

Thus, in the formula—

$$v = \frac{v_A m_A + v_B m_B}{m_A + m_B}$$

or, more conveniently—

$$v = \frac{v_A m + v_B(100 - m)}{100}$$

(where m is the percentage weight of the first component), the specific volume v_A of a substance capable only of existing in solution may be calculated if v, v_B, and m are known; or, again, the composition of a mixture may be ascertained by a determination of its specific volume, if those of its components are known. In most cases, however, the specific volume is not a strictly additive property, and it is therefore necessary, in the first place, to determine the actual specific volumes (or densities) of a series of mixtures, and to construct a table of values of v. It is in this way that the composition of mixtures of alcohol and water is usually ascertained, the tables in this case having been very carefully drawn up, not only for different percentages of alcohol at a given temperature, but for different temperatures also. The composition of a mixture is also frequently ascertained in a similar manner from its specific refractive power; but in this case the problem is complicated by the fact that the specific refractive power depends on the density as well as the refractive index.

In the formula

$$R = \frac{R_A m + R_B(100 - m)}{100},$$

if $R = \frac{\mu - 1}{s} = (\mu - 1)v$, $R_A = (\mu_A - 1)v_A$ . . . ; and if, according to the additive rule—

$$v = \frac{v_A m + v_B(100 - m)}{100}$$

then—

$$(\mu - 1)\{v_A m + v_B(100 - m)\} = (\mu_A - 1)v_A m + (\mu_B - 1)v_B(100 - m)$$

from which m can be calculated; but there may be deviations from the rule as regards both μ and v.

A convenient method of finding the value of m, after a sufficient number of determinations of the relation between μ and m have been made, is described by Zawidski.[1]

[1] *Zeit. physik. Chem.*, 35, 138 (1900).

There can be little doubt that, just as with the specific volumes, so with other properties, the closest agreement with the additive rule will be observed in the case of nearly related substances, and it has been found that, in general, the greatest deviations are met with when the molecules of one or both liquids are associated. Among the liquids of this class, those of most frequent occurrence—water, the lower alcohols, and the lower fatty acids—contain a hydroxyl group, and it has already been pointed out that the physical properties of these bodies are abnormal in many other respects.

The Vaporization of Mixed Liquids.

In studying the vaporization of mixtures, it is convenient to include pairs of non-miscible liquids, for which the relations between temperature, pressure, and composition of vapour are very simple.

Non-miscible liquids.

Vapour Pressures.—It was shown by Regnault that when two non-miscible liquids are placed together over the mercury in a barometer tube, the observed vapour pressure is equal to the sum of the vapour pressures of the two liquids when heated separately to the same temperature. It is only necessary that both liquids should be present in fair quantity, and that if the upper layer is deep, sufficient time should be allowed for the evaporation of the heavier liquid, or that its evaporation should be facilitated by bringing some of it to the surface by shaking or stirring. Under these conditions each liquid behaves quite independently of the other (or others, if more than two are present), and the total pressure is independent of the relative quantities of the different liquids and of the relative volumes of liquid and vapour.

Boiling Points.—Dalton's law of partial pressures is applicable to the case of non-miscible liquids, each vapour behaving as an indifferent gas to the others, and the boiling point of each liquid depends on the partial pressure of its own vapour. The temperature is necessarily the same for all the liquids present, and the total pressure, if the distillation is carried out in the ordinary manner, is equal to that of the atmosphere. The boiling point is therefore that temperature at which the sum of the vapour pressures of the components is equal to the atmospheric pressure. For example, at 90·23° the vapour pressure of water is 530·1 mm., and that of chlorobenzene is 210·1, total 740·2; and it was found that when chlorobenzene

and water were distilled together under a pressure of 740·2 mm., the temperature varied only between 90·25° and 90·35° until there was scarcely any chlorobenzene left in the residual liquid, when it rose rapidly to 100°. The boiling point is necessarily lower than that of the more volatile component, and may be far lower than that of the less volatile.

The process of distillation with steam is very frequently employed in the case of substances of high boiling point which are insoluble or only slightly soluble in water (aniline, nitrobenzene, oils, etc.).

Composition of Vapour.—The composition of the vapour from two or more non-miscible liquids, like the vapour pressure and boiling point, is independent of the relative quantities of the components, provided that they are all present in sufficient quantity, and that evaporation can take place freely.

Calling the vapour densities D_A and D_B, and the vapour pressures at $t°$ p_A and p_B, there will be, in a litre of the mixed vapour, 1 litre of A at $t°$ and p_A mm., and 1 litre of B at $t°$ and p_B mm. The masses of vapour will therefore be—

$$\frac{0{\cdot}0899 \times D_A \times 273 \times p_A}{(273 + t) \times 760} \text{ and } \frac{0{\cdot}0899 \times D_B \times 273 \times p_B}{(273 + t) \times 760}$$

respectively, and the relative masses will be $\frac{D_A \times p_A}{D_B \times p_B}$.[1]

The vapour density of chlorobenzene = 56·2, and that of water 9, and at 90·23° the relative masses of vapour will be

$$\frac{m'_A}{m'_B} = \frac{56{\cdot}2 \times 210{\cdot}1}{9 \times 530{\cdot}1} = 2{\cdot}475,$$

and the percentage mass of chlorobenzene will be 71·2.

In the actual experiment to which reference has already been made, the percentage of chlorobenzene in the distillate was found to be 71·4. Both the boiling point and the composition of the vapour, therefore, agree very well with the calculated values.

INFINITELY MISCIBLE AND CLOSELY RELATED LIQUIDS.

In the case of liquids which are miscible in all proportions, the simplest relations are observed when the substances are chemically closely related to each other.

[1] Naumann, *Ber.*, **10**, 1421, 1819, 2015, 2099 (1877); Brown, *Trans. Chem. Soc.*, **35**, 547 (1879).

Vapour Pressures.—The vapour pressure of a mixture of two such liquids, A and B, is given by the formula—

$$100p = Mp_A + (100 - M)p_B$$

where M is the molecular percentage of A, and p, p_A, and p_B are the vapour pressures of the mixture and of A and B respectively at the same temperature, t. In other words, the relation between vapour pressure and molecular composition is represented by a straight line.

Van der Waals[1] considered that this relation should be true when the critical pressures of the two liquids are equal and the molecular attractions agree with the formula of Galitzine and D. Berthelot, $a_{A.B} = \sqrt{a_A . a_B}$.

The relation has been found to hold accurately for chlorobenzene and bromobenzene, the critical pressures of which are almost certainly equal,[2] as will be seen from the table below.

M	t.	p_A.	p_B.	p.		
				Calculated.	Observed.	Δ
	degrees.	mm.	mm.	mm.	mm.	mm.
25·01	136·75	452·85	862·95	760·4	760·0	− 0·4
50·00	142·16	526·25	992·30	759·3	760·0	+ 0·7
73·64	148·16	618·40	1153·00	759·3	760·0	+ 0·7
Mean				759·7	760·0	+ 0·3

But the vapour pressure, p, may be calculated with very small error, even when the critical pressures, p_c, of the closely related liquids are different.[3]

Substances.		Δp_c.	p (mean).		
A.	B.		Calculated.	Observed.	Δ.
		atmos.	mm.	mm.	mm.
Ethyl propionate	Ethyl acetate .	4·83	755·6	760·0	+4·4
„ benzene .	Toluene . .	3·5	763·9	760·0	−3·9
n-Octane . .	n-Hexane . .	4·98	764·6	760·0	−4·6
Ethyl alcohol .	Methyl alcohol .	15·67	759·4	760·0	+0·6
Toluene . .	Benzene . .	8·5	762·7	760·0	−2·7

[1] *Proc. Roy. Acad. Amsterdam*, **3**, 170 (1900).
[2] Young, *Trans. Chem. Soc.*, **81**, 768 (1902).
[3] Young and Fortey, *Trans. Chem. Soc.*, **83**, 45 (1903).

The experiments of Guthrie [1] make it probable that the relation holds for ethyl bromide and iodide, and Zawidski [2] finds that mixtures of ethylene dibromide and propylene dibromide give results in conformity with the formula. It is not known, however, whether the critical pressures are equal in these cases or not.

Boiling Points.—In order to calculate the boiling points of all mixtures of two liquids under a given pressure, p, the vapour pressures of each substance must be known at all temperatures between their respective boiling points under that pressure. The percentage molecular composition of mixtures which would exert the vapour pressure p must then be calculated at a series of temperatures between these limits by means of the formula—

$$M = 100\frac{p_B - p}{p_B - p_A}$$

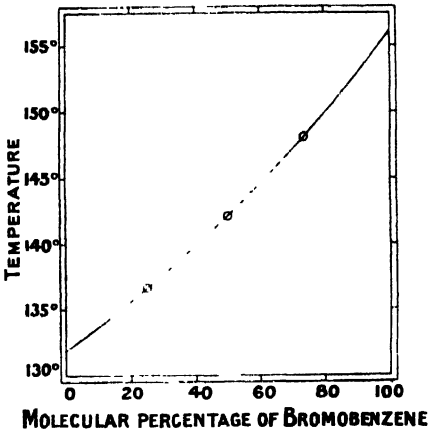


FIG. 62.

Lastly, the values of M must be mapped against the temperatures, and the curve drawn through the points will give the required relation between boiling point and molecular composition under the pressure p.

The calculated boiling points of mixtures of bromobenzene and chlorobenzene under normal pressure (p = 760 mm.) are given by the curve (Fig. 62), and the observed boiling points for M = 25·01, 50·00, and 73·64 respectively are indicated by circles. It will be seen that the agreement is perfectly satisfactory. It was found to be very good also for other pairs of closely related liquids. If the

[1] *Phil. Mag.* (V.), **18**, 495 (1884). [2] *Zeit. physik. Chem.*, **35**, 129 (1900).

boiling points of the two closely related substances were identical, the mixtures would boil at the same temperature, and the relation between temperature and molecular composition would be represented by a horizontal straight line; in all other cases a curve is obtained, and the greater the difference between the two boiling points the more marked is the curvature.

The vapour pressures and boiling points of a mixed liquid may be determined by either the statical or dynamical method, for, as in the case of pure liquids, the same curve represents the vapour pressures at different temperatures and the boiling points under different pressures.

The experimental difficulties and the liability to error are, however, much greater with mixtures than with pure substances. If the statical method is employed, it is necessary not only to expel dissolved air completely from the liquid, but also to determine accurately the composition of the mixture in the barometer tube. Moreover, as the composition of the vapour differs from that of the liquid in contact with it, both composition and vapour pressure necessarily depend, for a given quantity of the substance, on the relative volumes of liquid and vapour. In the dynamical method no difficulty is caused by dissolved air, but if the boiling points of a given mixture of known composition are determined at a series of pressures, it is very important that the volume of vapour should be as small as possible relatively to that of the liquid, and it must be remembered, if the thermometer bulb is immersed in the liquid, that the temperature of a boiling liquid is necessarily higher than the true boiling point—even when ebullition is taking place quite freely—owing to the pressure of the column of liquid itself; and whether the thermometer bulb is in the liquid or vapour, great care must be taken to diminish the amount of condensation on the walls of the bulb or tube as far as possible, because the composition of the liquid formed by condensation of the vapour differs from that of the boiling liquid, and the greater the amount of condensed liquid, the more will the composition both of the boiling liquid and of the vapour be altered. A suitable apparatus is described by Young.[1]

If, on the other hand, a distillation is carried out, either at constant temperature or under constant pressure, the composition of the liquid corresponding to each reading of pressure or temperature must be ascertained. In such experiments not only the relation be-

[1] *Trans. Chem. Soc.*, **81**, 768 (1902)

tween temperature and pressure has usually been investigated, but also that between the composition of liquid and vapour or distillate. Great care must be taken that all liquid formed by condensation of vapour shall be collected as distillate, and shall not return to the still.

Very careful distillations under constant pressure have been carried out by F. D. Brown,[1] and at constant temperature by Lehfeldt,[2] Zawidski,[3] Rosanoff, Lamb and Breithut,[4] and Rosanoff and Easley.[5] The method and results of Rosanoff and his co-workers are undoubtedly the best.

Composition of Liquid and Vapour Phases.—The relation between the composition of liquid and vapour has been investigated by the methods of isobaric and isothermal distillation just mentioned. A special method by which the ebullition of liquid and distillate is carried on simultaneously in the same flask has been devised by Carveth,[6] but his results do not agree well with Rosanoff's. Determinations of the relative compositions of liquid and vapour by passing a known volume of air through a mixture at constant temperature have been carried out by Winkelmann,[7] Linebarger,[8] Gahl,[9] and others, but the method does not seem to have given very satisfactory results.

Lastly, Brown observed, in the course of his experiments with a still-head kept at a constant temperature in a bath of liquid, that the composition of the distillate was independent of that of the mixture in the still, and depended only on the temperature of the still-head; he also found that the boiling points of mixtures which evolved vapour of the same composition as the distillates obtained with the still-head of constant temperature agreed very closely with the temperatures of the still-head. The relation between the composition of liquid and vapour could therefore be ascertained by determining (*a*) the relation between composition of liquid and boiling point, and (*b*) that between composition of distillate and temperature of still-head. This method[10] has been carefully investigated

[1] *Trans. Chem. Soc.*, **35**, 547 (1879), and **39**, 304 (1881).
[2] *Phil. Mag.* (V.), **46**, 42 (1898). [3] *Loc. cit.*
[4] *Zeit. physik. Chem.*, **66**, 349 (1909).
[5] *Journ. Amer. Chem. Soc.*, **31**, 953 (1909).
[6] *Journ. Phys. Chem.*, **3**, 193 (1899). [7] *Wied. Ann.*, **39**, 1 (1890).
[8] *Journ. Amer. Chem. Soc.*, **17**, 615 (1895).
[9] *Zeit. physik. Chem.*, **33**, 179 (1900).
[10] For a detailed account of these methods, and of the results obtained by them, see Young's "Fractional Distillation," chaps. v. and vi. (Macmillan & Co.).

by Rosanoff and Bacon,[1] who found that an annular form of constant temperature still-head gave better results than the usual spiral form. They obtained excellent results with mixtures of carbon disulphide and carbon tetrachloride, and found that the method was also applicable to two substances which form mixtures of constant boiling point, but in such a case the separation on distillation is into the mixture of constant boiling point and one or other of the two components depending on the composition of the original mixture (p. 259).

As a result of his experimental investigations, Brown arrived at the conclusion that the formula which had previously been proposed by Wanklyn and by Berthelot—

$$\frac{m'_A}{m'_B} = \frac{m_A D_A p_A}{m_B D_B p_B}$$

(where m' is the weight of vapour, and m that of liquid)—was not correct; he found that for the mixtures he had investigated a better result was obtained with the formula—

$$\frac{m'_A}{m'_B} = \frac{m_A p_A}{m_B p_B}$$

but that the agreement between the calculated and observed results was still closer when a constant c was substituted for the ratio of the vapour pressures $\frac{p_A}{p_B}$.

Even the simple formula—

$$\frac{m'_A}{m'_B} = c \times \frac{m_A}{m_B}$$

$\left(\text{or } \frac{M'_A}{M'_B} = c \times \frac{M_A}{M_B}\text{, for the relative quantities may, of course, be expressed either as grams or gram-molecules}\right)$

is not generally applicable to infinitely miscible liquids, but the experimental evidence seems to warrant the conclusion that it is true for those liquids for which the relation $100p = Mp_A + (100 - M)p_B$ holds good. It is probable, also, that for such liquids the constant c is equal, or nearly equal, to $\frac{p_A}{p_B}$.

The strongest evidence is afforded by two pairs of liquids, ethylene and propylene dibromides, and benzene and ethylene dichloride,

[1] *Journ. Amer. Chem. Soc.*, 37, 301 and 1072 (1915).

investigated by Zawidski,[1] for both of which the relation between vapour pressure and molecular composition is accurately represented by a straight line. For the two dibromides $t = 85{\cdot}05°$; $\frac{p_A}{p_B}$ at $85° = 1{\cdot}357$, and $c = 1{\cdot}31$; for benzene and ethylene dichloride $t = 49{\cdot}99°$; $\frac{p_A}{p_B}$ at $50° = 1{\cdot}135$, and $c = 1{\cdot}134$. Zawidski states that the errors of experiment were much greater in the first case than the second.

It has been stated that the formula $100p = Mp_A + (100 - M)p_B$ is generally applicable to closely related liquids (and occasionally to others), and it may perhaps be concluded that Brown's formula is generally true for such liquids, and probably also that $c = \frac{p_A}{p_B}$.

The number of closely related liquids so far examined is, however, very small, and further investigation is required before a definite statement can be made.

INFINITELY MISCIBLE LIQUIDS WHICH ARE NOT CLOSELY RELATED.

Vapour Pressures.—The relation between vapour pressure and molecular composition of mixed liquids which have no very close chemical relationship to each other is usually represented by a curve, and it may be stated generally that when the attraction of the unlike molecules is small, relatively to that of the like molecules, the vapour pressures will be higher than those calculated from the formula $p = Mp_A + (1 - M)p_B$ (where M is the molecular fractional amount of A), while if the mutual attraction of the unlike molecules is relatively great, the vapour pressures will be lower. Or, adopting the formula of Galitzine and D. Berthelot, it may probably be stated that when $a_{A.B} < \sqrt{a_A . a_B}$, then $p > M p_A + (1 - M) p_B$, and *vice versâ*. The relations are shown diagrammatically in Fig. 63.

The greater the difference between $a_{A.B}$ and $\sqrt{a_A . a_B}$, the greater will be the curvature, and it will be seen that, for any given values of p_A and p_B, if the deviation from the straight line exceeds a certain amount, there must be a point of maximum or minimum pressure on the curve. It is obvious, also, that the smaller the difference between p_A and p_B, the smaller will be the deviation required to give a maximum or minimum pressure.

[1] *Loc. cit.*

The influence of chemical relationship is well seen by the behaviour of the monohydric, aliphatic alcohols towards water. These alcohols may be regarded as derivatives of water, formed by the replacement of a hydrogen atom by the group C_nH_{2n+1}, thus HO—H → HO—C_nH_{2n+1}; or as derivatives of the paraffins, formed by replacement of a hydrogen atom by a hydroxyl group, thus $C_nH_{2n+1}H \rightarrow C_nH_{2n+1}OH$.

The smaller the alkyl group, the closer is the relationship to water; the larger the alkyl group, the smaller is the influence of the hydroxyl radical, and the closer is the relationship to the corresponding paraffin.

At the ordinary temperature methyl alcohol is miscible with water in all proportions, as also are ethyl and propyl alcohols.

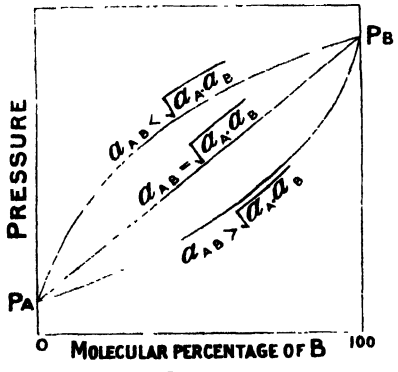


FIG. 63.

Normal butyl alcohol dissolves in about 12 parts of water, and isobutyl alcohol in about 10·5 parts, and the solubility of the higher alcohols in water diminishes as the molecular weight rises, cetyl alcohol, for example, being practically insoluble in water. The volume and temperature changes (p. 239) similarly indicate that the mutual attraction of the unlike molecules diminishes as the molecular weight of the alcohols increases. Lastly, the deviation of the vapour-pressure curves from straightness increases,[1] as may be seen from Fig. 64, in which the vapour pressure-molecular composition curves for four alcohols are given. The temperatures are such that the vapour pressure of each pure alcohol is 400 mm. The maximum differences between the pressures represented by the actual curves and the theoretical straight lines are roughly as follows:—

[1] Konowalow, *Wied. Ann.*, **14**, 34 (1881).

Methyl alcohol and water	.	.	.	43 mm.
Ethyl „ „ „	.	.	.	112 „
n-Propyl „ „ „	.	.	.	203 „
Isobutyl „ „ „	.	.	.	315 „

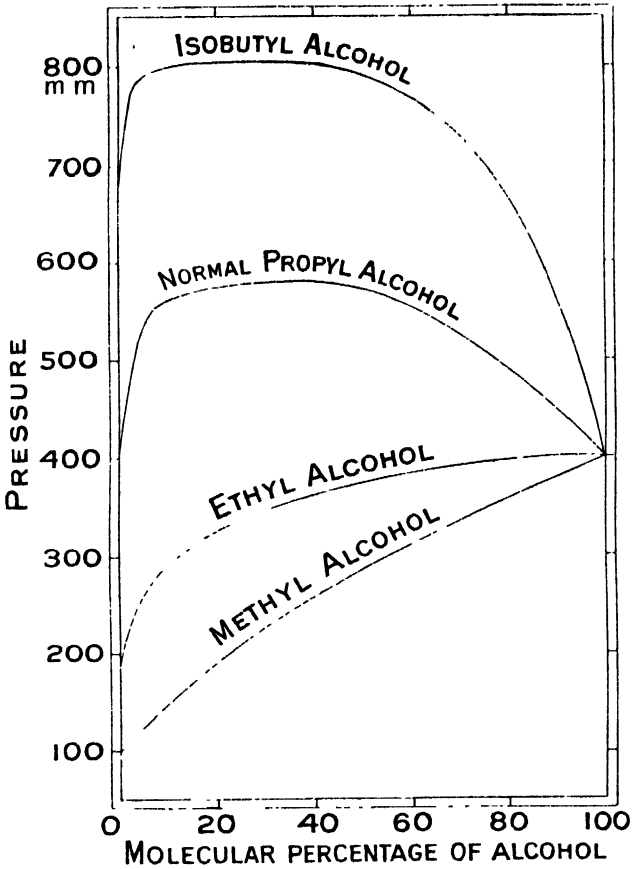


FIG. 64.

The miscibility of the alcohols with the paraffins from which they are derived has not yet been studied, because the lower paraffins are gaseous, but the behaviour of a single paraffin, normal hexane, towards the alcohols has been investigated. Methyl alcohol and n-hexane at the ordinary temperature are only miscible within limits, but the higher alcohols—at any rate, up to isoamyl alcohol—are miscible with the hydrocarbon in all proportions. Again, the fall in

temperature on mixing hexane with the alcohols in equimolecular proportions diminishes slightly as the molecular weights of the alcohols rise (ethyl alcohol, – 2·55°; n-propyl alcohol, – 2·40°; isobutyl alcohol, – 2·35°; isoamyl alcohol, – 1·85°). Lastly, n-hexane forms mixtures of maximum vapour pressure with the lower alcohols, but not with isoamyl alcohol or any other of higher boiling point. The behaviour of benzene towards the alcohols is very similar to that of n-hexane, and has been more completely studied. The temperature and volume changes are given in the table, p. 239; the percentage differences between the observed and calculated pressures (p' and p respectively) for equimolecular mixtures both with water and with benzene are given below.

Alcohol.	Mixtures with					
	Water.			Benzene.		
	p'.	p.	$\frac{100(p'-p)}{p}$.	p'.	p.	$\frac{100(p'-p)}{p}$.
Methyl . .	282	247·0	+ 14·2	760	475·0	+ 60·0
Ethyl . .	372	285·7	+ 30·2	760	507·3	+ 49·8
n-Propyl .	576	287·0	+ 48·8	760	535·4	+ 41·9
Isobutyl .	792	476·5	+ 66·2	760	562·2	+ 35·2
Isoamyl .	—	—	..	760	579·6	+ 31·1

Mixtures of minimum vapour pressure are of comparatively rare occurrence. The few which have been studied are mentioned on p. 254.

Worley[1] has made a careful study of the surface tensions of mixtures of miscible and partially miscible liquids, and has shown that there is a remarkably close analogy between the vapour pressures and surface tensions of such mixtures.

Boiling Points.—It has been stated (p. 245) that the boiling points of mixtures of closely related liquids under a pressure p can be calculated with considerable accuracy from the vapour pressures of the components by means of the formula $M = 100\frac{p_B - p}{p_B - p_A}$.

In the case of liquids which are not closely related the observed boiling points of mixtures do not, as a rule, agree with those calcu-

[1] *Trans. Chem. Soc.*, 105, 260 and 273 (1914).

lated in this way. If, as is usually the case, the vapour pressures of the mixtures are higher than are given by the formula—

$$100p = Mp_A + (100 - M)p_B$$

the observed boiling points will be lower than the calculated; if the vapour pressures are lower, the boiling points will be higher.

Moreover, when there is a point of maximum pressure on the curve which shows the relation between vapour pressure and molecular composition, there must be a corresponding point of minimum temperature on the boiling point-molecular composition curve, the composition of the mixture which exerts a maximum vapour pressure p at $t°$ being the same as that of the mixture which has a minimum boiling point $t°$ under the pressure p.

So, also, two substances capable of forming mixtures of minimum vapour pressure will also form mixtures of maximum boiling point.

Such mixtures of either minimum or maximum boiling point, when distilled, boil at a constant temperature like pure substances, and they have frequently been mistaken for chemical compounds. But mixtures of minimum boiling point are formed owing to the relatively small attraction of the unlike molecules for each other; moreover, the composition depends on the pressure, which would not be the case with a definite compound.

A most instructive example is that of ethyl alcohol and water. Under normal atmospheric pressure there is formed a mixture of minimum boiling point (78·15°) the percentage of water in which was found by Young and Fortey[1] to be 4·43, and the following results were obtained by Wade and Merriman[2] at a series of pressures higher and lower than the atmospheric pressure.

Pressure in mm.	Boiling Points.		Percentage of Water in Binary Mixture.
	Alcohol	Binary Mixture.	
	Degrees.	Degrees.	
1450	95·5	95·35	4·73
1075	87·26	87·03	4·67
760	78·39	78·13	4·41
400	—	62·85	3·77
200	47·97	47·95	2·70
130	39·35	39·34	1·25
100	34·2	34·2	0·54
75	29·35	—	[3]

[1] *Trans. Chem. Soc.*, 81, 717 (1902). [2] *Ibid.*, 99, 997 (1911).

[3] No mixture of minimum boiling point was formed at this or any lower pressure.

A table of mixtures of constant (minimum and maximum) boiling point is given in Young's "Fractional Distillation," pp. 67-69.

In the great majority of cases one of the two liquids is a hydroxyl compound—an alcohol, an acid, or water, or both liquids may be hydroxyl compounds; and it may probably be concluded that mixtures of constant boiling point are most readily formed when one or both of the liquids exhibit molecular association.

There is some evidence of molecular association in the case of acetone and probably of the lower aliphatic esters, and the following pairs of liquids are stated by Ryland[1] to form mixtures of minimum boiling point: carbon disulphide and acetone, carbon disulphide and methyl acetate, carbon disulphide and ethyl acetate, acetone and methyl acetate, acetone and ethyl iodide, ethyl iodide and ethyl acetate.

