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INTRODUCTION TO PHYSICAL CHEMISTRY

by

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THIRD EDITION

Revised by

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WITH 155 FIGURES



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PREFACE TO THE THIRD EDITION

In the present revised edition several changes have been made. While much of classical physical chemistry remains unchanged, in several fields considerable simplification and clarification has occurred. The chapters on velocity of chemical reaction and catalysis have been largely rewritten, combined, and transferred to almost the end of the book. This is more in accordance with the logical procedure in physical chemistry. Similarly the chapter on photochemistry has disappeared and the newer matter incorporated in the chapter dealing with chemical change. The chapters on the colloidal state and adsorption have also been revised with the inclusion of a small amount of high polymer physical chemistry as an indication of the more precise development of colloid chemistry.

It has been my desire to maintain the character of the book as an Introduction to Physical Chemistry, making no demands on the reader of advanced mathematical knowledge. Any discussion of the quantum mechanical theory of valence has therefore been omitted ; and, in the introductory chapter, no attempt has been made to deal with modern advances in nuclear physics since these have no important impact on elementary physical chemistry.

H. W. MELVILLE.

1952.

PREFACE TO THE FIRST EDITION

In the present *Introduction to Physical Chemistry*, which has been written at the request of former colleagues, the aim has been to provide a textbook which should not only serve as an introduction to the study of physical chemistry but should also carry the student on to such a point that he can read with profit the numerous special monographs which are now available. The work is designed, more especially, to meet the needs of the student of chemistry who desires to build his later specialised study on a broad foundation.

Owing to the rapid advances made in recent years by physical science the difficulty of selecting the subjects for treatment in an introductory course of physical chemistry is very great, and in making the selection one must be guided by one's experience as a teacher. In general, the historical method of treatment, a method which seems to be the soundest one educationally and one which is particularly needed at the present time, has been adopted. An acquaintance with the historical development of a subject is necessary for a true understanding and appreciation of its present state, and has a cultural value which should constantly be emphasised.

Physical chemistry is essentially an exact and quantitative branch of science, and requires for its proper understanding and for its advancement a sound knowledge of mathematics, covering at least the elements of the differential and integral calculus. Moreover, in order to secure a proper understanding of and familiarity with the subject, it is necessary that the student should practise himself in the solving of numerical problems. Examples of such problems are worked out in the body of the text, and a number of problems for solution by the student are collected together in an appendix. In such a work as the present, the number of such problems must, of course, be somewhat restricted ; but several special works dealing with calculations in physical chemistry are now available, and should be made use of by every serious student of the subject. The numerous references to the original literature which are given in the text will also furnish the teacher with the sources from which other problems can be obtained.

I would express my thanks to my colleagues, Dr J. E. Humphries and Dr A. R. Martin, for their valuable assistance in preparing this work and in reading the proof sheets.

ALEX. FINDLAY.

August 1933.

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CHAPTER I

THE CONSTITUTION OF MATTER

Atomic and Molecular Theory.—Although Robert Boyle had, in the seventeenth century, raised chemistry to the rank of a science, it was not till towards the end of the eighteenth century that chemistry became an exact science. During the course of the latter century many new substances, especially gases, had been discovered, but the facts of chemistry remained, to a large extent, isolated data of experience, unconnected by quantitative laws and uninterpreted by any exact theory capable of quantitative expression. With the recognition, however, by the brilliant French chemist, Antoine Laurent Lavoisier (1743-94), of the supreme importance of the balance as an essential aid in the study of chemical reactions, and with his enunciation and verification in 1785 of the law of conservation of mass, a new epoch in chemistry—the quantitative epoch—was inaugurated. At the beginning of the nineteenth century, therefore, the time was ripe for the enunciation by John Dalton (1766-1844), a Manchester schoolmaster, of the *atomic theory*, by means of which the laws of chemical combination (law of constant composition, law of multiple proportions, etc.) could be quantitatively explained and co-ordinated.

The general hypothesis of the atomic or discontinuous constitution of matter had been put forward by the Epicurean philosophers of ancient Greece in the fourth and fifth centuries B.C., but that hypothesis could not be of any real value in science until it had been developed in such a way that its deductions could be *quantitatively* tested. By postulating the existence of indivisible and indestructible *atoms* of matter which have definite weights or masses, different in the case of different elements, Dalton was able to give an explanation of the quantitative laws of chemistry and of the relative proportions in which the elements combine.

It was the introduction of this quantitative factor into the hypothesis of the atomic constitution of matter which made it possible for the atomic theory to become the basis of physical science during the nineteenth century. Of one important chemical property, however, the property of valence, the atomic theory gave no explanation.

Although it is possible, on the basis of the experimental investigations of the present century, to calculate the absolute masses of atoms, it is not with these absolute masses but with the *relative masses* of the atoms, the so-called *atomic weights*, that chemistry is mainly concerned; and in view of the importance of a knowledge of atomic weights for the application of the atomic theory, the Swedish chemist, Jöns Jakob Berzelius (1779-1848), Professor of Chemistry at the Medico-chirurgical Institute, Stockholm, devoted himself with great energy and ability to their determination.

For the determination of the atomic weights of elements it is necessary, in the first place, to determine, as accurately as possible, the chemical *equivalents*, or proportions by weight in which the elements can combine with a definite weight of some standard element; for example, with eight parts by weight of oxygen. But this is only the first step. If it could be assumed that all compounds are formed by the combination of only one atom of each element, then the value of the equivalent would also be the value of the atomic weight referred to the atomic weight of oxygen equal to eight. This assumption, however, cannot be made. Elements, it was soon discovered, combine in more than one proportion; and although it was clear that the atomic weight must be equal to the equivalent or to some multiple of the equivalent, it was not possible, without further information, to decide what multiple of the equivalent was to be taken as the atomic weight. In the case of solid elements some guidance was given by the law of Dulong and Petit, enunciated in 1819, and by the law of isomorphism, enunciated by Mitscherlich in 1820, but it was not until 1858-60 that chemists, led by Stanislao Cannizzaro (1826-1910), at that time Professor of Chemistry in the University of Genoa, realised that the molecular hypothesis of Avogadro and the determinations of molecular weights which were founded on it, furnished a sure means of deciding between conflicting values of the atomic weight.

with respect to physical properties (*e.g.*, atomic volume) by Lothar Meyer, and with respect to chemical properties by Mendeléeff.

Although the familiar Mendeléeff classification of the elements, according to ascending atomic weights, proved to be of much value both as a means of correcting doubtful atomic weights and as a guide in the discovery of new elements, it exhibited certain defects which indicated that the periodic law, as stated by Mendeléeff, was only an approximate law. Thus, in order that the proper periodicity of properties might be secured, the strict order of arrangement according to ascending atomic weights had, in some cases, to be altered. In order, for example, that iodine should come into the group of the halogen elements, it was necessary to place it after the element tellurium, although the atomic weight of iodine is less than that of tellurium. Similarly, cobalt, with higher atomic weight, had to be placed before nickel, and argon at a later time had to be placed before potassium, an element of lower atomic weight. For a large number of closely related elements, the so-called rare earth elements, no satisfactory position could be found in the Mendeléeff classification. In spite, however, of the anomalies which existed, and which have now been explained, the regularities which were observed clearly pointed to a close interconnection between the elements and aroused fresh interest in investigations relating to the nature of the atom and the problem of the constitution of matter.

Cathode Rays. Electrons.—In 1859 it was discovered by the German physicist, Julius Plücker (1801-68), that when an electric discharge is allowed to take place in a highly evacuated glass tube, the negative electrode, or *cathode*, emits a radiation which excites a luminescence in the glass of the tube opposite to the cathode. This radiation, known as the *cathode rays*, travels in straight lines, and if a solid object is placed in the path of the rays, a shadow is cast. A wheel, also, may be caused to rotate by allowing the cathode rays to strike against its vanes, and a number of minerals emit luminescence when bombarded by the cathode rays. Moreover, the rays may be brought to a focus by means of a concave cathode, and a metal placed at the focus can be raised to incandescence or even melted. When the cathode rays are suddenly checked in their motion by allowing them to impinge on a plate of

dense metal, electro-magnetic disturbances, of the same nature as ordinary light but of extremely short wave-length, are produced. These so-called X-rays are very penetrating, and have the property of ionising a gas through which they are passed.

In 1879 it was surmised by Sir William Crookes (1832-1919) that the cathode rays are composed of small particles or corpuscles, and the correctness of this surmise was proved in 1897 by Sir J. J. Thomson (1856-1940), at that time Cavendish Professor of Physics in the University of Cambridge. That the cathode rays are the carriers of negative electricity was already known from the fact that they are deflected in a particular manner by a magnet; and by determining the amount by which a narrow beam of cathode rays was bent under the action of a magnetic field of strength H, the ratio mv/e could be calculated from the relation $Hev = mv^2/r$. In this expression, e is the electric charge on the particle of mass m and velocity v, and r is the radius of curvature of the beam. Further, the rectilineal path of the rays could be restored by means of an electrostatic field placed at right angles to the magnetic field, the field required being given by the expression $Xe = Hev$, where X is the strength of the electrostatic field. From this expression the value of v was calculated and its average value found to be $2{\cdot}8 \times 10^9$ cm. per sec. When v is known, the ratio e/m can be calculated from the value of mv/e. Except when the velocity of the cathode rays approached that of light,[1] the ratio e/m was found to have a constant value of about $1{\cdot}79 \times 10^7$ electromagnetic units per gram, irrespective of the nature of the cathode and of the residual gas contained in the tube. A more recently determined value[2] is $1{\cdot}759 \times 10^7$ e.m.u./g.

The value of e, the unit electric charge, was determined by the American physicist Robert A. Millikan, Professor of Physics at the California Institute of Technology, Pasadena, by studying the rate of motion of a minute droplet of oil suspended in air between two horizontal plates which could be electrically charged.[3] The oil droplet is, normally, positively charged, and moves with a certain velocity, against

[1] The "mass" of an electron, it should be noted, increases with increase in the velocity of motion.

[2] R. T. Birge, *Phys. Rev.*, 1940, (ii), **58**, 658.

[3] *Phys. Rev.*, 1913, **2**, 143.

gravity, towards the upper, negatively charged plate. When the air is ionised by the passage through it of X-rays, the oil drop can take up one or more of the negatively charged particles so produced. Its positive charge is thereby reduced and the velocity of motion towards the negatively charged metal plate is retarded. The change in the velocity of motion, however, was found to be not continuous but abrupt, indicating that the oil drop had captured an ion carrying a certain definite amount of negative electricity ; and as each successive ion was captured the change of velocity of motion of the oil droplet was the same. That is to say, the charge on the droplet varies discontinuously by a definite unit amount, or by some multiple of this unit. From the magnitude of the charge on the metal plate and from the velocity of motion and mass of the droplet, it was possible to calculate the value of the unit charge, e. This was found to be $4{\cdot}80 \times 10^{-10}$ electrostatic units, the same value as the charge carried by a hydrogen ion in solution. From these experiments it is clear that electricity also must be atomic, and exists only as unit charges or as multiples of these.

Since, in the electrolysis of an aqueous solution, 96,500 coulombs (1 faraday) [1] of electricity liberate 1·008 g. of hydrogen, one electromagnetic unit [2] would liberate $1{\cdot}044 \times 10^{-4}$ g. Therefore the ratio $\frac{e}{m} = \frac{1}{1{\cdot}044 \times 10^{-4}} = 0{\cdot}9577 \times 10^4$ e.m.u./g.

In the case of cathode rays, we have seen, $\frac{e}{m} = 1{\cdot}759 \times 10^7$ e.m.u./g., and since the value of e is the same in both cases, it follows that the mass of the cathode particle must be smaller than that of the hydrogen atom in the ratio $\frac{0{\cdot}9577 \times 10^4}{1{\cdot}759 \times 10^7} = \frac{1}{1840}$.

One sees, then, that through the study of the discharge of electricity through gases the existence was revealed of negatively charged particles, or *electrons* as they are now called, having a mass of only $\frac{1}{1840}$ of that of the hydrogen atom, the lightest atom or particle of matter then known. The electron, moreover, may be regarded as the unit of negative electricity.

[1] We shall, in general, use the round number in place of the more exact value 96,494 coulombs.

[2] One electromagnetic unit = 10 coulombs = $2{\cdot}998 \times 10^{10}$ electrostatic units.

Investigation has shown that electrons can be produced in various ways : by the electric discharge as cathode rays, by the action of ultra-violet light on metals, and by the raising of metals to incandescence, as in the so-called thermionic emission used in wireless valves. In all cases the electrons are the same, and therefore the electron must be a constituent of many different substances. From this consideration there arose the conception of the electronic constitution of matter or of the atom.

In the phenomena of *radioactivity*, further, a very striking indication of the complex nature of the atom is given. According to the disintegration theory of radioactivity, the atom of a radioactive element is a complex system of particles which undergoes spontaneous change or disintegration with the emission of alpha (α), beta (β), and gamma (γ) rays.

The alpha rays are positively charged particles, which were shown by Sir William Ramsay (1852-1916), Professor of Chemistry in University College, London, and by Sir Ernest Rutherford (Lord Rutherford), to be positively charged helium atoms or helium nuclei. They have very slight penetrating power but, on account of their mass, have a relatively large amount of energy. The beta rays consist of negatively charged electrons which move with a velocity approaching that of light and have considerable penetrating power. The gamma rays are electromagnetic vibrations of very short wave-length, and are of the same nature as X-rays and ordinary light. They have very great penetrating power.

Atomic Structure.—Since negatively charged electrons constitute, as has been pointed out, a part of the atom of different substances, and since the atom, as a whole, is electrically neutral, it follows that there must be an amount of positive electricity within the atom equal to the total negative charge carried by the electrons. From the fact that an alpha particle, emitted by a radioactive substance, may pass in a straight line through the atoms of a gas and only occasionally suffer a sharp deflection,[1] Rutherford put forward the view that the positive electricity is concentrated on a very minute nucleus in which, also, practically the

[1] As shown by the fog-track experiments of C. T. R. Wilson (*Phil. Trans.*, 1897, A, **189**, 265). Rutherford's hypothesis was also based on the deflection of alpha particles on passing through thin metal foil (*Phil. Mag.*, 1906, **11**, 166). See also H. Geiger, *Proc. Roy. Soc.* .1908, A, **81**, 174 ; 1910, A, **83**, 492 ; Geiger and Marsden, *ibid.*, 1909, A, **82**, 495.

whole mass of the atom is supposed to reside, the mass of the electrons being, in comparison, negligibly small. Around this minute positively charged nucleus the negative electrons are arranged in various so-called orbitals.

And what is the nature of the positively charged nucleus ? The atoms of the radioactive elements, on disintegrating, emit, in some cases, alpha particles or positively charged helium nuclei, and in other cases beta rays or negatively charged electrons. In the case of the heavy atoms of the radioactive elements, therefore, the positively charged nucleus of the helium atom would seem to be one of the units of atomic nuclear structure ; but since the mass of the helium atom, or nucleus, is nearly four times that of the hydrogen atom, the helium nucleus must itself be regarded as complex. The conclusion, therefore, is reached that the positively charged nucleus of the hydrogen atom, the lightest atom, is itself the structural unit of positive charge. To this unit the name *proton* has been given.

For many years no positively charged particle of mass less than that of the proton was known, but in 1932, C. D. Anderson,[1] of the California Institute of Technology, while studying the bombardment of a gas by cosmic rays, discovered the production of positively charged particles with a mass equal to that of the negatively charged electrons. These positively charged particles, called *positrons*, were later found to be emitted by artificially produced radioactive substances.

While the nucleus of the hydrogen atom can be regarded as formed by a single proton, the nuclei of the other elements must be more complex structures and consist of both protons and electrons. Thus, in the case of helium the nucleus must contain four protons, because the mass of the helium atom is about four times the mass of the hydrogen atom. From the behaviour of the alpha rays, however, the conclusion must be drawn that the helium nucleus carries only two positive charges, and, consequently, the four protons of the nucleus must be associated with two electrons in order that the excess positive charge may be only two units.

It was, at first, considered that the protons and electrons exist free in the nucleus, but it was discovered in 1932 by

[1] *Science*, 1932, **76**, 238. See also P. M. S. Blackett and G. P. S. Occhialini, *Proc. Roy. Soc.*, 1933, A, **139**, 699.

(Sir) James Chadwick,[1] working in the Cavendish Laboratory, Cambridge, that when beryllium or boron is bombarded by alpha particles, stable uncharged particles of great penetrating power are emitted. The emission of these *neutrons*, as they are called, has led to the view that atomic nuclei consist of neutrons and protons, probably with helium nuclei as secondary units. These helium nuclei are themselves regarded as consisting of a very stable combination of two protons and two neutrons.

In the production of the atomic nuclei of the heavy elements there is a great loss of mass, and therefore a liberation of a very large amount of energy, with the result that a very stable nucleus of protons and neutrons is formed. At the same time helium nuclei, more loosely held, may also be present, as they probably are in the case of the radioactive elements, since helium nuclei are expelled from the latter as α-rays. The single protons, however, are too firmly held, and do not appear among the products of radioactive disintegration.

In general, then, an atom is to be regarded as consisting of a positively charged complex nucleus, made up of protons and neutrons, round which revolve planetary electrons equal in number to the excess positive charge on the nucleus.