Mixtures of minimum boiling point are not confined to associating liquids, but they only occur among normal liquids when the difference Δ_t between the boiling points of the components is small. Thus it is almost certain that benzene and normal hexane ($\Delta_t = 11{\cdot}3°$) and that benzene and carbon tetrachloride ($\Delta_t = 3{\cdot}44°$) form such mixtures, and Ryland states that a mixture of carbon disulphide and ethyl bromide (Δ_t = about 7·6°) boils 0·5° lower than ethyl bromide. Again, Zawidski finds that methylal and carbon disulphide ($\Delta_t = 4{\cdot}15°$) form a mixture of maximum vapour pressure.

Mixtures of maximum boiling point are not so frequently met with. In most of the known cases one of the substances is an acid and the other a base or a compound of basic character—formic, acetic, or propionic acid with pyridine (Zawidski), hydrochloric acid with methyl ether (Friedel); or the liquids are water and an acid—formic, hydrochloric, hydrobromic, hydriodic, hydrofluoric, nitric, or perchloric acid (Roscoe); but Rylands finds that such mixtures are also formed by chloroform and acetone ($\Delta_t = 4{\cdot}8°$), and chloroform and methyl acetate (Δ_t = about 4·3°), and these results have been confirmed by other observers.

In the case of three liquids, if each of the three possible pairs is able to form a mixture of minimum boiling point, it may happen that a particular mixture of all three liquids will boil constantly at a lower temperature than any of the pairs or single liquids. Thus benzene and water form such ternary mixtures of minimum boiling point with ethyl, n-propyl, isopropyl, and tertiary butyl alcohols,

[1] *Amer. Chem. Journ.*, **22**, 384 (1899).

and normal hexane and water do so with ethyl and n-propyl alcohols, and no doubt with the other two also.

Composition of Liquid and Vapour Phases.—The whole question of the relations between the composition of liquid mixtures and (*a*) the partial pressures of the vapours of the components, (*b*) the composition of the vapour, has been discussed mathematically by Duhem and by Margules, and they have arrived independently at the same formula—

$$\frac{d \log p_A}{d \log M} = \frac{d \log p_B}{d \log (1 - M)}$$

where p_A and p_B are the partial pressures of the vapours of the two liquids A and B, and M and $(1 - M)$ their molecular fractional amounts in the liquid mixture, taking the normal molecular weights as correct.

Starting from this equation, Lehfeldt adopts the formula—

$$\frac{m'_A}{m'_B} = k \times \left(\frac{m_A}{m_B}\right)^r$$

$$\text{or } \log \left(\frac{m'_A}{m'_B}\right) = \log k + r \log \left(\frac{m_A}{m_B}\right)$$

where m'_A and m'_B are the weights of A and B in the vapour, and m_A and m_B the weights in the liquid, and k and r are constants.

In this formula, when $r = 1$, $\frac{m'_A}{m'_B} = k \times \frac{m_A}{m_B}$, or Brown's formula holds good. On the other hand, if k is positive and r is less than unity, there must be a particular value of $\frac{m_A}{m_B}$ for which $\log \left(\frac{m'_A}{m'_B}\right) = \log \left(\frac{m_A}{m_B}\right)$, and there must therefore be a possible mixture of constant boiling point. Thus for benzene and carbon tetrachloride Lehfeldt gives $\log \left(\frac{m'_A}{m'_B}\right) = 0{\cdot}065 + 0{\cdot}947 \log \left(\frac{m_A}{m_B}\right)$. In this case the logarithms of the ratios are equal when $\log \frac{m_A}{m_B} = 1{\cdot}2264$ or $\frac{m_A}{m_B} = 16{\cdot}84$. There should thus be a mixture of constant boiling point containing 5·6 per cent. by weight or 10·5 molecules per cent. of benzene. Rosanoff, Bacon, and Schulze[1] find that the molecular percentage of benzene is 8·35.

[1] *Journ. Amer. Chem. Soc.*, **36**, 1993 (1914).

Zawidski adopts the following equations to express the relations between the partial pressures p'_A and p'_B of the components in the vapour from the mixture, the vapour pressures p_A and p_B of the pure components, and the molecular fractional amounts M and 1 − M of the two substances in the liquid mixture:—

$$p'_A = p_A M \times e^{\frac{\alpha_2}{2}(1-M)^2 + \frac{\alpha_3}{3}(1-M)^3}$$

$$p'_B = p(1-M)e^{\frac{\beta_2}{2}M^2 + \frac{\beta_3}{3}M^3}$$

and

$$\beta_2 = \alpha_2 + \alpha_3$$
$$\beta_3 = -\alpha_3$$

where α_2 and α_3 are constants, the values of which can be ascertained from the partial-pressure curves, or, by a method suggested by Margules, from the total-pressure curve.[1]

Zawidski points out that if α and β vanish, the equations become—

$$p'_A = p_A M \text{ and } p'_B = p_B(1-M)$$

whence

$$\frac{p'_A}{p'_B} = \frac{p_A}{p_B} \times \frac{M}{1-M} = k \times \frac{M}{1-M},$$

but for substances of normal molecular weight the pressures are proportional to the number of molecules present, and the equation may be written $\frac{M'_A}{M'_B} = k \times \frac{M_A}{M_B}$, which is Brown's formula, expressed in gram-molecules.

For ethylene and propylene dibromides, and for benzene and ethylene dichloride, Zawidski shows the correctness, not only of the relation—

$$p = p'_A + p'_B = p_A M + p_B(1-M)$$

but also of the formulæ—

$$p'_A = p_A M \text{ and } p'_B = p_B(1-M)$$

as may be seen from the diagram (Fig. 65), which is taken from his paper.

In the case of other mixtures of liquids with normal molecular weight investigated by Zawidski, the constants α and β were found

[1] See also Rosanoff and Easley, *Journ. Amer. Chem. Soc.*, 31, 953 (1909); Dolezalek, *Zeit. physik. Chem.*, 64, 727 (1908); 71, 191 (1909); 83, 40 (1913); Campbell, *Trans. Faraday Soc.*, 11, 91 (1915); Tinker, *Phil. Mag.*, 32, 295 (1916); Worley, *Trans. Chem. Soc.*, 105, 273 (1914); Kremann, *Monatsh.*, 37, 369 (1916); Hildebrand, *Journ. Amer. Chem. Soc.*, 38, 1452 (1916).

to have finite values, and the simple formulæ $p'_A = p_A M$ and $p'_B = p_B(1 - M)$ were not found to be applicable; the relations between molecular composition and pressure, whether total or partial, are, in fact, represented by curves which could be well represented by the formulæ given on p. 256. In the case of associating substances, Zawidski's formulæ could only be applied if the average molecular weights of the associating substances under the varying conditions of the experiment were known.

Investigations of the relation between the composition of liquid and vapour have, as a rule, been carried out at constant temperature, but in practice a liquid is almost always distilled under constant

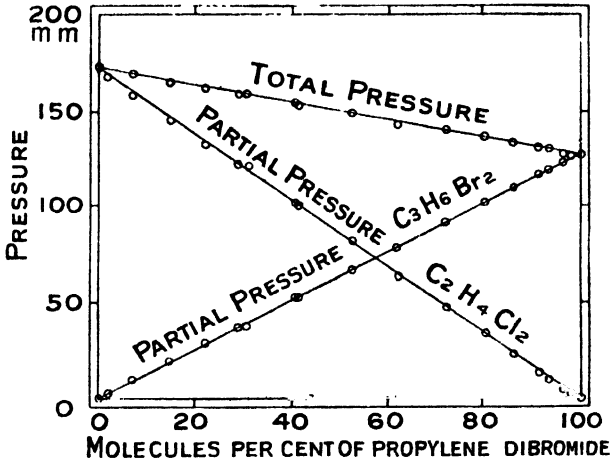


FIG. 65.

pressure. The ratio $\frac{p_A}{p_B}$ varies slightly with the temperature even for closely related substances, so that if Brown's formula were strictly true for a distillation at constant temperature, it could not be applicable without slight error to an ordinary distillation under constant pressure, or rather the value of $\frac{p_A}{p_B}$ ought, theoretically, to be calculated for any given temperature during the distillation.

Distillation of Mixtures.—It has been stated that for closely related liquids, Brown's formula, $\frac{M'_A}{M'_B} = c \times \frac{M_A}{M_B}$, in all probability holds good with a close approximation to accuracy, and that the con-

stant c is probably equal to the ratio of the vapour pressures $\frac{p_A}{p_B}$ at the boiling point of the mixture. The value of the constant is always such that the vapour is richer than the liquid in the more volatile component. The distillate obtained by condensation of the vapour will therefore be richer, and the residual liquid will be slightly poorer, than the original liquid mixture in that component. Continuing the distillation, the vapour evolved from the residual liquid will again be richer than the liquid in contact with it in the more volatile component, but it will contain a relatively smaller amount of it than the first portion of vapour. If successive portions of vapour be condensed, the percentage of the more volatile component in the distillates or *fractions* will steadily diminish until, if the constant c differs greatly from unity, in other words, if there is a great difference between the vapour pressures of the pure components, the residual liquid will consist of the liquid of lower vapour pressure and higher boiling point in a pure or almost perfectly pure state.

If the distillation is carried out under constant pressure, the boiling point will rise continuously until only the one component is left; if it is carried out at constant temperature, the vapour pressure will fall until it reaches that of the less volatile component.

If the components are not closely related, or, more generally, if the formula—

$$p = Mp_A + (1 - M)p_B$$

is not applicable, the composition of the vapour cannot be calculated from that of the liquid by Brown's formula, but the percentage of the more volatile component in the vapour will be greater than in the liquid, and the separation by distillation will take place in a similar manner unless the deviation from the formula

$$p = Mp_A + (1 - M)p_B$$

is so great that a mixture of minimum or maximum vapour pressure is formed.

If the fractions obtained by the first distillation were redistilled, each fraction could be separated into smaller fractions, the first richer and the last poorer in the more volatile component, and by a process of systematic fractional distillation it should, theoretically, be possible to effect a separation of the two components.

The mathematical investigation[1] of the behaviour on distillation

[1] Barrell, Thomas, and Young, *Phil. Mag.* (V.), **37**, 8 (1894).

of mixed liquids which follow Brown's law, show that with two components it is the liquid of higher boiling point which is the easier to separate, and that if there are three or more components boiling at fairly equal intervals of temperature, the substances of intermediate boiling point are the most difficult to separate, and the least volatile substance is the easiest.

For such substances, also, it may be stated quite generally that the greater the difference between the boiling points of the components, the more readily can a separation be effected by distillation. These rules do not necessarily apply to liquids which do not follow Brown's law, but the form of the curve representing the relation between boiling point and composition must be taken into account.

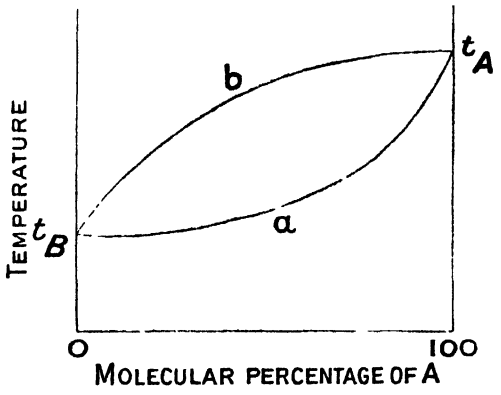


FIG. 66.

If the curve for two components were of the form *a* (Fig. 66), the substance of higher boiling point could be separated very easily, but the more volatile component only with great difficulty, if at all. On the other hand, if the curve were of the form *b*, nearly horizontal at the higher temperature, the more volatile component would be comparatively easy and the less volatile difficult to separate. The first case is frequently met with, the second seldom.

With curves of the forms *c* and *d* (Fig. 67), it would not, under any conditions, be possible to separate both components by distillation of any given mixture, but it would be possible to separate the mixture of maximum or minimum boiling point from that component which was in excess.

In a case represented by curve *c*, where the minimum temperature corresponds to the molecular composition *q*, the distillation might

proceed in either of three ways: (1) If the liquid mixture had the composition q, it would distil unchanged in composition and at a constant temperature like a pure liquid. (2) If the molecular percentage of A were less than q, the liquid would tend to separate into two components, the more volatile of which would be the mixture of minimum boiling point, and the less volatile the substance B. (3) If the molecular percentage of A were greater than q, the components separated by distillation would be, first, the mixture of minimum boiling point, and, second, the liquid A.

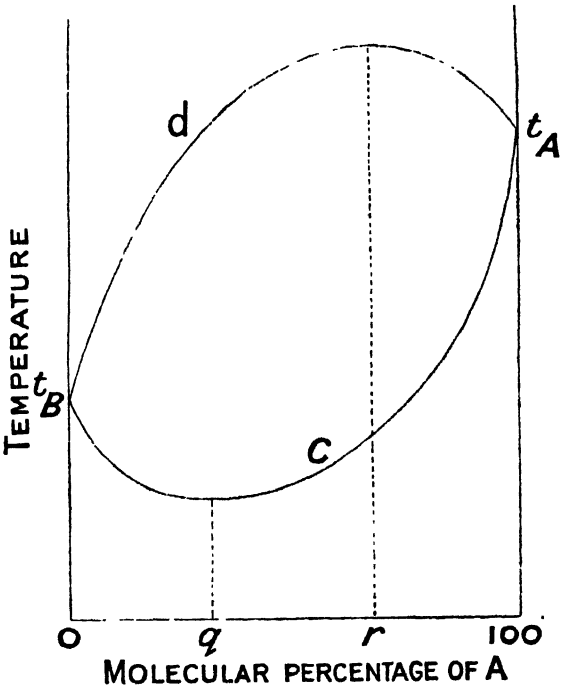


FIG. 67.

A well-known case of this kind is that of normal propyl alcohol and water. The boiling points under normal pressure are: water, 100°; n-propyl alcohol, 97·2°; mixture of minimum B.P. 87·7°. This mixture contains 71·7 per cent. by weight, or 43·2 molecules per cent. of propyl alcohol. It was described for many years as a hydrate of propyl alcohol.

If the boiling point composition curve has the form d (Fig. 67), the mixture will distil like a pure liquid at constant temperature if

it has the composition r, or it will tend to separate into two components, the first being either A if the molecular percentage of A in the original mixture is greater than r, or B if it is less, and the second the mixture of maximum boiling point. Formic acid and water

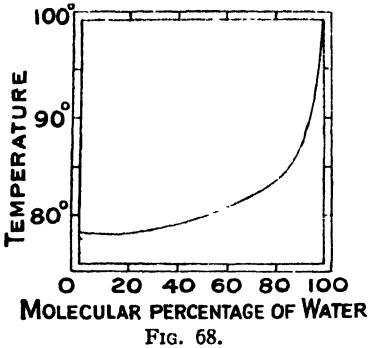


FIG. 68.

behave in this manner, as shown by Roscoe.[1] *Boiling points:* water, 100°; formic acid, 99·9°; mixture of maximum boiling point, 107·1°. *Composition of mixture* · percentage of acid by weight, 77; molecular percentage, 56·7.

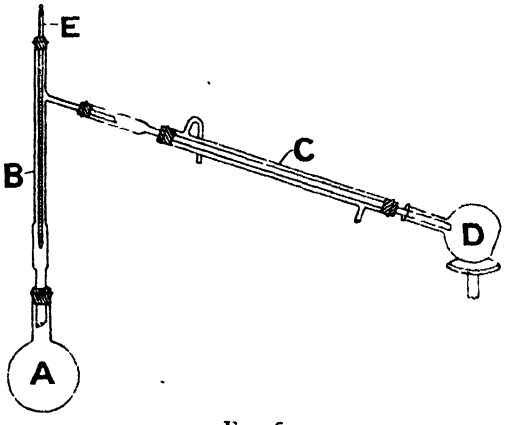


FIG. 69.

If, as in the case of ethyl alcohol and water (Fig. 68), the mixture of constant boiling point distils at very nearly the same temperature as one of the two pure liquids, it is impossible to separate that component in a pure state by distillation. In this case the curve is also

[1] *Trans. Chem. Soc.*, **13**, 146 (1861); **15**, 270 (1862).

exceedingly flat at the lower temperatures, and it is practically impossible to separate the mixture of minimum boiling point in a pure state even when water is in excess, although it is quite easy to separate pure water from such a mixture.

The apparatus required for carrying out the distillation of a liquid consists essentially of five parts (Fig. 69): A, the still; B, the still-head; C, the Liebig's condenser; D, the receiver; E, the thermometer. Each of these parts may be modified to meet special requirements, such as distillation under reduced pressure, distillation of large quantities of liquid, of very volatile liquids, and so on; but the most important modifications are those of the still-head, by which a more complete separation of the components can be obtained in a single distillation than with the plain vertical still-head.

For the chief modifications of the still-head and other parts, and for an account of the methods of systematic fractional distillation, and of the interpretation of the experimental results, Young's "Fractional Distillation" may be consulted.

Critical Constants of Mixed Liquids.

The behaviour of mixed liquids at or near the critical point has been investigated mathematically by Van der Waals,[1] and Duhem,[2] while the most valuable experimental work has been carried out by Kuenen[3] in Leiden and Dundee, Hartmann and Verschaffelt in Leiden[4] and Caubet[5] in Bordeaux.

Kuenen[3] pointed out that inasmuch as during the evaporation or condensation of the components of a mixture, change of composition is constantly taking place, and as the process of diffusion is exceedingly slow, it is practically impossible for either the liquid or

[1] "Die Continuität des gasförmigen und flussigen Zustandes" (1881); *Zeit. physik. Chem.*, **5**, 133 (1890); "Statique des fluides (Mélanges), Congrès internat. de physique" (Paris, 1900), vol. i., p. 583.

[2] *Trav. et Mem. des Facultés de Lille*, **11**, 90 (1892); *ibid.* [3], **13** (1893), and other papers (*vide* Caubet).

[3] *Archives Néerlandaises*, 26, 354; *Communications from the Physical Lab. Leiden*, Nos. 4, 7, 8, 11, 13, 16, 17; *Zeit. physik. Chem.*, **11**, 38 (1893); **24**, 667 (1897); **41**, 43 (1902); *Phil. Mag.* (V.), **40**, 173 (1895); **44**, 174 (1897); (VI.) **4**, 116 (1902); *Arch. Néerland., sci. exact. nat.* (2), **5**, 306 (1900).

[4] *Communications from Physical Lab. Leiden* (Professor H. Kamerlingh Onnes, director).

[5] "Liquéfaction des Mélanges gazeux" (Paris, 1901); *Zeit. physik. Chem.*, **40**, 257 (1902).

gaseous phase to be homogeneous unless complete admixture is brought about by vigorous stirring. He therefore placed in his experimental tube a little stirrer consisting of a fine rod of soft iron, about 2 cm. in length, provided at each end with a bead of enamel. This stirrer could be moved rapidly up and down by means of an electro-magnet outside the apparatus. Earlier experiments carried out without such a stirring arrangement are of little value, and need not be described.

When a mixed vapour is compressed at a constant temperature below its critical point it behaves like a pure substance, the pressure rising as the volume diminishes, until condensation begins. The process of condensation differs, however, from that of a pure vapour —unless, indeed, a mixture of maximum or minimum vapour pressure is formed—for a mixed liquid differs in composition from the vapour in contact with it (p. 247), being richer in the less volatile component. As condensation proceeds the successive quantities of liquid formed will be poorer and poorer in this component, and the vapour pressure will rise until condensation is complete, when the composition of the liquid as a whole will, of course, be the same as that of the original vapour. If both liquid and vapour are constantly stirred during the process, so that each phase is always homogeneous, the true relation between pressure and volume will be observed, but if the electro-magnetic or other stirrer is not used, and especially if the experiment is carried out in a long narrow tube, admixture of the successive portions of liquid formed by condensation will take place with extreme slowness, and the observed vapour pressures will always be too high.

In any case there will be a rise of vapour pressure during condensation, and the diagram representing the relation between pressure and volume for a given mixture at a series of temperatures will be of the form shown in Fig. 70.

The relation between vapour pressure and temperature will not be represented by a simple curve, as in the case of a pure substance, but by a surface enclosed by a *border* curve (Kuenen). The general form of the vapour-pressure surface is indicated by the curves VRPL in Figs. 71, 72, and 74.

It may safely be assumed that the relations between pressure, temperature, and composition are simplest in the case of mixtures of substances which are chemically closely related; but, unfortunately, the only determinations which have so far been made with such

substances[1] are not sufficiently complete, as regards range of composition, to allow of definite conclusions being drawn regarding the relation between composition and critical pressure or critical temperature.

Several pairs of infinitely miscible liquids which do not form mixtures of maximum or minimum pressure have, however, been carefully examined by Kuenen and by Caubet, and the results obtained by the latter observer with mixtures of carbon dioxide and sulphur dioxide are shown in Fig. 71. The vapour-pressure curves

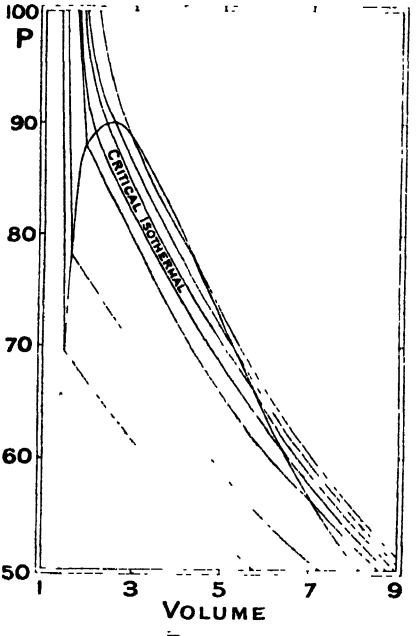


FIG. 70.

of the two pure substances terminate in their critical points, C_1 and C_2 respectively. The vapour-pressure areas enclosed by the border curves (VRPL) for the mixtures investigated lie between these curves and a third curve, called by Kuenen the *plait point* curve, drawn between C_1 and C_2 is tangential to the border curves. The point of contact P between a border curve and the plait point curve is termed by Kuenen the plait point temperature, and by Caubet the critical temperature. The point R at which the border curve has a tangent parallel to the p-axis is termed by Kuenen the critical

[1] Kuenen, "Ethane and Butane," *Proc. Roy. Soc. Edin.*, vol. 21.

point of contact; it gives the maximum temperature on the border curve.

At all temperatures below the plait point t_P, vaporization or condensation at constant temperature takes place in the ordinary manner; starting with saturated vapour and compressing the mixture, condensation takes place, and the volume of liquid continuously increases and the pressure rises until all the vapour has disappeared. At temperatures higher than the maximum t_R the substance behaves like a pure substance above its critical point, no liquid being formed under any pressure. At intermediate temperatures a remarkable phenomenon is observed, condensation beginning at the lower pressure at which the vertical line of constant temperature intersects

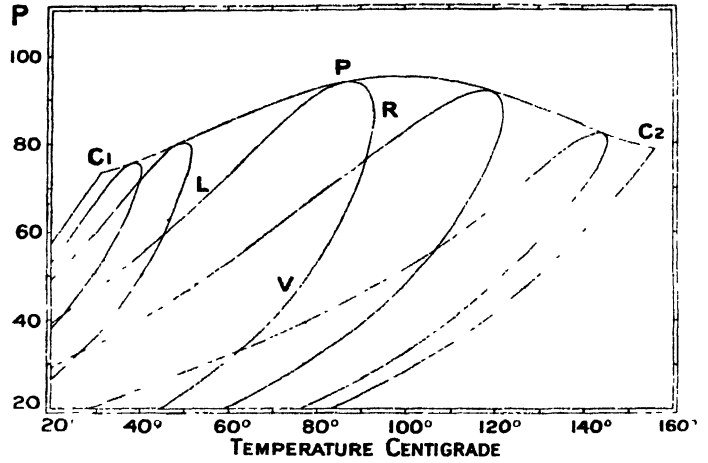


FIG. 71.

the border curve, the liquid increasing in amount with rise of pressure to a maximum, then diminishing and finally disappearing at the pressure corresponding to the point where the vertical line intersects the upper branch of the border curve.

This phenomenon was observed by Cailletet in 1880,[1] in the case of a mixture of carbon dioxide and air, and subsequently by Van der Waals, and by Andrews. It was carefully and thoroughly investigated by Kuenen, by whom it was termed *retrograde condensation.*

Several observers[2] described the appearance of three phases,

[1] *Compt. rend.*, **90**, 210.

[2] Pictet, *Compt. rend.*, **100**, 329 (1885); Wroblewski, *Wied. Ann.*, **26**, 134 (1885); Dewar, *Proc. Roy. Soc.*, **30**, 538 (1880).

two liquid and one vapour. Ramsay and Young [1] found that, with a mixture of alcohol and ether, two liquid phases could be temporarily produced at 210° by allowing some of the vapour in the upper part of the tube to cool so as to promote separation by distillation. When, however, the vapour was condensed by diminishing the volume, and the upper part of the tube was again cooled, convection currents were formed, and the apparent meniscus between the two liquid layers was seen to descend the tube until it became lost at the surface of the mercury.

By the use of his electro-magnetic stirrer, Kuenen (*loc. cit.*) was able to prove still more conclusively that the appearance of the two

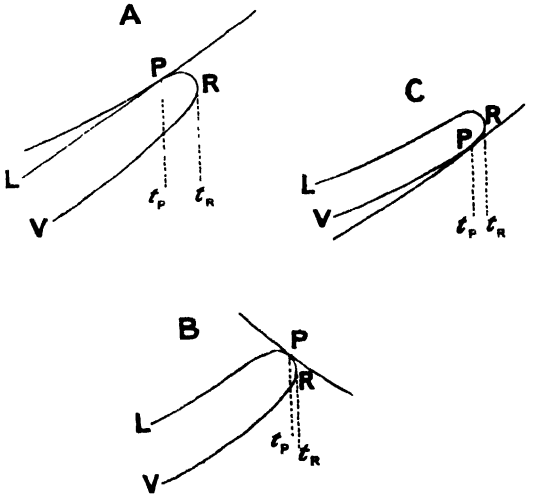


FIG. 72.

liquid phases was merely due to the temporary partial separation of the two components by a process of distillation, and that only one liquid phase remained after stirring.

Kuenen [2] has pointed out that a second kind of retrograde condensation during compression is possible, a vapour phase appearing, reaching a maximum, diminishing, and finally disappearing. The question which kind of retrograde condensation will occur is decided by considering whether, on passing along the border curve, starting from its lower branch, the point R or P is first reached. In Fig. 72, A, B, and C, three possible relative positions of plait point curve and border curve are shown. In A and B the point R is encountered

[1] *Trans. Chem. Soc.*, 51, 760 (1887). [2] *Communications*, No. 16.

before P, and the conditions are those under which retrograde condensation of the first kind is met with. In C, on the other hand, the border curve is above and to the left of the plait point curve, and the point P is reached before R. Under these conditions, retrograde condensation of the second kind should be observed. The conditions would be fulfilled if the plait point temperatures were between the critical temperatures of the pure substances for all mixtures and the component of higher critical temperature had the higher critical pressure, a case which does not frequently occur. They may also be fulfilled when the plait point curve is less simple.

Kuenen has investigated a considerable number of mixtures in the hope of observing retrograde condensation of the second kind; but although he has succeeded in finding mixtures which fulfil the conditions (Figs. 73 and 74, plait point curve between B and A), yet the difference in temperature between t_P and t_R in the case of ethane and nitrous oxide (Fig. 73)[1] was never greater than 0·1°, and the difficulties due to minute variations in temperature and to the action of gravity on the highly compressible fluid (Gouy) made it impossible to observe the phenomenon, or, indeed, to distinguish between the two temperatures. In the case of methyl ether and hydrochloric acid (Fig. 74), there was some chemical action at the higher temperatures, and trustworthy observations could not be made.

Kuenen, however, has succeeded in bringing to light several interesting facts. It has been stated that many pairs of infinitely miscible liquids form mixtures of minimum boiling point, and that a smaller number form mixtures of maximum boiling point. Kuenen has shown that certain pairs of substances also form mixtures of minimum, and others mixtures of maximum, critical point. To the first class belong ethane and nitrous oxide (Fig. 73), ethane and acetylene, and ethane and carbon dioxide; to the latter, methyl ether and hydrogen chloride (Fig. 74).

The results further showed that two substances which at a low temperature form a mixture of maximum or minimum vapour pressure form a similar mixture at higher temperatures up to the critical point. If the composition of the mixture of maximum or minimum pressure were the same at all temperatures there would be three vapour pressure curves on the P.T. diagram, the curves for the two pure substances, and a third for the mixture of maximum or minimum

[1] *Phil. Mag.*, Aug. (1897), 174.

vapour pressure. The composition, however, does vary with the temperature, although very slightly in the case of nitrous oxide and ethane.

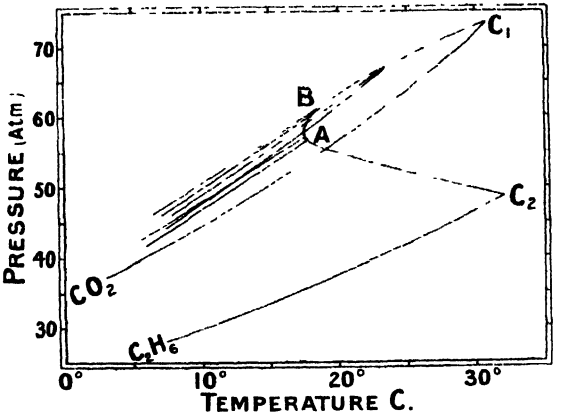


FIG. 73.

In the neighbourhood of the curve of maximum pressure, and also of the vapour pressure curves for the pure substances, the border curves are very narrow, that is to say, the rise of pressure during condensation is very slight. Under these conditions there is great difficulty in observing retrograde condensation of either kind.

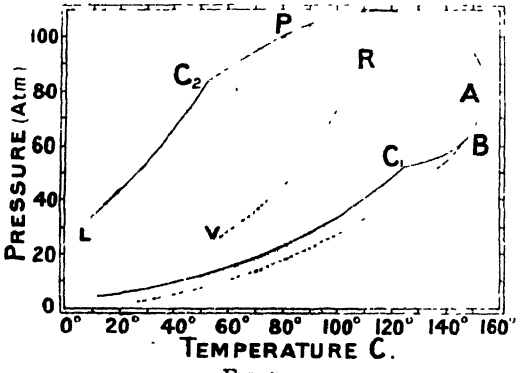


FIG. 74.

RELATION BETWEEN COMPOSITION AND CRITICAL TEMPERATURE OR CRITICAL PRESSURE.

By the *critical point* of a mixture is usually understood the *plait point*, or the point at which the border curve touches the plait point

curve. At the temperature and under the pressure corresponding to the plait point, the critical phenomena—opalescence, striæ, etc.—are visible; but the plait point temperature is not the highest at which condensation of vapour can be brought about, for retrograde condensation may take place at temperatures between the plait point and the "critical temperature of contact," that is to say, the maximum temperature on the border curve. It would therefore, perhaps, be more correct to speak of the critical region than the critical point of a mixture; but when the term *critical point* is employed, it must be understood to refer to the plait point.

It was stated in 1882 by Pawlewski[1] that the critical temperature of a mixture could be calculated by the formula—

$$T_c = mT_c' + (1 - m)T_c''$$

where T_c, T_c', T_c'' are the critical temperatures of the mixture and of the two components A and B respectively, and m is the fractional weight of A.

That Pawlewski's rule, however, cannot be of general applicability has been clearly proved by Kuenen, who has shown that the critical temperature of a mixture may in certain cases be considerably lower, in others considerably higher, than that of either component (Figs. 73, 74). For such pairs of liquids it is obvious that the relation between critical temperature and composition is not represented by any such formula as that of Pawlewski.

It was pointed out by Kuenen that the substances which form mixtures of minimum or maximum critical temperature form also mixtures of minimum or maximum boiling point under lower pressures; and it is very probable that many such mixtures of minimum or maximum critical temperature will be met with in the future.

The data at present available are insufficient to allow of any very definite conclusions being drawn, but it may be assumed that the relations between pressure, temperature, and composition will be simple in the case of mixtures of substances which are chemically closely related, and it is not improbable that they may be found to be even simpler when the critical pressures of the two substances are equal—as in the case of fluorobenzene and chlorobenzene—than when they are unequal—as in the case of homologous compounds.

It may, indeed, be conjectured that all mixtures of fluorobenzene

[1] *Berichte*, 15, 460.

and chlorobenzene will be found to have the same critical pressure; but the question whether any such simple rule as that of Pawlewski applies to the critical pressures of mixtures of homologous organic compounds, or to the critical temperatures of closely related substances of either equal or unequal critical pressure can only be decided by experiment. It seems not unlikely, also, that the formula should take the form $T_c = mT_c' + (1 - m)T_c''$ or $p_c = mp_c' + (1 - m)p_c''$, where m is the molecular fractional amount of A.

CHAPTER XIV.

SOLUBILITY AND MISCIBILITY.

It is customary to speak of a *mixture* of two or more gases or of two or more liquids, and the term *mixed* solids is also employed; but a mixture formed by bringing together a gas and a liquid or a solid and a liquid is usually termed a *solution*. There is, however, no real difference between miscibility and solubility; for example, tertiary butyl alcohol melts at 25·53°, and it is easy to cool the alcohol a few degrees below its freezing point without solidification taking place. We may then mix the liquid alcohol with water at 20°, or dissolve the solid alcohol in water at the same temperature, the product being precisely the same in the two cases, and it would be permissible to speak either of a mixture of the alcohol with water or of a solution of the alcohol in water.

Solubility of Gases in Liquids.

Some gases, such as ammonia, are exceedingly soluble in water; others, like hydrogen, very slightly. Thus at 0° and 760 mm., 1 volume of water dissolves 1050 volumes of ammonia gas, but only 0·02 of hydrogen.

It may, perhaps, be stated that no gas is absolutely insoluble in any liquid; but the solubility may be almost inappreciable, as, for example, that of hydrogen in mercury. On the other hand, no gas under ordinary pressures is known to be infinitely soluble in any liquid.

The solubility of gases in liquids diminishes with rise of temperature. Thus on warming a saturated solution of ammonia in water, gas is freely evolved, and may be obtained free from moisture by passing it over quicklime. On boiling the solution for some time, the whole of the ammonia gas is expelled.

In the case of gases such as hydrogen or nitrogen, which are only slightly soluble in water, the amount dissolved at a given temperature is directly proportional to the pressure; but the density varies

directly as the pressure, and the volume of gas dissolved is therefore independent of the pressure. This law, first stated by Henry, is, however, subject to limitations similar to those observed in the case of Boyle's law. It is not absolutely true for any gas under ordinary pressure, and the deviations increase with rise of pressure; they are greater, also, for the more soluble gases, such as carbon dioxide or ammonia, but it is probable that some chemical action takes place in these cases.

Dalton's law of partial pressures was first applied to solutions of mixed gases in water. The solubility of each gas depends on its own partial pressure, not on the total pressure of the mixture. Thus, in the case of air in contact with water, the amount of each gas dissolved depends on its specific solubility and on its partial pressure, that is to say, about one-fifth of the total atmospheric pressure for the oxygen, and about four-fifths for the nitrogen.

The deviations from Dalton's law are of the same kind as from Boyle's and Henry's laws.

Miscibility of Liquids, and Critical Solution Point.

It has been stated that if the mutual attraction of the molecules of two liquids, A and B, is very slight compared with the attractions of the like molecules, those of A for each other, and those of B for each other, or, making use of the formula of Galitzine and D. Berthelot (p. 238), if $a_{A.B}$ is very much smaller than $\sqrt{a_A \times a_B}$, the two liquids are likely to be either non-miscible or only miscible within limits. If, on the other hand, $a_{A.B} = \sqrt{a_A \times a_B}$ or $> \sqrt{a_A \times a_B}$, the liquids will be miscible in all proportions.

It is found, however, that the miscibility of two partially miscible liquids is dependent on the temperature, usually increasing, but in some cases diminishing with rise of temperature.

If the relation between $a_{A.B}$ and $\sqrt{a_A \times a_B}$ remains the same, it is to be expected that the miscibility will increase with rise of temperature, because the kinetic energy of rectilinear motion of the molecules increases with rise of temperature, and also the mean distance between the molecules increases. It may, in short, be said that the penetrating power of the molecules becomes greater as the temperature rises. The general increase in miscibility with rise of temperature may then be attributed to this purely physical cause.

An increase in the ratio of $a_{A.B}$ to $\sqrt{a_A \times a_B}$ will also tend to

cause increased miscibility; but the ratio may increase as the temperature falls, and the increase in miscibility due to this change may be greater than the decrease due to the diminution in kinetic energy and specific volume, so that the miscibility may actually become greater as the temperature falls.

The subject was first studied experimentally by Alexéeff,[1] who found that several pairs of liquids, which at the ordinary temperature are only partially miscible, become infinitely miscible at some higher temperature. This temperature has been termed the critical solution temperature by Orme Masson, who has drawn attention to the close analogy between the critical point of a pure liquid and the critical solution point of a pair of liquids. This analogy will be discussed after the laws of osmotic pressure have been considered. Since the publication of Alexéeff's results many cases have been observed of liquids, which are partially miscible at ordinary temperatures, becoming infinitely miscible at a higher temperature.

It has also been found that with certain liquids, notably derivatives of ammonia, the miscibility increases with fall of temperature, and Rothmund[2] has observed several cases of partial miscibility at high temperatures increasing to infinite miscibility at a lower temperature.[3]

Many lactones are characterized by the fact that an aqueous solution, saturated at the ordinary temperature, becomes turbid when warmed, but, on raising the temperature still higher, becomes clear again. There is thus a temperature of minimum miscibility, generally about 40°, for these substances.

Lastly, nicotine and water are stated by Hudson to be partially miscible between 61° and 210°, but miscible in all proportions above and below these temperatures. This pair of substances has therefore both a superior and an inferior critical solution temperature. We may thus have the three cases represented in Figs. 75-77. The first shows the superior critical solution point, the second the inferior point, and the third both superior and inferior critical solution points.

It has been shown by Crismer[4] that the critical solution temperature of a pair of liquids is greatly altered by the presence of even a small quantity of a third substance, soluble in one or both of the

[1] *Wied. Ann.*, **28**, 305 (1886). [2] *Zeit. physik. Chem.*, **26**, 433 (1898).
[3] See also Centnerszwer and Zoppi, *Zeit. physik. Chem.*, **54**, 690 (1906).
[4] *Compt. rend. du Congrès de Chimie de Liège* (1905).

liquids, and he recommends the determination of this temperature as a delicate test of the purity of a liquid.

This subject has been further studied by Timmermans,[1] who points out that the critical solution temperature is raised by the addition of a substance which is soluble in only one of the two liquids, but is lowered when the added substance is soluble in both. The observation of a superior or inferior critical solution point may thus be rendered possible at a convenient temperature.

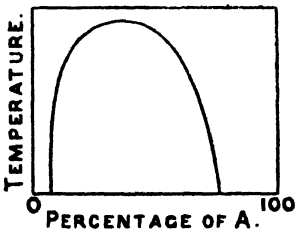


FIG. 75.

To take a single example, normal hexane and ethyl alcohol are miscible in all proportions at the ordinary temperature, but they become only partially miscible on addition of a very small quantity of water, which is miscible with alcohol but not with hexane. The critical solution temperature may thus be raised to, say, 30° or 40°.

On the other hand, the critical solution temperature of phenol

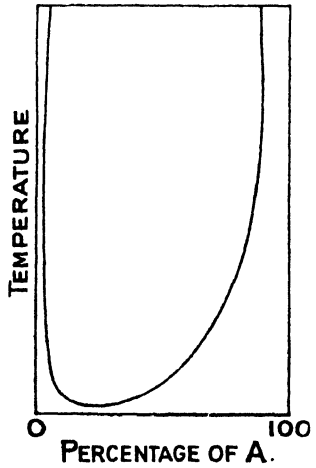


FIG. 76.

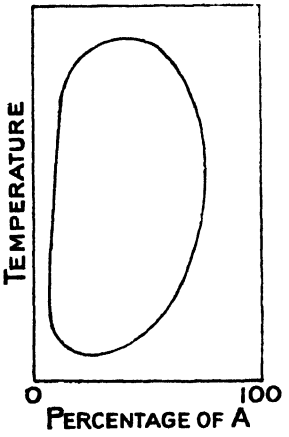


FIG. 77.

and water was found by Alexéeff to be 66°, but by adding a little soap, which dissolves in both liquids, the critical temperature may be so greatly reduced that infinite miscibility at the ordinary tem-

[1] *Bull. Soc. Chim. Belg.* (1906); and *Zeit. physik. Chem.*, 58, 129 (1907); Recherches expérimentales sur les Phénomènes de Démixtion des Mélanges Liquides, Brussels (1911).

perature results. The disinfectant known as *lysol* is prepared in this way.

Dolgolenko[1] states that an inferior critical solution temperature is not observed with pure secondary butyl alcohol and water, but that it is when the secondary contains a little tertiary alcohol. Again, a mixture of methyl ethyl ketone and water can be made to exhibit a lower critical solution point by the addition of 1·5 per cent. of ethyl alcohol. Dolgolenko is of opinion that the inferior critical solution point is only observed in the case of ternary mixtures, but the correctness of this assumption would be difficult to prove.

The influence of pressure on the miscibility of liquids has not been much studied, but it is probable that the question whether the miscibility is increased or diminished by rise of pressure depends partly on the change of volume on admixture and partly on the heat change. There is little doubt that when the volume of the mixture is considerably smaller than the sum of the volumes of the components, miscibility is increased by raising the pressure.

Solubility of Solids in Liquids.

Influence of Temperature.—As a general rule the solubility of a solid in a liquid is increased by raising the temperature, but the rate of change differs widely for different substances, and there are many cases in which the rate for a given substance alters abruptly at a definite temperature—a rapid increase of solubility being followed by a much slower increase, or even by a decrease.

The influence of change of temperature on the solubility of a few typical substances is indicated in Fig. 78, temperatures being measured as abscissæ, and the weights of anhydrous salt dissolved in 100 parts of water as ordinates.

The fact that there are two distinct solubility curves for strontium nitrate and for sodium sulphate is, no doubt, to be explained by the existence of hydrates, $Sr(NO_3)_2,4H_2O$ and $Na_2SO_4,10H_2O$, respectively, in solution at the lower temperatures, and of the anhydrous salts at the higher temperatures. The point of intersection of the curves indicates in each case the temperature of dissociation of the hydrate, but it is not to be assumed that complete dissociation takes place at that temperature. There are doubtless molecules of the anhydrous salt present at lower temperatures, and of the hydrate at

[1] *Zeit. physik. Chem.*, **62**, 499 (1908).

higher temperatures, and the diminution in the apparent solubility of sodium sulphate is probably due to the gradual dissociation of the residual hydrate with rise of temperature. Tilden and Shenstone [1] proved, in fact, by heating solid sodium sulphate with water in closed tubes of gun-metal, that the solubility reaches a minimum at about 120°, and increases slowly at higher temperatures, the actual measurements having been taken to 240°.

Influence of Pressure on Solubility.—According to Sorby,[2]

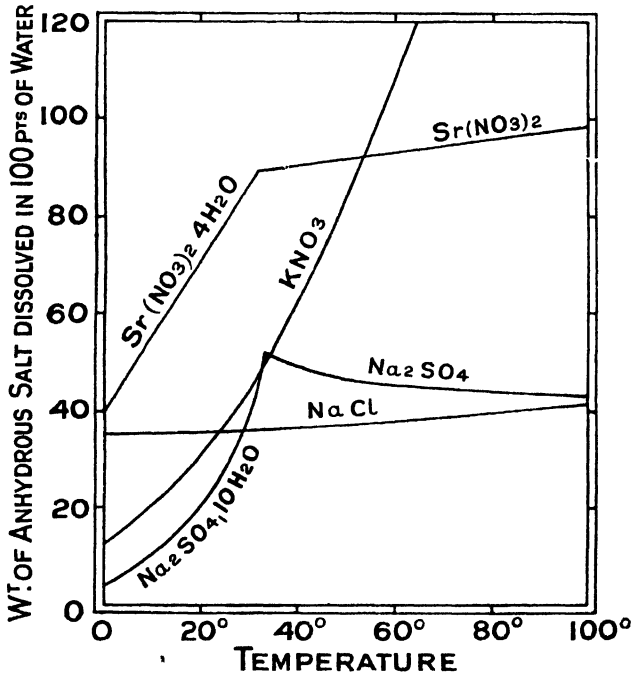


FIG. 78.

the solubility of a solid in a liquid increases with rise of pressure when there is contraction on dissolution, but diminishes when there is expansion. Braun, however,[3] basing his reasoning on the mechanical theory of heat, concludes that the change in solubility depends, not only on the alteration of volume on dissolution, but also on the temperature, the heat of dissolution, and the temperature coefficient of solubility.

[1] *Phil. Trans.*, 1884, 23.
[2] *Proc. Roy. Soc.*, **12**, 538 (1863).
[3] *Wied. Ann.*, **30**, 250 (1887).

Solidification of Liquid Mixtures.

It will be convenient to include under the heading "liquid mixtures" not only mixed liquids, but also solutions of gases and solids in liquids.

There is a fairly close analogy between vaporization and solidification. A pure liquid under a given pressure has a definite boiling point and a definite freezing point, although under certain conditions the liquid may be heated above its boiling point or cooled below its freezing point. A mixed liquid may either boil at a constant temperature, when the composition of the vapour must be the same as that of the liquid; or the temperature may rise during distillation, when the vapour will be richer than the residual liquid in the more volatile component.

So, also, a mixed liquid may freeze at a constant temperature, in which case the solid will have the same composition as the residual liquid (mother liquor), or the temperature may fall during solidification, the composition of the solid differing from that of the mother liquor.

Again, the freezing point of a liquid mixture may lie between the freezing points of the pure components, or it may be lower or, rarely, higher than either of them. When the two substances are chemically closely related and are isomorphous, they separate together from the liquid, but as a rule the solid which separates differs in composition from the remaining liquid (mother liquor), and the temperature falls steadily during solidification. If the freezing points of all mixtures lie between those of the pure compounds, it is theoretically possible to separate both components from the mixture by fractional crystallization.

As an example of two isomorphous substances one may take potassium chromate and potassium sulphate, the freezing points of mixtures of which are given below:—

Percentage of K_2SO_4.	Freezing Point.
	Degrees
0	940
13·7	950
30·6	960
47·2	985
63·5	1000
100	1045

If, on the other hand, the curve representing the relation between freezing point and composition shows a maximum or minimum point, it is only possible to separate the mixture of maximum or minimum freezing point, termed the *eutectic* mixture, from that component which is in excess. Here, again, there is a close analogy between solidification and distillation.

The freezing points of mixtures of potassium nitrate and sodium nitrate are given below. A mixture in equi-molecular proportions (54·3 per cent. of potassium nitrate by weight) freezes at 225°.

Percentage of KNO_3.	Freezing Point.
	Degrees.
100	338·3
90	311
80	280
70	250
60	230
54·3	225
50	229
40	244
30	262
20	281
10	298
0	313

A more complex case is that in which the freezing points of all mixtures are lower than that of either pure component, but a double compound is formed with a freezing point higher than that of either of the two possible eutectic mixtures. Such a case is that of potassium carbonate (M.P. 860°) and lithium carbonate (M.P. 710°). Here there are two eutectic mixtures containing 26 per cent. and

POTASSIUM CARBONATE AND LITHIUM CARBONATE.

Percentage of Li_2CO_3.	Freezing Point.
	Degrees.
0	860
5·0	777
9·6	720
19·4	590
26·0	500
29·9	505
34·9	515
39·1	505
46·6	492
51·6	525
73·0	638
100·0	710

46·6 per cent. of lithium carbonate, and freezing at 500° and 492° respectively, whilst the double salt, Li_2CO_3,K_2CO_3, contains 34·9 per cent. of lithium carbonate and freezes at 515°. Here the possible separations would be (1) potassium carbonate from the first eutectic mixture; (2 and 3) the double salt from one or other eutectic mixture; (4) lithium carbonate from the second eutectic mixture.

In the case of substances which are closely related but of different crystalline form, or of substances which are not closely related, the freezing point of a mixture is usually lower than that of either component. This, for example, is the case with aqueous solutions of most salts and of many other substances.

When a dilute solution of common salt, for example, is cooled below 0°, solid ice begins to separate when the freezing point of the mixture is reached. The mother liquor thus becomes richer in salt, and its freezing point falls. If the solution is further cooled, more ice continues to separate, and the concentration of the residual liquid increases, but the solubility of sodium chloride in water diminishes as the temperature falls, and a point is finally reached at which the residual solution is saturated. Further removal of ice would then cause the solution to become supersaturated, and though the concentration might increase and the temperature fall to a small extent, separation of solid salt would soon occur, and the temperature would rise again until the point was reached at which the solution first became saturated. After this, the solution being now in contact with both solid ice and solid salt, both components would continue to separate at a constant temperature, and the composition of the residual solution would undergo no further change. A mixture or solution of constant freezing point would, in fact, be obtained.

Starting with a saturated solution of sodium chloride at 0°, and cooling the solution, the solubility diminishes, solid salt separates, and the concentration of the mother liquor falls. This process goes on until the freezing point of the residual solution is reached. It may be possible to cool the solution a few degrees below its freezing point before solidification takes place, but as the temperature continues to fall, the concentration diminishes owing to further separation of salt, and the freezing point of the mother liquor therefore rises. A point is therefore very soon reached at which ice begins to form, when the temperature at once rises, and equi-

librium is finally attained under the same conditions as in the previous case, both solid ice and solid salt being in contact with the solution. In such a case there is not a continuous freezing point temperature curve, but the minimum freezing point is given by the intersection of the freezing point curve AB with the solubility curve CB (Fig. 79).

The freezing of such solutions was first studied by Guthrie, who termed the mixtures of constant freezing point "cryohydrates". They are, however, not hydrates in reality, for the ice and salt crystallize separately, and not in the form of hydrates or even of mixed crystals.

Many substances, when they crystallize from aqueous solution,

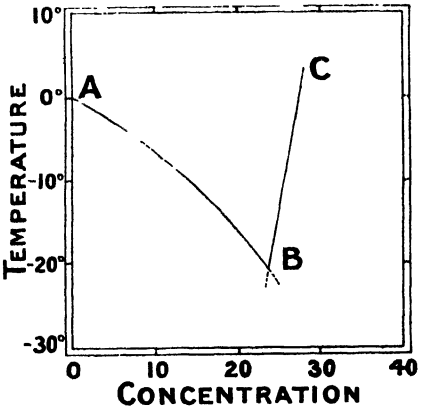


FIG. 79.

form definite hydrates, such, for example, as $MgSO_4,7H_2O$; $Na_2SO_4,10H_2O$. On cooling solutions of such substances either ice or the solid hydrate separates, and a point is finally reached at which the solid hydrate, solid ice, and the residual solution are in equilibrium. Some substances, such as ferric chloride, form more than one hydrate, and the freezing of solutions of these substances may be a less simple process, because the final equilibrium may be between ice, the highest hydrate, and the residual solution, or between two solid hydrates and solution, or lastly between a solid hydrate, the solid anhydrous salt, and the solution, according to the concentration of the original solution. Such a case resembles that of lithium carbonate and potassium carbonate.

When an aqueous solution of two or more salts is concentrated

by evaporation, or when the solubility of the salts is diminished by cooling, the dissolved substances solidify separately unless they are isomorphous, in which case mixed crystals are formed.

In the former case, if the saturation point of one substance is reached before that of the other, the first substance separates in a nearly pure state, and by repeated dissolution and crystallization may be obtained quite pure.

In the latter case the relative quantities of the salts in the mixed crystal may differ from those in the solution, and separation by fractional crystallization may be possible, though more difficult.

Some salts, such as chrome alum and ordinary alum, are miscible in all proportions in the solid state, so that the composition of the mixed crystal may vary indefinitely from that of the one pure salt to that of the other.

In other cases the solids are only miscible within limits, and in some cases the pure salts crystallize normally in quite different forms; for example, magnesium sulphate, $MgSO_4,7H_2O$ and ferrous sulphate, $FeSO_4,7H_2O$. Mixed crystals of these salts may be obtained in either form; thus from a solution rich in magnesium sulphate the crystals will take the rhombic form of that substance, but if the original solution contains a large excess of ferrous sulphate, the crystals will take the monoclinic form of that salt. Rhombic crystals containing more than 18·8 per cent. of ferrous sulphate and monoclinic crystals with more than 54 per cent. of magnesium sulphate cannot be obtained by evaporation of mixed solutions at the ordinary temperature.

The specific volumes of mixed crystals may usually be calculated without great error from those of the components by the method described on p. 239, and other physical properties appear to be approximately additive.

For a fuller account of the solidification of mixed liquids, see Findlay, "The Phase Rule," in this series. See also Roozeboom, *Zeit. physik. Chem.*, **30**, 385 (1899).

Absorption and Adsorption of Gases and Solutes by Solids.—Certain metals, notably palladium and platinum, especially when in a finely divided state, have the power of absorbing or *occluding* hydrogen and oxygen.

There is experimental evidence [1] that when oxygen is absorbed by platinum black or palladium black, chemical combination with

[1] Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, **62**, 50 and 290 (1898).

the metal takes place. On the other hand, there appears to be no evidence of the formation of a hydride of either metal.

One volume of pure spongy palladium occluded 852 volumes of hydrogen under atmospheric pressure, and of this 92 per cent. could be extracted in a vacuum at the ordinary temperature. When the palladium contained oxygen, a larger amount of hydrogen was absorbed, the excess forming water with the oxygen.

Charcoal and other porous substances possess the property of absorbing gases; it is found that the denser forms of charcoal have greater absorptive power than the lighter, and that cocoa-nut charcoal gives especially good results.

McBain [1] heats in a muffle the white tissues of the fruit of the cocoa-nut to a temperature just below redness for several hours until no more fumes are evolved. The temperature is then allowed to rise to a dull red heat for about thirty seconds. The charcoal from the interior of the mass is employed, and is dried at 160° before use. Hempel and Vater [2] recommend blood charcoal formed at 600° in preference to cocoa-nut charcoal as an absorbent.