The picture which is thus obtained of the atom is that of a very open-spaced system of particles, the diameters of which are very small compared with that of the system as a whole, or of the *atomic domain* as it is called. The diameter of an electron, it has been calculated, is only about one forty-thousandth of the diameter of the atom, and the diameter of the proton is still less, being about one eighteen-hundred and fortieth ($\frac{1}{1840}$) of the diameter of an electron. The structure of an atom of hydrogen, therefore, has been compared with that of the solar system, and it has been pointed out that since the diameter of the earth is one twenty-thousandth of the diameter of its orbit round the sun, one can think of a hydrogen atom as a system in which the earth represents an electron circling round a nucleus (much smaller than itself) at a distance equal to twice the distance of the earth from the sun. The atom, therefore, is mainly void, a thing of specks and spaces, and one can understand how an alpha particle can pursue a straight path through the atoms of matter and be only occasionally

[1] *Proc. Roy. Soc.*, 1932, A, **136**, 692; 1933, A, **142**, 1.

diverted from its course by a near approach to or collision with the massive, positively charged nucleus. Moreover, from a study of the scattering of α-rays in their passage through different substances, *e.g.*, gold, silver, and copper, Rutherford was able to calculate the charge on the nucleus of the different atoms. In all cases this charge was found to be approximately equal to about half the atomic weight of the element.[1]

Atomic Number.—The relation which was shown by Rutherford to exist between the number of unit charges on the nucleus and the atomic weight of an element was in harmony with the conclusion arrived at by C. G. Barkla from a study of the scattering of X-rays, namely, that the number of extranuclear electrons is about half the atomic weight.[2] The number of these electrons must, of course, be equal to the number of unit positive charges on the nucleus.

One of the most important advances in connection with the problem of atomic structure was the identification of the number of excess positive charges on the atomic nucleus with the serial number, or *atomic number* as it is now called, of the element in the periodic classification.[3] By determining the serial number, therefore, a knowledge could be obtained of the number of extranuclear electrons in the atom, or of the excess positive charge on the nucleus. Such a determination was first made by Henry Gwyn Jeffreys Moseley (1887-1915), working in the physics laboratory of the University of Manchester.[4]

It has already been pointed out that when cathode rays are allowed to impinge on a target X-rays are generated; and it was found by Moseley, in 1913, that when these X-rays are analysed by means of a crystal, which acts as a diffraction grating (Chap. VI.), each substance used as a target emits, not only a general radiation, but also X-rays of definite wave-length characteristic of the material of the target. In other words, each substance gives a definite X-ray spectrum; and the spectra so obtained are exceedingly simple and consist of groups of lines known as the K, L, M, etc., series.

[1] *Phil. Mag.*, 1911, (6), **21**, 669; H. Geiger and E. Marsden, *ibid.*, 1913, **25**, 604. See also C. G. Barkla, *Phil. Mag.*, 1911, **21**, 648.

[2] *Phil. Mag.*, 1911, (6), **21**, 648.

[3] A. van den Broek, *Physikal. Z.*, 1913, **14**, 32; Niels Bohr, *Phil. Mag.*, 1913, (6), **26**, 476; J. Chadwick, *ibid.*, 1920, (6), **40**, 734.

[4] *Phil. Mag.*, 1913, (6), **26**, 1024; 1914, (6), **27**, 703.

As is seen from Fig. 1, which reproduces the K series of lines in the spectra of the elements from calcium to copper, omitting scandium, there are two well-marked lines, a stronger (α) and a weaker (β). There is, moreover, an obvious regularity in the shift of the corresponding lines as

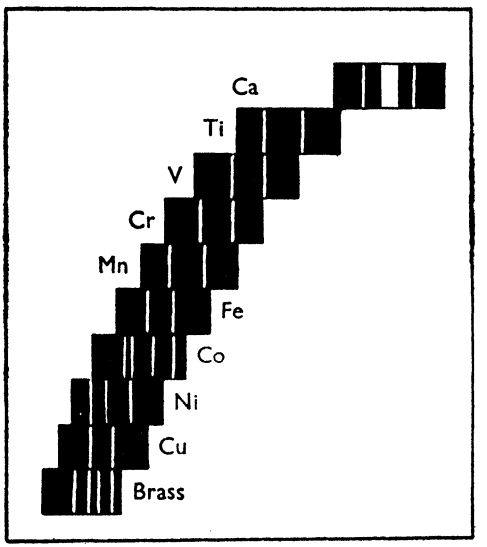


FIG. 1.
(From *Philosophical Magazine*, by permission.)

one passes from element to element, and Moseley found this shift to be in accordance with the equation,

$$\sqrt{\bar{\nu}} = \sqrt{1/\lambda} = a(Z - b),$$

where $\bar{\nu}$ is the wave number [1] and λ is the wave-length of the particular lines in centimetres; a and b are constants, and Z is an integer which is characteristic of the element and was called by Moseley the *atomic number*. It is clear, therefore, from this relationship, that if the square root of the wave number is plotted against the values of Z, a straight line will be obtained. In other words, the square root of the wave number of the corresponding line in the X-ray spectra of the elements increases by *equal amounts* as one passes from element to element. As Moseley wrote: "There

[1] The wave number is the reciprocal of the wave-length measured in centimetres.

is in the atom a fundamental quantity which increases by regular steps as we pass from one atom to the next. This quantity can only be the charge on the central positive nucleus."

The investigation of the X-ray spectra of the elements, then, has shown that to each element there may be given a whole number which represents its serial number in the list of elements, starting from hydrogen which has the atomic number 1, up to californium which has the atomic number 98; and the important conclusion can be drawn that as one passes from element to element, ascending the series, there is, at each step, an addition of one unit of positive electricity to the nucleus, and a corresponding increase in the number of extranuclear electrons.

When one arranges the elements in order of their atomic numbers (Fig. 2),[1] it is found that the anomalies of the Mendeléeff classification according to atomic weights (p. 5) disappear. That is, argon and potassium, tellurium and iodine, cobalt and nickel, follow regularly in the order of their atomic numbers as given by their X-ray spectra and as required by their chemical properties. Since it is now recognised that the chemical and most of the physical properties of an element depend on the number and arrangement of the extranuclear electrons, rather than on the atomic weight, the periodic law may be restated in the form: *The properties of the elements are a periodic function of the* ATOMIC NUMBER. The recognition of the fact that the atomic number is more definite and fundamental than the atomic weight as an index of the properties of an element, constitutes one of the most important advances in chemical theory in modern times.

The existence, moreover, of a series of integral atomic numbers not only shows that the elements are limited in number but also throws light on the number of elements still to be discovered. This fact is of especial importance in the case of the elements of the rare earth group, which occupied an ill-defined position in the periodic table of Mendeléeff and offered no internal evidence regarding the possible number of elements belonging to the group. By means of their X-ray spectra the identity of the rare earth metals, so difficult to separate and distinguish by chemical methods, can readily be confirmed.

[1] J. Thomsen, *Z. anorgan. Chem.*, 1895, **9**, 190, 283; N. Bohr, *Ann. Physik*, 1923, **71**, 228.

In the arrangement of the elements in ascending order of atomic numbers (Fig. 2), it is seen that the elements fall into a number of series or " periods," the fuller significance of which will appear later. After the first two elements, hydrogen and helium, which stand at the head of the two groups of related elements (the alkali metals and the inert gases) forming the end members of the succeeding periods,

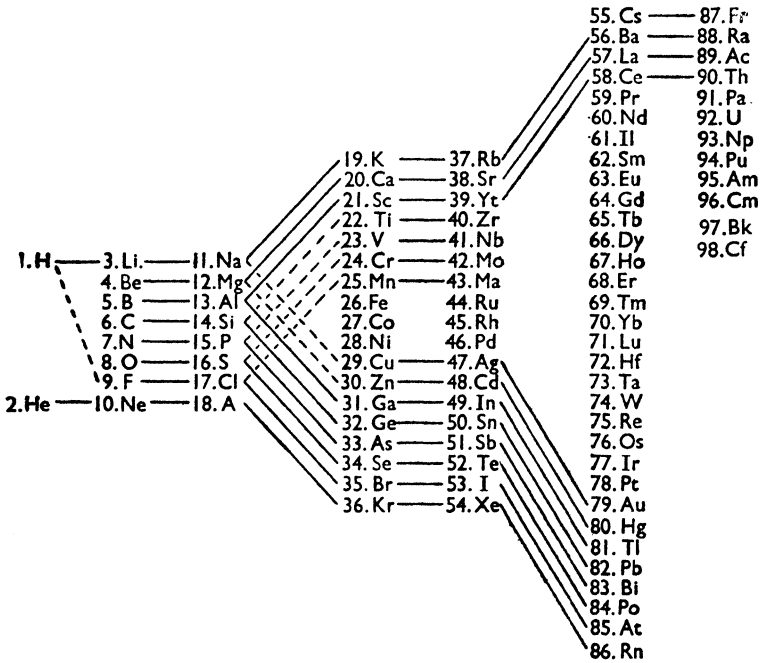


FIG. 2.—Periodic Classification of the Elements.

there come two short periods of eight elements each. Thereafter, two periods of eighteen elements each, one period of thirty-two elements, and, lastly, a fragmentary period of twelve elements. Owing to the periodicity of properties, elements of similar or analogous character fall into corresponding places in the various periods, and in Fig. 2 the members of these " natural families " or groups of related elements are joined together by full-drawn lines. The dotted lines join elements which are related to each other in certain respects, although not so closely as the members of the " natural families " just mentioned.

Hydrogen, it may be noted, is unique in that it may show a certain analogy both to the alkali metals and to the halogens. Thus, by the loss of an electron, hydrogen forms a positively charged ion (proton), just as sodium, for example, by the loss of an electron, forms positively charged sodium ion. Hydrogen, therefore, like sodium, has a positive electrovalency of 1. Moreover, hydrogen may, in certain circumstances, add on an electron and so form a negative ion, as in lithium hydride, just as chlorine, by accepting an electron, forms chloride ion. Hydrogen, therefore, may also show a negative electrovalency of 1.

Between the values of the atomic numbers of related elements, certain numerical relationships have been discovered. Thus the atomic numbers of the inert gases, 2, 10, 18, 36, 54, 86, form a series represented by the expression :—

$$Z = 2 \times 1^2 + 2 \times 2^2 + 2 \times 2^2 + 2 \times 3^2 + 2 \times 3^2 + 2 \times 4^2.$$

This series, known as the *Rydberg series*, is, of course, also found in the number of elements forming a period. As we have seen, the number of elements in the different periods are 2, 8, 8, 18, 18, 32, or 2×1^2, 2×2^2, 2×2^2, 2×3^2, 2×3^2, 2×4^2. We shall learn, presently, that this arrangement of the elements has also a basis in the spectroscopic behaviour of the elements.

It will be evident that the relationship, $\sqrt{1/\lambda} = a(Z - b)$, gives a means not only of ascertaining the atomic number Z from the experimentally determined value of λ, but also of calculating the value of λ from a given value of the atomic number Z. Since the atomic numbers form a series of integers increasing by single units, the atomic numbers of hitherto undiscovered elements are known, and therefore the wave-length of the X-ray spectral lines can be calculated. Guidance is thus given in the search for missing elements, and, since 1917, the existence of several new elements (protactinium, hafnium, and others) has been discovered by means of their X-ray spectra.

Isotopes.—Since the nucleus of the heavier elements is a complex structure, made up of protons and neutrons, it is clear that if one neutron were removed from the nucleus the atomic weight would be reduced by unity (the mass of one neutron), but the positive charge on the nucleus would be unaltered—that is to say, the atomic number or the number

of extranuclear electrons would be unchanged. The theory of atomic structure discussed in the preceding pages, therefore, opens up the astounding possibility of the existence of elements which have the same atomic number (and are therefore chemically identical) but have different atomic weights. The existence of such elements was first realised in the case of radioactive elements—a fact which is not surprising, since radioactive change is associated with a disintegration of the nucleus.

In 1906, B. B. Boltwood (1870-1927), of Yale University, found that if salts of the two radioactive elements, ionium and thorium, are mixed it is impossible to separate them again by any chemical process ; and the spectra, also, of the two elements were later found to be identical. Moreover, in 1911, it was pointed out [1] by Frederick Soddy that the emission of an α-ray from the nucleus of a radioactive element corresponds to a lowering of the atomic number by two units and a diminution of the atomic weight by four units, because the atomic weight of helium is 4, whereas its atomic number is 2. In the disintegration, for example, of radium to form radium-B, we have the series :

	Radium	$\longrightarrow$ (α-ray.)	radon	$\longrightarrow$ (α-ray.)	radium-A	$\longrightarrow$ (α-ray.)	radium-B
Atomic weight .	226		222		218		214
Atomic number .	88		86		84		82

The atomic number of radium-B, therefore, is the same as that of lead, but its atomic weight (214) is greater than the atomic weight of lead (207·2).

On the other hand, the emission of a β-ray (an electron) from the nucleus will increase the atomic number (or positive charge) by one unit, but, owing to the negligible mass of an electron, will leave the atomic weight unchanged. On pursuing the investigation of the radium disintegration series further, one finds the following series of changes :—

	Radium-B	$\longrightarrow$ (β-ray.)	radium-C	$\longrightarrow$ (β-ray.)	radium-C_1	$\longrightarrow$ (α-ray.)	radium-D
Atomic weight .	214		214		214		210
Atomic number	82		83		84		82

	Radium-D	$\longrightarrow$ (β-ray.)	radium-E	$\longrightarrow$ (β-ray.)	radium-F	$\longrightarrow$ (α-ray.)	radium-G
Atomic weight .	210		210		210		206
Atomic number	82		83		84		82

[1] F. Soddy, *Chemistry of the Radio-elements*, Part II (Longmans).

Radium-D and radium-G, therefore, with their different atomic weights, have the same atomic number as radium-B and lead. Elements which have the same atomic number but different atomic weights were called by Soddy *isotopes*.[1] Radium-B and radium-D are, therefore, isotopes of lead.

The final disintegration product of radium and the final disintegration product of thorium have been identified with the element lead. They have all the same atomic number. On calculating the atomic weight of the lead formed by the disintegration of radium, one finds the value 206, whereas the lead derived from thorium is calculated to have the atomic weight 208·4. Soddy, therefore, predicted that the atomic weight of lead would depend on its provenance, and this prediction proved to be correct, the atomic weight of lead derived from different sources having been found to vary from 206·08 to 207·694. One cannot escape the conviction, therefore, that ordinary lead is a mixture of isotopes of different atomic weights, and that the atomic weight value, 207·2, is merely an average value (*see below*).

The occurrence of istopes is not confined to the products of radioactive disintegration, but is met with also in the case of many of the ordinary elements. This was most abundantly proved by Sir J. J. Thomson and by F. W. Aston (1877-1945), of the University of Cambridge, who, by the method of *positive ray analysis*, were able to determine, with a high degree of accuracy, the mass of the positively charged nuclei of different elements.[2]

The cathode rays, produced by an electric discharge through a rarefied gas, ionise the atoms and molecules of gas present in the tube; that is, by collision, they split off electrons from the gaseous atoms and molecules and thus produce, also, positively charged particles, the mass of which depends on the nature of the atoms and molecules present. Under the fall of potential existing in the discharge tube, these " positive rays " pass to the cathode, and if the latter is perforated, they will pass through the perforations, forming what were originally called " canal rays." Since the particles are positively charged, they can be deflected by a magnet; and since the amount of deflection will depend on

[1] Thereby signifying that isotopes occupy the same place (from the Greek *isos* = the same, and *topos* = place) in the periodic classification.

[2] See F. W. Aston, *Isotopes* (Arnold).

the charge and mass of the particles, it is possible, from the amount of deflection produced, to draw conclusions regarding the mass of the positively charged particles.

The apparatus—the so-called *mass spectrograph*—devised by Aston,[1] is shown diagrammatically in Fig. 3. C is the

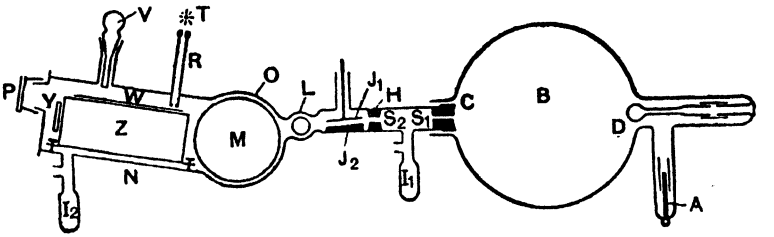


FIG. 3.—Mass Spectrograph.
(From F. W. Aston's *Isotopes*, by permission of Edward Arnold & Co.)

perforated cathode of an X-ray bulb from which electrons are projected. These ionise the gas atoms or molecules in the tube. The positive rays pass to the cathode and, having a high velocity, they pass through the perforated cathode and are formed into a fine ribbon of rays by passage through the slits S_1 and S_2. The rays are then passed through an electric field, J_1J_2, which bends the rays through a certain angle depending on the mass of the particles. A portion of the rays is selected by means of a diaphragm, and the selected part is passed through a magnetic field M, arranged in such a way that the rays are bent back again in the same plane but through an angle which is greater than the original angle of deflection. By this means a separation of the particles according to their mass is effected, analogous to the dispersion of different light waves by passage through a prism. All particles with the same ratio e/m are deviated from the original path to the same extent and fall, therefore, on the same line on a photographic plate placed in the camera at W, and particles of different mass will fall on different lines. In this way a "spectrum" can be produced in which the position of the lines depends on the mass of the positive ray. It is therefore called a *mass-spectrum*. By means of the mass-spectrograph the mass of the positively charged atomic

[1] *Proc. Camb. Phil. Soc.*, 1919, **19**, 317; *Proc. Roy. Soc.*, 1937, A, **163**, 391. A spectrograph of a different type was devised by K. T. Bainbridge, *J. Franklin Inst.*, 1933, **215**, 509.

nucleus or of a positively charged molecule can be determined with an accuracy of nearly 1 part in 100,000. A very sensitive method is thus given for determining the atomic weights of *individual atoms*. (In Fig. 3, I_1 and I_2 are tubes with charcoal which could be immersed in liquid air in order to maintain a vacuum in the apparatus, and T is a small lamp which throws a spot of light on the photographic plate through the tube R in order to give a reference point for measurements of the spectral lines.)[1]

On determining, by means of the mass-spectrograph, the mass of the positive nuclei, and therefore the mass of the atoms, of different elements, it was found that if the mass of the oxygen atom is put equal to 16·00, the masses of the atoms of other elements are all represented by whole numbers (*see below*). In some cases, *e.g.*, helium, fluorine, etc., it is found that the elements consist entirely of atoms having the same mass, but in most cases the elements are found to consist of a mixture of isotopes, the atomic masses of which, however, are represented by whole numbers : thus chlorine, the atomic weight of which as determined by chemical methods is 35·457, was found to be a mixture of two isotopes having atomic weights or mass numbers of 35 and 37 respectively, mixed together in the proportion of 3 to 1 (75·4 to 24·6). The two isotopes have the same number of extranuclear electrons (namely 17), and are therefore chemically identical,[2] but in one case the nucleus consists of 35 protons and 18 electrons, while in the other case it consists of 37 protons and 20 electrons. These isotopes are represented as ^{35}Cl and ^{37}Cl respectively. Similarly, argon, with an atomic weight of 39·944, is a mixture of isotopes having mass numbers 36, 38, and 40 ; and krypton (atomic weight = 83·80) is a mixture of no fewer than six isotopes, the mass numbers of which are 78, 80, 82, 83, 84, and 86.