McBain has made a careful study of the "absorption" of hydrogen by cocoa-nut charcoal, prepared as described above. He shows that the process is of a dual nature, surface condensation or *adsorption* taking place with great rapidity, and diffusion into the interior—solid solution or *absorption*—far more slowly, many hours, in fact, elapsing before equilibrium is attained. In one series of experiments charcoal was saturated with hydrogen by long contact at constant temperature. It was then suddenly exposed to a vacuum and finally left in contact with hydrogen at low pressure. In this case the pressure registered by the manometer first fell and then slowly rose to a higher point than the initial value. The exposure to a vacuum removed the "adsorbed" hydrogen; then, in presence of hydrogen at low pressure, gas was at first rapidly "adsorbed" as shown by the fall in pressure, but afterwards the partial slow escape of the "absorbed" hydrogen caused the gradual rise of pressure.

In a second set of experiments the interior of the charcoal was at first free from hydrogen, but the surface was supersaturated by very short exposure to a high pressure of gas. A portion of the hydrogen was then removed and pressure readings were taken from time to time. In this case the pressure rose for a short time owing to the rapid escape of the adsorbed gas, and then fell slowly for

[1] *Phil. Mag.*, **18**, 916 (1909). [2] *Zeit. Elektrochem.*, **18**, 724 (1912).

several hours while the gas was being absorbed. Most of the experiments were carried out at the temperature of liquid air, a few at the ordinary temperature. The solubility of hydrogen in carbon at room temperature is not nearly so great as that at the temperature of liquid air even when the pressure is sixty times as high.

As regards the influence of pressure, McBain finds that at liquid air temperature the amount of hydrogen absorbed varies as the square root of the pressure, whilst the amount adsorbed is proportional to the cube root of the pressure. From the relation between solubility and pressure the conclusion is drawn that the absorbed hydrogen is dissociated into atoms.

Sieverts and Hagenacker [1] observe that at 822° and 923° the amount of hydrogen absorbed by nickel is nearly proportional to the square root of the pressure and [2] that the same law holds for the solubility of hydrogen in platinum, palladium, and copper, and of oxygen in silver and silver-gold alloys. These authors conclude that the hydrogen and oxygen are in the atomic state. Sieverts and Bergner [3] find that the absorption of hydrogen by tantalum at temperatures above 450° follows the law, but Sieverts [4] has since observed that while the law holds good for hydrogen in palladium between 138° and 821° and from 1 to 760 mm. the solubility increases more rapidly at higher pressures, the relation $L_p = K_1 p^{\frac{1}{2}}$ becoming $L_p = K_1 p^{\frac{1}{2}} + K_2 p$, where L_p is the amount of hydrogen absorbed at pressure p, and K_1 and K_2 are constants depending on the temperature. Sieverts draws the conclusion that at high pressures molecules as well as atoms of hydrogen are present in solution.

As regards the dual nature of the process pointed out by McBain, Davis [5] has shown that when charcoal extracts iodine from solutions in various solvents, there is a rapid adsorption and slow absorption, and Ritzel [6] has observed the same phenomena in the extraction of uranium X from solution by charcoal. McBain proposes the general term "sorption" to cover the two processes of adsorption and absorption.

Arrhenius,[7] on the other hand, is of opinion that in most cases it is only the surface condensation or adsorption that is of importance,

[1] *Ber.*, **42**, 2 (1909). [2] *Zeit. physik. Chem.*, **68**, 115 (1909).
[3] *Ber.*, **44**, 2394 (1911). [4] *Zeit. physik. Chem.*, **88**, 451 (1914).
[5] *Trans. Chem. Soc.*, **91**, 1683 (1907).
[6] *Zeit. physik. Chem.*, **67**, 724 (1909).
[7] *Medd. K. Vetensh. Nobelinst.*, **2**, No. 7 (1912).

and that solid solution or absorption is negligible except for highly penetrating gases such as hydrogen and helium. He finds that in certain cases of both gases and solutions there is a maximum of adsorption and he proposes the formula—

$$\frac{\log_{10} s}{s - x} - \frac{0{\cdot}4343x}{s} = \frac{c}{k},$$

where x represents the quantity of substance taken up by 1 gram of charcoal, s the maximum value of x, c the pressure of the gas or osmotic pressure of the solute, and k a constant.

Schmidt [1] proposes a more complex formula which represents the experimental results better than that of Arrhenius.

It has been shown by Titoff [2] that the adsorption of a gas increases simultaneously with the a term of Van der Waals' equation, and Arrhenius concludes that while compressibility is determined by the sum of the external pressure and that due to molecular attraction, adsorption is determined by the sum of the external gas pressure or osmotic pressure and the attraction pressure between adsorbed molecules and adsorbent. The formula of Arrhenius represents Amagat's data for the compressibility of liquids with considerable accuracy, x representing the density of the liquid, c the total pressure, internal and external, and s the maximum density.

At a given temperature and pressure gases which are easily condensed are absorbed much more freely than those which have very low critical temperatures; but Dewar has shown that under atmospheric pressure the volumes of different gases absorbed by unit volume of charcoal at their respective condensing points do not show wide differences.

At constant pressure the quantity of any given gas absorbed increases greatly with fall of temperature.

Miss Homfray [3] has measured the volumes of argon and of nitrogen absorbed at definite pressures and temperatures, and finds that the "isosteric" curves, showing the relation between temperature and pressure for equal volumes of either gas absorbed, have the same form as a vapour pressure curve. Moreover, if the isosteric curve for argon or nitrogen is compared with the vapour pressure curve for a pure liquid, the relation—

[1] *Zeit. physik. Chem.*, **77**, 641 (1911); **78**, 667 (1912).
[2] *Ibid.*, **74**, 641 (1910). [3] *Brit. Ass. Rep.* for 1906.

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + \alpha(T_A' - T_A)$$

(p. 133) is found to hold good.

Very good vacua can be obtained, as pointed out by Dewar, by the removal of the last traces of air by means of cocoa-nut charcoal cooled to the temperature of liquid air, and this method is now largely employed.

CHAPTER XV.

PROPERTIES OF DILUTE SOLUTIONS.

Freezing Points.—It has long been known that the freezing point of sea-water is lower than that of fresh-water, and Blagden,[1] in 1788, observed that the depression of the freezing point of water is, within limits, proportional to the amount of a salt, such as sodium chloride, dissolved in it; and that if two different substances are dissolved together, the observed depression of the freezing point is equal to the sum of the depressions which the two would cause separately.

These results were, however, entirely overlooked until attention was called to them by de Coppet[2] in 1871. Meanwhile, in 1861, similar observations had been made by Rudorff.[3] De Coppet himself proceeded further, and by taking quantities of different salts proportional to their molecular (formula) weights, he was able to show that, for analogous substances, the molecular depression of the freezing point is constant.

The whole subject was investigated with great care and thoroughness by Raoult,[4] who employed not only water, but also benzene, acetic acid, and other liquids as solvents, and examined solutions of more than two hundred different substances.

If Δt is the observed depression of the freezing point caused by dissolving m grams of substance of molecular weight M in 100 grams. of solvent, the molecular depression of the freezing point is given, according to Raoult, by the equation $E' = \frac{\Delta t \,.\, M}{m}$.

Raoult found that in the majority of cases E′ is constant for a given solvent, but a number of exceptions were met with. With water as solvent, for example, organic compounds and many weak acids and bases gave values of E′ about 18·5 or 19, but inorganic

[1] *Phil. Trans.*, **78**, 277 (1788).

[2] *Ann. Chim. Phys.* (4), **23**, 366 (1871); **25**, 502 (1872); **26**, 98 (1872).

[3] *Pogg. Ann.*, **114**, 63 (1861); **116**, 55 (1862); **145**, 599 (1871).

[4] *Compt. rend.*, **94**, 1517 (1882); **95**, 188 and 1030 (1882); *Ann. Chim. Phys.* (5), **28**, 137 (1883); (6), **2**, 66 (1884).

acids and bases and the salts derived from them gave higher values; thus for strong monobasic acids, monacid bases, and the salts derived from them double values were obtained, while hydroxides and halides of the dyad alkaline earth metals gave nearly triple values.

On the other hand, with organic solvents, the value of E′ was generally constant, but with certain substances the value was only half as great. Raoult thought it probable that these exceptional values of E′ were due to molecular association of the dissolved substance.

Van't Hoff[1] showed that E′ may be calculated for any solvent from its heat of fusion L′, expressed in gram-calories, and its melting point on the absolute scale of temperature; thus—

$$E' = \frac{0{\cdot}02T^2}{L'}.$$

In the table on page 288 the values of E′ are given for a few solvents. The "observed" values are obtained from Raoult's formula, $E' = \frac{\Delta t \,.\, M}{m}$, a large number of substances of known molecular weight having been dissolved in the solvent, and the mean value of E′ being adopted; the calculated values are derived from Van't Hoff's formula.

The experimental method of determining the freezing points of solvent and solution has been perfected by Beckmann[2] (Fig. 80).

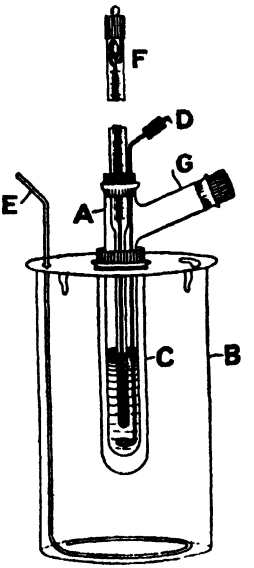


FIG. 80.

A weighed quantity of the pure solvent is placed in the tube A and is cooled by water, ice, or a freezing mixture in the large bath B, direct contact between the tube A and the material in the bath being prevented by means of the tube C, which contains only air. Two stirrers are provided, one, D, for the solvent, the other, E, for the bath. The temperature is read on a very delicate thermometer F, of a special form devised by Beckmann. The actual freezing points of the solvent and solutions are not required, but only the differences,

[1] *Zeit. physik. Chem.*, 1, 481 (1887).
[2] *Ibid.*, 2, 638 (1888); 7, 323 (1891); 21, 239 (1896); 44, 169 (1903).

	E.	
	Calculated.	Observed.
Water . . .	18·9	18·5 to 19
Acetic acid . .	38·8	39·0
Benzene . . .	51·0	49·0
Phenol . . .	76·0	74·0
Formic acid . .	28·4	27·7
Nitrobenzene . .	76·3	71·0

and the thermometer has a range of only five or six degrees. The amount of mercury in the bulb may be adjusted so that readings may be taken on the same thermometer with liquids of widely different freezing points.

After the freezing point of the solvent has been determined, a weighed quantity of the substance is introduced through the side tube G, the solvent having previously been melted; and the freezing point of the solution is determined. It is usual to make a series of determinations, further small quantities of the substance being added.

For substances of low freezing point a pentane thermometer has been used, and Beckmann and Waentig [1] have employed a platinum resistance thermometer and have determined the constants for a number of solvents freezing at temperatures between -24° and -117°. It was found that alcohols are polymerized when dissolved in carbon tetrachloride or chloroform, but that they have normal molecular weights in ether.

Vapour Pressures.—It seems to have been first observed by Gay Lussac that the vapour pressure of an aqueous solution of sodium chloride is lower than that of pure water, and it was found by Princep that the ratio of the vapour pressure of the solution p' to that of pure water p was constant at different temperatures. Von Babo afterwards obtained similar results with aqueous solutions of other salts.

In 1856 Wüllner [2] concluded, from his experiments, that the lowering of the vapour pressure of water produced by a dissolved non-volatile substance is proportional to the amount of solute.

Tammann, in 1885,[3] determined the vapour pressures of aqueous

[1] *Zeit. Anorg. Chem.*, **67**, 17 (1910).
[2] *Pogg. Ann.*, **103**, 529; **105**, 85 (1858); **110**, 564 (1860).
[3] *Wied. Ann.*, **24**, 523 (1885).

solutions of a great number of salts. He found that Wullner's law was strictly true in only a few cases, but, on the other hand, he showed that the molecular lowering of the vapour pressure, $E'' = \frac{p - p'}{p} \cdot \frac{M}{m}$, is approximately the same for similar salts (M is the molecular weight of the salt, and m its percentage weight in the solution). Further experiments by Moser,[1] v. Helmholtz,[2] Emden,[3] Bremer,[4] and J. Walker[5] indicated that Von Babo's law was correct, but that Wullner's law was only approximately true.

In all the older experiments aqueous solutions had been examined, but Raoult[6] employed other solvents, notably ether, and carried out a long series of investigations, employing the barometric method for the measurement of the vapour pressures.

Raoult found that Von Babo's law was true for ethereal solutions between 0° and 20°, that Wullner's law was true for moderate concentrations, and that the molecular lowering of the vapour pressure $\frac{p - p'}{p} \times \frac{M}{m}$ (where m is the weight of substance in 100 parts of ether) was the same for different substances.

After making similar experiments with other solvents, he was led to the wider generalization that the relative lowering of the vapour pressure is equal to the ratio of the number of molecules of solute to the total number of molecules, or—

$$\frac{p - p'}{p} = \frac{N}{n + N}$$[7]

which may be written—

$$\frac{p - p'}{p'} = \frac{N}{n}.$$

It has been stated (p. 244) that for closely related substances, when mixed in any proportions—

$$p = Mp_A + (1 - M)p_B,$$

[1] *Wied. Ann.*, **14**, 72 (1881). [2] *Ibid.*, **27**, 508 (1886).
[3] *Ibid.*, **31**, 145 (1887). [4] *Rec. tr. Pays-Bas.*, **6**, 122 (1887).
[5] *Zeit. physik. Chem.*, **2**, 602 (1888).
[6] *Compt. rend.*, **103**, 1125 (1886); **104**, 976 and 1430 (1887); **107**, 442 (1888); *Zeit. physik. Chem.*, **2**, 353 (1888).
[7] Raoult first gave the equation in the form—

$$\frac{p - p'}{p} = \frac{N}{n}$$

but this he afterwards found to be incorrect.

where p, p_A, and p_B are the vapour pressures of the mixture and the two substances, A and B, respectively, and M is the fractional number of gram-molecules of A.

$$\text{If } p_B = 0,\ p = Mp_A, \text{ or } p_A = \frac{p}{M},$$

$$\therefore p_A - p = p \times \frac{(1 - M)}{M}$$

$$\text{and } \frac{p_A - p}{p} = \frac{1 - M}{M} = \frac{N}{n},$$

an equation which is identical with Raoult's (p_A and p in the above equation corresponding to p and p', respectively, in Raoult's). But the equation $p = Mp_A + (1 - m)p_B$ does not, as a rule, hold for substances which are not closely related, and one would therefore not expect Raoult's law to be true for such substances even when $p_B = 0$. It appears, however, that for dilute solutions the errors are small, and the law may be taken as, at any rate, approximately true.

Raoult found that while the molecular lowering of the vapour pressure was generally constant for a given solvent, there were exceptions similar to those observed in the case of the molecular depression of the freezing point.

The chief experimental methods which have been employed for the determination of the vapour pressures of solutions or mixtures of liquids are the following:—

1. The statical method, in which the difference between the vapour pressures of the pure solvent and of solutions or mixtures of known composition is measured at a known temperature, the vapour pressure of the pure solvent having been previously determined. This method was employed by Konowalow[1] in his research on the vapour pressures of mixtures of water with the lower alcohols and fatty acids, by Emden, Raoult, and others. Frazer and Lovelace[2] make use of the manometer designed by Lord Rayleigh (p. 30) for the determination of $p - p'$ in the case of very dilute solutions.

The statical method is open to the serious objection that there is great difficulty in getting rid of traces of air from a solution without altering its concentration, and there is also some danger that the surface layer of solution may differ in composition from the liquid below.

[1] *Wied. Ann.*, **14**, 34 (1881).
[2] *Journ. Amer. Chem. Soc.*, **36**, 2439 (1914).

2. The dew point method. Air in presence of pure water gives a mist when very slightly cooled by sudden expansion, but in presence of a salt solution a greater cooling is required before the dew point is reached. A method based on this principle has been devised by R. von Helmholtz (*loc. cit.*).

3. Dry air is passed through two Liebig's absorption tubes containing the salt solution, then through one containing pure water, and lastly through a drying tube, in which the moisture is completely absorbed. In passing through the first Liebig's tube the air takes up moisture, and the solution gradually becomes slightly more concentrated; but the amount of moisture taken from the second solution is very small, and the concentration of this solution remains almost constant. The air becomes fully saturated in passing through the pure water. The ratio of the loss of weight of the water tube to the increase of weight of the absorption tube is equal to the ratio $\frac{p - p'}{p}$.

This method was first suggested by Ostwald, and was employed by J. Walker (*loc. cit.*). Will and Bredig[1] used a similar method for alcoholic solutions, determining the loss of weight of the solution and of the pure solvent, and thus obtaining the ratio $\frac{p'}{p - p'}$, and the method has since been employed by many experimenters, notably by Lord Berkeley, Hartley and Burton,[2] who determined the losses in weight of the two saturators by weighing them before and after the experiment, and by Washburn and Heuse,[3] who absorbed the moisture in absorbers of such form and size that they could be accurately weighed. Accurate results were obtained in both cases, but the time required for a determination was very great.

4. A small flask, containing firstly the pure solvent, and secondly the solution, is brought into contact with an exhausted globe, and the loss of weight is determined in each case. In this method, which was employed by Beckmann,[4] the ratio of p to p' is directly obtained.

5. A simple, convenient, and accurate method has been described by Menzies,[5] in which the difference between the vapour pressures of the solvent and of the very dilute solution is measured by the

[1] *Ber.*, **22**, 1084 (1889). [2] *Trans. Roy. Soc.*, **209**, 177 (1909).
[3] *Journ. Amer. Chem. Soc.*, **37**, 309 (1915).
[4] *Zeit. physik. Chem.*, **4**, 532 (1889).
[5] *Journ. Amer. Chem. Soc.*, **32**, 1615 (1910).

difference in height of two columns of the liquid itself. There seems no reason why the apparatus devised by Menzies should not come into general use.

The bulb A, Fig. 81, is about two-thirds filled with pure solvent, a little being also placed in the graduated tube B. The clip C is closed and the stopper D raised to allow escape of vapour. The liquid is boiled for some time; the vapour passes down the narrow tube E, which is graduated in millimetres, bubbles through the liquid in B and so removes dissolved air; most of it condenses and flows back into B. After a time the stopper D is placed in position and the clip C is opened. The levels of liquid in E and B should now be the same except for the small difference due to capillarity. The process may be repeated until the difference is constant. A weighed quantity of the substance is now introduced into B and the liquid in A is again boiled for some time with C closed and D raised a little. Then the stopper is inserted and the clip C opened, and the difference in level again read. The volume of solution is read on the scale on B and the difference in level on that on E. This difference must be corrected for capillarity as indicated by the zero reading.

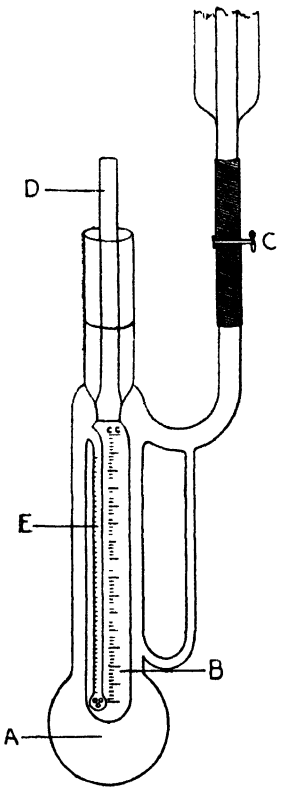


FIG. 81.

The molecular weight is calculated from the formula—

$$M = \frac{1000W \times k \times B}{l \times v \times 760}$$

where W is the weight of solute added, l is the measured lowering of pressure in millimetres, v the volume of solution in cubic centimetres, B the barometric pressure, and k a constant, the value of which at 760 mm. pressure for several solvents is given in the paper.

Boiling Points.—The first four methods described above are

somewhat inconvenient, and are not very accurate unless the experiments are carried out with extreme care, and Beckmann [1] proposed to determine the boiling points of the solvent and solution under the same pressure, instead of the vapour pressures at the same temperature.

The molecular rise of the boiling point E is given by the equation—

$$E = \frac{\Delta t \times M}{m}$$

where M is the molecular weight of the dissolved substance, m is the weight of substance in 100 grams of solvent, and Δt is the observed rise of the boiling point.

The value of E for a given solvent may be ascertained by determining the rise of boiling point for a number of substances of known molecular weight; or, as pointed out by Van't Hoff,[2] it may be calculated from the equation—

$$E = \frac{0{\cdot}02T^2}{L},$$

where T is the boiling point of the solvent on the absolute scale of temperature, and L is its heat of vaporization.

The following are the values of E for a few useful solvents:—

Solvent	E.
Benzene	26·7
Chloroform	36·6
Acetic acid	25·3
Ether	21·2
Water	5·2
Aniline	32·2

There are two methods in general use for the determination of the boiling points of solutions. In that of Beckmann (Fig. 82) a weighed quantity of the pure solvent is first boiled in a glass tube A, the temperature being registered by a delicate thermometer, similar to that employed for the determination of freezing points. Ebullition is facilitated by fusing a short length of stout platinum wire B into the bottom of the tube, and by placing in the tube a

[1] *Loc. cit.* and *ibid.*, **8**, 223 (1891); **21**, 239 (1896); **40**, 129 (1902); **44**, 161 (1903).

[2] *Loc. cit.*

number of glass beads or crystals of garnet. The glass tube is placed inside a wider vessel C (Fig. 82*a*) in which some of the pure solvent is boiled. Both the experimental tube and the jacketing vessel are provided with reflux condensers, either spiral in form or fitted with water-jackets (D and E).

After reading the position of the mercury when the thermometer bulb is immersed in the boiling solvent, a small quantity of the substance under investigation is introduced through the side tube, and after the temperature has become constant a second reading is taken. Additional small quantities of the substance are introduced, and the rise of boiling point determined in each case. The rela-

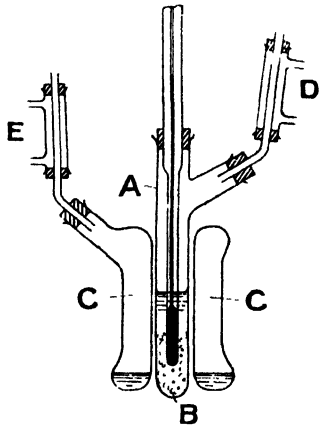


FIG. 82.

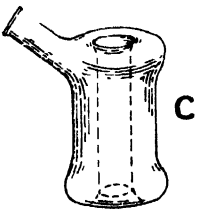


FIG. 82*a*.

tion between concentration and rise of boiling point may thus be studied.

Landsberger[1] has devised a somewhat different method. The solvent and solution respectively are not heated directly by a flame, but by passing the vapour of the pure solvent through them. Modifications of the original method have been proposed by Walker and Lumsden,[2] Smits,[3] Ruber,[4] and Ludlam.[5] The apparatus devised by Ludlam is shown in Fig. 83.

A quantity of the pure solvent is boiled in the flask A; the vapour passes through the opening in the side of the tube B, up through the valve C (shown separately on a larger scale) in the

[1] *Berichte*, **31**, 458 (1898). [2] *Trans. Chem. Soc.*, **77**, 503 (1898).
[3] *Proc. K. Akad. Wetensch. Amsterdam*, **3**, 86 (1900).
[4] *Berichte*, **34**, 1060 (1901). [5] *Trans. Chem. Soc.*, **81**, 1194 (1902).

bottom of the experimental tube D (which is graduated in cubic centimetres), and out by the side tube E, which is connected with a Liebig's condenser. If necessary, a little of the pure solvent is first placed in D. Condensation takes place at first in the tube B and in the lower part of D, but after the apparatus has become thoroughly heated, the amount of condensation is very small. Any liquid formed by condensation of vapour in the upper part of D is carried off into the condenser. It is usual to employ a thermometer graduated in tenths or fifths of a degree. The boiling point of the pure solvent is first determined, and then a small quantity of the substance is introduced through the side tube F. When the thermometer bulb is quite covered with liquid and the temperature has become steady (the time required is much shorter than with the Beckmann apparatus), the current of vapour is stopped for a few moments by cooling the flask A by touching it with the hand. The liquid is prevented by the valve C from flowing out of the experimental tube, and a reading of the volume of the solution is taken. The vapour is allowed to pass through the solution again, and successive readings are taken with larger volumes of solution. In the Beckmann apparatus the quantity of substance is gradually increased, the solution becoming more concentrated; in the Landsberger-Ludlam apparatus the quantity of solvent is gradually increased, the solution becoming more dilute.

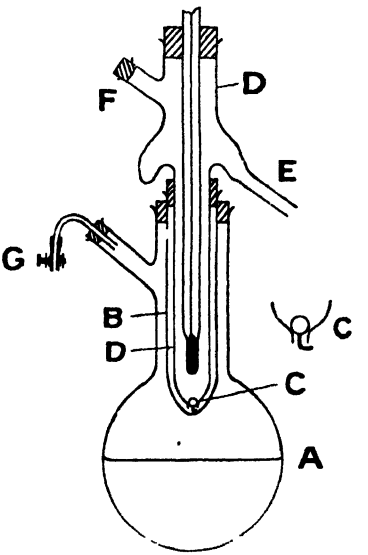


FIG. 83.

When the last reading has been taken, the clip G is opened in order to admit air into the flask.

DIFFUSION OF LIQUIDS AND OSMOSIS.

Just as two gases, when brought into contact or when separated only by a porous diaphragm, diffuse into each other until a homo-

geneous mixture is produced, so also admixture of two liquids will take place under similar conditions.

The process of diffusion, however, in the case of liquids is exceeding slow, as may be seen by carefully pouring a strong solution of a coloured substance, such as copper sulphate, through a thistle funnel, so as to form a layer at the bottom of a cylinder of water. Weeks or even months will elapse before the salt is evenly distributed through the water.

The processes are similar in this respect also, that they are not reversible. The gases or liquids may, indeed, be separated again,

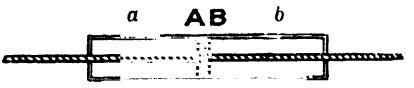


FIG. 84.

but not by a simple reversal of the process by which admixture was effected.

It is possible, however, by the employment of what are termed *semipermeable* diaphragms, to make the process a strictly reversible one. Imagine a cylinder (Fig. 84) divided by means of two pistons into two chambers, *a* and *b*. Let each piston consist of a solid rod attached to a semipermeable diaphragm, such that the diaphragm A will allow a gas placed in the chamber *a* to pass freely through it, but not a gas placed in *b*. Conversely, let B be permeable to the gas in *b*, but not to that in *a*.

FIG. 85.

The gas in *a* will then pass freely through A, but it will exert a pressure on B tending to move it to the right, while the gas in *b* will pass freely through B, but will tend to force A to the left. If the pistons were frictionless, they would therefore move apart until they reached the extremities of the cylinder, and a mixture of the two gases would then be obtained (Fig. 85). Let the two pistons be now brought together again by the application of external force. As B moves to the left, it compresses the gas originally present in *a*, but the other gas passes through it; and as A moves to the right, the gas originally in *a* passes through it, but that which was in *b* is

compressed. The pistons may thus be brought into their original positions, the two gases being completely separated, and the work done in bringing the pistons together will be exactly equal to that done by the gases in moving them apart.