[1] Modern instruments of high precision and sensitivity now record the intensity of the positive ion beams by electronic methods, the result being displayed on a paper chart or on the screen of a cathode ray tube. Such instruments are also used for the analysis of very complex gas mixtures such as, for example, hydrocarbons.

[2] Isotopes are not really chemically or physically identical, although in the case of the isotopes of the heavier elements the differences are small. Isotopes have, in some cases, been separated by physical processes, *e.g.*, by diffusion or by electrolysis (due to different ionic mobilities) ; and, chemically, the heavier isotope reacts more slowly than the lighter. Similarly, the slightly different masses give rise to different equilibrium constants for reactions involving the isotopes and their compounds.

In the table on the opposite page is given a list of the chief simple and complex (isotopic) elements,[1] the mass numbers being given in order of the relative proportions or abundance ratios of the isotopes.

Isotopes of Carbon, Nitrogen, Oxygen, and Hydrogen.—Mass spectroscopic analysis of compounds containing carbon, nitrogen, oxygen, and hydrogen revealed no evidence for supposing these elements consisted of more than one atomic species. The earlier mass spectrographs, however, had an experimental limitation in that small percentages of an isotope could not easily be detected. This was the reason for isotopy remaining undetected in these common elements. This evidence was provided in quite a different way. As will be seen later (p. 25), emission or absorption of radiation by individual atoms gives rise to line spectra. Similarly molecules give rise to spectra, but such spectra consist of a great multiplicity of lines which often condense apparently into bands. This complexity arises because molecules can vibrate and rotate, thus giving rise to many more energy levels in a molecule than in an atom. If we consider two molecules identical in every respect, except that one consists of atoms isotopic with those in the other molecule, then in virtue of the fact that isotopes have similar electronic extranuclear structure and that electrons are responsible for the binding force or valence between atoms, such valency forces will be identical in magnitude. The frequency of vibration of the molecule (ν) is controlled by the valency forces and the reduced mass of the system μ, then $\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$. Hence isotopic molecules will vibrate at different frequencies. Analysis of line spectra with instruments of high dispersion have revealed the existence of the isotopes ^{13}C, ^{15}N, and of ^{17}O and ^{18}O. The confirmation of the isotopes discovered by the mass spectrograph has been established by similar technique. The discovery of isotopes in oxygen revealed a discrepancy between the atomic weights of hydrogen as determined by physical and chemical methods, and thus led to a search for an isotope of hydrogen. This isotope was discovered by H. C. Urey (1932) by examining under great dispersion the atomic spectrum of hydrogen in the

[1] For a complete list of isotopes see *Fifteenth Report of the Committee on Atoms* (*J. Chem. Soc* **1951,** 1); Hahn, Flügge, and Mattauch, *Physikal. Z.*, 1940, **41,** 1: *Ber.*, 1940, **73,** A, 1.

Simple Elements.				Complex Elements.			
Atomic Number.	Element.	Atomic Weight.	Mass Number.	Atomic Number.	Element.	Atomic Weight.	Mass Numbers of Isotopes.
2	He	4·003	4	1	H	1·008	1, 2
4	Be	9·013	9	3	Li	6·940	7, 6
9	F	19·00	19	5	B	10·82	11, 10
11	Na	22·997	23	6	C	12·010	12, 13
13	Al	26·98	27	7	N	14·008	14, 15
15	P	30·98	31	8	O	16·000	16, 18, 17
21	Sc	44·96	45	10	Ne	20·183	20, 22, 21
22	Ti	47·90	48	12	Mg	24·32	24, 25, 26
23	V	50·95	51	14	Si	28·09	28, 29, 30
25	Mn	54·93	55	16	S	32·066	32, 34, 33
33	As	74·91	75	17	Cl	35·457	35, 37
39	Yt	88·92	89	18	A	39·944	40, 36, 38
53	I	126·91	127	19	K	39·100	39, 41, 40
55	Cs	132·91	133	20	Ca	40·08	40, 44, 42, 48, 43, 46
57	La	138·92	139	24	Cr	52·01	52, 53, 50, 54
59	Pr	140·92	141	26	Fe	55·85	56, 54, 57, 580
79	Au	197·2	197	27	Co	58·94	59, 57
83	Bi	209·00	209	28	Ni	58·69	58, 60, 62, 61, 64
90	Th	232·12	232	29	Cu	63·54	63, 65
				30	Zn	65·38	64, 66, 68, 67, 70
				35	Br	79·916	79, 81
				36	Kr	83·80	84, 86, 82, 83, 80, 78
				37	Rb	85·48	85, 87
				38	Sr	87·63	88, 86, 87, 84
				40	Zr	91·22	90, 92, 94, 91, 96
				42	Mo	95·95	98, 96, 95, 92, 94, 97, 100
				46	Pd	106·7	106, 108, 105, 110, 104, 102
				47	Ag	107·880	107, 109
				48	Cd	112·41	114, 112, 111, 110, 113, 116, 106, 108
				50	Sn	118·70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
				51	Sb	121·76	121, 123
				54	Xe	131·3	132, 129, 131, 134, 136, 130, 128, 124, 126
				56	Ba	137·36	138, 137, 136, 135, 134, 130, 132
				58	Ce	140·13	140, 142
				74	W	183·92	184, 186, 182, 183, 180
				76	Os	190·2	192, 190, 1 9, 188, 187, 186, 184
				78	Pt	195·23	195, 194, 196, 198, 192
				80	Hg	200·61	202, 200, 199, 201, 198, 204, 196
				82	Pb	207·21	208, 206, 207, 204

Balmer series; spectroscopic theory was in a sufficiently advanced state to predict the position of the line due to it, namely, for H 0·05A. Urey found such a line in the spectrum and showed conclusively that the intensity of this line could be significantly increased by evaporating off the lighter isotope from a large volume of liquid hydrogen.[1] Normally this heavy isotope is present to the extent of 1 part in 6,000 of ordinary hydrogen. Its accepted name is *deuterium*.

Physical and Chemical Atomic Weights.—Besides the established methods of determining atomic weights relative to oxygen, 16·0000, the mass spectrograph makes it possible to determine physically atomic weights because the relative abundance of the various isotopes may be measured and a suitable average value for the atomic weight computed. The difficulty arises as to the standard. The standards for the two are different, for in the mass spectrograph the standard is the oxygen isotope of mass 16. The atomic weight of oxygen, as used chemically, is higher because of the existence of oxygen isotopes of mass 17 and 18.

It will now be clear that the claim can no longer be made that the chemical atomic weights of the elements are fundamental constants, for the existence of isotopes, with their integral atomic weights, shows that the fractional atomic weights are merely average values for mixtures of different atoms. And yet, for practical purposes, the atomic weight has lost little of its former importance in chemistry on account of the fact that Nature, apparently, for some reason still unknown, mixes the isotopes in constant, or practically constant, proportions; and the chemist, in his practical operations, is concerned, not with single atoms but with very large collections of atoms.

Packing Fraction.—The earlier determinations of atomic mass by means of the mass-spectrograph had shown, as we have seen, that the atomic masses are whole numbers ("whole-number rule") when referred to the atomic mass of oxygen equal to 16·0000. To this rule, hydrogen was a marked exception. The more recent and exact determinations, however, have shown that the atomic masses of nearly all

[1] H. C. Urey, F. G. Brickwedde and G. M. Murphy, *Phys. Rev.*, 1932, **40**, 1. See also G. N. Lewis, *J. Amer. Chem. Soc.*, 1933, **55**, 1297. The ratio of ^2H to ^1H in natural waters is about 1 : 6500.

isotopes deviate to a slight extent from whole numbers, the masses of the lighter elements being greater and those of the heavier elements (up to mercury) being less than the nearest whole number. The divergence of the atomic mass from the nearest whole number divided by the mass number or number of protons in the nucleus is called the *packing fraction*, and its importance lies in its being a measure of the gain or loss of mass per proton, when the nuclear packing is changed from that of oxygen to that of the atom in question. Large packing fractions indicate looseness of packing and low stability; small packing fractions, the reverse. Of the different elements, hydrogen has the largest packing fraction, namely, $81{\cdot}2 \times 10^{-4}$. In the following table are given the isotopic weights and packing fractions of a number of the elements.[1]

TABLE OF PACKING FRACTIONS AND ISOTOPIC WEIGHTS

Symbol.	Isotopic Weight.	Packing Fraction $\times 10^4$.
^{1}H	$1{\cdot}00812 \pm 0{\cdot}00004$	$+81{\cdot}2$
^{4}He	$4{\cdot}00391 \pm 0{\cdot}00016$	$+\ 9{\cdot}77$
^{10}B	$10{\cdot}0161\ \pm 0{\cdot}0003$	$+16{\cdot}1$
^{12}C	$12{\cdot}00355 \pm 0{\cdot}00015$	$+\ 2{\cdot}96$
^{14}N	$14{\cdot}0073\ \pm 0{\cdot}0004$	$+\ 5{\cdot}28$
^{19}F	$19{\cdot}0045\ \pm 0{\cdot}0005$	$+\ 2{\cdot}36$
^{20}Ne	$19{\cdot}9986\ \pm 0{\cdot}0006$	$-\ 0{\cdot}70$
^{28}Si	$27{\cdot}9863\ \pm 0{\cdot}0007$	$-\ 4{\cdot}90$
^{31}P	$30{\cdot}9836\ \pm 0{\cdot}0005$	$-\ 5{\cdot}30$
^{32}S	$31{\cdot}9823\ \pm 0{\cdot}0003$	$-\ 5{\cdot}53$
^{35}Cl	$34{\cdot}9800\ \pm 0{\cdot}0008$	$-\ 5{\cdot}71$

If the nucleus, as is now believed, is made up of protons and neutrons, the mass of the heavier atoms, referred to $0 = 16{\cdot}00$, should be a multiple of the mass of the hydrogen nucleus or proton, 1·00812. But this is not the case. In the case of helium, the atomic mass is 4·00391, whereas $4 \times 1{\cdot}00812 = 4{\cdot}03248$, a difference of 0·02857. An explanation of this fact can be found in the assumption that

[1] Aston, *Proc. Roy. Soc.*, 1937, A, **163**, 391. See also Hahn, Flügge and Mattauch, *loc. cit.*, where also data relating to number of neutrons in the nucleus, isotopic weights, relative abundance of isotopes, packing fractions, etc., are given.

when two protons and two neutrons combine to form the helium nucleus, energy is liberated; and, according to the theory of Einstein, electromagnetic mass and energy are interrelated (1 g. $= 9 \times 10^{20}$ ergs), so that emission of energy corresponds to a reduction of mass.[1]

Arrangement of Extranuclear Electrons.—While the mass of the atom depends almost entirely on the nucleus, the chemical behaviour (*e.g.*, valence, formation of ions in solution, etc.), and the physical properties (*e.g.*, visible and X-ray spectra) depend on the number and arrangement of the extranuclear electrons. Regarding the arrangement of these electrons various suggestions have been made, and the atomic model which is now generally accepted is that due, essentially, to Niels Bohr,[2] Professor of Physics in the University of Copenhagen, but modified in various details. So far as the *number* of electrons in different layers or orbitals is concerned, this model is similar to that suggested, from the chemical point of view, by C. R. Bury,[3] of University College of Wales, Aberystwyth, and based on an earlier model proposed, in 1919, by Irving Langmuir,[4] of the General Electric Company, Schenectady, New York. For the interpretation of chemical properties and valence, a static model,[5] in which the electrons are fixed in their positions, will suffice; but for an explanation of the dynamic stability of the atom and of the optical properties, it is necessary to assume that the electrons are in motion, and that they are revolving round the nucleus in circular or elliptical orbitals. The electrons in the outer orbitals are responsible for the visible spectra, those in the inner orbitals for the X-ray spectra.

According to Bohr's theory of atomic structure there

[1] The loss of mass which accompanies the combination of four protons and two electrons to form a helium nucleus corresponds to the liberation of no less than 6×10^{11} gram calories per gram-atom (4 g.) of helium. It may perhaps be pointed out that the discovery of the hydrogen isotope ^2H introduces the possibility that this isotope may be a structural unit of the nucleus. If so, then arguments based on defects of mass and packing fractions may have to be revised. Views and knowledge regarding the constitution of the atomic nucleus are in process of rapid growth.

[2] *Phil. Mag.*, 1913, **26**, 1, 476, 587; *The Theory of Spectra and Atomic Constitution* (Cambridge University Press).

[3] *J. Amer. Chem. Soc.*, 1921, **43**, 1602. For certain modifications, see J. D. Main Smith, *Chem. and Ind.*, 1923, **42**, 1073; 1924, **43**, 323; *Phil. Mag.*, 1925, **50**, 878; E. C. Stoner, *Phil. Mag.*, 1924, **48**, 719.

[4] *J. Amer. Chem. Soc.*, 1919, **41**, 868, 1543; 1920, **42**, 274.

[5] Such models had been suggested as early as 1902 and elaborated in 1916 by G. N. Lewis, and also in 1916 by W. Kossel.

exist certain orbitals in which alone an electron can move without emitting radiation,[1] and these states of motion of the electrons are called *stationary states*. These stationary states are such that the angular momentum of the electron round the nucleus is equal to $h/2\pi$, or to some multiple of this, the multiple which defines the particular stationary state being known as the *quantum number* of that state. The constant h is known as *Planck's constant*. It has the dimensions of energy multiplied by time and has the value of $6{\cdot}62 \times 10^{-27}$ erg-second.

To account for the emission spectra of a gaseous element, Bohr postulated, also, that energy of radiation may be absorbed by an extranuclear electron, which is thereby raised to a higher energy level, or is caused to pass into an orbital in which the electron has a greater potential energy. Moreover, invoking the quantum theory of the German mathematical physicist, Max Planck, Bohr assumed that radiation taken up by an electron is not absorbed continuously but as a *quantum* of energy, or in integral multiples of energy quanta. A quantum of energy of radiation is not a fixed and constant quantity but depends on the frequency of the radiation and is equal to $h\nu$, where h is Planck's constant. The frequency ν is equal to c/λ, where c is the velocity of propagation and λ is the wave-length of the radiation. The shorter the wave-length, therefore, the greater is the energy of the quantum.

Moreover, when an electron falls back again from an orbital of higher energy level, E_2, to an orbital of lower energy level, E_1, a quantum of energy is emitted equal to that absorbed when the electron passes from the energy level E_1 to the energy level E_2; and the frequency of the radiation (or the wave-length of the spectral line) so emitted is given by the relationship, $E_2 - E_1 = h\nu = hc/\lambda$.

The important hypothesis that the extranuclear electrons of an atom are arranged only in certain definite orbitals or energy levels, and do not revolve in every conceivable orbital, has been confirmed by experimental determination of the energies of electrons ejected from atoms by the action of X-rays of different frequencies and by the study of the emission spectra of the elements; and the theory developed

[1] If energy were emitted as radiation, the electron orbit would become smaller and smaller, and, finally, the electron would fall into the nucleus. The above postulate is made in order to take into account the permanence of the atom.

by Bohr has been of great value in interpreting the visible and X-ray spectra.

It has been pointed out that when an electron jumps from an energy level with the quantum number n_2 to a lower energy level with the quantum number n_1, monochromatic radiation is emitted, the frequency of which is given by $E_{n2} - E_{n1} = h\nu$. The energy associated with the different orbitals or energy levels can be calculated, and it is found that

$$\nu = K \cdot \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or

$$\bar{\nu} = K' \cdot \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

where $\bar{\nu}$ is the wave number $(1/\lambda)$ or the number of waves in 1 cm., λ being expressed in centimetres. It had, however, been observed by the German physicist, J. J. Balmer,[1] as long ago as 1885, that the lines of the visible hydrogen spectrum form a series, the wave numbers of which are given by the expression

$$\bar{\nu} = \boldsymbol{R} \cdot \left(\frac{1}{2^2} - \frac{1}{m^2}\right),$$

where $\boldsymbol{R}$ is a constant, known as the Rydberg constant, and m has successive values of 3, 4, 5, etc. On calculating the value of K', derived from the Bohr theory, the value 109,486 was obtained in good agreement with the Rydberg constant, 109,677·76.

According to the Bohr theory the lines of the Balmer series are produced by the jump of an electron from orbitals with the quantum numbers $n = 3, 4, 5$, etc., to the orbital with the quantum number $n = 2$.

Similarly, other series of hydrogen spectral lines in the ultra-violet and infra-red have been found, which are also in agreement with the general expression $\bar{\nu} = \boldsymbol{R} \cdot \left(\frac{1}{n^2} - \frac{1}{m^2}\right)$, the values of m being whole numbers greater than n. When $n = 1$, $\bar{\nu}$ gives the wave numbers of the lines of the *Lyman series*; when $n = 3$ one obtains the wave numbers of the *Paschen series*, and when $n = 4$ one obtains the wave numbers of the *Brackett series*. These series of lines are formed by the fall of electrons from higher energy levels to orbitals having the quantum numbers 1, 3, and 4 respectively.

To sum up. According to the Bohr theory, there are, for any given nucleus, only certain orbitals or energy levels which an electron can occupy, and these are defined by what are known as the *principal quantum numbers*, $n = 1, 2, 3$, etc. These numbers also denote the electron sheath or shell, $n = 1$ being the orbital or shell nearest to the nucleus. These shells are also known as the K, L, M, etc., shells, and the K, L, M series of X-ray spectral lines previously referred to (p. 12) are produced when an electron falls from an outer shell to a place in the K, L, M shell respectively, rendered vacant by the X-ray bombardment.

Besides the principal quantum numbers, it has been found necessary, in order to account for the fine structure of spectra, to introduce *subsidiary quantum numbers* defining

[1] *Ann. Physik*, 1885, **25**, 80.

(1) the angular momentum of the system, (2) the orientation of this angular momentum in a magnetic field, (3) the magnetic moment or "spin" of the electron. The first of these is generally represented by l, and this may have different values equal in number to the principal quantum number. The electrons in a given sheath or shell can therefore be separated into different sub-groups, and the values of $l=0$, 1, 2, and 3 are frequently represented by the letters s, p, d, and f respectively.[1] Into a fuller discussion of these, however, it is not possible to enter.

The maximum number of electrons which can exist in the different shells, or at the different energy levels, is given by the series, 2×1^2, 2×2^2, 2×3^2, etc.—that is, the number is equal to twice the square of the principal quantum number, and according to what is known as *Pauli's exclusion principle*,[2] no two electrons in an atom can have an identical set of quantum numbers.

In all the electronic arrangements, even in those suggested by R. Abegg (1904), J. J. Thomson (1904), G. N. Lewis (1916), and W. Kossel (1916), the maximum number of electrons existing in the outermost layer was taken to be eight, forming what is called an *octet*. This octet of electrons is particularly stable and is found in the case of all the inert gases except helium. The arrangement of the extranuclear electrons, therefore, which has been adopted as expressing most completely the chemical and optical behaviour of the inert gases, is shown in the following table :—

ARRANGEMENT OF EXTRANUCLEAR ELECTRONS IN THE INERT GASES

Element.	Atomic Number.	Number of Electrons in Quantum Group.					
		$n=1$.	$n=2$.	$n=3$.	$n=4$.	$n=5$.	$n=6$.
Helium	2	2	...	...	...	...	...
Neon	10	2	8	...	...	...	...
Argon	18	2	8	8	...	...	...
Krypton	36	2	8	18	8	...	...
Xenon	54	2	8	18	18	8	...
Radon	86	2	8	18	32	18	8

[1] These letters are the initial letters of the words *subsidiary, principal, diffuse* and *fundamental*, which are used to describe spectral series connected with the corresponding l values.

[2] *Z. Physik*, 1925, 31, 765.

Of the eight electrons in the outermost shell of the elements, neon to radon, two are in the sub-group s and six in the sub-group p.

Electronic Arrangement and the Periodic Classification.—In the first period of the table (p. 14) stand the elements hydrogen and helium, the former with one extranuclear electron and the latter with two. The orbit with quantum number $n=1$ is now complete, and the helium system is a very stable one. When a third electron is added, in the case of lithium, it enters a new shell with quantum number $n=2$, and a new period, the first of the two short periods, is begun. On passing to elements of higher atomic number, the number of electrons in this second shell increases up to eight, when the stable configuration of neon is reached. Thereafter, with sodium, a new shell ($n=3$) is formed and progressively built up so that one has the arrangements 2, 8, 1 ; 2, 8, 2 ; 2, 8, 3, etc., up to 2, 8, 8, the stable configuration of argon. In the two short series the outer shell is built up in a similar manner in both cases, and the elements of the second short series exhibit a gradation of properties similar to that shown by the elements of the first short series. The elements of the two short periods, and the members of the closely related families of which they are the types, are known as *typical elements*.

One now comes to the first long period, and with potassium a new shell of electrons ($n=4$) begins to be formed, potassium having the electronic structure 2, 8, 8, 1, and calcium the configuration 2, 8, 8, 2. This fourth shell, however, is not built up continuously, for with the presence of the two electrons in the fourth shell, the third incomplete shell can now be built up. With scandium, then, a new type of element, not represented in the two short periods, is introduced ; and for the elements following scandium (2, 8, 9, 2) the *third* shell is built up, unit by unit,[1] until one reaches zinc (2, 8, 18, 2). The elements scandium to zinc are known as *transition elements* ; they do not belong to the family of any of the elements of the short periods. After zinc, the third shell being now complete, the filling up of the fourth shell, which had been interrupted at the element calcium, is resumed for the typical elements gallium (2, 8, 18, 3) to krypton (2, 8, 18, 8).

[1] An exception to this rule is found in the case of chromium with the structure 2, 8, 13, 1, and of copper with the structure 2, 8, 18, 1.

A similar behaviour is found in the next long period, yttrium to cadmium being transition elements. After strontium, with the configuration 2, 8, 18, 8, 2, the fourth shell is built up, with slight interruptions, and the regular building up of the fifth shell, interrupted at strontium, is resumed for the typical elements indium (2, 8, 18, 18, 3) to xenon (2, 8, 18, 18, 8).

The principles of electronic arrangement which have just been discussed and which are based mainly on spectroscopic evidence have proved of great value in considering the electronic structure of the elements of the longest period with atomic numbers 55 to 86. A discussion of the complex structures met with in these cases would, however, lead us too far. They are shown in the table of atomic structures (p. 31).

On considering the periodic classification of the elements in the light of the extranuclear electronic structures, it is found that elements belonging to the same natural group or family have similar structures so far as the outer layer or shell of electrons is concerned. Thus, in the case of the inert gases, as has been pointed out, there is always, except in the case of helium, an outer layer of *eight* electrons. Such elements are chemically inert. The elements of the alkali metal group which, in all cases, follow the inert gases, all have *one* electron in the outermost layer and, except in the case of lithium, eight electrons in the adjacent layer. Similarly, the elements of the natural group, Be, Mg, Ca, Sr, Ba, Ra, have *two* electrons in the outermost shell and, except in the case of beryllium, eight electrons in the preceding shell. The elements of the halogen group, on the other hand, have *seven* electrons in the outermost layer, and the elements of the oxygen group have *six*.

It may be pointed out that elements like copper, silver and gold, which show certain remoter resemblances to the alkali metals (*e.g.*, univalency) also have one electron in the outermost shell, but have eighteen, not eight, electrons in the adjacent shell. The atoms of the rare earth metals, the properties of which are very similar, all have the same number of electrons in the outermost shell, and are, moreover, nearly of the same size.

With regard to the transition elements, more especially of the fourth period, the electrons which exist in the outermost layer are not very strongly bound. For this reason

ARRANGEMENT OF THE EXTRANUCLEAR ELECTRONS IN THE ELEMENTS

Quantum Number.		1.	2.		3.			4.				5.		
Atomic Number.	Element.	*s.*	*s.*	*p.*	*s.*	*p.*	*d.*	*s.*	*p.*	*d.*	*f.*	*s.*	*p.*	*d.*
1	H	1												
2	He	2												
3	Li	2	1											
4	Be	2	2											
5	B	2	2	1										
6	C	2	2	2										
7	N	2	2	3										
8	O	2	2	4										
9	F	2	2	5										
10	Ne	2	2	6										
11	Na	2	2	6	1									
12	Mg	2	2	6	2									
13	Al	2	2	6	2	1								
14	Si	2	2	6	2	2								
15	P	2	2	6	2	3								
16	S	2	2	6	2	4								
17	Cl	2	2	6	2	5								
18	A	2	2	6	2	6								
19	K	2	2	6	2	6		1						
20	Ca	2	2	6	2	6		2						
21	Sc	2	2	6	2	6	1	2						
22	Ti	2	2	6	2	6	2	2						
23	V	2	2	6	2	6	3	2						
24	Cr	2	2	6	2	6	5	1						
25	Mn	2	2	6	2	6	5	2						
26	Fe	2	2	6	2	6	6	2						
27	Co	2	2	6	2	6	7	2						
28	Ni	2	2	6	2	6	8	2						
29	Cu	2	2	6	2	6	10	1						
30	Zn	2	2	6	2	6	10	2						
31	Ga	2	2	6	2	6	10	2	1					
32	Ge	2	2	6	2	6	10	2	2					
33	As	2	2	6	2	6	10	2	3					
34	Se	2	2	6	2	6	10	2	4					
35	Br	2	2	6	2	6	10	2	5					
36	Kr	2	2	6	2	6	10	2	6					
37	Rb	2	2	6	2	6	10	2	6			1		
38	Sr	2	2	6	2	6	10	2	6			2		
39	Yt	2	2	6	2	6	10	2	6	1		2		
40	Zr	2	2	6	2	6	10	2	6	2		2		
41	Nb	2	2	6	2	6	10	2	6	4		1		
42	Mo	2	2	6	2	6	10	2	6	5		1		
43	Tc	2	2	6	2	6	10	2	6	5		2		
44	Ru	2	2	6	2	6	10	2	6	7		1		
45	Rh	2	2	6	2	6	10	2	6	8		1		
46	Pd	2	2	6	2	6	10	2	6	10				
47	Ag	2	2	6	2	6	10	2	6	10		1		
48	Cd	2	2	6	2	6	10	2	6	10		2		
49	In	2	2	6	2	6	10	2	6	10		2	1	
50	Sn	2	2	6	2	6	10	2	6	10		2	2	
51	Sb	2	2	6	2	6	10	2	6	10		2	3	
52	Te	2	2	6	2	6	10	2	6	10		2	4	
53	I	2	2	6	2	6	10	2	6	10		2	5	
54	Xe	2	2	6	2	6	10	2	6	10		2	6	

ARRANGEMENT OF THE EXTRANUCLEAR ELECTRONS IN THE ELEMENTS—*continued.*

Quantum Number.		1.	2.		3.			4.				5.			6.			7.
Atomic Number.	Element.	*s.*	*s.*	*p.*	*s.*	*p.*	*d.*	*s.*	*p.*	*d.*	*f.*	*s.*	*p.*	*d.*	*s.*	*p.*	*d.*	*s.*
55	Cs	2	2	6	2	6	10	2	6	10		2	6		1			
56	Ba	2	2	6	2	6	10	2	6	10		2	6		2			
57	La	2	2	6	2	6	10	2	6	10		2	6	1	2			
58	Ce	2	2	6	2	6	10	2	6	10	1	2	6	1	2			
59	Pr	2	2	6	2	6	10	2	6	10	2	2	6	1	2			
60	Nd	2	2	6	2	6	10	2	6	10	3	2	6	1	2			
61	Il	2	2	6	2	6	10	2	6	10	4	2	6	1	2			
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6		2			
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6		2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1	2			
65	Tb	2	2	6	2	6	10	2	6	10	8	2	6	1	2			
66	Dy	2	2	6	2	6	10	2	6	10	9	2	6	1	2			
67	Ho	2	2	6	2	6	10	2	6	10	10	2	6	1	2			
68	Er	2	2	6	2	6	10	2	6	10	11	2	6	1	2			
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6		2			
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6		2			
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1	2			
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2	2			
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	2			
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4	2			
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5	2			
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6	2			
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	9				
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9	1			
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10	1			
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10	2			
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	2	1		
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2		
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3		
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10	2	4		
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10	2	5		
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		1
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		2
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	3	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	4	2

the transition elements can give rise to positively charged ions and are therefore to be classed as metals. In the case of these elements, moreover, an electron may take its place in the outermost shell or in the adjacent shell, and so a variable electrovalency may be found, as in the case of chromium ($Cr^{\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$), manganese ($Mn^{\cdot\cdot}$ and $Mn^{\cdot\cdot\cdot}$), iron

($Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$), etc. It is in the case of these elements, also, that one meets with coloured ions.

Although the Bohr theory has proved very useful and gives a satisfactory general explanation of the periodicity of properties and of the simpler optical properties of the elements, it fails to give a completely satisfactory account of all the facts, and has had to be supplemented and modified by the concepts and equations of wave mechanics, introduced by Prince Louis Victor de Broglie and E. Schrödinger. These rather abstract conceptions and their difficult mathematical treatment cannot, however, be discussed here.

Electronic Constitution and Valency.—The conception of an atom as a complex structure formed by a positively charged nucleus surrounded by extranuclear electrons, and the manner in which these extranuclear electrons are built up into shells with a maximum of eight electrons in the outer layer, furnish a physical basis for the doctrine of valency which was first put forward as an empirical doctrine descriptive of the combining capacity of atoms. A discussion of valency from this point of view was first most fully undertaken by Gilbert N. Lewis (1876-1946), of the University of California,[1] and Walter Kossel,, now Professor of Theoretical Physics in the University of Kiel.[2]

Reference has already been made to the particular stability of the electronic arrangement in the atoms of the inert gases, associated with the presence, in the case of helium of two and in the case of the other gases of eight electrons in the outermost shell. If, then, chemical combination be regarded as due to the transfer or to a rearrangement of electrons between atoms so as to yield the stable configurations of the inert gases, it will be clear that it is the electrons of the outermost shell, the so-called valency electrons, which are involved. Valency, accordingly, may be regarded as the expression of the number of electrons which an atom must gain or lose in order to form a system with an outermost shell of eight electrons, or in order to assume the structure of the nearest inert gas.

Electrovalency.—The formation of salts which, like sodium chloride, are not only completely ionised in aqueous solution but which, in the fused state, have a high electrical

[1] *J. Amer. Chem. Soc.*, 1916, **38**, 762; *Valence and the Structure of Atoms and Molecules* (Chemical Catalog Company).

[2] *Ann. Physik*, 1916, **49**, 229.

conductivity, can best be interpreted as due to electron transfer. The sodium atom has one electron in its outermost shell and by giving up this electron it forms a positively charged system (ion) having the stable extranuclear electronic arrangement of neon. Chlorine, on the other hand, which has seven electrons in its outermost shell, can take up one electron to complete the octet, thereby forming a negatively charged system having the electronic arrangement of the inert gas, argon. Combination between sodium and chlorine, therefore, can readily occur by the transfer of one electron from the sodium atom to the outer shell of the chlorine atom. By the loss of an electron the sodium atom acquires a positive charge, and by the gain of an electron the chlorine atom acquires a negative charge, and union takes place by electrostatic attraction. In this reaction the sodium and chlorine atoms act as univalent atoms, the sodium being *electropositive* and the chlorine *electronegative*. Similarly, calcium, which has two electrons in its outer shell, can give up these electrons and so act with an electrovalency of two; oxygen, with six electrons in its outer shell, can take up two electrons to complete the octet, and it also is bivalent. The valency which is thus manifested by the transfer of electrons is known as *electrovalency*, and the compounds formed in this way are called *electrovalent* (sometimes also *polar*) compounds. The ordinary salts, *e.g.*, sodium chloride, calcium bromide, etc., are electrovalent compounds.

The action of electrovalency cannot, however, extend indefinitely. The electrons in the outermost shell are subject to the attraction of the positive nucleus, and the ease with which an electron is removed from an outer layer will depend on its distance from the nucleus. In the case, for example, of lithium, in the first short period, the valency electron exists in the second shell with quantum number $n=2$, whereas in the case of sodium the single electron exists in the third shell; farther away, therefore, from the nucleus. The removal of the electron will, in this case, take place more easily than in the case of lithium. Moreover, after one electron has been removed, the removal of a second electron takes place with greater difficulty. Accordingly, in the first short period, although beryllium can lose two electrons and form a bivalent ion, boron shows no electrovalency. The electrons in the third shell, however, can be

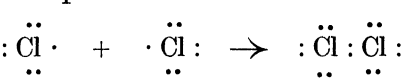
removed more easily, and it is found that in the second short period aluminium can form a trivalent ion. Similarly, atoms can take up electrons only to a limited extent, and the negative charge on an elementary anion seldom exceeds two units.

The restriction placed on the action of electrovalency is also illustrated by the behaviour of hydrogen. Under certain conditions it would appear that hydrogen can take up an electron and so form a negative ion with the configuration of helium, because when fused lithium hydride, LiH, is electrolysed, hydrogen is evolved at the anode. Apparently, however, hydrogen cannot exercise a positive electrovalency through the loss of an electron. Anhydrous acids, *e.g.*, liquid hydrogen chloride, are not electrolytes, and the union of the elements, therefore, is not to be ascribed to the action of electrovalency. When an acid is dissolved in water, it is true, a cation is formed which is usually spoken of as hydrogen ion, but this is not a bare proton, formed by the loss of an electron, but an oxonium ion, H_3O^+, in which the atoms are not held together by electrovalencies but by covalencies.

Covalency.—Reference has already been made to the particular stability of the electronic arrangement in the atoms of the inert gases associated with the presence, in the case of helium, of two and, in the case of the other inert gases, of eight electrons in the outermost shell. It is found, therefore, that the formation of stable compounds can take place by the *sharing* of electrons by atoms so as to form a *duplet* or an *octet*, the atoms thereby acquiring the configuration of an inert gas. Only the electrons in the outermost layer, the valency electrons, will be concerned in this process. Thus, in the combination of two atoms of hydrogen to form a molecule, each atom of hydrogen shares its single electron with the other, thus: $H\cdot + \cdot H \rightarrow H : H$. The single chemical bond, therefore, so generally represented in the older graphic formulæ by a line, H – H, is seen to be formed by a pair of shared electrons, or a *duplet*. Similarly, in the case of other non-metals, especially in the case of the carbon compounds, chemical combination by the sharing of electrons is frequently found.