Such an arrangement is not realizable in practice, because frictionless pistons of this kind could not be made, but diaphragms which are almost perfectly semipermeable are obtainable. Thus metallic palladium at a high temperature will allow hydrogen gas to pass freely through it, while it is practically impermeable to oxygen or nitrogen. Again, a moist piece of bladder or parchment is almost impermeable to hydrogen or air, but will allow the passage of easily soluble gases such as ammonia.

Nernst[1] has described a simple method of showing the action of a semipermeable membrane. The tube of a thistle funnel is bent in the form of a U, and a little mercury is placed in the tube to close it, and to serve as an indicator of any change of pressure. A piece of moistened bladder is tied tightly round the funnel (Fig. 86), and an inverted beaker is held over it. Ammonia gas is now passed upwards into the beaker, when it is found that the pressure in the funnel increases, as shown by the movement of the mercury. Ammonia gas passes through the moist bladder into the funnel, while air is unable to escape from the funnel, and the process continues until the partial pressure of the ammonia in the funnel is equal to that outside. The process is reversible, for when the inverted beaker is removed the ammonia passes back again through the moistened bladder into the air outside; or by increasing the pressure on the mercury in the open limb, the beaker being left in position, the gas in the funnel may be compressed, and ammonia will pass back again, so long as its partial pressure in the funnel is greater than that in the beaker.

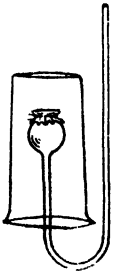


FIG. 86.

Osmotic Pressure.—If an aqueous solution of cane-sugar and pure water were separated from each other in a cylinder by a frictionless piston formed of a material through which water could pass freely, but which was impermeable to cane-sugar (Fig. 87), diffusion would take place, the piston would slowly move upwards, and eventually a homogeneous dilute solution of cane-sugar would be obtained. Here again the process would be reversible, because

[1] *Theoretische Chemie* (1893) p. 90.

on increasing the pressure on the piston from above, water would pass through it, and the solution remaining below the piston would become more concentrated. The work done by the cane-sugar in raising the piston would be equal to that done in forcing the piston down to its original position. The pressure exerted on the piston forcing it upwards is termed the *osmotic pressure* of the solution.

It would be very difficult to make a frictionless and semipermeable piston strong enough and fitting the cylinder well enough to allow of this experiment being actually performed, but semipermeable membranes exist in nature, and others can be prepared in the laboratory.

Moritz Traube,[1] in 1867, observed that a membrane of copper ferrocyanide, formed by the action of copper sulphate on potassium ferrocyanide in aqueous solution, is permeable to water, but not to cane-sugar, nor to many other dissolved substances.

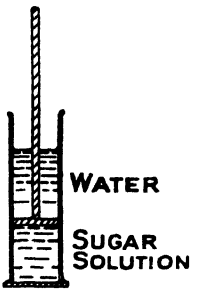


FIG. 87.

Other substances, for example, ferric hydroxide, tannate of gelatine, calcium phosphate, prussian blue, or silicic acid, may be employed in place of copper ferrocyanide, and semipermeable membranes are found naturally in plant cells, such as those in the leaves of *Tradescantia discolor*, in red blood-corpuscles, and in bacteria. The osmotic pressure in such cells frequently amounts to four or five atmospheres, and may be considerably higher when the cells contain dissolved reserve materials, such as the sugar in beetroot.

A copper ferrocyanide membrane would not be strong enough to withstand even moderate pressures, but this difficulty was overcome by Pfeffer,[2] who caused the precipitation to take place in the interior of the walls of a porous earthenware cell. The procedure has been modified from time to time, and Morse and Horn [3] found that the quality of the copper ferrocyanide membrane could be greatly improved by assisting the process of diffusion by the electrical transport of the ions. The cell is first filled with and placed in a dilute solution of potassium sulphate, and an electric current is passed between electrodes placed inside and outside the cell, the cathode

[1] *Archiv. f. Anatomie u. Physiologie* (1867), p. 87.
[2] *Osmotische Untersuchungen*, Leipzig (1877).
[3] *Amer. Chem. Journ.*, **26**, 80 (1901).

being inside. By the "electrical endosmose" so set up, the air filling the pores of the cell is completely swept out. The cell is then repeatedly washed with distilled water, and the current is passed until the conductivity falls to that of pure water. The cell is now filled with a solution of potassium ferrocyanide and placed in a solution of copper sulphate, and a current is passed from a copper anode in the solution of copper sulphate to a platinum cathode in the solution of potassium ferrocyanide. The ferrocyanide solution must be renewed from time to time to prevent accumulation of alkali which would injure the membrane. After the action has gone on for some time the membrane should be tested with a sugar solution, and the making process should be repeated until there is no further increase in the measured osmotic pressure. The membrane should be deposited as near the inner surface of the cell as possible.

In making actual determinations it is advisable that the liquids inside and outside the cell should contain a little potassium ferrocyanide and copper sulphate respectively in osmotically equivalent amounts,[1] so that any weak points which happen to develop in the membrane may be made good.[2]

In the earliest experiments the cell was fitted with a stopper, through which passed a long vertical glass tube. The cell was filled with a dilute solution of cane-sugar to a height a little above the top of the stopper, and was immersed in pure water. Under these conditions the water slowly enters the cell, and the solution rises in the vertical tube until equilibrium is established between the hydrostatic pressure of the column of solution and the osmotic pressure which tends to cause the passage of more water into the cell from outside.

The simple apparatus first devised by Pfeffer is not suitable for accurate measurements of osmotic pressure for two reasons. In the first place, the pressures to be measured are so great that glass tubes of inconvenient height would be required; thus the osmotic pressure of an aqueous solution containing 1 per cent. of cane-sugar was found to be 0·649 atmos. at 0°, which would correspond to a column of water 6·7 metres in height. In the second place, the solution becomes diluted as the process goes on, and, diffusion being a very slow process, the concentration would not become uniform until after the lapse of a long period of time, although admixture would doubtless be facilitated to some extent by convection currents. It would,

[1] Solutions which have the same osmotic pressure as each other are termed *isosmotic* or *isotonic*.

[2] Earl of Berkeley and E. G. J. Hartley, *Trans. Roy. Soc.*, **206**, 486 (1906).

therefore, not be easy to ascertain the true concentration of th solution in the cell itself.

Pfeffer overcame these difficulties by the employment of an ai manometer in place of the open water manometer. The apparatus as further modified by Adie,[1] is shown in Fig. 88. The glass cove B is fixed to the porous cell by means of sealing wax ; the manomete is closed above, and contains air above C, and mercury from C to D A solution of cane-sugar of the required strength is poured into th cell through the tube E until the remainder of the apparatus is com pletely filled, the tube E is then sealed at the blow pipe, and the cell is immersed in a vessel of pur water.

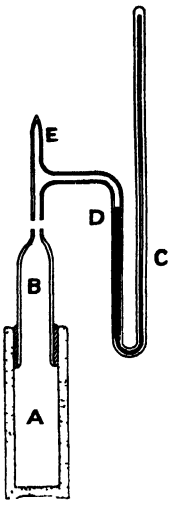


FIG. 88.

The water enters slowly, and the pressure o the air in the manometer rises until it become constant after several days or perhaps weeks. Th quantity of water that enters the cell is so smal that the dilution is of little importance, and i may, of course, be estimated by the diminution i volume of the air.

Further great improvements in the construc tion of the apparatus have been made by Morse and his co-workers in America, and by the Ear of Berkeley and E. G. J. Hartley[2] in England Morse's apparatus is similar in principle to th simple form shown in Fig. 88, but very great car was taken in the selection, preparation, and ad mixture of suitable clays, and in making the pots which were so constructed as to withstand high pressures ; the metho of attachment of the manometer tube to the pot was greatly im proved ; a hollow needle was provided to facilitate the closing of th cell at the beginning of an experiment and the subsequent opening o the cell ; the temperature of the bath and of the air was very care fully regulated, and various sources of error were eliminated. Morse' apparatus and that of Lord Berkeley and Hartley are figured an fully described in Findlay's "Osmotic Pressure".

[1] *Trans. Chem. Soc.*, **59**, 344 (1891).

[2] *Amer. Chem. Journ.*, **26**, 80 (1901) ; **28**, 1 (1902) ; **29**, 137 (1903) ; **32**, 9 (1904) ; **34**, 1 and 39 (1905) ; **37**, 324, 425, and 558, **38**, 175 (1907) ; **39**, 667, 40 1, 194, 266, and 325 (1908) ; **41**, 1 and 557 (1909) ; **45**, 91, 237, 283, 517, and 55 (1911) ; **48**, 29 (1912).

[3] *Trans. Roy. Soc.*, **206**, 486 (1906).

The method employed by Lord Berkeley and Hartley is different from that of Morse. A porcelain tube is used and the semi-permeable membrane is deposited as near the outer surface as possible. The water is inside the tube and the solution outside, and the solution is subjected to a gradually increasing pressure until the flow of the solvent through the membrane is just reversed in direction. The apparatus is specially adapted for the measurement of the osmotic pressures of concentrated solutions.

In continuation of the work of Morse and Frazer, Frazer and Myrick [1] have recently modified the original apparatus by depositing the membrane on the outer surface of the cell, and placing the solution outside and the water inside. Very much higher pressures could thereby be dealt with, and the osmotic pressures of the most concentrated solutions of cane-sugar determined. The pressure required to produce equilibrium is measured by the alteration of the resistance of a metallic conductor formed of "Thirlo" wire, an alloy of copper, manganese, and aluminium.

The experiments were carried out at 30° and the results are in close agreement with those of Lord Berkeley and Hartley, corrected from 0° to 30° by the use of the ordinary gas constant.

Grams of sucrose per litre. . . .	180·1	300·2	420·3	540·4	660·5	750·6
Grams of sucrose per 1000 grams of water	202·0	370·0	569·0	820·0	1133·0	1430·0
Osmotic pressure (F. and M.) . . .	15·59	29·78	47·88	73·06	109·1	148·8 atm.
Osmotic pressure (B. and H.) . . .	15·48	29·72	48·81	74·94	111·87	148·46 „

The highest pressure reached by Frazer and Myrick was 270 atmospheres.

Amongst other methods of measuring osmotic pressure the following may be mentioned :—

1. Dynamical method of Lord Berkeley and Hartley.[2] In this the initial rate of flow of the solvent into the solution is measured, and the mechanical pressure which would produce the same rate of flow of pure water through the same membrane is also measured. This mechanical pressure should be numerically equal to the osmotic pressure, and for dilute solutions the results obtained were satisfactory.

[1] *Journ. Amer. Chem. Soc.*, **38**, 1907 (1916).
[2] *Proc. Roy. Soc.*, **82**, 271 (1909).

2. Trouton's solubility method.[1] The solubility of water in ether is diminished by dissolving a substance such as cane-sugar in the water, but it is increased by external pressure. With a solution containing 600 grams of sucrose to the litre, in contact with ether, an external pressure of 79 atmos. was required to enable the ether to take up as much water as it would have done if in contact with pure water at atmospheric pressure. For a solution of this strength the osmotic pressure, deduced from Lord Berkeley and Hartley's data, would be 81 atmospheres.

3. Electrolytic method of Cohen and de Bruin.[2] A Pfeffer pot containing the solution is closed by a stopper through which passes a capillary tube and a copper wire to which is attached a copper electrode. A second copper electrode is placed in the water outside the pot. After the solution has risen a little in the capillary tube an electromotive force E_1, just sufficient to stop the rise, is applied to the electrodes, and the height h_1 of the liquid in the capillary is measured. From this, $\mathbf{p} - h_1 = kE_1$, where k is a constant. A second measurement, after breaking the circuit and waiting a short time, gives $\mathbf{p} - h_2 = kE_2$, and from the two equations $\mathbf{p}$ may be calculated. The method is rapid and very little solvent passes into the solution.

Indirect methods of determining osmotic pressure will be considered later.

Quantitative experiments with cane-sugar solutions of different concentrations and at different temperatures, carried out by Pfeffer, and later by Adie, Griffiths, and others, prove that for dilute solutions the osmotic pressure is directly proportional to the concentration, and, approximately at any rate, to the absolute temperature. The osmotic pressure of a dilute cane-sugar solution may, in fact, be calculated by the formula—

$$\mathbf{p} = n \times 0{\cdot}649(1 + 0{\cdot}00367t) \text{ atmos.}$$

where n is the percentage of cane-sugar.

Laws of Osmotic Pressure.

It was pointed out by Van't Hoff[3] that the laws of osmotic pressure in the case of dilute solutions are similar to those relating to

[1] *Proc. Roy. Soc.*, **86**, 149 (1912).

[2] *Proc. K. Akad. Wet. Amsterdam*, **16**, 160 (1913).

[3] *Arch. Néerland.*, 20 (1885), *K. Svensk. Ak. Hand.*, 21; *Zeit. physik. Chem.*, 1, 481 (1887).

gascous pressure. Pfeffer, as already stated, found that the osmotic pressure of a dilute cane-sugar solution was directly proportional to the weight of cane-sugar in 100 grams of the solution, which may be taken, without sensible error, to occupy 100 c.c.

Let c be the number of gram-molecules of cane-sugar dissolved in 1 litre of solution at a given temperature; then—

$$p = c \times \text{constant.}$$

But $c = \frac{1}{V}$, where V is the volume of solution in litres that contains 1 gram-molecule of sugar; therefore—

$$pV = \text{const. at constant temperature.}$$

The range of temperature over which experiments are possible is limited, but it may be stated that the results obtained by Pfeffer are not inconsistent with the statement that the osmotic pressure is directly proportional to the absolute temperature, or for a 1 per cent. cane-sugar solution—

$$p = 0{\cdot}649 \times \frac{T}{273}.$$

Confirmatory evidence was afforded by experiments with living cells, which showed that solutions of different substances in osmotic equilibrium with the cell contents at 0° were also in equilibrium at 34°. The relation of osmotic pressure to temperature is therefore the same for aqueous solutions of different substances.

The equation for gases—

$$PV = T \times \text{constant},$$

representing the laws of Boyle and Gay Lussac, is therefore found to hold good for substances in dilute solution.

The value of the constant in the above equation may be deduced from Pfeffer's observation that the osmotic pressure of a 1 per cent. cane-sugar solution is 0·649 atmos.

The volume of 100 grams of solution at 0° = 99·7 c.c.; that is to say, 1 gram of cane-sugar is present in 99·7 c.c. of solution, and therefore 1 gram-molecule, or 342 grams of sugar in 342 × 99·7 c.c., or 34·1 litres. But in the equation for gases—

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

R = 0·0821, and if V = 34·1 litres for 1 gram-molecule of gas, and T = 273, then—

$$P = \frac{0{\cdot}0821 \times 273}{34{\cdot}1} = 0{\cdot}658 \text{ atmos.}$$

The agreement of this pressure with that found by Pfeffer—0·649 atmos.—is as close as could be expected from the nature of the experiments, and the conclusion is therefore apparently justified that the equation—

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

is applicable not only to gases under moderate or low pressures, but also to dilute solutions; in other words, that the osmotic pressure of a substance in dilute solution is equal to the pressure which it would exert as a gas at the same temperature and occupying the same volume as the solution, if it could exist as a gas under such conditions. Griffiths has determined the osmotic pressures of very dilute solutions of cane-sugar, and has obtained an excellent agreement between the observed pressures and those calculated from the formula $PV = RT$.

The experiments carried out, however, by Morse and his co-workers, and by Lord Berkeley and Hartley are far more complete and trustworthy than the earlier ones. As a result of their investigations, which extended over many years, Morse and his collaborators find that the osmotic pressures of even fairly dilute solutions of cane-sugar are higher than the calculated gas pressures, as will be seen from the following table which gives the pressures at 20° observed and calculated.

Weight Normal Concentration.[1]	Volume Normal Concentration.[2]	Osmotic Pressure Observed in Atmosphere.	Osmotic Pressure in Atmosphere Calculated according to	
			Van't Hoff.	Morse.
0·1	0·098	2·59	2·34	2·39
0·2	0·192	5·06	4·59	4·78
0·3	0·282	7·61	6·74	7·17
0·4	0·369	10·14	8·82	9·56
0·5	0·452	12·75	10·81	11·95
0·6	0·533	15·39	12·72	14·34
0·7	0·610	18·13	14·58	16·73
0·8	0·684	20·91	16·36	19·12
0·9	0·756	23·72	18·08	21·51
1·0	0·825	26·64	19·73	23·90

Morse points out that a better agreement is obtained if the theoretical values are calculated on the assumption that the osmotic

[1] Gram-molecules of sugar in 1000 grams of water.

[2] Gram-molecules of sugar in 1000 c.c. of solution.

pressure is equal to the pressure which the sugar would exert as a gas occupying a volume equal to that of the solvent at 4° instead of the solution at the experimental temperature. The difference naturally becomes more marked as the concentration increases, the calculated pressure for a normal solution being 23·90 instead of 19·73 atmos. But, even so, the observed osmotic pressure is considerably higher than the calculated.

As regards the relation between osmotic pressure and temperature, Morse[1] gives the following table showing the ratio of the observed osmotic pressure to the gas pressure calculated by his method for the same concentrations at temperatures from 0° to 80°.

Weight Normal Concentration.	Ratio of Osmotic Pressure to Gas Pressure at											
	0°.	5°.	10°.	15°.	20°.	25°.	30°.	40°.	50°.	60°.	70°.	80°.
0·1	(1·106)	1·082	1·082	1·082	1·084	1·084	1·000	1·003	1·000	1·000	—	—
0·2	1·061	1·063	1·060	1·061	1·062	1·059	1·020	1·011	1·002	1·001	—	—
0·3	1·061	1·058	1·059	1·061	1·060	1·060	1·031	1·024	1·009	0·999	—	—
0·4	1·060	1·059	1·060	1·059	1·060	1·059	1·040	1·038	1·017	1·000	—	—
0·5	1·069	1·067	1·066	1·068	1·067	1·065	1·050	1·046	1·025	1·006	1·000	—
0·6	1·077	1·074	1·073	1·073	1·073	1·071	1·060	1·054	1·032	1·015	1·002	—
0·7	1·083	1·084	1·083	1·083	1·084	1·083	1·069	1·059	1·041	1·020	0·999	—
0·8	1·093	1·093	1·092	1·093	1·093	1·093	1·081	1·067	1·049	1·027	1·008	1·001
0·9	1·104	1·102	1·102	1·102	1·103	1·102	1·089	1·076	1·059	1·033	1·015	1·000
1·0	1·115	1·115	1·113	1·115	1·115	1·113	1·101	1·085	1·071	1·044	1·023	1·000

It will be seen that while the osmotic pressures are higher than those calculated at the lower temperatures, the ratios diminish above 25° and become equal to unity at a temperature which rises as the concentration increases. Below 25° it would seem that the osmotic pressure is proportional to the absolute temperature, but the range of temperature is not great enough to show whether the proportionality would again hold above the temperatures at which the ratio becomes equal to unity.

It should be pointed out, however, that the Earl of Berkeley and Hartley[2] have recently determined the osmotic pressures of more dilute solutions than those they previously studied, and have obtained values lower than those of the American observers. To facilitate comparison with the table on p. 304 the concentrations are given in gram-molecules of cane-sugar in 1000 grams of water.

[1] *Amer. Chem. Journ.*, **48**, 29 (1912). [2] *Proc. Roy. Soc.*, **92**, 477 (1916).

Weight Normal Concentration.	Osmotic Pressures.		
	Lord Berkeley and Hartley.	Morse.	Difference per Cent.
0·0986	2·23	2·13	8·2
0·2959	6·85	7·02	2·4
0·5963	14·21	14·38	1·2
0·8892	21·87	21·92	0·2
0·9862	24·55	24·57	0·1

At the lowest concentration the osmotic pressure observed by Lord Berkeley and Hartley differs but slightly from the calculated gas pressure.

In view of the fact that the osmotic pressures of very dilute solutions appear to follow the same laws, as regards volume and temperature, as gases, Van't Hoff suggested that osmotic pressure might be explained as due to the bombardment of the membrane by the molecules of the solute, but he did not insist on this and admitted that it might be due to the attraction between solvent and solute. The bombardment theory has been accepted by many physicists, and attempts have been made to explain the deviation from the simple law at higher concentrations on the lines of Van der Waals' theory.

Among the numerous equations tried, the two following, suggested by the Earl of Berkeley,[1] were found to give good results over the range of the actual observations :—

$$(A/v - p + a/v^2)(v - b) = RT \quad . \quad . \quad . \quad (1)$$

$$(A/v + p - a/v^2)(v - b) = RT \quad . \quad . \quad . \quad (2)$$

The units adopted were the atmosphere and the litre, and R was taken as equal to 0·08207. In the first equation v = the volume of solvent which contains 1 gram-molecule of solute, and in the second equation v = the volume of solution which contains a gram-molecule. The temperature was 0° C.

The calculated and observed results for cane-sugar are given below; the concentration is in grams per litre of solution. The highest osmotic pressure was not directly measured, but was calculated from vapour pressure measurements. The constants for the equations were calculated from the three highest pressures, and were used for the calculation of the lower pressures.

[1] *Proc. Roy. Soc.*, 79A, 125 (1907); *Trans. Roy. Soc.*, **209**, 177 and 319 (1909).

Concentration.	v.		Osmotic Pressure.		
	Of Eqn. (1).	Of Eqn. (2).	From Eqn. (1).	From Eqn. (2).	Observed.
850	0·18270	0·39722	(183·0)	(183·0)	183·0
760	0·23656	0·45025	(133·7)	(133·7)	133·7
660	0·29883	0·51177	(100·8)	(100·8)	100·8
540	0·41431	0·62570	68·4	67·7	67·5
420	0·59471	0·80492	45·0	43·4	44·0
300	0·91883	1·12764	27·7	25·4	26·8
180	1·67368	1·88094	14·6	12·2	14·0

The constants are—	A	*a*	*b*
For equation (1) . .	45·3689	3·5696	0·05266
,, (2) . .	6·7166	7·2960	0·25139

The values of T, **p**, *v* for the critical point derived from the two equations are impossible ones, and it therefore appears, as the Earl of Berkeley points out, that the equations can only be regarded as holding good over a limited range of values.

Moreover, it has been pointed out by Callendar that this method of attacking the problem is not satisfactory, because so many types of equation are possible and the constants are purely empirical.

Findlay in "Osmotic Pressure," p. 30, recommends the general thermodynamic equation as the starting point, and the consideration of *perfect* or *ideal* solutions rather than infinitely dilute solutions, a method first adopted by the Dutch physicists Boldingh, Van der Waals, and van Laar in the years 1890 to 1894.

Just as in the study of the vapour pressure, specific volumes, critical constants, and so on, of mixed liquids it is best to start with closely related substances which exhibit no heat changes or volume changes on admixture,[1] so also with the osmotic pressures the simplest results will be obtained with such ideal mixtures or solutions.

The following general equation, valid for all concentrations, has been obtained for such solutions,

$$\mathbf{p} = p - p_0 = \frac{RT}{V_0}[-\log_e(1-x)] - \tfrac{1}{2}a\mathbf{p}^2$$

where p is the pressure on the solution and p_0 that on the solvent, when the solvent and solution are in equilibrium through a membrane permeable only to the solvent; x is the molar fraction of the solute or the ratio of the number of molecules of the solute to the total number of molecules; V_0 is the molecular volume of the solvent

[1] Pres. Address to Chem. Section of British Association, Cambridge, 1904.

under the standard pressure; and a is the coefficient of compressibility.

Since a is negligible except under very high pressures the equation may be simplified to

$$p = \frac{RT}{V_o}[-\log_e(1-x)] - \frac{RT}{V_o}(x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 + \ldots) \quad . \quad . \quad (A)$$

Most of the direct determinations of osmotic pressure have been made with aqueous solutions, which are not "ideal," but the osmotic pressure may be determined indirectly from the vapour pressures of solvent and solution (p and p' respectively) thus,

$$p = \frac{RT}{V_o}\log_e\frac{p}{p'} \quad . \quad . \quad . \quad . \quad (B)$$

The vapour pressures of mixtures of ethylene dibromide and propylene dibromide have been determined by Zawidski (p. 275) and the osmotic pressures have been calculated by Lewis.[1] It is found that the osmotic pressures given by the formula (B) agree extremely well with those calculated by the thermodynamical equation (A), but not at all with those calculated by the formula of Van't Hoff or of Morse.

As regards aqueous solutions, the heat of dilution is of great importance in such a case as that of sulphuric acid, but with cane-sugar and most neutral organic compounds the chief points to be considered are (*a*) the association of the water molecules and (*b*) the possible formation of hydrates. Findlay [2] shows that by taking the association factor for water as 1·65 and assuming that cane-sugar forms a pentahydrate in solution, a very fair agreement between the observed and calculated osmotic pressures is obtained. At the highest concentration the calculated pressure is a little too high, whereas if the association of the water molecules is neglected it is a little too low. There is, however, some doubt as to the degree of association of water and the degree of hydration of the sugar.[3]

That the osmotic pressure of cane-sugar solutions is proportional to the absolute temperature between 0° and 25°, but falls below the

[1] *Journ. Amer. Chem. Soc.*, **30**, 668 (1908).

[2] "Osmotic Pressure," p. 41.

[3] *Cf.* Frazer and Myrick, *loc. cit.*, and Wood, *Trans. Faraday Soc.*, **11**, 29 (1915).

calculated value at higher temperatures, may be due to the dissociation of the pentahydrate above 25°.

Various theories have been brought forward to explain the nature of osmotic pressure :—

1. The bombardment theory, based on the statement that in very dilute solutions the osmotic pressure is equal to the gaseous pressure which the solute would exert at the same temperature if it occupied the same volume as the solution.

The thermodynamical equation involves the volume of the solvent, or rather the increase of volume when the solvent is added to the solution, and not the volume of the solution. In the case of a hydrated solute, it would be the volume of the uncombined solvent.

2. Attempts have been made by Jager[1] and others to connect osmotic pressure with surface tension, but no exact relationship between the two has been discovered.

3. Moritz Traube considered that the osmotic pressure was due to the attraction between the molecules of the solute and those of the solvent, and this idea has been developed by I. Traube,[2] Kahlenberg,[3] and Armstrong.[4] Some chemists think that a considerable number of unstable hydrates may be formed in aqueous solution, others believe that one or a very few stable hydrates are formed.

4. Callendar[5] considers that the semipermeable membrane consists of fine capillaries which are not wetted by the liquids but which allow the passage of vapour. With a pure solvent at one end of a capillary and solution at the other end, distillation from solvent to solution would take place unless the vapour pressure of the solution were made equal to that of the solvent by a hydrostatic pressure on the solution.

5. Tinker[6] has determined the changes in concentration brought about by immersing dried colloidal copper ferrocyanide in cane-sugar solutions of various strengths. He finds that water is taken up by the ferrocyanide but that sugar is not, and that the amount of water taken up decreases as the strength of the solution increases.