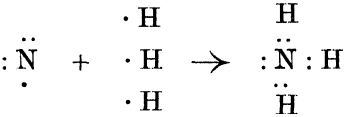
In the case of the univalent halogen elements, for example, molecules are formed by the sharing of electrons, and the molecules so formed possess great stability owing to the

fact that the shared duplet forms part of an octet. Thus, since the halogen elements have seven electrons in the outermost layer, the combination of two atoms to form a molecule may be represented thus :



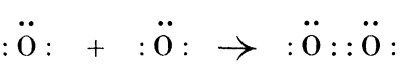
Each single atom is shown here with seven electrons, whereas, in the molecule, two electrons are held in common (forming a *duplet*), and so each atom has its completed octet. Valency due to the sharing of electrons is spoken of as *covalency*. The maximum covalence of a non-metal is equal to the number of electrons in its outer layer in defect of eight. It will be seen that each chlorine atom has three pairs of unshared electrons. These are spoken of as " lone pairs."

In the production of ammonia by the combination of nitrogen and hydrogen, the nitrogen atom with its outer layer of five electrons shares three pairs of electrons with the three hydrogen atoms, as shown by the diagram



In ammonia, each hydrogen atom has the stable configuration of helium, and nitrogen has the stable octet. In the case of ammonia there are three duplets and one *lone pair* of electrons.

In the molecule of oxygen two pairs of electrons are shared, thus :



This sharing of two pairs of electrons corresponds to a double bond, and, similarly, the sharing of three pairs of electrons corresponds to a triple bond.

In some cases the two shared electrons constituting a single linkage are supplied by only *one* of the two atoms concerned. In such cases of " co-ordinate covalency," or " dative covalency " as it is called, the molecule becomes polar, or forms a " dipole," the " donor " atom, which supplies the electrons, becoming positive while the other atom, the " acceptor " atom, becomes negative. These

compounds, unlike those in which only an electrovalency is present, do not undergo ionisation in solution, and the linkage is therefore frequently referred to as a semi-polar double bond and is represented by the symbol $\rightleftharpoons$. In this symbol the half arrow-head points towards the negative portion of the molecule.

The further deductions which may be made from the electronic theory of valency are of great importance, but they cannot be discussed more fully here.[1] Nor is it possible to discuss here the important advances which have been made in the interpretation of valency on the basis of wave mechanics.[2]

[1] See, for example, N. V. Sidgwick, *The Electronic Theory of Valency* (Oxford University Press); *Some Physical Properties of the Covalent Link in Chemistry* (Cornell University Press).

[2] A useful little book on valency is *An Introduction to the Modern Theory of Valency* by J. C. Speakman (Arnold). See also L. E. Sutton, "The Present State of Valency Theory" (*J. Chem. Soc.*, **1940**, 544).

1 ml. of a gas, and as this calculation was first carried out in 1865 by Joseph Loschmidt (1821-95), a schoolmaster in Vienna, the number is generally spoken of as the *Loschmidt number*. From this, one can obtain the actual number of molecules in 1 gram-molecule of a substance (or in 22,414 ml. of a gas at N.T.P.), the so-called *Avogadro number*. For the determination of this number various methods have been employed, and the best value, calculated by R. A. Millikan,[1] is $6{\cdot}031 \pm 0{\cdot}006 \times 10^{23}$.

The value of this constant has been ascertained most accurately from determinations of the unit charge of electricity (p. 7).[2] By international agreement the atomic weight of silver is taken as 107·88, and in order to liberate 1 gram-atom of silver by electrolysis of a solution of a silver salt, 96,494 coulombs or 9649·4 electromagnetic units must be passed through the solution. This amount of electricity is equal to $9649{\cdot}4 \times 2{\cdot}998 \times 10^{10}$ electrostatic units. This quantity of electricity must be equal to the unit charge e ($=4{\cdot}802 \times 10^{-10}$ e.s.u.), multiplied by the Avogadro constant N, or the number of molecules (or atoms) in 1 gram-molecule (or 1 gram-atom) of silver.[3] That is,

$$4{\cdot}802 \times 10^{-10} \times N = 9649{\cdot}4 \times 2{\cdot}998 \times 10^{10}$$

or,

$$N = 6{\cdot}024 \times 10^{23}.$$

A similar value was also obtained by Rutherford,[4] who succeeded in counting the number of alpha particles emitted by a known weight of radium, by an electrical method and also by allowing the particles to pass through a small hole and impinge on a fluorescent screen. At each impact of an alpha particle a flash of light was seen. Since each alpha particle becomes a helium atom, it is possible, by measuring the volume of helium produced by a given weight of radium in a given time, to calculate the number of helium atoms (or molecules) in a given volume. The number obtained by Rutherford was $2{\cdot}75 \times 10^{19}$ in 1 ml. at N.T.P., or $6{\cdot}16 \times 10^{23}$ in 22·4 litres.

If one divides the molecular weight of a substance by the Avogadro number the weight of one molecule of the substance is obtained. Thus, the weight of one molecule of hydrogen is calculated to be $\frac{2{\cdot}016}{6{\cdot}031 \times 10^{23}} = 3{\cdot}343 \times 10^{-24}$ g., and the weight of the atom $1{\cdot}671 \times 10^{-24}$ g.

The van der Waals Equation of State.—In deducing the gas laws on the basis of the kinetic hypothesis two factors were omitted from consideration, the attractive force between the molecules and the volume occupied by the molecules themselves. In order to represent more accurately, therefore,

[1] *Ann. Physik*, 1938, (v), **32**, 34, 520.

[2] For a summary of the determinations of the Loschmidt number see S. E. Virgo, *Science Progress*, 1933, **27**, 634.

[3] This follows from the fact that the ion of silver carries unit charge (Chap. X).

[4] See Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, A, **81**, 141, 162; Rutherford and Boltwood, *Phil. Mag.*, 1911, **22**, 586.

the relation between pressure and volume of a gas, account must be taken of these factors, and this was first done successfully in 1873 by Johannes Diderik van der Waals (1837-1923) while a student at the University of Leyden.

That a force of attraction or cohesion does exist between molecules is shown by the condensation of a gas or vapour to liquid when the temperature is lowered ; and although this mutual attraction will be negligible when a gas is under a low pressure, it can become quite appreciable when the volume of the gas is diminished by increase of pressure. Since this mutual attraction of the molecules has the effect of diminishing the volume of the gas, it acts like an external pressure ; and the volume of a gas will therefore depend on the external pressure and on the *internal pressure*, due to the mutual attraction of the molecules. According to the theory developed by van der Waals, the attractive force between the molecules is inversely proportional to the square of the volume, and the effective pressure on a gas will therefore not be p, the external pressure, but $\left(p + \frac{a}{v^2}\right)$, where a is a constant and v is the volume of the gas.

According to Boyle's law, moreover, the compressible volume of a gas is taken as equal to the total volume occupied by the gas, and the volume occupied by the incompressible molecules is neglected. Although, under moderate pressures, the error thereby introduced may be small, yet at high pressures, when the volume of the gas becomes small, the fraction of the total volume occupied by the incompressible molecules becomes increasingly large ; and the error involved in putting the compressible volume equal to the total volume increases. To correct this error, van der Waals substituted for v in the gas equation the quantity $(v - b)$, or, the total volume minus a quantity which is proportional to the actual volume of the molecules and which was assumed to be constant for any given gas. The value of b is, according to different assumptions, equal to 4 times or to $4\sqrt{2}$ times the actual volume of the molecules.

From these considerations, then, van der Waals put forward the expression

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

as giving the relation between the pressure and volume of a

gas. That this equation reflects more nearly the behaviour of a gas is shown by the numbers in the following table, which apply to ethylene at 20° ($a = 0{\cdot}00786$; $b = 0{\cdot}0024$) :—

Pressure in Atmospheres.	1000 pv		Pressure in Atmospheres.	1000 pv	
	Observed.	Calculated.		Observed.	Calculated.
31·6	914	895	133·3	520	520
45·8	781	782	233·6	807	805
84·2	399	392	329·1	1067	1067
110·5	454	456	398·7	1248	1254

The Specific Heats of Gases.[1]—The specific heat is the ratio of the amount of heat taken up by a substance to the rise of temperature produced. Usually it is defined as the amount of heat in calories required to raise the temperature of 1 g. of a substance by 1° c., 1 calorie being the amount of heat required to raise the temperature of 1 g. of water from 15° to 16° c.

Owing to the fact that when a gas expands against an external pressure, work is thereby done, it follows that the specific heat of a gas at constant pressure will be greater than the specific heat at constant volume by an amount equivalent to the work done on expansion. That is to say,

$$c_p = c_v + \text{work done on expansion} = c_v + p(v_2 - v_1).$$

In these expressions, c_p and c_v are the specific heats at constant pressure and constant volume respectively ; p is the pressure and $(v_2 - v_1)$ the increase of volume which takes place when the gas expands.

If one multiplies the value of the specific heat (per gram) by the molecular weight of the substance, the product is known as the molecular heat, and is represented by C_p and C_v respectively. For a gram-molecule of a gas, the expansion which takes place when the temperature is raised from 0° to 1° is $\frac{22414}{273{\cdot}16}$, and therefore the work done on expansion against atmospheric pressure is

$$p(v_2 - v_1) = \frac{1013250 \times 22414}{273{\cdot}16} = 8{\cdot}314 \times 10^7 \text{ ergs} = 1{\cdot}9866 \text{ cal.}$$

From this, then, it follows, $C_p = C_v + 1{\cdot}987$ calories.

[1] See Partington and Shilling, *The Specific Heat of Gases.*

The **specific heat at constant pressure** can be determined, by the method of Regnault, by passing a known amount of gas heated to a constant temperature t_2, through a tube immersed in a calorimeter containing water at a lower temperature t_1. From the rise of temperature produced, the amount of heat given out by the known amount of gas can be calculated in accordance with the ordinary methods of calorimetry. In this way one obtains the *mean* specific heat between the temperatures t_2 and t_1.

By a modification of this method,[1] it is possible to determine the *true* specific heat, $\Delta Q/\Delta t$, at the temperature t. Gas, heated to a definite temperature t, is passed through a tube immersed in a bath at a temperature $t+\Delta t$. To maintain the temperature of the bath constant, heat is added by means of an electric heater. From the known amount of electrical energy supplied to the heater and the amount of gas passed through the tube in the bath, the true molecular heat at constant pressure is given by the expression $C_p = \frac{H}{n\Delta t}$, where H = the energy supplied to the heater and n = the number of gram-molecules of gas passed through the calorimeter. The heat energy supplied by the heater is given by $I^2R/4{\cdot}185$ cal. per sec. where I is the current in amperes and R is the resistance of the heater in ohms.

The specific heat at constant pressure can also be determined by passing a known amount of gas, heated to a temperature t, over an electric heater, so that its temperature is raised to $t+\Delta t$. From the amount of electrical energy supplied and the rise of temperature produced in a known amount of gas, the specific heat can be calculated.[2]

One of the first to carry out successful determinations of the **specific heat at constant volume** was John Joly (1857-1933), Professor of Geology, Trinity College, Dublin, who made use of the differential steam calorimeter.[3]

Two hollow copper spheres A and C, about 7 cm. in diameter, attached to the scale-pans of a balance, were suspended in a steam chamber B (Fig. 13). Each sphere was provided with a small cup c, to catch the condensed steam. The sphere A was empty and the sphere C was filled with a gas at known temperature and pressure. When equipoise had been attained, steam was admitted into the chamber B and condensed on the two spheres. Owing to the presence of gas in C, more steam was condensed on this sphere than on A, the excess being determined by the weights which had to be placed on the scale-pan of the balance in order to restore equilibrium. From the amount of excess steam condensed, the specific heat of the gas could be calculated.

The values obtained by this method represent the mean specific heats at constant volume.

The true specific heats at constant volume have been

[1] E. D. McCollum, *J. Amer. Chem. Soc.*, 1927, **49**, 28.

[2] See Scheel and Heuse, *Ann. Physik*, 1912, (iv), **37**, 79; 1913, **40**, 473; Heuse, *ibid.*, 1919, **59**, 86.

[3] *Proc. Roy. Soc.*, 1889, A, **45**, 33; 1891, A, **48**, 440; *Phil. Trans.*, 1892, A, **182**, 73; 1895, A, **185**, 943, 961.

determined by adding a known amount of heat (by means of an electrically heated platinum wire or otherwise) to an insulated mass of gas and determining the increase of pressure produced.[1] The specific heat of gases at high temperatures has also been determined by mixing the gas with an explosive mixture (*e.g.* hydrogen and oxygen), and determining the rise of temperature which is produced by the heat of reaction. This will evidently depend on the specific heat of the gas.

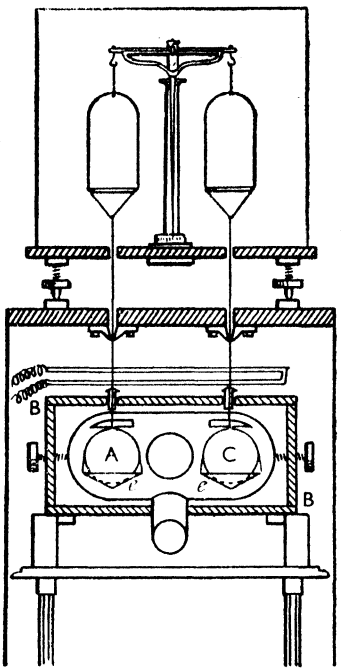


FIG. 13.—Joly's Differential Steam Calorimeter.

As experiment has shown, the specific heat at constant volume is independent of the temperature in the case of monatomic gases, but increases with the temperature in the case of polyatomic gases.

The molecular heat of hydrogen at $-238°$ is 2·98; at $-173°$, 3·42; and at 0°, 4·85. It may be concluded, therefore, that at low temperatures the molecular heat of a diatomic gas approaches that of a monatomic gas.

MOLECULAR HEATS OF GASES AT CONSTANT VOLUME

	Molecular Heat at			
	0°.	100°.	500°.	2000°.
Argon	2·98	2·98	2·98	3·0
Nitrogen, Oxygen, Carbon monoxide	4·97	4·99	5·13	6·55
Hydrogen	4·85	4·92	5·20	6·25
Carbon dioxide	6·70	7·14	8·69	11·62

[1] Voller, *Dissertation*, Berlin, 1908; Trautz and Grosskinsky, *Ann. Physik*, 1922 (iv), **67**, 462; Trautz and Blum, *ibid.*, 1933, **16**, 362 See also Eucken and Bertram, *Z. physikal. Chem.*, 1936, B, **31**, 361.

From the point of view of the kinetic theory the heat which is taken up by a gas may serve (1) to increase the kinetic energy of translational motion of the molecules; (2) to increase the rotational velocity of the molecules; (3) to increase the motion of the atoms within the molecule. In the case of monatomic gases it can be assumed that, if the gases are perfect, all the heat taken up is converted into kinetic energy of translational motion. On this assumption the molecular heat at constant volume can be calculated. For 1 gram-molecule, as has been pointed out, $E=\frac{3}{2}RT$, where E is the total kinetic energy. At any two temperatures, T_1 and T_2, the total kinetic energies will be $E_1=\frac{3}{2}RT_1$ and $E_2=\frac{3}{2}RT_2$. Consequently, $\frac{E_2-E_1}{T_2-T_1}=\frac{3}{2}R$. When the temperature difference is equal to 1°, that is, when the heat added to the gas suffices to raise its temperature by 1°, then the energy difference, which is equal to the heat added to the gas, is equal to $\frac{3}{2}R$: that is, $C_v=\frac{3}{2}R=2{\cdot}980$ cal. This, then, is theoretically the minimum value for C_v, and this is the value which has been obtained experimentally for argon and other monatomic gases.

It may be noted here that a single atom has three degrees of freedom, corresponding to motion along three axes, and since, according to Maxwell's *principle of equipartition of energy*, each degree of freedom entails an equal increase of energy, the energy for each degree of freedom amounts to 0·993 calorie, or approximately 1 calorie.

Further, for an ideal monatomic gas, $C_p=C_v+1{\cdot}987=4{\cdot}967$ calories, and, consequently, the ratio $\frac{C_p}{C_v}=\frac{4{\cdot}967}{2{\cdot}980}=1{\cdot}667$. This ratio is generally represented by the Greek letter gamma (γ). It can be argued, therefore, that in the case of mercury, argon, etc., for which the ratio of specific heats is 1·66, we are dealing with monatomic gases; and it was from the value of the ratio of specific heats that Ramsay and Travers inferred that argon, helium, etc., are monatomic.

As the molecule of a gas becomes more and more complex, more and more of the heat taken up may go to increasing the rotational and intramolecular motions, and the specific

heats will therefore have higher values. Thus, neglecting intramolecular motion, a diatomic molecule has not only three degrees of freedom of translational motion but also two degrees of freedom of rotational motion, and the minimum value of the specific heat will be $2{\cdot}980 + 1{\cdot}987 = 4{\cdot}967$ calories, which is in agreement with the experimental numbers shown in the table on p. 65. But the higher the values of the specific heats, the lower will be the value of the ratio, and so it is found, as theory predicts, that the ratio of specific heats decreases as the molecules become more complex. For diatomic gases the maximum value of the ratio will be about $\frac{7}{5} = 1{\cdot}4$; for triatomic gases, about $\frac{8}{6} = 1{\cdot}33$; but, the greater the amount of heat used up in increasing intramolecular motion, the larger will be the specific heats and the smaller will be the ratio. These points are illustrated by the numbers in the following table :—

RATIO OF SPECIFIC HEATS OF GASES

	γ.		γ.		γ.
Helium	1·63	Oxygen	1·40	Ozone	1·29
Argon	1·67	Nitrogen	1·40	Carbon dioxide	1·30
Mercury vapour	1·67	Hydrogen	1·41	Nitrous oxide	1·30
Potassium vapour	1·69	Carbon monoxide	1·40	Ammonia	1·31
Sodium vapour	1·68	Hydrogen chloride	1·41	Ethylene	1·26
		Chlorine	1·36	Ether	1·08

Experimental Determination of the Ratio of Specific Heats.—The ratio of the specific heats at constant pressure and volume can not only be calculated from a knowledge of the individual values, but can also be determined experimentally by various methods, of which the simplest is, perhaps, that introduced by the German physicist August Kundt (1839-94) in 1866.[1]

A glass tube T (Fig. 14), 1 metre or more in length, into which a light powder (lycopodium, ignited silica, etc.) has been introduced, is closed at either end by means of metal caps or rubber stoppers. Passing through the cap or stopper A at one end of the tube is a glass or metal rod, firmly clamped at its middle point. By "stroking" the rod with a cloth coated with resin or moistened with alcohol, the rod is made

[1] *Ann. Physik*, 1866, **127**, 497.

to vibrate, and the vibrations set up waves in the gas contained in the tube and cause the light powder, which had previously been made to form a thin layer along the tube, to arrange itself in regular, striated heaps. (The rod passing through the stopper B is adjusted so as to give the best

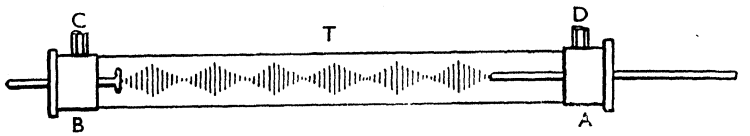


FIG. 14.—Kundt's Tube.

results.) The distance between the corresponding points of two neighbouring heaps is equal to half a wave-length. By means of the side tubes C and D the tube T can be filled with different gases.

The velocity of sound in a gas is given by the expression $c=\sqrt{\frac{\gamma \cdot p}{d}}$, where $\gamma=\frac{C_p}{C_v}$. If λ is the wave-length of the sound waves and n the frequency, then $n\lambda=c$. The value of n for any given rod can be found by carrying out an experiment with air. Since the velocity of sound in air is known (340 metres per sec.), and λ can be measured by means of the dust heaps, $n=\frac{c}{\lambda}$ can be calculated. If the tube be filled with a gas other than air, and λ be determined, we have

$$\frac{\lambda_1}{\lambda_2}=\frac{c_1}{c_2}=\sqrt{\frac{\gamma_1 d_2}{\gamma_2 d_1}},$$

and if the value of γ_1 (say, for air) is known, the value of γ_2 can be calculated.

Kundt's dust-figure method was improved by Behn and Geiger,[1] who replaced the vibrating rod by a tube A in which the gas under investigation was sealed up along with a light powder. The tube was clamped at its middle point and one end was inserted in the end of an open tube B containing air, in which also there was a layer of light powder (Fig. 15). When the closed tube was caused to vibrate, the powder arranged itself in striated heaps in both tubes. To secure the proper formation of the dust figures in the closed tube,

[1] *Verh. deutsch. physikal. Gesell.*, 1907, **9**, 657.

the ends of the latter were weighted with metal discs in order to bring its vibration frequency into harmony with the wave-length of the vibrations in the tube. The wave-length of the sound waves in air and in the enclosed gas could then be directly compared.

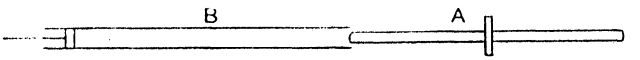


FIG. 15.

The ratio of specific heats may also be determined with an accuracy of about 0·1 per cent., by measuring, by means of a thermocouple or otherwise, the fall of temperature which takes place when a gas under pressure is allowed to expand adiabatically against the pressure of the atmosphere.[1] The method requires a considerable volume of gas (say, 60 litres), and is a variant of the method originally proposed by Clement and Désormes.[2] The ratio of specific heats is given by the expression

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{\gamma-1}{\gamma}}, \text{ or } \gamma = \frac{\log (p_1/p_2)}{\log (p_1/p_2) - \log (T_1/T_2)}.$$

[1] H. W. Moody, *Physikal. Z.*, 1912, **13**, 383. See also O. Lummer and E. Pringsheim, *Ann. Physik*, 1898 (iii), **64**, 555.

[2] See also P. A. Müller, *Ann. Physik*, 1883, **18**, 94; E. Rüchardt, *Physikal. Z.*, 1929, **30**, 58.

CHAPTER III

LIQUEFACTION OF GASES AND CRITICAL PHENOMENA

In the gaseous state the molecules of matter are relatively far apart and in perpetual rapid motion, and this motion is sufficient to overcome the attractive forces which exist between the molecules. These, therefore, lead an existence of practically complete independence. As the temperature of a gas is lowered, the kinetic energy of the molecules may be reduced to such an extent that the more sluggish molecules (for all do not move with the same velocity) are no longer able to overcome the force of mutual attraction or cohesion. They cohere to one another, therefore, and a liquid is formed. This process of condensation or liquefaction will be helped by an increase of pressure (or diminution of volume of the gas) as well as by reduction of the temperature. The conditions of temperature and pressure necessary to bring about liquefaction vary greatly for different gases, for while sulphur dioxide can be liquefied, under atmospheric pressure, at a temperature of $-8°$, carbon dioxide must be cooled to below $-78{\cdot}2°$, and oxygen to below $-182{\cdot}5°$. Since however, pressure assists condensation, sulphur dioxide can be liquefied even at 20° if the pressure is increased to 3·24 atmospheres.

Liquefaction of Gases.—While the attempts of the earliest workers—of whom the most important was Michael Faraday (1791-1867), of the Royal Institution, London—to liquefy gases were crowned with a large measure of success, a certain number of gases, *e.g.*, hydrogen, oxygen, nitrogen, methane, proved refractory. All attempts to obtain these substances in the liquid state having proved unsuccessful, even when the pressure was raised to 2790 atmospheres,[1] the gases were regarded as being non-liquefiable and were

[1] Natterer, *Ann. Physik*, 1855, **94**, 436.

therefore spoken of as *permanent gases.* In 1869, however, the reason for the failure to liquefy these gases became clear when, as will be discussed more fully presently, Thomas Andrews, (1813-85) Professor of Chemistry in Belfast, showed that for each gas there exists a temperature, the *critical temperature,* above which the gas cannot be liquefied no matter how great may be the pressure.

After the conditions necessary for the liquefaction of gases had been established, Raoul Pierre Pictet (1842-1929), in Geneva, and Louis Paul Cailletet (1832-1913), Ironmaster at Chatillon-sur-Seine, succeeded in liquefying a number of the so-called permanent gases, the former by cooling the gas, under pressure, by means of liquid carbon dioxide boiling under reduced pressure, and the latter by rapidly reducing the pressure and so allowing the compressed gas to expand adiabatically. In the latter case the gas, on expanding against the pressure, does a certain amount of work, and the heat corresponding to the work is taken from the gas itself. The temperature of the gas, therefore, falls, and may reach the point of liquefaction. This principle of adiabatic expansion is employed in the Claude process for the liquefaction of air on an industrial scale.

The change of temperature produced by the adiabatic expansion or compression of a gas is given, for an ideal gas, by the expressions $\left(\frac{v_1}{v_2}\right)^{\gamma-1}=\frac{T_2}{T_1}$ and $\left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}=\frac{T_2}{T_1}$, where γ is the ratio of the specific heats at constant pressure and constant volume. From these expressions one can calculate that when air ($\gamma=1{\cdot}41$) at 0° C. is allowed to expand adiabatically against the pressure of the atmosphere to twice its volume ($v_1=1$; $v_2=2$), the temperature falls to $-67{\cdot}5$° C. Or, again, when air at 0° and under a pressure of 10 atmospheres is allowed to expand adiabatically to a pressure of 1 atmosphere, the temperature falls to $-133{\cdot}2$°.

When a gas is compressed adiabatically, its temperature will be raised.

In 1853 it was shown by Sir William Thomson (Lord Kelvin) (1824-1907), Professor of Natural Philosophy in the University of Glasgow, and James Prescott Joule (1818-89), an English brewer, that when compressed air, and certain other gases, at temperatures between 0° and 100°, are allowed to expand through a porous plug or valve, the

temperature falls; but that in the case of hydrogen a rise of temperature takes place. This heat effect on expansion is known as the *Joule-Thomson effect*, and it was later shown that there is, for each gas, a certain temperature at which the sign of the heat effect undergoes change. This temperature is known as the *temperature of inversion of the Joule-Thomson effect*. When, therefore, a compressed gas is allowed to expand at a temperature below the temperature of inversion of the Joule-Thomson effect, cooling takes place; and the degree of cooling is all the greater the lower the initial temperature of the compressed gas.[1] For air (under a pressure of 200 atmospheres) the temperature of inversion of the Joule-Thomson effect is 240°; for hydrogen it is −79°, and for helium, −173°.

In 1895, C. von Linde, in Germany, and W. Hampson, in England, patented apparatus in which the Joule-Thomson effect is applied to the liquefaction of air and other gases. In these apparatus the compressed gas is allowed to expand at a nozzle and the cooled gas is caused to pass around the tube by which the compressed gas reaches the nozzle (Fig. 16). The incoming gas is thus progressively cooled, and at length a temperature is reached such that when the gas expands the ensuing fall of temperature is so great that the gas is liquefied. By this method even hydrogen and helium have been obtained in the liquid state.

The Joule-Thomson effect is due to the fact that gases do not obey Boyle's law and Joule's law. For moderate increase of pressure at the ordinary temperature, most gases, we have seen, are more compressible than according to Boyle's law; that is, the value of the product pv at the higher pressure is less than its value at the lower pressure, owing to the attraction between the molecules. When, therefore, expansion takes place, work has to be done against the attraction of the molecules, and the heat corresponding to this work is taken from the gas itself: its temperature, therefore, falls. In the case of hydrogen at the ordinary temperature, however, the product pv has a greater value at a higher pressure than it has at a lower. When, therefore,

[1] In the case of air, the cooling (Δt) on expansion is given by the expression $\Delta t = \frac{\Delta p}{4} \times \left(\frac{273}{T}\right)^2$, where Δt is the fall of temperature in degrees centigrade, Δp the difference of pressure in atmospheres, and T the absolute temperature of the gas before expansion. Calculation shows that if $T = 288°$ and $\Delta p = 199$ atmospheres (expansion from 200 atmospheres to 1 atmosphere), $\Delta t = 44{\cdot}7°$.

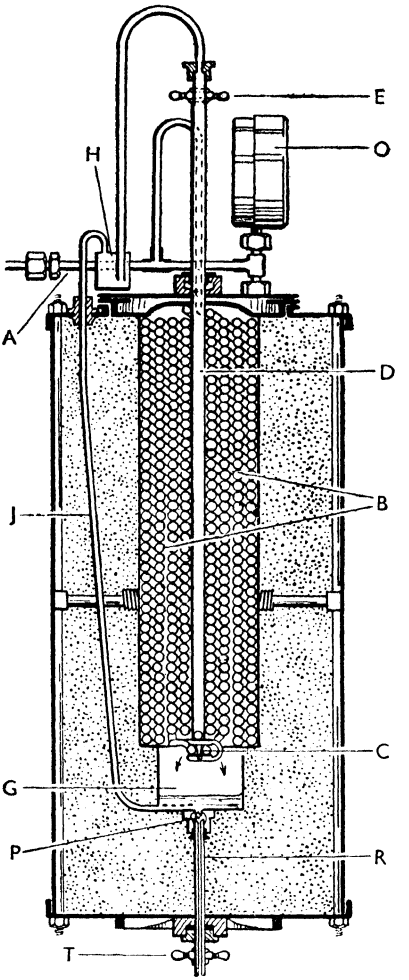


FIG. 16.—Hampson Apparatus for Liquefying Air.

A, tube by which air enters; B, section through spirals of copper tubing; C, expansion valve; D, central spindle; E, wheel for opening and closing expansion valve; G, tank in which liquid air collects; H, gauge to indicate amount of liquid air in G; J, tube connecting tank with gauge; O, pressure gauge to indicate pressure at which the air enters the apparatus; P, valve, closing tube R, through which the liquid air is withdrawn; T, wheel for opening the valve P.

the compressed gas is allowed to expand there is a decrease in the value of pv, as if work were done on the gas, and this work shows itself in a rise of temperature. The Joule-Thomson effect also is due to the fact that real gases do not obey Joule's law which states that the total internal energy of a given mass of a perfect gas at constant temperature is independent of the volume. In an actual gas, on expanding internal work is done in overcoming the cohesion between the molecules.

Critical Phenomena.—"On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 88° Fahr., the surface of demarcation between the liquid and 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 its entire mass. At temperatures above 88° no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results." So wrote Thomas Andrews in 1863.[1]

The occurrence of a critical temperature at which liquid and vapour become identical was established by Andrews in the course of his study of the pressure-volume relations of carbon dioxide at different temperatures.[2] The behaviour will best be understood with the help of the diagram (Fig. 17), in which pressure is plotted against volume.

When one considers the isothermal curve for 13·1°, it is seen that as the pressure increases the volume of the gas diminishes, until, at a certain pressure (49·8 atmospheres), liquefaction takes place (point B). On diminishing still further the volume of the gas (vapour), the pressure remains constant, until the whole of the vapour has been condensed to liquid (point C). Thereafter, the liquid being only slightly compressible, a great increase of pressure is required to effect even a slight diminution of volume. The pressure-volume curve, therefore, rises almost vertically. At higher

[1] Published in Miller's *Chemical Physics*, 3rd Edition, p. 328. The phenomenon referred to here had been observed as early as 1822 by Cagniard de la Tour. For a discussion of the critical state see *Chem. Rev.*, 1938, **23**, 1.

[2] *Phil. Trans.*, 1869, **159**, 575; 1876, **166**, 421. See also Ostwald's *Klassiker*, No. 132.

temperatures, *e.g.*, 21·1°, a similar behaviour is found, but as the temperature is raised, the pressure at which liquefaction takes place becomes higher and the length of the horizontal portion of the isotherm becomes shorter and shorter until, at a certain temperature, it dwindles to a point. The isothermal curve then becomes continuous. This is shown by the isotherm for 31·1°. At this temperature, although a flattening of the curve is shown, there is no horizontal portion

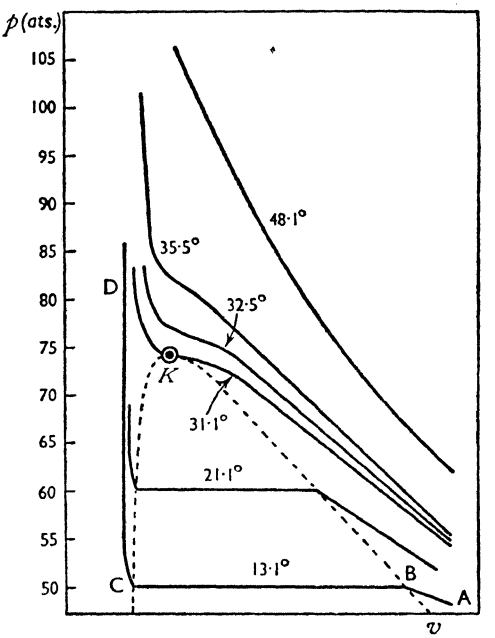


FIG. 17.

and no abrupt change from the gaseous to the liquid state. At temperatures above 31·1° the flattening of the curve becomes less marked and, at 48°, is no longer observable. Andrews was thus able to show that for carbon dioxide there is a certain temperature, which he called the *critical temperature*, below which the gas can be liquefied by increase of pressure, but above which liquefaction cannot take place no matter how great the pressure may be.[1] Other gases behave in a similar manner.

[1] A vapour is sometimes defined as being a gas below its critical temperature.

At the critical temperature the vapour pressure of the liquid must have a definite value, and this is known as the *critical pressure*; at this temperature, also, the substance must have a definite density (*critical density*), the reciprocal of which is called the *critical volume*.

Determination of the Critical Constants.—The **critical temperature** of a substance which is liquid under ordinary conditions can be most easily determined by sealing up a quantity of the liquid in a strong glass tube from which all air must be removed. The tube is then heated in a suitable oven, the temperature of which can be slowly raised. As the temperature of the critical point is approached, the liquid meniscus becomes billowy and indistinct, and then suddenly disappears altogether when the critical temperature is reached. On cooling through the critical temperature, formation of a mist and a liquid meniscus is observed.[1] In the case of a gas the substance may be compressed in a capillary glass tube until liquid is formed. The tube is then heated until the meniscus disappears, the pressure being increased during the process so as to keep the meniscus in a fixed position.

For the determination of the **critical pressure,** the method due to Michael Altschul[2] may be employed. The substance (liquid) is contained in a strong glass tube *d*, the lower end of which is closed by a movable thread of mercury *e*, and the tube is connected with a pressure pump A (Fig. 18). The upper end of the tube is heated to above the critical temperature, the pressure being at the same time increased so as to maintain the liquid in the tube. The lower end of the tube is kept at the ordinary temperature (that is, below the critical temperature), and, therefore, at some intermediate point the temperature must be the critical temperature. At that point a meniscus will be formed, and the critical pressure

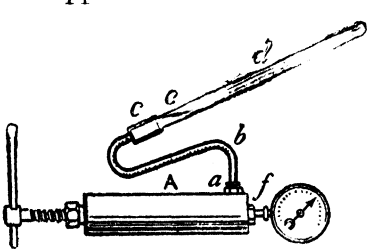


FIG. 18.

[1] For accurate determinations, the relative volumes of liquid and vapour in the tube must be adjusted, and the liquid must be stirred. See F. B. Young, *Phil. Mag.*, 1910 (vi), **20**, 793.

[2] *Z. physikal. Chem.*, 1893, **11**, 577.

will be produced. This pressure can be read off on the manometer attached to the pump.