[1] *Wiener Ber.*, **100**, 245 and 493 (1891).

[2] *Ber.*, **17**, 2294 (1884); *Phil. Mag.* [VI.], **8**, 704 (1904), Pflugers Archiv der Physiologie (1904).

[3] *Journ. Physical Chem.*, **10**, 141 (1906).

[4] *Proc. Roy. Soc.*, **78**, 264 (1906).

[5] *Ibid.*, **80**, 466 (1908); *Proc. Roy. Inst.*, **19**, 485 (1911).

[6] *Proc. Roy. Soc.*, **93**, 268 (1917).

He concludes from his experiments that copper ferrocyanide forms a stable hydrate, $Cu_2Fe(CN)_6,3H_2O$, and that in dilute solutions more water is taken up by adsorption on to the surfaces of the colloidal particles. In the case of a copper ferrocyanide membrane the adsorbed moisture-content is greater on the water side of the membrane than it is on the solution side, consequently a continual flow across the membrane from the water to the solution must take place unless sufficient pressure is applied to the solution to prevent such diffusion.

Kahlenberg[1] has carried out a large series of qualitative experiments on osmosis in which various liquids and septa were employed. The process of admixture of solution and solvent in the cell was accelerated by stirring.

Kahlenberg states that osmotic pressures are equilibrium pressures, and that in the osmotic process there is always a current in both directions, though the major current may, in specific cases, be so much stronger than the minor that the latter almost sinks into insignificance. He terms the septum "semipermeable" in such cases, and he found that vulcanized caoutchouc was "semipermeable" when used as a septum separating a pyridine solution of silver nitrate, lithium chloride, or cane-sugar from the pure solvent. Kahlenberg made quantitative measurements of osmotic pressure with these solutions, and found that the laws relating to gases did not hold; he therefore concludes that these laws cannot serve as a basis for a satisfactory theory of solutions.

It may be pointed out, however, that the theory assumes that the membrane is absolutely impermeable to the solute, and that deviations must occur if the solute is able to penetrate the septum. An imperfectly semipermeable membrane would, in fact, behave like a piston which was not quite air-tight, the measured pressures of a compressed gas being necessarily too low. Morse,[2] in his experiments on the osmotic pressure of cane-sugar solutions, found that with a copper ferrocyanide membrane a pressure of 12 atmospheres remained quite constant for 60 days.

That the osmotic pressure, which is measured by the hydrostatic pressure of the column of solution in a cell of Pfeffer's original simple form, is simply related to the vapour pressures of

[1] *Journ. Physical Chem.*, 10, 141 (1906).
[2] *Amer. Chem. Journ.*, 45, 558 (1911).

the solution and solvent, is evident from the following considerations :— [1]

Let a vessel A (Fig. 89), containing a small quantity of a solution, be placed in a shallow cylindrical vessel B containing the pure solvent; let the apparatus be covered by a bell-jar C connected with a pump, and let all air be removed from the vessel and the liquids. The vapour pressure of the pure solvent will be higher than that of the solution, and distillation will therefore take place. The volume of the solution will increase, and if the temperature be kept quite constant, and time enough be allowed for diffusion of the condensed solvent into the solution to take place completely, a state of equilibrium will finally be attained when the diluted solution has reached a certain height h measured from the level of the pure solvent.

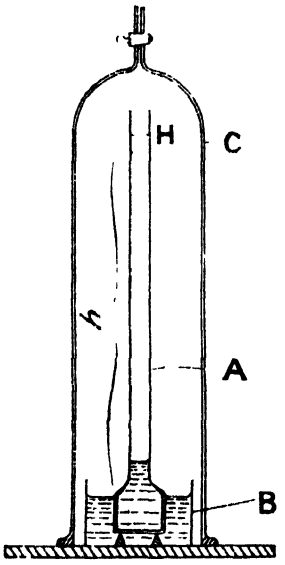


FIG. 89.

The vapour pressure of the pure solvent will still be higher than that of the solution at their respective surfaces, but the pressure of the saturated vapour just above the surface of the solvent is greater than that of the vapour at the height H, by the pressure of the column of vapour between the two levels, $\frac{s \times h}{76s'}$ atmos., where s is the mean mass of 1 c.c. of the vapour, and s' is the mass of 1 c.c. of mercury.

Calling the vapour pressure of the solvent and solution p and p' respectively, equilibrium takes place when $p - p' = \frac{sh}{76s'}$.

Imagine, now, that without disturbing the apparatus, the bottom of the cylinder is replaced by a truly semipermeable diaphragm. The solvent could now pass into or out of the cylinder, but if it were to do so the height of the column of solution above the level of the solvent would be altered, and there would no longer be

[1] Arrhenius, *Zeit. physik. Chem.*, **3**, 115 (1889).

equilibrium between the vapour pressure of the solution and the pressure of the vapour of the pure solvent at the new height H'.

Distillation in one direction or the other would therefore take place and would go on continuously. There would, in fact, be a perpetual circulation, the solvent passing in one direction by osmosis through the diaphragm, and in the other direction by distillation.

It is, in fact, evident that the osmotic pressure of a solution, as measured by the hydrostatic pressure of the solution in the vessel with a semipermeable base, must be definitely related to the difference between the vapour pressures of solvent and solution at the same temperature. The osmotic pressure may, indeed, be calculated from the lowering of the vapour pressure. The theory of this relation is discussed in the volume on Thermodynamics; it is shown that the osmotic pressure may also be calculated from the depression of the freezing point, the rise of the boiling point, and also, as Nernst [1] has shown, by the diminution in the solubility of one liquid in another caused by the dissolution in it of a third substance.

It will be sufficient here to give the formulæ expressing these relations. The osmotic pressure may be calculated—

1. From the lowering of the vapour pressure, by the equation—

$$\mathbf{p} = \frac{p - p'}{p'} \times \frac{82{\cdot}1\mathrm{T}}{\mathrm{M}} \times s \text{ atmos.}$$

where T is the absolute temperature, s is the specific gravity of the solution at T°, and M is the molecular weight of the solvent; or, for stronger solutions, with greater accuracy by the formula—

$$\mathbf{p} = \frac{82{\cdot}1\mathrm{T}}{\mathrm{M}} \times s \log_n \frac{p}{p'} \text{ atmos.};$$

2. From the rise of the boiling point, by the equation—

$$\mathbf{p} = \frac{1000s \times \mathrm{L}}{24{\cdot}17} \times \frac{\Delta t}{\mathrm{T}} \text{ atmos.}$$

where L is the heat of vaporization of the solvent, Δt the rise of the boiling point, and T the boiling point of the pure solvent on the absolute scale of temperature;

3. From the depression of the freezing point, by the equation—

$$\mathbf{p} = \frac{1000s \times \mathrm{L}'}{24{\cdot}17} \times \frac{\Delta t}{\mathrm{T}} \text{ atmos.}$$

[1] *Zeit. physik. Chem.*, **6**, 16 (1890).

where L′ is the heat of fusion of the solvent, T its freezing point on the absolute scale, and Δt the depression of the freezing point;

4. From the diminution in solubility, by the equation—

$$p = \frac{\mathfrak{S} - \mathfrak{S}'}{\mathfrak{S}'} \times \frac{82{\cdot}1T}{M} \times s \text{ atmos.}$$

where $\mathfrak{S}$ is the solubility of the first liquid in the second before the addition of the solute, and $\mathfrak{S}'$ the solubility after its addition, T is the absolute temperature, and s and M are the specific gravity and molecular weight, respectively, of the first liquid.

CHAPTER XVI.

DISSOLUTION AND VAPORIZATION.

It has been pointed out (pp. 272, 275) that the miscibility of two liquids and the solubility of a solid in a liquid generally increase with rise of temperature, and that Alexéeff[1] was the first to observe the gradual change from partial miscibility of two liquids at a low temperature to infinite miscibility at a higher temperature. This temperature, at which two liquids become miscible in all proportions, has been termed by Orme Masson[2] the critical solution temperature; and he has called attention, not only to the analogy between the critical solution temperature of two liquids and the critical temperature of a pure substance, but also, more generally, to that between dissolution (or admixture) and vaporization.

Consider two liquids, miscible within limits at the ordinary temperature, placed in contact with each other. For convenience, call the liquid A the solute, and B the solvent. Exerting a definite osmotic pressure, the liquid A proceeds to dissolve until, if there is sufficient present, the maximum osmotic pressure is reached and the solution becomes saturated; just as a liquid, when placed in a vacuous space, proceeds to evaporate until the maximum vapour pressure is exerted. At the same time dissolution of the solvent in the solute takes place until equilibrium is reached.

Two layers will thus be formed—one, which may be termed the A layer, consisting of solute A, containing a little of the solvent B in solution; the other, the B layer, consisting of solvent with some dissolved solute. If the amount of solute is insufficient, the whole of it will dissolve, and a single layer of unsaturated or just saturated solution will be formed; in the same way that unsaturated or just saturated vapour may be formed when a small amount of liquid is placed in a vacuous space. The volume occupied by 1 gram of solute is termed by Masson the specific solution volume; that occupied by 1 gram-molecule the molecular solution volume. It is clear that

[1] *Loc. cit.* [2] *Nature*, **43**, 345 (1891); *Zeit. physik. Chem.*, **7**, 500 (1891).

the specific solution volume of the solute in the A layer must be relatively small, and in the B layer relatively great, just as the specific volume of a liquid under ordinary conditions is small compared with that of its saturated vapour. The specific solution volume of A in the unsaturated solution must also obviously be greater than in the saturated solution, just as the specific volume of vapour is greater when unsaturated than when saturated.

Suppose, now, that the temperature is raised when both layers are present. The osmotic pressure increases, and more solute dissolves, until the solution again becomes saturated; at the same time more of the solvent dissolves in the solute. The specific solution volume of the solute in the A layer thus increases, while that in the B layer diminishes. [The changes in specific solution volume due to expansion by heat are generally inconsiderable compared with those due to increase in miscibility; the increase in specific solution volume of the A layer is slightly greater, and of the B layer very slightly less, than if there were no expansion.] The case of a pure liquid is quite analogous; on raising the temperature further evaporation takes place until the vapour again becomes saturated. The specific volume of the liquid becomes greater owing to expansion, that of the vapour less owing to increased evaporation.

Each time that the temperature is raised the osmotic pressure and the miscibility increase; the specific solution volume of the solute in the A layer increases, while it diminishes in the B layer.

If either solute or solvent is present in insufficient quantity, it will eventually be completely dissolved in the other layer. In the same way, if the liquid placed in the vacuous space is too small in quantity, it will completely evaporate, and if too large it will completely fill the space.

If, however, the quantities are such that the two layers remain, the specific solution volume of the solute in the A layer will at last become equal to that in the B layer. The two layers will, in fact, become identical, and the two liquids infinitely miscible, and the critical solution temperature will be reached. There is thus a close analogy with the critical temperature of a pure substance, the temperature at which the specific volume of the liquid becomes equal to that of its saturated vapour.

In many cases the substance is solid at the ordinary temperature, but the *solution melting point*, that is to say, the temperature at which the solid in contact with a solvent melts, is generally lower than the

ordinary melting point, because the melted solid dissolves a portion of the solvent, and the freezing point of a solution is generally lower than that of a pure substance.

Among other solutions Alexéeff examined those of phenol, salicylic acid, benzoic acid, aniline phenylate, and aniline in water, and of chlorobenzene, benzene, toluene, aniline, and mustard oil in molten sulphur, and in each of these cases he observed reciprocal partial solubility at lower temperatures, leading to infinite miscibility at some definite higher temperature. In several cases, also, he observed that the solution melting point was lower than the melting point of the pure substance.

Alexéeff determined the temperatures at which different relative quantities of the same two liquids are just converted into homogeneous liquids; in other words, he determined the strengths of the saturated solutions corresponding to different temperatures.

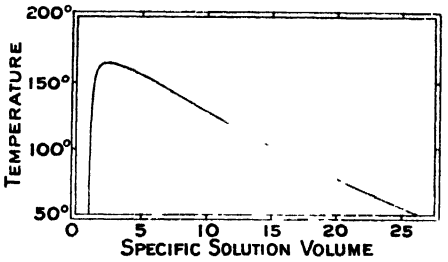


FIG. 90.

From Alexéeff's results Masson calculated the weight of water capable of dissolving or of being dissolved by 1 gram of aniline at each observed temperature so as to form a saturated solution. From the known specific volumes of aniline and water Masson then calculated the approximate specific solution volumes of aniline, on the assumption that the volume of solution is equal to the sum of the volumes of the components. Finally, he plotted the specific solution volumes against the temperatures. The actual data are given in the table on p. 317, and the curves are shown in Fig. 90. The specific volumes of isopentane are plotted against the temperatures in Fig. 91, in order that the two diagrams may be compared.

In the isopentane diagram a few isobaric curves for liquid and saturated vapour are given. The corresponding curves for aniline and water cannot be drawn, because the osmotic pressures have not yet been determined. It is also impossible as yet to draw the

diagram representing the relations between osmotic pressure and specific solution volume at constant temperature, but with regard to these relations and to the comparison of the diagram with the iso-

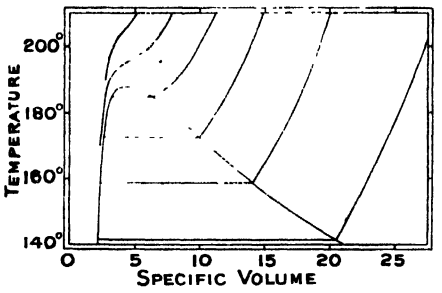


FIG. 91.

thermal diagram for gases and liquids (Figs. 21 and 22), the following points may be noticed.

Temperature.	Specific Solution Volume of Aniline.	
	In Aniline Layer.	In Water Layer.
Degrees.		
8·0	1·015	—
16·0	—	32·16
25·0	1·036	—
39·0	1·053	—
55·0	—	28·27
68·0	1·087	—
77·0	—	19·55
137·0	1·297	—
142·0	—	7·696
156·0	—	5·248
157·5	1·498	—
164·5	—	3·412

When unsaturated isopentane vapour is compressed at constant temperature the volume diminishes and the pressure rises until the vapour becomes saturated. Liquefaction then takes place, and the pressure remains quite constant until it is complete, the volume diminishing greatly during this process. Lastly, the pressure rises again, but the volume of liquid diminishes very slowly.

The specific solution volume of aniline in the B layer depends on the concentration of the solution; it may be diminished by removal of water, and for dilute solutions, as Pfeffer has shown, the osmotic pressure is directly proportional to the concentration, or

inversely proportional to the specific solution volume. For stronger solutions there is little doubt that the pressure rises somewhat more slowly; in other words, the product pv falls in the same way that pv does for compressed gases. In any case, the specific solution volume diminishes and the osmotic pressure increases until the solution becomes saturated. On further removal of water the second phase—the A layer, consisting of aniline saturated with water—appears, and its volume slowly increases, while that of the B layer rapidly diminishes. The concentration, and therefore the osmotic pressure, of each layer remains unaltered during this process, and, as the two layers are in equilibrium, the osmotic pressure must be the same for both. The layer B finally disappears, and, as the remaining A layer contains very little water, hardly any further change in the specific solution volume of the aniline can be effected by removal of solvent, but the corresponding rise in osmotic pressure is very great.

The process may be exactly reversed by the gradual addition of water to aniline. There is thus a very close analogy between the changes produced by compressing unsaturated isopentane vapour and those caused by concentrating an aqueous solution of aniline by gradual removal of water.

But the analogy is even closer, for by careful removal or addition of solvent it is generally possible to obtain supersaturated solutions. Thus, starting with the unsaturated B layer, it would be possible to obtain a supersaturated solution of aniline in water, or, beginning with the unsaturated A layer, a supersaturated solution of water in aniline would be obtained. In neither case, however, could the process, as a rule, be carried very far; after a time an abrupt separation into the A and B layers would take place. The osmotic pressure of the supersaturated B layer would be greater, and of the supersaturated A layer less than that of the saturated solutions, and with the sudden formation of the two layers the osmotic pressure would at once fall or rise to that of the saturated solution.

The formation of the supersaturated aqueous solution of aniline is precisely analogous to the formation of a supersaturated vapour by compression beyond the condensing point at constant pressure, as observed by Aitken. On the other hand, the supersaturated A layer is analogous to a superheated liquid, which may be obtained either by lowering the pressure below the vapour pressure of the liquid at constant temperature, or by raising the temperature above the boiling point at constant pressure. In either case the change

of state, when it occurs, takes place abruptly, and the pressure at once falls or rises to the true vapour pressure (or the temperature falls or rises to the true boiling point).

If the compression of the vapour or the concentration of the solution is carried out at a higher temperature, but still below the critical or critical solution temperature, the changes observed are similar in kind, the only differences being that the specific volume and specific solution volume of the saturated vapour and B layer respectively are smaller, while those of the liquid and A layer respectively are greater than at the lower temperature.

When the process is carried out at the critical and critical solution temperatures, respectively, the separation into two phases does not take place, but in both cases, between certain limits of volume, the opalescence so characteristic of the critical state is observed. This opalescence is also to be seen in both cases at temperatures slightly above and slightly below the critical temperature.

At still higher temperatures no visible change whatever occurs during compression, but there is a continuous rise of gaseous or osmotic pressure.

Law of Cailletet and Mathias.—Rothmund,[1] who has carried out an important investigation of the influence of temperature on the miscibility of liquids, discusses the question whether the law of Cailletet and Mathias is applicable to mixtures of liquids. Strictly speaking, the density of one of the substances, that is to say, the mass of it in 1 c.c. of liquid, should be determined for each layer at each temperature. The two densities would then correspond to those of liquid and saturated vapour in the case of a pure substance. The mean densities should then be plotted against the temperature. In order to do this, however, a knowledge not only of the composition but also of the density of each layer would be required, and in most cases these densities have not been ascertained. Rothmund, however, points out that if the concentration of the liquid A is expressed by the equation—

$$C = \frac{m_A}{m_A + m_B} \times 100$$

where m_A and m_B are the masses of the two liquids, and if C_1 and C_2 are the concentrations of the liquid A in the two layers, then the

[1] *Zeit. physik. Chem.*, **26**, 433 (1898).

mean concentration at any temperature t should be given by the formula—

$$\frac{C_1 + C_2}{2} = A + Bt,$$

and the critical concentration would be—

$$C_c = A + Bt_c.$$

The law of the rectilinear diameter, stated in this form, was found to hold in the case of eight pairs of substances which became infinitely miscible at high temperatures.

In the case of aniline and water, investigated by Alexéeff, Masson has calculated the approximate specific solution volumes of aniline in the two layers, and the reciprocals of these values give the required densities.

The densities were plotted against the temperatures, and the values given in the table below were read from the curves. The mean densities given in the last column were calculated from the equation—

$$s_t = 0{\cdot}512 - 0{\cdot}00048t.$$

Temperature	Densities of Aniline.			
	In A Layer.	In B Layer.	Mean.	Mean Calculated.
Degrees.				
20	0·972	0·030	0·501	0·502
40	0·951	0·033	0·492	0·493
60	0·928	0·040	0·484	0·483
80	0·902	0·050	0·476	0·474
100	0·867	0·067	0·467	0·464
120	0·821	0·089	0·455	0·454
140	0·762	0·127	0·445	0·445
150	0·719	0·160	0·440	0·440
160	0·633 (?)	0·221	0·427 (?)	0·435

The agreement is very good except at 160°, but the number of observations is small, and the density of aniline in the A layer at 160° was obtained by extrapolation.

It may be noticed that, as in the case of pure liquids, the coefficient B in the formula—

$$s_t = A + Bt$$

is negative, and that it is of the same order of magnitude; thus for normal pentane the value of B is – 0·00046.

In the case of two pairs of liquids, triethylamine and water, and

β-collidine and water, Rothmund found that the miscibility increased with fall of temperature, reaching infinity at about 18·7° with the first pair, and at about 6·4° with the second.

If, as has been suggested (p. 272), the increasing miscibility with fall of temperature is due to the attraction between the unlike molecules becoming greater relatively to that between the like molecules, there would be no close analogy between the inferior and superior critical solution temperatures, and it could not be expected that the law of the rectilinear diameter should hold. In point of fact, the diameter is markedly curved in both these cases.

CHAPTER XVII.

THE DETERMINATION OF MOLECULAR WEIGHT.

From Chemical Considerations.

If the percentage composition of a substance and the atomic weights of its component elements are known, the empirical formula of the compound may be calculated by dividing the percentage amounts of the elements by their respective atomic weights, and the quotients so obtained by the lowest of them.

Taking acetic acid as an example—

C	40·0	$\frac{40{\cdot}0}{12} = 3{\cdot}3$	$\frac{3{\cdot}3}{3{\cdot}3} = 1$
H	6·7	$\frac{6{\cdot}7}{1} = 6{\cdot}7$	$\frac{6{\cdot}7}{3{\cdot}3} = 2$ (approximately)
O	53·3	$\frac{53{\cdot}3}{16} = 3{\cdot}3$	$\frac{3{\cdot}3}{3{\cdot}3} = 1$
	100·0		

the empirical formula is CH_2O.

But $\frac{1}{4}$ of the total hydrogen is replaceable by a metal, and $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ of the hydrogen by chlorine, and the substitution cannot be effected in any other proportions. It is therefore concluded that there are 4 atoms of hydrogen in the molecule, and the molecular formula $C_2H_4O_2$ is adopted, the corresponding molecular weight being 60 (taking as atomic weights C = 12, H = 1, O = 16). Again, the empirical formula of benzene is found to be CH, and as the hydrogen can be replaced by chlorine in six equal stages, it is concluded that the molecular formula is C_6H_6, and that the molecular weight is 78.

From the percentage composition of ammonia, its empirical formula is found to be NH_3, that of ammonium chloride is similarly found to be NH_4Cl, and of platinic chloride $PtCl_4$, and the two latter substances unite to form a crystalline compound which has the empirical formula $N_2H_8PtCl_6$, thus—

$$2NH_4Cl + PtCl_4 = (NH_4)_2PtCl_6.$$

But the hydrogen in ammonia can be replaced in three equal stages by various monovalent groups of carbon and hydrogen atoms, such as CH_3, C_2H_5, etc., forming amines, whilst the hydrogen in hydrochloric acid can be replaced in only one stage; and the molecular formulæ of ammonia, ammonium chloride, and ammonium platinichloride, for these and other reasons, are taken to be the same as their empirical formulæ, namely, NH_3, NH_4Cl, and $(NH_4)_2PtCl_6$.

The amines unite with hydrochloric acid to form substituted ammonium chlorides, and these will combine with platinum chloride to form crystalline compounds similar to ammonium platinichloride. All these platinichlorides, when strongly heated, decompose and leave a residue of pure platinum.

Therefore the weight of platinichloride is to the weight of platinum as the molecular weight of the platinichloride is to the atomic weight of platinum; and as the atomic weight of platinum is known, the molecular weight of the platinichloride may be calculated.

Writing the formula of the platinichloride $(NRR'R''H)_2PtCl_6$ (where R, R', and R'' may be monad radicles or hydrogen), and subtracting from its molecular weight the atomic weights of Pt, 6Cl, and 2H, there is left twice the molecular weight of NRR'R''. This method is commonly employed for determining the molecular weights of amines.

So, also, the silver salts of organic acids, when strongly heated, decompose and leave a residue of metallic silver. The equivalent of the acid may thus be directly determined, and its molecular weight may be calculated by multiplying the equivalent by the basicity. By one or other of these various methods it is frequently possible to determine what may be called the *chemical* molecular weight of a compound, but it does not necessarily follow that this molecular weight is identical with that of the smallest particle of the compound that exists in the free state. The methods of determining the *physical* molecular weight of a substance will now be considered.

Molecular Weights of Gases and Vapours.

The molecular weight of a gas or vapour is usually calculated from its density compared with that of a standard gas, hydrogen, oxygen or air, at the same temperature and pressure. It is now customary to take the atomic weight of oxygen as 16, and as the molecules of this gas are diatomic, the molecular weight of oxygen = 32.

The densities of gases and vapours were formerly almost invariably expressed in terms of that of air, but this method of comparison has the obvious disadvantage that air is a mixture of slightly variable composition and density. If d_A is the density of a gas or vapour compared with that of air, taken as unity, the molecular weight (O = 32) is calculated by the formula—

$$M = 28{\cdot}95d_A.$$

When the atomic weight of hydrogen was taken as unity it was most convenient to make the density of hydrogen = 1, and many results are stated in this way. But if the molecular weight of oxygen = 32, that of hydrogen = 2·016, and the molecular weight of the substance considered will be given by the formula—

$$M = 2{\cdot}016d_H.$$

When the density is stated in terms of that of oxygen taken as 16, the equation becomes—

$$M = 2d_O.$$

These equations are based on the assumption that the molecular weights of gases and vapours are strictly proportional to their densities under the same conditions of temperature and pressure; in other words, that Avogadro's hypothesis is invariably true. This could only be the case if the laws of Boyle and Gay Lussac were of universal applicability, and it has been shown (Chap. II.) that this is very far from being the case.

Even gases with very low critical temperatures, such as hydrogen, oxygen, and nitrogen, show slight deviations from Boyle's and Gay Lussac's laws under ordinary conditions of temperature and pressure; but it has been shown by Lord Rayleigh and by D. Berthelot that it is possible to find the corrections necessary to convert the observed densities of these gases into the theoretical densities which they would possess as perfect gases.

At ordinary temperatures and under pressures less than three or four atmospheres, the relation between pv and p for these gases may be represented without sensible error by a straight line, and D. Berthelot has shown (p. 34) that under infinitely low pressures the coefficient of expansion under constant pressure must become numerically equal to the coefficient of increase of pressure at constant temperature; that under these conditions the gases behave as perfect gases, and that Avogadro's hypothesis is strictly applicable to them. The molecular weights of these gases, calculated from their corrected

densities, agree exceedingly well with those derived from the atomic weights determined by other methods. That is also the case with a few gaseous compounds. For the above-mentioned gases at lower temperatures and for more easily condensable gases at ordinary temperatures, the relation between pv and p is less simple and is represented by a curve, but D. Berthelot concludes that even then the gases would behave as perfect gases under infinitely low pressures. There is always, however, greater liability to error in the extrapolation of a curve than of a straight line.

Ramsay and Steele[1] have very carefully determined the vapour densities of methyl alcohol, ether, benzene, toluene, normal hexane, normal octane, and $\beta\epsilon$-dimethyl hexane at 100°, 115°, and 130°, and under pressures from about 600 mm. to either 40 or 75 mm. The observed values of $\frac{pv}{T}$ were plotted against the pressures, and the curves drawn through the points were extrapolated to zero pressure. The molecular weights calculated from the values of $\frac{pv}{T}$ at zero pressure were, however, in some cases higher, in others lower, than those derived from the atomic weights C = 12, O = 32, H = 1·007, the difference varying from 1 part in 2500 in the case of normal hexane to 1 part in 182 in that of toluene. No satisfactory explanation of these differences has yet been suggested.