The **critical volume** is usually determined indirectly by making use of the *law of rectilineal diameters* discovered by Cailletet and Emile Mathias,[1] Professor of Physics in the University of Clermont, France. If in a system of rectangular co-ordinates the density of the liquid and of the vapour is plotted against the temperature, a curve is obtained of the form shown in Fig. 19. This curve, which applies to

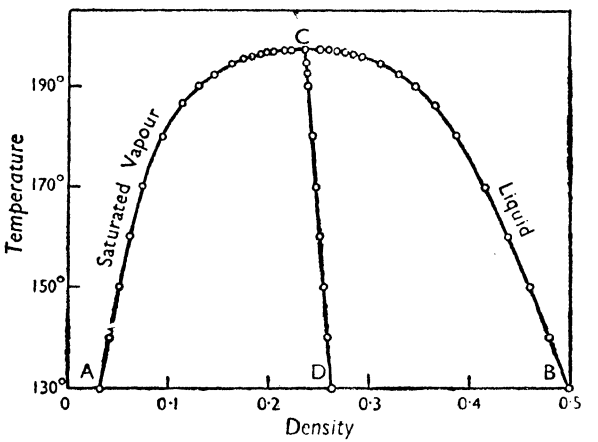


FIG. 19.

n-pentane,[2] shows clearly that as the temperature rises the density of the saturated vapour increases and the density of the liquid decreases, the density of liquid and vapour becoming identical at the critical point. If, also, one plots the means of the densities of the liquid and vapour, Cailletet and Mathias found that these values lie on a straight line CD, which passes through the critical point. This is the *law of rectilineal diameters.*

In order to determine the critical density or critical volume of a substance, therefore, one determines the density of the liquid and of the saturated vapour at a series of temperatures, *not too far removed from the critical point,*[3] and one plots these values against temperature in rectangular

[1] *Compt. rend.*, 1886, **102,** 1202; 1887, **104,** 1563.

[2] See S. Young, *Phil. Mag.*, 1900 (v), **50,** 291.

[3] When the temperatures are far below the critical point, the line of mean density may show a slight curvature.

co-ordinates. The corresponding values of density are joined by straight lines; these lines are bisected, and, through the points of bisection, a line is drawn until it

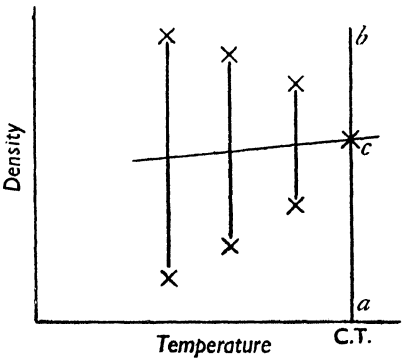


FIG. 20.

cuts the perpendicular *ab*, drawn from the critical temperature (Fig. 20). The point of intersection *c* gives the value of the critical density, and the reciprocal of this is the critical volume.

The following table gives the critical constants [1] of a number of substances :—

CRITICAL CONSTANTS

	Critical Temperature T_c°K.	Critical Pressure in Atmospheres p_c.	Critical Volume per Gram-molecule (ml.) V_c.	$\frac{RT_c}{p_cV_c}$.
Helium	5·2°	2·25	61·55	3·08
Hydrogen	33·2°	12·8	69·68	3·06
Nitrogen	126·0°	33·5	90·0	3·43
Argon	150·7°	48·0	77·07	3·35
Oxygen	154·3°	49·7	74·4	3·42
Carbon dioxide	304·2°	72·8	94·2	3·64
Nitrous oxide	311·9°	77·5	96·9	3·41
Ethyl ether	467·0°	35·5	282·0	3·82
n-Pentane	470·3°	33·0	310·2	3·76
Methyl alcohol	513·1°	78·5	117·7	4·56
Benzene	561·6°	47·9	256·4	3·76
Acetic acid	594·7°	57·1	171·2	4·99
Water	647·3°	218·5	55·4	4·39

[1] For the prediction of critical constants, see Meissner and Redding, *J. Ind. Eng. Chem.*, 1942, **34**, 521.

Continuity of the Liquid and Gaseous States.—Although one is accustomed to think of the liquid and gaseous states as being sharply distinguished one from the other, a consideration of the critical phenomena which have just been discussed will show convincingly that one is scarcely justified in so thinking. A liquid and its vapour when heated together approach *continuously* to each other in their properties and become identical in all respects at the critical point: there is no abrupt change of properties. Moreover, as a study of Fig. 17 will make clear, one can pass continuously from the liquid to the gaseous, and from the gaseous to the liquid state without there being at any time a discontinuity in the properties of a substance, and without there being any separation into two phases or distinct forms of matter.

When the ends of the horizontal portions of the isotherms are joined together, a so-called "border curve" is obtained, shown in Fig. 17 by a dotted line. At the summit of this curve lies the critical point K, and within this curve lie all the values of pressure, volume, and temperature at which liquid and vapour can coexist; outside this curve only homogeneous systems, liquid or vapour alone, can exist. Suppose, then, that carbon dioxide gas, under atmospheric pressure, is heated to a temperature above the critical temperature, say to 48°, and that it is then subjected to a pressure greater than the critical pressure, say, to 100 atmospheres, the system will change in volume, as shown by the isotherm for 48°. If the temperature be now lowered to 13·1°, while the pressure is maintained at 100 atmospheres, a point on the curve CD will be reached, a curve which applies to *liquid* carbon dioxide. At no point in the process is there any abrupt change of state; the change from gas to liquid is continuous. Similarly, one may start with liquid carbon dioxide under the conditions represented, say, by the point C. If the pressure on the liquid is increased, say, to 100 atmospheres and the temperature raised to 48°, the condition of the system will be represented by a point on that isotherm; and on reducing the pressure to that of the atmosphere and then allowing the temperature to fall to 13·1°, we shall have the carbon dioxide as a gas, and at no time during the whole process will any discontinuity of properties be observed, or any separation into liquid and vapour. The passage from the liquid to the gaseous state is continuous.

The van der Waals' Equation and the Critical State.— The equation put forward by van der Waals for the relation between the pressure and volume of a gas is also of great value in the study of critical phenomena and the passage from the gaseous to the liquid state. When the van der Waals' equation is multiplied out and arranged in powers of v, it takes the form

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

This is a cubic equation and, as such, may have only one real root, or one value of v which, at a given temperature and

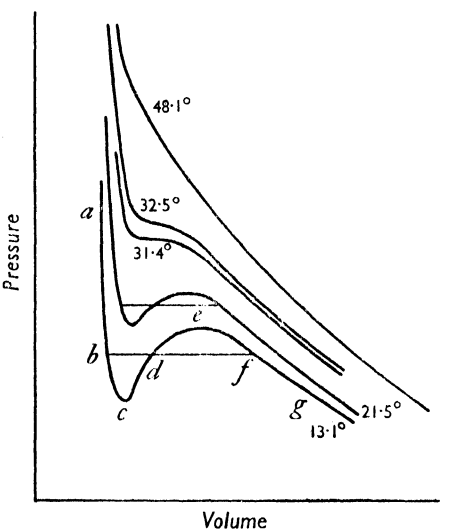


FIG. 21.

pressure, will satisfy the equation ; or it may have three real roots, or three values of v at a given temperature and pressure. The behaviour predicted by the equation will best be understood from the graphic representation (Fig. 21).

If for constant values of a and b one inserts varying values of T, the relation between pressure and volume at different temperatures is given ; and on plotting these values, one obtains a series of isotherms, such as are shown in Fig. 21. At higher temperatures, *e.g.*, 48°, the curve clearly indicates that at any given pressure the volume has a single definite

value. This corresponds to the case where the equation has only one real root. At lower temperatures, however, sinuous curves, such as *abcdefg*, are obtained, showing that at a given pressure, represented by the line *bf*, there may be three values for *v*, represented by the points *b*, *d*, and *f*. These represent the three real unequal roots of the cubic equation. Only two of these values, however, are experimentally realisable, namely, *b* and *f*.

When a gas, having the volume *g*, is compressed at a temperature below the critical point, liquefaction normally takes place at a certain pressure, represented by the point *f*; and the pressure then remains constant until the gas is completely liquefied at the point *b*. The experimental curve, therefore, differs from the theoretical curve in being discontinuous, and the vapour-pressure line *bf* cuts the theoretical curve in such a way that the areas of the loops *bcd* and *def* are equal. Although the portion of the curve *cde*, which indicates a concurrent increase of pressure and volume, is not experimentally realisable,[1] parts of the curves *bc* and *fe* can sometimes be realised.

Normally, when the pressure on a liquid is lowered to that corresponding to the point *b*, or the vapour pressure of the liquid at the given temperature, vapour formation will take place; but under special conditions the formation of vapour may remain suspended and the pressure on the liquid may be lowered to below that corresponding to the point *b* without vapour being formed. The liquid will then be in a condition corresponding to a point on the curve *bc*. Thus, although the vapour pressure of methyl formate, at 80°, is 350 cm. of mercury, it has been found possible, by using a very clean tube and pure methyl formate free from dissolved air, to lower the pressure on the liquid to 80 cm. without vapour formation taking place. Further, when a clean barometer tube has been filled with and inverted over mercury, the mercury may remain filling the whole tube instead of falling to the height representing the atmospheric pressure. The mercury is then under a negative pressure, and is in a condition represented by a point on the curve *bc*.

Similarly, the formation of liquid from vapour may remain suspended, and so a portion of the curve *fe* may be realised.

[1] It must be emphasised that the van der Waals' equation is empirical. There is therefore no physical reason why the *pv* curve should follow the course shown in Fig. 21.

Thus it has been found that when water vapour has been very carefully freed from dust particles or other condensation nuclei its temperature may be lowered considerably below the point of condensation before liquefaction takes place.

As the temperature is raised, the loops on the sinuous curves become smaller and smaller, and the values for the volume of liquid and of gas approach each other until, at a certain temperature, the loops shrink to a point and the three values of v become identical. This temperature is the critical temperature, and the volume of the gas at this temperature is the critical volume v_c. At the critical point, then, the three roots of the van der Waals' equation become identical and equal to v_c; and since this is the value of the three roots of the van der Waals' equation at the critical point, $(v-v_c)^3=0$, or $v^3-3v_cv^2+3v_c^2v-v_c^3=0$.

This equation must be identical with the van der Waals' equation when the temperature is equal to the critical temperature and the pressure is equal to the critical pressure. We have, therefore,

$$v^3-3v_cv^2+3v_c^2v-v_c^3\equiv v^3-\left(b+\frac{RT_c}{p_c}\right)v^2+\frac{a}{p_c}v-\frac{ab}{p_c},$$

where p_c and T_c represent critical pressure and critical temperature (absolute). On equating the coefficients of the equal powers of v in the two equations, one obtains the important relations,

$$3v_c=b+\frac{RT_c}{p_c};\quad 3v_c^2=\frac{a}{p_c}\text{ and }v_c^3=\frac{ab}{p_c}.$$

From these equations one can deduce the values of the critical constants in terms of the constants a and b of the van der Waals' equation. Thus, since $v_c^3=\frac{ab}{p_c}$ and $3v_c^2=\frac{a}{p_c}$ it follows that

$$v_c=3b.$$

Similarly, for the critical pressure, one finds

$$p_c=\frac{a}{27b^2},$$

and for the critical temperature,

$$T_c=\frac{8a}{27Rb}.$$

Since the values of a and b in the van der Waals' equation can be deduced from measurements on compressed gases, it is clear that such measurements can also be employed for the purpose of calculating the critical constants.[1]

If, in the above expressions, v is the volume in litres of 1 mole, and if p is expressed in atmospheres, then a will be expressed in atm. × lit.^{2}, b in litres, and $\boldsymbol{R}$ in litre-atmospheres (0·08205). v_c is then the volume in litres of 1 mole at the critical point. If the volume is expressed in millilitres, a will be expressed in atm. × ml.^{2} and b in millilitres. The new value of a will therefore be 10^6 times and that of b 10^3 times greater than when the volume is expressed in litres. $\boldsymbol{R}$, similarly, will be 10^3 times greater (82·05). Sometimes, however, v is expressed as a *fraction* of the volume at N.T.P., and, in this case, v_c is the volume at the critical point of that amount of gas which at N.T.P. would have unit volume. In other words, v_c is the *ratio* of the volume of a gas at the critical point to that which it would have at N.T.P. Representing the constants expressed in the former units by a, b, and $\boldsymbol{R}$, and the constants expressed in the latter (or Amagat) units by a', b', and $\boldsymbol{R}'$, one has the relations $a' = a/v_m^2$, $b' = b/v_m$, and $\boldsymbol{R}' = \boldsymbol{R}/v_m$, where v_m is the volume of 1 gram-molecule at N.T.P. (22·414 l. or 22,414 ml.). Moreover, if the volume is put equal to unity when the pressure is 1 atmosphere, the van der Waals' equation takes the form,

$$(1+a')(1-b') = \boldsymbol{R}' \times 273{\cdot}16, \text{ and } \boldsymbol{R}' = \frac{(1+a')(1-b')}{273{\cdot}16}.$$

Example.—Given that the van der Waals' constants for 1 gram-molecule of carbon dioxide are $a = 3{\cdot}609 \times 10^6$ and $b = 42{\cdot}75$ (volume in millilitres and

---

[1] The relation between the constants of the van der Waals' equation and the critical data can also be obtained in another way. Since the critical point is a maximum point at which the two points c and e (Fig. 21) on the isothermal curve coalesce, the tangent to the curve at this point must be horizontal and parallel to the volume axis. That is to say, the first differential of the equation of state, $p_c = \frac{\boldsymbol{R}T_c}{v_c - b} - \frac{a}{v_c^2}$, must be equal to zero; or, $\left(\frac{\partial p}{\partial v}\right)_T = \frac{-\boldsymbol{R}T_c}{(v_c-b)^2} + \frac{2a}{v_c^3} = 0$. Further, the critical point is a point of inflexion on the isothermal curve, and therefore the second differential must also be equal to zero. That is, $\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2\boldsymbol{R}T_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0$. On dividing the third equation by the second, one obtains $\frac{v_c - b}{2} = \frac{v_c}{3}$, or, $v_c = 3b$. On inserting this value in the second equation one obtains $T_c = \frac{8a}{27\boldsymbol{R}b}$; and hence, from the first equation, $p_c = \frac{a}{27b^2}$.

pressure in atmospheres), calculate the values of the critical pressure and critical temperature.

$$p_c = \frac{a}{27b^2} = \frac{3{\cdot}609 \times 10^6}{27 \times (42{\cdot}75)^2} = 73{\cdot}2 \text{ atmospheres.}$$

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 3{\cdot}609 \times 10^6}{27 \times 82{\cdot}1 \times 42{\cdot}75} = 304{\cdot}7^\circ \text{ K.}$$

Not only can one calculate the values of the critical constants from the constants of the van der Waals' equation, but one can, conversely, calculate the constants of the van der Waals' equation from the esperimentally determined values of the critical constants. From the relations expressed above, one deduces

$$a = \frac{27R^2T_c^2}{64p_c} \text{ and } b = \frac{RT_c}{8p_c}.$$

Example.—The critical temperature and critical pressure (millilitres, gram-molecule, atmospheres) of chlorine are 419·0° K. and 93·5 atmospheres respectively. Calculate the values of the constants a and b.

$$a = \frac{27R^2T_c^2}{64p_c} = \frac{27 \times 82{\cdot}05^2 \times 419^2}{64 \times 93{\cdot}5} = 5{\cdot}33 \times 10^6.$$

$$b = \frac{RT_c}{8p_c} = \frac{82{\cdot}05 \times 419}{8 \times 93{\cdot}5} = 45{\cdot}96.$$

The values of the van der Waals' constants, in millilitre-atmosphere units per gram-molecule, for a number of gases, are given in the following table :—

Gas.	a.	b.	Gas	a.	b.
Cl_2 . .	$5{\cdot}33 \times 10^6$	45·96	He . .	$0{\cdot}033 \times 10^6$	23·42
CO_2 . .	$3{\cdot}61 \times 10^6$	42·75	O_2 . .	$1{\cdot}36 \times 10^6$	31·87
H_2 . .	$0{\cdot}244 \times 10^6$	26·53	SO_2 . .	$6{\cdot}69 \times 10^6$	56·5

Although the van der Waals' equation, as we have seen, represents fairly closely the behaviour of a gas even under high pressures at temperatures above the critical point, it does not accurately represent the transition from the gaseous to the liquid state, as is shown by the fact that the values of the critical constants calculated from the values of a and b of the van der Waals' equation are only approximately in agreement with the values determined experimentally. A similar lack of strict agreement is shown when one calculates the value of the ratio $\frac{RT_c}{p_cV_c}$, where V_c is the volume in millilitres of 1 gram-molecule of the substance at the critical

point. If the van der Waals' equation represented accurately the transition from the gaseous to the liquid state, the ratio $\frac{RT_c}{p_cV_c}$ should have the value $\frac{R \times 8a \times 27b^2}{27Rb \times 3b \times a} = \frac{8}{3} = 2{\cdot}67$. As the numbers given in the last column of the table on p. 78 show, however, the actual value of the ratio [1] is distinctly higher than 2·67. In the case of non-associated substances to which alone van der Waals' equation applies, the value of the ratio varies from about 3·3 to 3·8; but in the case of associated substances, *e.g.*, methyl alcohol, water, acetic acid, the value is much higher.

Since the equation of van der Waals does not accurately express the pressure-volume relations of a gas below its critical temperature or correctly represent the transition from the gaseous to the liquid state, various attempts have been made to modify the van der Waals' equation so as to bring it into closer agreement with the actual behaviour of gases. The most successful of these attempts was made in 1899 by Conrad Dieterici,[2] Professor of Physics, University of Kiel, who suggested the expression $p \cdot e^{\frac{a}{vRT}}(v-b) = RT$. In this expression, a is a constant depending on the mutual attraction of the molecules, and e is the base of the natural logarithms. Under certain but not under all conditions, the Dieterici equation of state is rather more satisfactory than that of van der Waals. The value of the expression RT_c/p_cV_c given by the Dieterici equation is 3·695.

An interesting equation of state has also been put forward by James A. Beattie and Oscar C. Bridgeman.[3]

The Reduced Equation of State.—In the neighbourhood of the critical point all gases give an isotherm of the same type; but, since the values of the van der Waals' constants a and b are different for different gases, the isotherms do not coincide. These individual differences, however, disappear if the gases are studied, not under the same conditions of temperature and pressure but at temperatures and under pressures which are the *same fraction* of the critical temperatures and pressures. Thus, if p_r, v_r, and T_r represent the ratios p/p_c, v/v_c, and T/T_c, the so-called *reduced* pressure, volume and temperature, and if these reduced values are substituted for p, v, and T in the van der Waals' equation, one obtains the expression

$$\left(p_rp_c + \frac{a}{v_r^2v_c^2}\right)(v_rv_c - b) = RT_rT_c.$$

[1] Since the gram-molecular volume is expressed in millilitres, R has the value 82·1.