Under high pressures large deviations from Boyle's and Gay Lussac's laws are met with, but, according to Van der Waals, if the *reduced* temperatures, pressures, and volumes are the same for any two substances which do not exhibit molecular association or dissociation, the ratio $\frac{d}{D}\left(=\frac{s}{S}\right)$ of the actual to the theoretical vapour density should be the same for both (p. 208).

Taking the special case of saturated vapours, the ratio of the actual to the theoretical density should be the same for all *normal* substances at corresponding temperatures, or at their boiling points under corresponding pressures. As the critical temperature is more easily determined than the critical pressure, the first method of comparison is the more generally convenient. The relation is not strictly true, but in most cases the variations from the mean values are not large. For the first twenty-six substances referred to in the table on p. 211

[1] *Zeit. physik. Chem.*, 44, 348 (1903).

the values of $\frac{d}{D}$ at a series of reduced temperatures lie, with a very few doubtful exceptions, between the limits given in the table below; the approximate mean values are stated in the last column. In no case does the difference between the extreme values given in the table amount to 4 per cent. except at the critical temperature, where it is more than 7 per cent. Some of the ratios for methyl, ethyl, and propyl alcohol fall within the same limits, but others are quite outside. At the critical points the ratios are 4·549, 4·024, and 3·995 for methyl, ethyl, and propyl alcohol respectively. The ratios for acetic acid are much higher than those for the other substances, and it will be seen from Fig. 92 that the curve representing the relation of $\frac{d}{D}$ to θ for this substance is of a different form.

Reduced Temperature, $\theta = \frac{T}{T_c}$.	Ratio of Actual to Theoretical Vapour Density, $\frac{d}{D}$.	
	Range of Values.	Mean.
Degrees.		
0·60	—	1·024
0·65	1·026–1·055	1·041
0·70	1·058–1·084	1·071
0·75	1·102–1·136	1·119
0·80	1·173–1·206	1·190
0·85	1·266–1·310	1·288
0·90	1·424–1·470	1·447
0·93	1·578–1·620	1·599
0·95	1·720–1·762	1·741
0·97	1·936–1·990	1·963
0·98	2·10 –2·17	2·135
0·99	2·39 –2·45	2·42
1·00	3·67 –3·94	3·80

The mean curve for the twenty-six substances indicates that at the lowest temperatures the ratio $\frac{d}{D}$ would not differ sensibly from unity; in other words, the saturated vapours of these substances would behave practically as perfect gases. The curves for the alcohols are of the same general form, and the same remark applies to their saturated vapours at very low temperatures.

In the case of acetic acid, however, the ratio $\frac{d}{D}$ has a minimum value 1·65 at about the reduced temperature 0·69; as the temperature falls the ratio rises, reaching 1·907 for $\theta = 0{\cdot}5164$, and if the trend of the curve remained the same the ratio would be 2 when $\theta = 0{\cdot}487$,

and would be still higher at lower temperatures. It is impossible to say, however, whether the ratio would continue to increase or whether it would rise more slowly below $\theta = 0{\cdot}5$ and finally maintain the constant value 2.[1]

As regards the unsaturated vapour, the ratio $\frac{d}{D}$ in all cases tends to fall as the temperature is raised or the pressure lowered, until a constant value is reached. This value is taken as unity, and in the case of acetic acid the unit value is that corresponding to a perfect gas with the formula $C_2H_4O_2$. The same formula, as already stated (p. 322), is arrived at from purely chemical considerations.

But at low temperatures the actual density is much greater than that corresponding to this formula, and an explanation of this fact must be found.

The behaviour of acetic acid vapour is precisely similar to that of nitric peroxide, and there is strong evidence (p. 111) that at low temperatures the molecular formula of this substance is N_2O_4, but that as the temperature rises or the pressure falls, dissociation into the simpler NO_2 molecules occurs. Similarly, it may be concluded with much probability that at low temperatures the molecular formula of acetic acid is $C_4H_8O_4$, and that, on raising the temperature or lowering the pressure, these complex molecules undergo dissociation into the simpler molecules $C_2H_4O_2$. It is, however, possible, though not very probable, that molecules even more complex than $C_4H_8O_4$ may be capable of existence in the state of vapour.

Starting at the lowest temperature, the ratio $\frac{d}{D}$ for the saturated vapour of acetic acid falls with rise of temperature from about 2 until the minimum 1·65 is reached; it then rises again, slowly at first, but more and more rapidly up to 4·986 at the critical temperature.

It can hardly be supposed that the increase in the ratio both with rise and fall of temperature can be due to the same cause, and it is most probable that the explanation of the increase with rise of temperature, which is observed with all substances without exception, is to be found in the fact that the vapour pressure rises very rapidly with the temperature, so that the molecules are brought much closer

[1] Drucker and Ullmann, *Zeit. physik. Chem.*, **74**, 567 (1910), attribute the increase in the density of saturated vapour at low temperatures to adsorption on the walls of the tube.

together, and the general attractive force between them comes strongly into play.

In other words, the molecular attraction which causes the ratio $\frac{d}{D}$ to rise with fall of temperature at low temperatures in the case of acetic acid, nitrogen peroxide, and some other substances is selective and chemical in nature; that which produces a similar effect with rise of temperature in the case of all substances (apparent only at high temperatures in that of acetic acid) is general and physical in nature.

If the critical temperature of any substance of normal behaviour is known, and also the density of its saturated vapour at any tem-

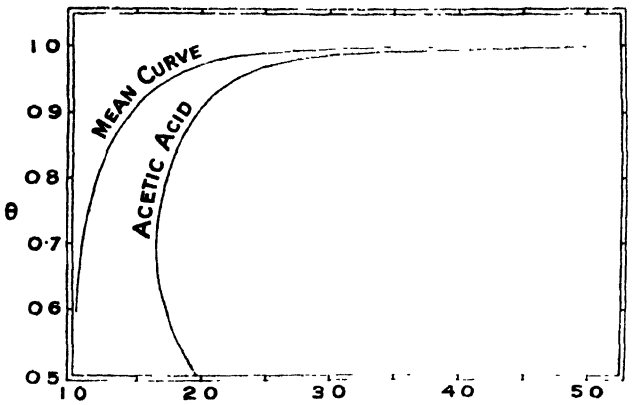


FIG. 92.

perature, the approximate theoretical density for the perfect gas may be calculated by dividing the observed density by the ratio $\frac{d}{D}$ corresponding to the reduced temperature θ, read from the mean curve (Fig. 92) or derived from the table. The molecular weight may then be calculated from the corrected density.

In the case of a substance such as acetic acid, the corrected density, calculated in the same manner, may be regarded as that of a perfect gas consisting of both simple and complex molecules. For a normal substance the corrected densities would be approximately the same at all temperatures; for dissociating substances the density should fall with rise of temperature. The approximate corrected densities for acetic acid are given below:—

Reduced Temperature.	Corrected Density.	Percentage Number of Molecules of $C_4H_8O_4$ Dissociated.
0·50	58·3	2·9
0·55	53·9	11·3
0·60	50·7	18·3
0·65	48·0	25·0
0·70	46·3	29·6
0·75	45·2	32·8
0·80	43·5	37·9
0·85	42·2	42·2
0·90	40·7	47·4
0·95	39·3	52·7
1·00	39·3	52·7

Assuming that dissociation takes place according to the equation—

$$C_4H_8O_4 = 2C_2H_4O_2$$

the percentage number of complex molecules dissociated may be calculated by the method explained on p. 180, and the values so obtained are given in the third column.

In the case of acetic acid, the constant density of unsaturated vapour observed at high temperatures and low pressures corresponds to the formula arrived at from chemical considerations. In many cases, however, the molecular weight calculated from the density is lower than that derived from the simplest possible formula. Thus, the empirical formula for ammonium chloride is NH_4Cl, and the molecular weight calculated from this formula is 53·5; but the observed vapour density is about 13·4, and the molecular weight calculated from this would be 26·8, or only half that derived from empirical formula. In such cases it is assumed that dissociation has taken place, and that the vapour consists of a mixture of the dissociation products. Experimental proof of the correctness of this assumption has been obtained in many cases (p. 107).

It has been shown by H. B. Baker and his co-workers that when all moisture is very carefully removed, the stability of ammonium chloride, nitrogen trioxide, nitrogen peroxide and other dissociating substances is greatly increased, and vapour densities corresponding to the formulæ NH_4Cl and N_4O_6 have been observed by them.

In the case of the alcohols, the curves showing the relation between $\frac{d}{D}$ and θ are of the usual form, but the values of $\frac{d}{D}$ at the critical temperatures are abnormally high, especially for methyl alcohol. It can hardly be supposed that there is definite chemical

combination between the simple molecules such as occurs in all probability with acetic acid and nitric peroxide, since there is no molecular association in the state of vapour at low temperatures, but there is evidence of considerable association, probably of a looser kind, in the liquid state, and it appears as though this association persisted to some extent up to the critical point.

Molecular Weights of Liquids.

The most important researches on the molecular weights of liquids are those of Eötvos,[1] Ramsay and Shields,[2] Ramsay and Aston,[3] Renard and Guye,[4] and J. Livingston R. Morgan.[5] It has already been stated (p. 136) that the surface tension of a liquid is usually measured by the height to which it rises in a capillary tube of known radius. The surface tension, in absolute units, is calculated from the formula—

$$\gamma = \tfrac{1}{2}hrsg$$

where h is the height of the liquid in the tube above that outside, r is the radius of the tube, and s the specific gravity of the liquid.

A number of determinations were made by an optical method in 1886 by Eötvös, who deduced from his results the equation—

$$\gamma V^{\frac{2}{3}} = k(t_0 - t)$$

where t_0 is the temperature at which $\gamma V^{\frac{2}{3}} = 0$, t the temperature of observation, and V ($= Mv$) is the molecular volume. $V^{\frac{2}{3}}$ is the area of a face of a cube of which V is the volume. Since the molecular volumes of different liquids contain the same number of molecules, the *molecular surfaces* $V^{\frac{2}{3}}$ would be surfaces on which an equal number of molecules are distributed.

The temperature t_0 was found by Eötvös to be identical with the critical temperature, or at least not far removed from it.

Eötvös found that the value of k is nearly the same (0·227 for the units adopted) for a considerable number of substances; but that for ethyl alcohol, water, and acetic acid it is much lower, the difference from the mean value diminishing, however, as the tem-

[1] *Wied. Ann.*, **27**, 448 (1886).

[2] *Phil. Trans.*, **184**, 647 (1893); *Trans. Chem. Soc.*, **63**, 1089 (1893).

[3] *Zeit. physik. Chem.*, **15**, 91 (1894).

[4] *Journ. Chim. phys.*, **5**, 81 (1907).

[5] *Journ. Amer. Chem. Soc.*, numerous papers in Vols. 30, 33, 35 and 37 (1908 to 1915).

perature rises. These abnormal values were attributed by him to molecular association in the liquid state.

Ramsay and Shields determined the surface tension of six very carefully purified liquids from low temperatures to their critical points, and found that the equation of Eotvos requires modification.

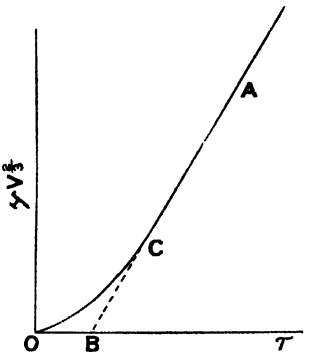


FIG. 93.

Plotting $\gamma V^{\frac{2}{3}}$ against τ, where $\tau = t_c - t$, a diagram of the form shown in Fig. 93 is obtained. It is true that when $t = t_c$, and therefore $\tau = 0$, $\gamma V^{\frac{2}{3}} = 0$, but with fall of temperature (increase of τ) $\gamma V^{\frac{2}{3}}$ increases slowly at first, then more rapidly, and the rate of increase only becomes constant when the temperature has fallen some 30 to 50° below the critical temperature. The relation between $\gamma V^{\frac{2}{3}}$ and τ is represented by the line OCA, which is curved from O to C, but straight beyond C. Producing AC to B and calling OB Δ, the formula of Eotvos becomes—

$$\gamma V^{\frac{2}{3}} = k(\tau - \Delta)$$

For benzene the values of k and Δ were found to be 2·1043 and 6·5 respectively, the critical temperature t_c being 288·5° C., and the calculated and observed values of $\gamma V^{\frac{2}{3}}$ are given in the table below :—

t° C.	τ.	$\gamma V^{\frac{2}{3}}$.	
		Observed	Calculated.
80	208·5	425·1	425·1
100	188·5	384·0	383·0
120	168·5	341·6	340·9
140	148·5	299·0	298·8
160	128·5	256·9	256·7
180	108·5	213·8	214·6
200	88·5	172·5	172·5
220	68·5	131·0	130·5
240	48·5	89·0	88·4
250	38·5	68·7	67·3
260	28·5	48·6	46·3
270	18·5	28·8	25·3
275	13·5	19·9	14·8
280	8·5	9·0	4·2
288·5	0	0	− 13·7

The curvature is hardly noticeable for values of τ between 208·5 and 48·5, but becomes very marked as the critical point is approached.

The values of k for six pure substances are given below:—

	k.
Ether	2·1716
Methyl formate	2·0419
Ethyl acetate	2·2256
Carbon tetrachloride	2·1052
Benzene	2·1043
Chlorobenzene	2·0770
Mean	2·1209

The linear equation does not hold for the alcohols nor for acetic acid, but it will be seen that the above six substances have nearly the same value of k; and Ramsay and Shields conclude that 2·12 may be taken as the normal value for non-associating liquids.

Consider now the effect of molecular association, and suppose that two simple molecules unite to form a complex molecule. If the association were complete, the number of molecules in unit volume would be reduced to one-half, and the number of molecules on unit surface would be altered in the ratio of $1 : (\frac{1}{2})^{\frac{2}{3}}$; a similar change would also take place in the surface energy, one of the factors of which is $V^{\frac{2}{3}}$. The value of the differential of surface energy with temperature would be similarly altered, and, according to Ramsay,[1] the amount of association may be calculated in any given case by the equation—

$$\gamma V^{\frac{2}{3}} = 2{\cdot}12 \times \frac{1}{x^{\frac{2}{3}}} \times (\tau - \Delta)$$

where x is the unknown factor of association. Comparing this equation with one which represents with greater accuracy the behaviour of associating liquids, viz.—

$$\gamma V^{\frac{2}{3}} = \frac{k(\tau - \Delta)}{1 + \mu\tau}$$

it is evident that x corresponds to the expression—

$$\left\{\frac{2{\cdot}12}{k} \times (1 + \mu\tau)\right\}^{\frac{3}{2}}$$

For acetic acid and methyl alcohol the following values were obtained:—

[1] *Proc. Roy. Soc.*, **56**, 171 (1894).

ACETIC ACID.

$k = 1{\cdot}910$; $\Delta = 11{\cdot}9$; $\mu = 0{\cdot}00163$; critical temperature = 321·5°.

$t°$ C.	τ.	x.	Molecular Weight $= x \times 60$.
20	301·5	2·13	137·8
100	221·5	1·86	111·6
200	121·5	1·53	91·8

METHYL ALCOHOL.

$k = 1{\cdot}489$; $\Delta = -4{\cdot}22$; $\mu = 0{\cdot}00104$; critical temperature = 240·0°.

$t°$ C.	τ.	x.	Molecular Weight $= x \times 32$.
− 89·8	329·8	2·65	84·8
+ 20·0	220·0	2·32	74·2
150·0	90·0	1·94	62·1

In both cases the amount of association diminishes as the temperature rises, and for equal values of τ it would appear that the factor of association is even higher for methyl alcohol than for acetic acid.

On the other hand, the ratios of the actual to the theoretical density indicate that at the critical temperatures the association is greater in the case of acetic acid.

Ramsay and Shields have examined a large number of liquids at a few comparatively low temperatures. In the great majority of cases normal values of k were found, and it was therefore concluded that there was no molecular association in the liquid state. On the other hand, evidence of association was obtained in the case of the alcohols, the fatty acids, and water, and, to a smaller extent, of acetone, propionitrile, and nitroethane. As regards the alcohols and fatty acids, it was found that in each homologous series the amount of association—under similar conditions—diminishes with rise of molecular weight.

J. Livingston R. Morgan and his co-workers, in their determinations of the weights of falling drops, have examined some two hundred carefully purified liquids and solutions, for more than one hundred of which the surface tensions—lying between 15·3 and 76 dynes per centimetre—have been determined by some other method.

For these liquids, belonging to widely diverse types and possessing widely diverse properties, it was found that, under specified conditions, at any given temperature $\gamma = c \times w$, where γ is the surface tension, w the weight of the falling drop, and c a constant depending on the form and diameter of the tip of the dropping tube. Hence cw can be employed in place of γ in determining the molecular weight of a liquid, c being best calculated from the observed values of w for benzene and water.

It is clear that the equation—

$$\gamma = \left(\frac{M}{s}\right)^{\frac{2}{3}} = k(t_c - t - 6)$$

may be employed for the calculation of either M or t_c if the other value is known, and Morgan proposes to divide liquids into three classes, including—

1. Those liquids for which the normal (benzene) value of k leads in the above equation at all temperatures to a value of t_c which agrees closely with the observed critical temperature.

2. Those liquids for which the normal value of k leads in the above equation to the same calculated value of t_c (with a reasonable allowance for error) at all temperatures, but a value which differs from the observed critical temperature, considerably in some cases.

3. Those liquids for which the normal value of k leads to a calculated value of t_c which is not only lower than that observed but increases as the temperature of observation rises. In such cases $w\left(\frac{M}{s}\right)^{\frac{2}{3}}$ is not a rectilinear but a curvilinear function of the temperature.

Liquids belonging to classes 1 and 2 are to be regarded as non-associated, those belonging to class 3, for example, water, methyl alcohol, ethyl alcohol, and acetic acid, as associated.

It is now generally admitted that it is the constancy and not the absolute value of the temperature coefficient of the molecular surface energy which is the essential characteristic of normal liquids or of those of which the molecular complexity is independent of the temperature. It has been pointed out by Bennett and Mitchell [1] that for normal liquids the total molecular surface energy $\left(\gamma - t\frac{d\gamma}{dt}\right)(Mv)^{\frac{2}{3}}$ remains nearly constant over a wide range of temperature, extending

[1] *Zeit. physik. Chem.*, **84**, 475 (1913).

nearly to the critical point. For water and the alcohols, the association of which varies with the temperature, the total molecular surface energy increases rapidly with rise of temperature. In this respect, however, acetic acid has been shown by Bennett[1] to behave like a normal liquid, at any rate between 15° and 150°, and he concludes that between these limits of temperature liquid acetic acid consists exclusively of molecules of the formula $(CH_3 . COOH)_2$.

D. Berthelot[2] has shown that the molecular weight of a substance may be calculated with fair accuracy from its critical temperature and pressure, and its density in the liquid state at a convenient temperature.

It has been shown by Young that the mean value of the ratio of the actual to the theoretical density at the critical point for a large number of *normal* substances is about 3·8. For carbon dioxide the ratio deduced from Amagat's results is somewhat lower, 3·6, and for the elementary gases—hydrogen, oxygen, and nitrogen—it is still lower. D. Berthelot adopts the value 3·6, and points out that—

$$M = \frac{s_c}{3\,6} \times 22{\cdot}4 \times \frac{T_c}{273} \times \frac{1}{p_c} \quad . \quad . \quad . \quad (1)$$

where s_c is the critical density, T_c the critical (absolute) temperature, and p_c the critical pressure measured in atmospheres. The volume of 1 gram-molecule of a perfect gas ($O_2 = 32$) at 0° C. and 1 atmos. is 22·4 litres.

Mathias[3] has shown that, in accordance with the law of the rectilinear diameter, the critical density may be calculated by means of the formula—

$$s_c = \frac{s_L - s_V}{2\left(2 - \frac{T}{T_c}\right)}$$

where s_L and s_V are the densities of liquid and saturated vapour at the absolute temperature T.

If the temperature is not above the boiling point under atmospheric pressure, s_V may, for the present purpose, be neglected, and the equation becomes—

$$s_c = \frac{s_L}{2\left(2 - \frac{T}{T_c}\right)} \quad . \quad . \quad . \quad . \quad (2)$$

[1] *Trans. Chem. Soc.*, **107**, 351 (1915). [2] *Compt. rend.* (March, 1899).
[3] "Le Point Critique des Corps purs" (1904), p. 164.

From equations (1) and (2)—

$$M = 11{\cdot}4 s_L \times \frac{T_c}{p_c\left(2 - \frac{T}{T_c}\right)}.$$

For example, the density of liquid nitrogen at its boiling point, − 194·4° C., is 0·885; its critical temperature and pressure are − 146° C. and 33 atmos. respectively; therefore

$$M = 11{\cdot}4 \times 0{\cdot}885 \times \frac{127}{33\left(2 - \frac{78{\cdot}6}{127}\right)} = 28{\cdot}1,$$

which agrees very well with the value 28·0 deduced from the atomic weight.

For substances which are liquid at the ordinary temperature the molecular weights given by the above formula are usually a little too high.

The Gaseous and Liquid States of Matter.

When a gas is compressed at a temperature lower than its critical temperature, the pressure rises until the vapour pressure is reached; then, under ordinary conditions, liquefaction begins, and the system consists of two phases, the gaseous and liquid, until the vapour is completely condensed. If the gas is very carefully freed from dust-particles, the pressure may rise somewhat higher than that at which liquefaction usually commences, but sooner or later the second phase appears abruptly.

Andrews, however, pointed out that if the gas is first heated above its critical temperature, then compressed, and finally cooled again, the change from the gaseous to the liquid state takes place continuously. There is never more than one phase, and it is impossible to say when the substance ceases to be gaseous and becomes liquid. Andrews concluded that there is no essential difference between the two states; that the molecules of the liquid are precisely similar to those of the gas; and that the properties of a liquid differ from those of a gas merely in consequence of the greater proximity of the molecules, involving greater mutual attraction or cohesion.

Van der Waals, in his great work on the *Continuity of the Gaseous and Liquid States of Matter*, adopts the same view, and expressly states that his equation of state, and the generalizations based upon it, cannot be applicable to substances which are characterized by molecular association or dissociation in either the gaseous or liquid condition.

The contrary view that the molecules of the liquid are in all cases more complex than those of the gas, that there are, in fact, *liquidogenic* and *gasogenic* molecules, or, to quote Traube's terms, *fluidonen* and *gasonen*, has been taken at various times by a few chemists and physicists. In recent years the arguments in favour of the complexity of the molecules of liquid have been drawn chiefly by De Heen and by Traube[1] from the behaviour or supposed behaviour of matter at or near the critical point, and chiefly from the remarkable differences of density observed at different levels in a column of fluid at or about its critical point.

Some experimenters also, notably Battelli, Galitzine, and De Heen, have observed differences between the temperature at which the meniscus disappears when a given liquid occupying approximately its critical volume is slowly heated and that at which the meniscus reappears when the fluid is cooled; and the argument has been advanced that the theory of Andrews and Van der Waals is inadequate to explain the supposed facts. It has, however, already been pointed out that there is a striking lack of agreement between the observations of these workers, and that the most trustworthy experimental evidence leads to the conclusion that the temperature at which the meniscus disappears is the same as that at which it reappears, and that this *apparent* critical temperature is the same as that at which the densities of liquid and vapour become equal.

That there must of necessity be great differences of density in a long vertical column of fluid at its critical temperature, when the mean density does not differ greatly from the critical density, has been proved on theoretical grounds by Gouy (p. 166), the reasoning being based on the almost infinite compressibility of a fluid at its critical point, and its very great compressibility in the neighbourhood of that point. An elegant and ingenious method of determining the densities at different levels of such a column of fluid, and of demonstrating their remarkable differences, has been devised by Teichner,[2] who places a number of minute coloured glass bulbs in the rather

[1] *Annalen der Physik*, (4), 8, 267 (1902); *Zeit. anorg. Chem.*, 37, 225 (1903); *ibid.*, 38, 399 (1904). But in a recent paper, *Zeit. physik. Chem.*, 58, 475 (1907), Traube expresses much less confidence in his theory, and states his opinion that the phenomena observed at and near the critical point can best be explained by Bakker's purely physical theory (*Zeit. physik. Chem.*, 49, 616 (1904)) of the broadening of the surface layer as the critical temperature is approached.

[2] Inaug. Dissert., Vienna (1903); *Ann. d. Phys.* (4), 13, 595 (1904); also Traube, *Zeit. anorg. Chem.*, 38, 399 (1904).

wide sealed tube containing the liquid under investigation. The density of such a bulb depends on the ratio of the volume of glass to that of glass plus enclosed air, and this ratio is capable of great variation. The bulbs can be distinguished by the shapes of the bits of capillary tubing left attached to them, and their densities are determined once for all by placing them in a liquid of very low specific gravity, such as isopentane, heating the liquid in a sealed tube, and observing the temperatures at which the bulbs sink.

It is necessary to employ a liquid of high specific gravity for the experiments at and near the critical point, and Teichner chose carbon tetrachloride for the purpose. In his earlier experiments Teichner observed very great differences in density at different levels, and found that these differences persisted for many hours at temperatures far higher than that at which the meniscus disappeared. There was no doubt, however, that the carbon tetrachloride had not been purified with sufficient care, and it is probable that the removal of dissolved air was not complete. Even in the later experiments, in which great care was taken in purifying the liquid and removing air, much greater differences were observed for a considerable time in some cases than could be accounted for by Gouy's explanation. Teichner admits that after a sufficient length of time, or after stirring, the observed densities are not too great, and he attributes the extreme slowness with which the change to the final state of equilibrium occurred to the perfection of his method of heating the tubes. Other experimenters place their tubes either in a bath of well-stirred liquid heated by a flame, or in the vapour from a boiling pure liquid; Teichner places his tube in a rather wider one containing paraffin, and this is heated by the vapour from a boiling liquid.

Teichner insists on the purity of his carbon tetrachloride both before and after being heated; but there is reason to think that this substance undergoes very slow decomposition at high temperatures, such as 280° or 290°; and Verschaffelt[1] has clearly shown that Teichner's results may be explained by the presence of a minute amount of permanent gas or very volatile impurity in the liquid.

Carbon dioxide would be a far more suitable substance than carbon tetrachloride on account of its convenient critical temperature and perfect stability, were it not that its lower critical density would necessitate the preparation and standardization of still lighter

[1] *Comm. Phys. Lab. Leiden*, Suppl. No. 10 (1904).

density bulbs. This difficulty has, however, been overcome by Kamerlingh Onnes and Fabius,[1] who, by greatly improved heating arrangements, were able to keep the temperature of the tube containing the carbon dioxide constant to within 0·002°. The height of the tube was 100 mm., and the meniscus disappeared 56 mm. above the bottom of the tube. The observed critical temperature was 30·985°.

When the meniscus appeared on allowing the temperature to fall from 30·986° to 30·984° the observed difference in density between the liquid and vapour phases was certainly less than 10 per cent. and probably not greater than 5 per cent. This is a smaller difference than had previously been observed by any experimenter.

Again, after keeping the tube for three hours at a constant temperature 0·9° above the critical point, the difference of density at the top and bottom of the tube was less than 3·5 per cent. From Verschaffelt's calculation, impurity to the extent of 1 molecule in 10,000 of carbon dioxide would be far more than sufficient to account for the difference of density in excess of that caused by gravity.

Onnes and Fabius consider that their results are in complete agreement with the theory of Andrews and Van der Waals.

Experiments with sulphur dioxide and carbon dioxide on similar lines have been carried out by P. Hein[2] at Traube's suggestion. His results are in general agreement with those of Onnes and Fabius, but both Hein and Traube consider that they do not invalidate the theory of "fluidonen" and "gasonen".

In any case, the question is merely that of the length of time required to bring about the final state of equilibrium, and it does not appear to the author that any sufficient reasons have been advanced for rejecting the simple theory of Andrews and Van der Waals.

Molecular Association.

For the reasons which have been given in the preceding section of this chapter, it will be assumed that the molecules of what may be termed a normal liquid are simple, like those of its vapour; but it has been pointed out that with some substances, such as acetic acid, there is molecular association in the gaseous state, as shown by

[1] *Comm. Phys. Lab. Leiden*, Suppl. No. 98 (1907).

[2] *Zeit. physik. Chem.*, 86, 385 (1914); Traube, *Ver. Deut. Phys. Gessell.*, 15, 1219 (1913).

the changes in vapour density, and there must undoubtedly be association in the liquid state also. There are reasons, also, for believing that with some other substances, notably water and the alcohols, there is molecular association of some kind in the liquid state, though not in that of vapour.

The criteria for the existence of molecular association have been discussed by Guye,[1] who refers especially to the following points :—

1. The variation of the constant k in the equation

$$\gamma V^{\frac{2}{3}} = k(\tau - \Delta)$$

from the mean value 2·12 (Ramsay and Shields, p. 330). Very low values, indicating a high degree of association, were observed in the case of water, the alcohols, and the fatty acids, moderately low values in the case of acetone, propionitrile, and nitroethane. In the homologous series of alcohols and fatty acids, the amount of association diminishes at a given temperature as the molecular weight increases, and in all cases the association diminishes as the temperature rises. More recent researches on this subject are described on pp. 136, 333.

2. Molecular association at the critical temperature is indicated when the ratio of the actual to the critical density is much higher than 3·85 (p. 211). The four highest values observed were 4·992, 4·559, 4·026, and 3·998, respectively, for acetic acid, methyl alcohol, ethyl alcohol, and propyl alcohol. The values for the lower aliphatic esters are also somewhat high—3·866 to 3·949—and it seems not improbable that there may be a slight degree of association in these cases also.

3. From a consideration of Van der Waals' equation of state, Maxwell's electromagnetic theory of light, and Clausius' equation connecting the dielectric constant with the ratio of the actual to the apparent volume of the molecules of a substance, Guye deduces the relation

$$\frac{T_c}{p_c} = \frac{1}{f} \cdot MR$$

where T_c is the absolute critical temperature, p_c the critical pressure, MR the molecular refraction, and f is a constant which for a large number of normal substances is about 1·8, but for water, methyl alcohol, and acetic acid is only about 1·1.

4. According to the law of Cailletet and Mathias (p. 154), the mean

[1] *Archives des Sciences phys. et nat., Geneva*, (3), 31, pp. 38, 164, 463 (1894); *Journ. Chim. phys.*, 9, 505 (1911).

densities of liquid and saturated vapour are a rectilinear function of the temperature. It has been shown by Young that the law requires modification to this extent—that there is in most cases very slight curvature, the mean densities being accurately given by the formula

$$s = s_0 + at + \beta t^2,$$

the coefficient β being very small.

In the case of the alcohols, the curvature of the diameter is very marked, and a fourth term, γt^3, would have to be added to reproduce the mean densities at all satisfactorily. The simpler formula suffices for acetic acid; but with this substance there is association not only in the liquid, but also in the gaseous state. The conclusion arrived at by Guye is that marked curvature indicates molecular association, but that the absence of marked curvature does not preclude the possibility of molecular association.

5. When there is no change in molecular complexity on the passage of a substance from the liquid to the gaseous state, the work done in vaporizing the liquid is wholly expended in overcoming the mutual attraction (cohesion) of the molecules, and in causing expansion against external pressure. In such a case the heat of vaporization L always diminishes with rise of temperature. But when the molecules of vapour are less complex than those of the liquid, work is also required to overcome the selective or chemical attraction between individual molecules. An irregularity is thus introduced into the relation between heat of vaporization and temperature, and in the case of acetic acid the values of L show a well-defined maximum at about 110° (Ramsay and Young). Ethyl alcohol shows a similar but less striking maximum at about 10°; and although no maximum has been observed in the case of methyl alcohol, it is not improbable that it may exist at some temperature lower than 0° C.

Acetic Acid.		Ethyl Alcohol.	
t.	L.	*t*.	L.
Degrees.	Cal.	Degrees.	Cal.
20	84·05	0	220·9
50	88·14	10	**221·2**
80	91·59	20	220·6
100	92·32	30	220·1
110	**92·79**	40	218·7
120	92·71	50	216·0
130	92·42	70	209·9
150	91·91	100	197·1

From these results Guye concludes that the heats of vaporization do not show a maximum unless there is molecular association; but it is, of course, possible that there may be association when a maximum has not been observed.

6. Regnault[1] called attention in 1862 to the fact that the vapour-pressure curves of different substances do not usually cut each other, but that water, the alcohols, and acetic acid form exceptions to the rule. The question is discussed, in the light of more recent investigations, by Guye, who arrives at the general conclusion that when the vapour-pressure curve of a given substance cuts the curves for normal substances, the first substance is associated.

It is more convenient, however, to consider the ratios of the boiling points (on the absolute scale) of the liquid to those of a normal substance at a series of equal pressures (Ramsay and Young, p. 133). If the relation

$$\frac{T_B'}{T_A'} = \frac{T_B}{T_A} + c(T_L' - T_B)$$

does not hold (where T_L' and T_B are the boiling points of the normal substance), in other words, if the relation between $\frac{T_L'}{T_A'}$ and $T_B' - T_B$ is not represented by a straight line,[2] it may be concluded that there is molecular association (or dissociation) in the case of the substance A.

7. It may also be noticed that for the alcohols, water, and acetic acid, the values of $\frac{dp}{dt} \times T$ at the boiling point under atmospheric pressure are very high. There is, however, considerable variation in the values of $\frac{dp}{dt} \times T$ among normal substances; thus for oxygen it is 6854, and for anthracene 9240. In a homologous series the value rises as the molecular weight increases; for example, methane 7434, n-pentane 7980, n-octane 8415. For ethyl alcohol, water, and acetic acid the values are 10,660, 10,150, and 9357 respectively.

Trouton's rule, $\frac{ML}{T} = \text{constant}$, comes under this heading (p. 145).

[1] *Mem. Acad. Sc. Paris*, vol. 26.

[2] If c has not an exceptionally high value, the somewhat more convenient equation $\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + c(T_B' - T_B)$ may be employed without sensible error (p. 134).

8. Longinescu[1] has brought forward the two following relations:—

(1) $\left[\frac{T}{100s}\right]^2 = n$, where T is the absolute boiling point, s the density of the liquid at 0°, and n the number of atoms in the molecule. In the case of normal substances n is usually equal to the number of atoms in the chemical formula, but in that of associated substances it is higher; thus, for acetic acid $n = 14$ instead of 8, and for water it is also 14 instead of 3. Some results, however, are quite improbable, thus for sodium $n = 108$.

(2) $\frac{T}{\sqrt{M}} + \frac{1000\sqrt{M}}{T} = 64$ for normal substances, but for associated substances the "constant" is higher; for example, it is 99 for water. In the case of aliphatic acids the value falls from 72 for acetic acid to 66 for œnanthylic acid, and in the series of alcohols it falls from 76·8 for methyl alcohol to 65·3 for octyl alcohol.

9. Dunstan and Thole[2] point out that the quantity

$$\frac{\text{viscosity}}{\text{molecular volume}} \times 10^{6}$$

is nearly constant, namely, about 60 for the liquids which are generally regarded as unimolecular, but that for hydroxyl compounds, which are considered to be associated, the values are much higher; thus—

Benzene	65	Methyl alcohol . .	138
Chloroform . . .	67	Ethyl „ . .	189
Carbon disulphide . .	60	Acetic acid . . .	195
Water	493	Glycerol . . .	106,000

In many other respects the properties of water, the alcohols, and the fatty acids differ from those of normal substances, but with regard to the homologous series of alcohols and acids, it is to be noted that these differences become less marked as the molecular weight increases. It seems probable that with these substances the tendency for molecular association to occur is due to the presence of the hydroxyl group, and that the influence of this group becomes less marked as the complexity of the alkyl or other group increases.

That water is associated in the liquid state is indicated by the following considerations.[3] By replacement of oxygen in methyl

[1] *Journ. Chim. phys.*, 1, 289, 296, and 391 (1903); 6, 552 (1908).

[2] *Proc. Chem. Soc.*, 23, 19 (1907); *Zeit. physik. Chem.*, 51, 732 (1905).

[3] Walden, *Zeit. physik. Chem.*, 55, 683 (1909).

ether by sulphur, the boiling point is raised 60°, and by similar replacement in ethyl ether the rise is 58·4°. Substitution of oxygen by sulphur, therefore, raises the boiling point, on the average, about 59°. But hydrogen sulphide boils at −61°, and therefore the boiling point of unassociated water should be about −120°, whereas the actual boiling point is 220° higher.

For further information on this subject, Turner's "Molecular Association" may be consulted.

Molecular Weights of Dissolved Substances.

The methods of determining molecular weights so far described are not generally applicable to substances which are only volatile at very high temperatures, or which decompose when vaporized. Such substances may, in most cases, be dissolved in water or some other solvent, and the following methods are now known by which their molecular weights may be determined :—

1. *From the Osmotic Pressure.*—Let m grams or $\frac{m}{M}$ gram-molecules of a substance be present in 1 litre of solution, and call the osmotic pressure, measured in atmospheres, p at t° C.

It has been shown that for 1 gram-molecule—

$$p \times v = 0{\cdot}0821T \text{ litre-atmos.},$$

therefore for $\frac{m}{M}$ gram-molecules—

$$p \times v = 0{\cdot}0821T \times \frac{m}{M}.$$

If $v = 1$ litre, then—

$$p = 0{\cdot}0821T \times \frac{m}{M},$$

$$\text{and } M = 0{\cdot}0821T \times \frac{m}{p}.$$

But the direct measurement of osmotic pressure is difficult, and is rarely employed in practice.

2. *From the Depression of the Freezing Point.*—Let m grams of a substance be dissolved in 100 grams of solvent, and call the observed depression of the freezing point Δt.

$$\text{Then } M = \frac{E' \times m}{\Delta t} \text{ (Raoult)}$$

where E' is the molecular lowering of the freezing point of the

particular solvent employed, and M is the molecular weight of the dissolved substance.

$$\text{Also } E' = \frac{0{\cdot}02T^2}{L'} \text{ (Van't Hoff)}$$

where T is the melting point of the solvent on the absolute scale of temperature, and L′ is its heat of fusion in gram-calories.

Values of E′ for a few useful solvents are given on p. 288, and the apparatus required is shown in Fig. 80.

3. *From the Lowering of the Vapour Pressure.*—It was found by Raoult (p. 289) that for dilute solutions—

$$\frac{p - p'}{p'} = \frac{N}{n}$$

where p and p' are the vapour pressures of solvent and solution respectively at the temperature of observation, and N and n the relative number of molecules of substance and solvent.

Let m grams of substance be dissolved in 100 grams of solvent; then—

$$N = \frac{m}{M} \text{ and } n = \frac{100}{M'}$$

where M and M′ are the molecular weights of solute and solvent respectively.

$$\text{Then } \frac{N}{n} = \frac{mM'}{100M} = \frac{p - p'}{p'}.$$

$$\therefore M = \frac{mM'}{100} \times \frac{p'}{p - p'}.$$

4. *From the Rise of the Boiling Point.*—Let m grams of substance be dissolved in 100 grams of solvent, and call the observed rise of boiling point Δt; then—

$$M = \frac{E \times m}{\Delta t}$$

and, as shown by Van't Hoff—

$$E = \frac{0{\cdot}02T^2}{L}$$

where T is the boiling point of the solvent on the absolute scale of temperature, and L is its heat of vaporization in gram-calories.

Values of E for a number of useful solvents are given on p. 293, and the apparatus required is shown in Figs. 82 and 83.

5. *From the Diminution in Solubility of one Solvent in another.*—Consider two liquids such as ether and water, miscible only within

comparatively small limits, and call the solubility of pure ether in water $\mathfrak{S}$ at the temperature of observation.

Let m grams of a substance be dissolved in 100 grams of ether, and call the solubility of the impure ether in water $\mathfrak{S}'$ at the same temperature, and the molecular weights of substance and ether M and M′ respectively; then—

$$M = \frac{M' \times m}{100} \times \frac{\mathfrak{S}'}{\mathfrak{S} - \mathfrak{S}'}, \text{ (Nernst, p. 313).}$$

Dissociation, Molecular Association, and Electrolytic Dissociation.

The molecular weights of many substances may be determined by several of the methods described: (1) from their chemical behaviour, (2) in the gaseous state, (3) in the liquid state, and (4) in solution; and the same value is frequently found by each method. There are, however, numerous cases in which discordant results are obtained. For example, from the chemical properties of acetic acid, together with its percentage composition, chemists are led to adopt the molecular formula $C_2H_4O_2$, and the molecular weight corresponding to this formula is 60 (approximately).

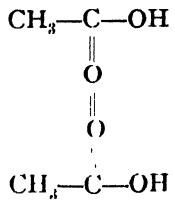
Determinations of the vapour density of acetic acid at high temperatures and low pressures give the constant value 30, and the molecular weight 60; but at low temperatures higher values are obtained, and from the curve (Fig. 92, p. 328) it is clear that the density of the saturated vapour would reach, if not exceed, the double value 60, corresponding to the molecular weight 120 and the formula $C_4H_8O_4$.

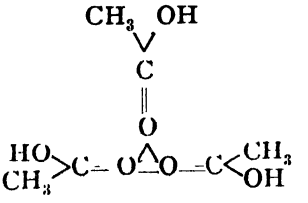
In the liquid state, a very high factor of association has been observed by Ramsay and Shields at low temperatures ($x = 2{\cdot}13$ and M = 137·8 at 20°).

The molecular weights of acetic acid calculated from the depression of the freezing points and the rise of the boiling points of solvents are very variable, depending on the concentration of the solutions, and still more on the nature of the solvent. Thus with benzene as solvent, and when the solution is not too dilute, the molecular weight 120 is obtained; with ether the molecular weight 60; while with water, when the solution is very dilute, the value 30 is obtained.

As already stated, the high values are in all probability to be

explained by the association of the chemical molecules $C_2H_4O_2$ or $CH_3 . COOH$. It is known that oxygen, although usually divalent, acts in some cases as a tetravalent element, and such formulæ as—





and so on, are possible.

But the lower molecular weight, 30, indicates dissociation or decomposition; and as the acetic acid can be recovered from the dilute solution, the change must be one of dissociation rather than decomposition.

Many oxy-acids, when heated, break up into the anhydride and water; but acetic acid can be strongly heated without undergoing this change, and it is only by the action of a powerful dehydrating agent that the anhydride can be prepared from the acid. It is exceedingly unlikely that such a change would occur in dilute aqueous solution; and, in any case, no explanation of the facts would be afforded by it, for the number of molecules must be doubled to reduce the apparent molecular weight to one-half, whereas the formation of anhydride and water from the acid is expressed by the equation—

$$2CH_3 . COOH = (CH_3 . CO)_2O + H_2O.$$

The amount of solvent, water, would be slightly increased, and the number of molecules of anhydride would be only half as great as the number of molecules of acid.

A similar difficulty arises in the determination of the molecular weights of strong mineral acids and bases, and of salts derived from them. Thus the molecular weight of hydrochloric acid calculated from the freezing point or boiling point of a dilute aqueous solution is only half as great as that calculated from the chemical formula HCl, that of sulphuric acid is only one-third, and so on. But the equations which represent the dissociation which these substances suffer on heating are—

$$2HCl = H_2 + Cl_2$$
$$\text{and } H_2SO_4 = SO_3 + H_2O$$

respectively. With hydrochloric acid there is no change in the

number of molecules, and with sulphuric acid the number is only doubled. Moreover, in a dilute solution of hydrochloric acid there is certainly no free hydrogen or chlorine present.

Theory of Electrolytic Dissociation.—It was observed that those substances which cause abnormally large alterations in the freezing point, boiling point, and vapour pressure of water behave as electrolytes in aqueous solution, while others, such as the sugars and many other organic compounds, which produce the normal effect when dissolved in water, do not act as electrolytes.

Again, while pure water and pure liquefied hydrogen chloride are non-conductors of electricity, aqueous hydrochloric acid conducts electricity freely, hydrogen gas being evolved at the negative pole and chlorine[1] at the positive pole.

On the other hand, carbon tetrachloride is not an electrolyte either in the pure (liquid) state or when dissolved in dilute alcohol (it is practically insoluble in water).

When an aqueous solution of silver nitrate is added to aqueous hydrochloric acid, a precipitate of silver chloride is at once formed; but when added to a solution of carbon tetrachloride in dilute alcohol, no change whatever occurs.

In the light of these and other facts, Arrhenius[2] was led to his theory of electrolytic dissociation. According to this theory, when a substance such as carbon tetrachloride, which is not an electrolyte even in solution, is dissolved in water (water and alcohol in this case), no decomposition or dissociation occurs; the molecules of dissolved carbon tetrachloride differ in no respect from those of the substance in the gaseous state.

On the other hand, when hydrogen chloride is dissolved in water, some of the molecules of the chloride are at once dissociated, not into ordinary atomic hydrogen and chlorine, but into *ions*, that is to say, into atoms of these elements endowed with very large electrical charges. So long as the atoms retain these charges, they do not behave like free atoms; but when the solution is electrolyzed, the hydrogen ions carry their positive charges to the negative electrode, and, giving them up, become free atoms, which unite together to form diatomic molecules of gaseous hydrogen. Similarly the chlorine ions travel to the positive electrode and surrender their

[1] From strong solutions; but when the solution is dilute, the nascent chlorine may act chemically on the water.

[2] *Zeit. physik. Chem.*, 1, 631 (1887).

negative charges, and the atoms of chlorine then either unite together to form molecules or they act on the water, forming oxyacids of chlorine or hydrochloric acid and free oxygen.

In the case of very dilute aqueous solutions of hydrochloric acid, the molecular weight of the acid calculated from the depression of the freezing point of the water has half the normal value, and it is concluded that electrolytic dissociation is complete or very nearly so; that there are, in fact, very few, if any, molecules of dissolved hydrogen chloride, but only hydrogen and chlorine ions. With stronger solutions the calculated molecular weight is somewhat higher, but still far below that corresponding to the formula HCl, and it is concluded that dissociation is not complete.

So also with other strong acids, with strong bases, and with salts derived from them, and even with salts derived from strong acids and weak bases or strong bases and weak acids; in very dilute aqueous solution the molecular weight calculated from the depression of the freezing point or the rise of the boiling point is in general a simple sub-multiple of that corresponding to the molecular formula. In all such cases it is concluded that complete or nearly complete electrolytic dissociation occurs. Thus, in dilute aqueous solution—

	Number of Ions from Molecule of Acid, Base, or Salt.
$NaCl = Na^{\cdot} + Cl'$	2
$HNO_3 = H^{\cdot} + NO_3'$	2
$AgNO_3 = Ag^{\cdot} + NO_3'$	2
$KOH = K^{\cdot} + OH'$	2
$FeSO_4 = Fe^{\cdot\cdot} + SO_4''$	2
$Na_2SO_4 = 2Na^{\cdot} + SO_4''$	3
$K_2C_2O_4 = 2K^{\cdot} + C_2O_4''$	3
$K_4Fe(CN)_6 = 4K^{\cdot} + Fe(CN)_6''''$	5
and so on	

The dot, $\cdot$, represents the + sign; the dash, $'$, the − sign.

In the case of weak acids, weak bases, and the salts derived from them, the molecular weights (M′) calculated from the depression of the freezing point or the rise of the boiling point approach more closely to those (M) corresponding to the chemical formulæ, and it is believed that electrolytic dissociation is incomplete, the solutions containing both undissociated molecules and ions.

Let n be the number of ions derived from one molecule of substance, and x the fractional number of molecules dissociated; then—

$$x = \frac{(M - M')}{(n - 1)M'}.$$

It is believed that the changes which are observed in qualitative analysis take place through interaction of the ions, and not of the molecules. Thus when aqueous solutions of silver nitrate and hydrochloric acid are mixed together, the formation of insoluble silver chloride is expressed by the equation—

$$Ag^{\cdot} + NO_3' + H^{\cdot} + Cl' + Aq = AgCl + H^{\cdot} + NO_3' + Aq.$$

If none of the substances which would be formed by such a reaction are insoluble, no change at all takes place. Again, on adding silver nitrate to a solution of carbon tetrachloride in dilute alcohol, the substances present are—

$$Ag^{\cdot} + NO_3' + CCl_4 + Aq(+ \text{alcohol})$$

and no reaction is possible.

The theory of electrolytic dissociation is supported by the following, among other considerations:—

1. When equivalent quantities of strong acids and bases are mixed together in dilute aqueous solution, the amount of heat evolved is almost independent of the nature of the acid or base.

According to the theory, the reactions which occur are expressed by such equations as the following:—

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + H_2O$$
$$H^{\cdot} + NO_3' + K^{\cdot} + OH' = K^{\cdot} + NO_3' + H_2O$$
$$\tfrac{1}{2}\{2H^{\cdot} + SO_4'' + 2Na^{\cdot} + 2(OH)' = 2Na^{\cdot} + SO_4'' + 2H_2O\}$$
$$\tfrac{1}{2}\{2H^{\cdot} + 2Cl' + Ca^{\cdot\cdot} + 2(OH)' = Ca^{\cdot\cdot} + 2Cl' + 2H_2O\}.$$

The change—combination of hydrogen with hydroxyl to form water—is the same in each case.

On the other hand, with a weak acid and a weak base, the amount of heat evolved is smaller; and this is accounted for by the assumption that the solutions contain not only ions but undissociated molecules. The number of hydrogen and hydroxyl ions which unite to form water is therefore smaller. For details of this subject, see Thomsen's "Thermo-Chemistry," translated by Miss Burke (this series).

2. The molecular (electrical) conductivity of an electrolyte may be defined in the following manner:—

Imagine a vessel formed of two very large electrodes 1 cm. apart, the other two walls and the bottom of the vessel being formed of non-conducting material. Let an aqueous solution containing 1 gram-molecule of the electrolyte be placed in the cell. The con-

ductivity of the system will then be called the molecular conductivity of the electrolyte.[1]

The molecular conductivity depends on the substance and on the temperature, increasing about 2 per cent. per degree. For a given substance at constant temperature it increases with the dilution, the increase being small with good conductors, but considerable with bad ones. In all cases it approximates with increase of dilution to a limiting value, which can be reached in practice with good conductors, but not with bad ones.

If the electricity is conveyed by the ions, the conductivity of a given electrolyte must be proportional to the number of ions present; and it is believed that when the maximum molecular conductivity is reached in very dilute solutions, electrolytic dissociation is complete. It was discovered by Hittorf in 1853 that when aqueous solutions of different substances are electrolyzed, the change in concentration in the neighbourhood of the two electrodes is usually different, and in order to explain the facts he advanced the theory that the velocities of migration of the ions are different. He showed, also, how the relative velocities could be calculated from the relative changes in concentration. Kohlrausch, in 1876, pointed out that the conductivities of salts, acids, and bases may be regarded as the sum of two values, one depending on the positive, the other on the negative ion; and that, when dissociation is complete, the conductivity of electrolytes affords a measure of the relative velocities of migration of the ions.

In the following table the conductivities of equivalent quantities of a few electrolytes are given for different states of dilution at the same temperature:—

Dilution.	Conductivity.			
	KCl.	NaCl.	$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}MgSO_4$
litres.				
1	91·9	69·5	67·2	27·0
10	104·7	86·5	89·7	47·4
100	114·7	96·2	109·8	71·5
1,000	119·3	100·8	120·7	93·5
10,000	120·9	102·9	124·9	103·4
50,000	121·7	102·8	126·0	105·2
100,000	121·6	102·4	127·5	105·6

[1] For a full account of the methods of determining molecular conductivity, and of the results obtained, see Lehfeldt's "Electro-Chemistry" (this series).

In each case the conductivity is nearly constant for the three highest states of dilution, and the mean of the three values may be taken as the maximum; namely, KCl, 121·4; NaCl, 102·7; $\frac{1}{2}K_2SO_4$, 126·1; $\frac{1}{2}MgSO_4$, 104·7.

With solutions of potassium chloride the concentration is very nearly the same at both electrodes, and it is therefore concluded that the velocity of migration of the K and Cl ions is the same. Adopting the arbitrary value $\frac{121\cdot4}{2} = 60\cdot7$ as the velocity of these ions, that of the Na ions, $102\cdot7 - 60\cdot7 = 42$; of the SO_4 ions, $126\cdot1 - 60\cdot7 = 65\cdot4$; and of the Mg ions, $105\cdot6 - 60\cdot7 = 44\cdot9$.

The conductivity of the strong acids and bases is greater than that of salts; thus for HCl the maximum value is about 346; hence the velocity of the H ions is about $346 - 61 = 285$, and that of the OH ions, derived from the conductivity of potassium hydroxide, about 154.

Strong acids and bases obey the law of Kohlrausch, but weak acids and bases do not; and it has already been stated that the dissociation of these substances appears to be incomplete. On the other hand, the law applies to salts derived from strong acids and weak bases, or from weak acids and strong bases, and the velocities of all the ions can therefore be determined. If μ is the molecular conductivity, and u and u' are the velocities of migration of the ions, the equation $\mu = u + u'$ holds for very dilute solutions of strong acids and bases and of salts derived from a strong acid or a strong base; but for stronger solutions of these substances and for dilute solutions of weak acids and bases and of salts derived from them the equation should be written—

$$\mu = x(u + u')$$

where x is the fractional number of molecules dissociated.

If the solution is infinitely diluted, dissociation is complete, and—

$$\mu_\infty = u + u'.$$

It would, of course, be impossible to determine directly the conductivity of a solution of infinite dilution; but, as already stated, the values of u and u' may be indirectly determined for all ions, and thus the value of μ_∞ may be ascertained.

From the two equations—

$$\mu = x(u + u')$$

and $$\mu_\infty = u + u'$$

the degree of electrolytic dissociation may be calculated, for—

$$x = \frac{\mu}{\mu_\infty}.$$

The values of x determined in this way agree satisfactorily with those calculated from the depression of the freezing point and the rise of the boiling point.

From what has been mentioned with regard to the influence of temperature on the solubility of salts (p. 275), it follows that in strong solutions there may be at the same time (*a*) ions formed by electrolytic dissociation, (*b*) molecules of the anhydrous salt, (*c*) molecules of the salt in one or more states of hydration.

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