[2] *Ann. Physik*, 1899 (iii), **69**, 685; 1901 (iv), **5**, 51; 1903, **12**, 144; 1911, **35**, 220.

[3] *J. Amer. Chem. Soc.*, 1927, **49**, 1665; 1928, **50**, 3133, 3151.

Further, if for p_c, v_c, and T_c one substitutes their values in a, b, and R already found, there is obtained the equation

$$\left(\frac{p_r a}{27b^2}+\frac{a}{v_r^2.9b^2}\right)(3bv_r-b)=\frac{8aRT_r}{27Rb}.$$

This reduces to

$$\left(p_r+\frac{3}{v_r^2}\right)(3v_r-1)=8T_r.$$

An expression has thus been obtained which does not involve the factors a and b or the values of the critical constants, and which does not depend, therefore, on the nature of the substance. It should apply, therefore, to all substances in the liquid or gaseous state. From this expression one deduces that if two substances have the same reduced temperature and pressure they will also have the same reduced volume. Under such conditions the substances are said to be in *corresponding states*, and the generalisation just stated is sometimes known as the *law of corresponding states*. The degree of accuracy of this law is illustrated by the numbers in the following table :—

SUBSTANCES IN CORRESPONDING STATES

$p_r=0{\cdot}08846$ $T_r=0{\cdot}73-0{\cdot}74$

	v_r.	
	Liquid.	Vapour.
Benzene	0·4065	28·3
Iso-pentane	0·4085	27·7
n-Pentane	0·4061	28·4
n-Hexane	0·4055	29·1
Fluorobenzene	0·4067	28·4
Ether	0·4030	28·3
Methyl formate	0·4001	29·3

Although, as is clear from the preceding table, the law of corresponding states holds only approximately, it is, nevertheless, very useful as giving a means for the approximate calculation of the specific volume of a liquid. One example of its application may be given,

The specific volume of ethyl ether at 10° C. is 1·3794. What is the specific volume at 33·8° ?

Since the critical temperature of ether is 466·8° K, the reduced temperatures corresponding to the given temperatures are—

$$(T_r)_1 = 283°/466·8° = 0·6063.$$
$$(T_r)_2 = 306·8/466·8° = 0·6572.$$

Taking, now, fluorobenzene, the critical temperature of which is 560° K, as comparison liquid, one calculates the absolute temperatures corresponding to the reduced temperatures $(T_r)_1$ and $(T_r)_2$ to be $560° \times 0·6063 = 339·5°$ K, and $560° \times 0·6572 = 368·1°$ K, respectively. At these two temperatures the specific volumes of fluorobenzene are 1·0339 and 1·0741. The relative increase of volume is $(1·0741 - 1·0339)/1·0339 = 0·0389$. For ether, according to the law of corresponding states, the relative increase of volume will be the same, so that the specific volume of ether at 33·8° will be $1·3794 \times 1·0389 = 1·4331$. The experimentally determined volume is 1·4351.

From what has been said it will be readily understood that when the physical properties of liquids, which may undergo change with pressure and temperature, are to be studied, the comparison should be made when the liquids are in corresponding states. In practice this means that the properties of the liquids should be determined when the liquids are at the same reduced temperature, because, as a rule, pressure has only a slight influence on the properties of liquids. Since it has been found that, for different liquids, the boiling-point in degrees absolute and under a pressure of 76 cm. of mercury is approximately two-thirds of the critical temperature, it follows that liquids at their boiling-points under atmospheric pressure are approximately in corresponding states. In studying, therefore, the relation between the physical properties of substances and the chemical constitution, which is one of the important tasks of the physical chemist, the physical properties should be determined at the boiling-point of the substances or at some other corresponding temperature, the same for all.

Berthelot's Equation and the Calculation of Molecular Weights of Gases.—The relation between the critical constants and the quantities a and b of the van der Waals' equation was made use of by Daniel Berthelot (1865-1927), Professor of Physics at the École de Pharmacie, Paris, for the purpose of deriving an equation of state applicable only at low pressures far removed from the critical point. Substituting for the numerical coefficients of the van der Waals' equation coefficients which corresponded to experimental results $\left(e.g., R = \frac{32}{9} \cdot \frac{v_c p_c}{T_c}$ instead of $R = \frac{8}{3} \cdot \frac{v_c p_c}{T_c}\right)$, Berthelot derived

the expression

$$pv = RT\left[1 + \frac{9}{128} \cdot \frac{p}{p_c} \cdot \frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right].$$

This equation can be used to extrapolate the value of volume or density to low pressures, and was used by Guye for the calculation of exact molecular weights (p. 51). Thus the true molecular weight of a gas is given by the expression

$$M = \frac{mRT}{pv}\left[1 + \frac{9}{128} \cdot \frac{p}{p_c} \cdot \frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right],$$

where M is the true molecular weight, m is the mass of the substance, R is the gas constant, p and p_c are the corrected barometric pressure and the critical pressure, T and T_c are the temperature of the experiment and the critical temperature of the substance respectively on the absolute scale. For m/v one may also write d, the density at N.T.P. The equation is of the form: $M = \frac{mRT}{pv}(1 + Ap)$ or, $M = \frac{d.RT}{p}(1 + Ap)$, where d is the density (g./l.) under pressure p and A is a constant. Exact molecular weight values may therefore be calculated from determinations of the density at the temperature T and at two different pressures. From the above equation one learns that when the temperature is such that $T^2 = 6T_c^2$, $M = \frac{mRT}{pv}$. That is, the gas, even although not perfect, obeys Boyle's law. This temperature is known as the *Boyle point*.

CHAPTER IV

LIQUIDS AND THEIR PROPERTIES

A. Vaporisation and Vapour Pressure

LIQUIDS differ from gases in that they do not fill completely the whole space which may be offered to them ; they possess no definite form, but, owing to cohesion, they have a definite volume. The compressibility of liquids, which is small, and their expansion with temperature depend on the nature of the liquid. The volume of liquid is, therefore, not a colligative property.

Although, in the case of liquids, no such simple relations obtain as in the case of gases, the subject of the molecular weights of substances in the liquid state will be briefly reviewed, after the physical properties on which much of our knowledge of the molecular weights of liquids chiefly depends, have been studied.

Structure of Liquids.—Until a few years ago the liquid state was considered to be similar to the gaseous state, although, owing to closer packing of the molecules, the intermolecular forces are necessarily greater than for gases. As in the case of gases, so in the case of liquids, the molecules were regarded as being distributed in a disordered or random manner. This view, however, which might have persisted if one could have regarded the molecules as being completely symmetrical spheres, has had to be abandoned. The introduction of the conception of dipoles and the conclusion, based on experiment, that molecules may have a geometrical shape—linear, like carbon dioxide, or flat, like benzene—has necessarily led to the belief that such molecules must tend to pack in some sort of ordered array. Notable examples of the orderly parallelwise arrangement of molecules in the liquid state are found in the case of the turbid

liquids formed by a number of compounds with long-chain molecules (*e.g.*, *p*-azoxyanisole). Although X-ray examination has shown that no space-lattice in the ordinary sense of the term exists, some kind of asymmetry must be present as these liquids are anisotropic and show the property of double refraction (see Chap. VI.).

Although "ideal liquids," or assemblages of closely packed spheres, oscillating over a certain range, do exist (in the case of fused metals, for example), evidence of the existence of a structure in some liquids, at least, apart from those just referred to, is given by the diffraction of X-rays, the study of which has so greatly advanced our knowledge of the crystalline state (Chap. VI.).[1] It has been shown, in fact, that there is a general similarity between the X-ray patterns for liquids and those of the corresponding solids; and so there has gradually grown up the view that there is a tendency for a liquid to imitate the solid in general atomic or molecular arrangement. The diffraction of X-rays has shown that water, for example, has a marked structure, based on a tetrahedral arrangement of the molecules. In ice, the tetrahedra are arranged in a fairly open structure, like the tetrahedra of tridymite, one of the crystalline forms of silica. When ice melts, however, there is a partial change-over to the more compact arrangement shown by quartz, and the relative amount of the "quartz" structure increases to a maximum as the temperature is raised to 4°. As the temperature is raised above 4°, there is a progressive break-down of the "crystalline" structure with an increasing randomness in the distribution of the molecules. Above 150° the random distribution is complete and the molecular arrangement approximates to that of an "ideal" liquid.

It seems clear, therefore, that in some liquids, at least, the molecules are arranged with some degree of orderliness; and such packing of the molecules in ordered array, and the formation of polymerised or associated molecules have an influence, as we shall learn, on the physical properties of liquids, such as viscosity, heat of vaporisation, etc.[2]

Vaporisation and Vapour Pressure.—Although the molecules of a liquid, as a whole, are unable to overcome the force

[1] See J. T. Randall, *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids, and Gases* (Chapman and Hall).

[2] See *Trans. Faraday Soc.*, 1937, **33**, 2; Hildebrand, *Science*, 1939, **90**, 1.

of cohesion, yet the molecules are not all moving with the same velocity, and it may happen that some, having a higher velocity than the average, are able to tear themselves away from the general mass and escape into space, where they move about freely as the molecules of a gas or vapour. The liquid evaporates.

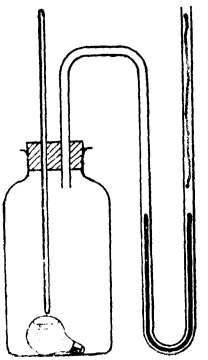


Fig. 22.—Vapour Pressure of Liquids.

If the liquid is placed in a closed vessel so that the escaping molecules cannot pass away into unlimited space, it is found that a pressure is produced, as can readily be shown by breaking a bulb of ether in a closed bottle fitted with a manometer or pressure gauge (Fig. 22). The pressure thus produced, however, does not go on increasing indefinitely. As more and more vapour is produced, some of the molecules will strike the surface of the liquid and be recaptured; and the number of such molecules will increase as the pressure or concentration of the vapour molecules increases. As more and more vapour is formed, therefore, a point will at length

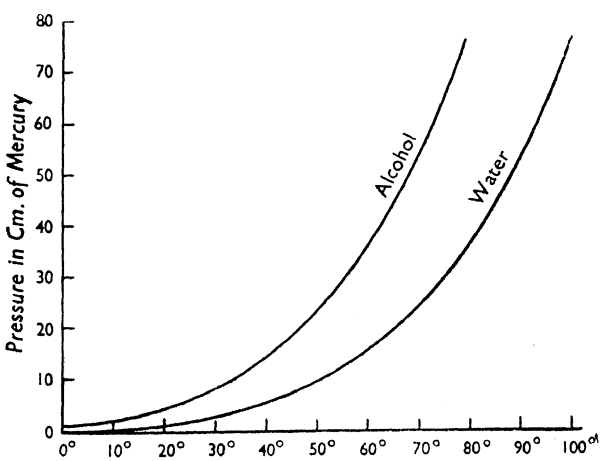


Fig. 23.—Vapour-pressure Curves.

be reached when the number of molecules recaptured by the liquid will be equal to the number which escape from the liquid. A state of equilibrium will thereby be attained, and

the pressure of the vapour in this state of equilibrium is known as the *vapour pressure* of the liquid. The vapour pressure, or pressure of the *saturated vapour* as it is sometimes called, increases with the temperature, but has, at each temperature, a definite value.

Although, at any given temperature, the vapour pressure of different liquids may differ greatly—some liquids being, as it is said, more volatile than others—yet, when one plots the values of the vapour pressure against the temperature, it is found that the curve so obtained *has the same form for all liquids*, and is convex to the temperature axis. This is illustrated by the curves shown in Fig. 23, which have been obtained by plotting the vapour pressures of ethyl alcohol and of water given in the following table :—

VAPOUR PRESSURE OF ETHYL ALCOHOL AND OF WATER

Temperature.	Vapour Pressure in Millimetres of Mercury.		Temperature.	Vapour Pressure in Millimetres of Mercury.	
	Alcohol.	Water.		Alcohol.	Water.
0°	12·7	4·58	40°	133·4	55·1
10°	24·1	9·21	60°	350·2	149·2
20°	44·0	17·5	80°	...	355·1
30°	78·4	31·7	100°	...	760·0

When the temperature is raised the vapour pressure increases, and when the pressure of the vapour becomes equal to the atmospheric pressure or to the external pressure on the liquid, bubbles of vapour are formed within the liquid and the liquid is then said to boil. The *boiling-point* of a liquid is therefore the temperature at which the vapour pressure of the liquid becomes equal to the external pressure on the liquid. If the external pressure is increased, the boiling-point is raised ; and if the external pressure is diminished, the boiling-point is lowered. A liquid will boil at a lower temperature on the top of a mountain than it will on the seashore.[1] For this reason, substances which undergo decomposition at a temperature below the boiling-point

[1] The boiling-point of water falls by 1° C. for a rise of 295 metres (or about 960 ft.).

under atmospheric pressure can frequently be distilled at a lower temperature, without decomposition, by carrying out the distillation under reduced pressure. This fact is widely taken advantage of for the purification of substances both in industry and in the scientific laboratory.

Determination of the Vapour Pressure of a Liquid.—For the determination of the vapour pressure various methods, both static and dynamic, may be employed.

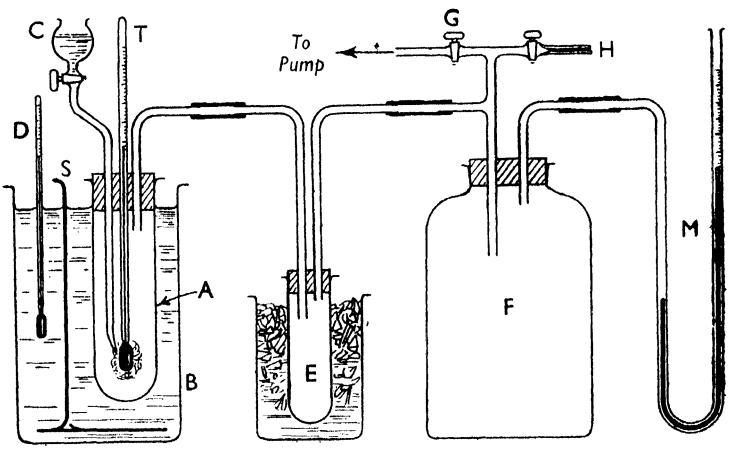


FIG. 24.

1. *Dynamic Methods.*—Among the first to determine the vapour pressure of liquids with accuracy by a dynamic method were William Ramsay and Sydney Young[1] (1857-1937), a diagram of whose apparatus is shown in Fig. 24.[2] According to this method, one maintains a constant pressure and ascertains the temperature at which the liquid boils under that pressure.

The bulb of the thermometer T, which passes through a rubber bung, is covered with cotton-wool, and the lower end of the dropping funnel C is drawn out to a point and bent so that it just touches the cotton-wool. The boiling tube A is supported in a suitable heating bath B. E is a tube to condense vapour, F is a large bottle which acts as a reservoir and serves to maintain a steady pressure, and M is a manometer.

[1] Later, Professor of Chemistry in Trinity College, Dublin.
[2] *Phil. Trans.*, 1884, **175**, 37; *J. Chem. Soc.*, 1885, **47**, 42.

A quantity of the pure liquid is placed in C and the pressure within the apparatus is reduced by means of an exhaust pump to a definite value, say 30 mm. of mercury. Liquid is allowed to flow slowly from the funnel so as thoroughly to moisten the cotton-wool surrounding the bulb of the thermometer T. As evaporation takes place, the temperature recorded by the thermometer T will alter and will reach a steady value, if the pressure in the apparatus is kept constant. This temperature is the boiling-point of the liquid under the pressure within the apparatus ; or, in other words, the pressure shown by the manometer represents the vapour pressure of the liquid at the temperature recorded by the thermometer T. The pressure within the apparatus is then altered by allowing air to enter through the tap G, and the boiling-point under the new pressure determined. In this way the vapour pressure at a series of different temperatures can readily be determined.

The boiling-point method introduced by Alexander Smith (1865-1922), Professor of Chemistry, Columbia University, and Alan W. C. Menzies,[1] of Princeton University, is somewhat simpler than that of Ramsay and Young, and requires the use of only a small quantity of liquid.

The liquid under investigation is placed in a small bulb-tube A (Fig. 25), which is then attached by thread to the thermometer T. Tube B is nearly filled with a liquid of considerably higher boiling-point than that under investigation. Tube B is connected by means of C with a manometer and pressure-regulating bottle, as shown in Fig. 24. The temperature of the liquid in B is regulated by means of the bath D.

To carry out a determination, the tube B is heated to a constant temperature, say 15°, and the pressure in the apparatus is then reduced. As the pressure falls, air escapes from the bulb-tube A. Later, the liquid in A begins to boil, and a stream of bubbles escapes from the capillary of A. Air is now allowed to enter slowly through a very fine capillary H (Fig. 24), until the liquid in A just ceases to boil. At this point the temperature on the thermometer T and the pressure are read. Similar determinations are then carried out at higher temperatures.

Reference has already been made (p. 93) to the transpiration method of determining vapour pressures by bubbling

[1] *J. Amer. Chem. Soc.*, 1910, **32**, 897, 907.

an indifferent gas through a liquid. This method has been widely used for the determination of the vapour pressure of solutions.

2. *Static Method.*—The vapour pressure may also be determined by means of the *isoteniscope.* This instrument, which we owe to Smith and Menzies,[1] has the form shown in Fig. 26. The liquid under investigation is introduced into the isoteniscope in such amount that the bulb is about half full, and the liquid stands about half-way up the limbs of the U-tube. The apparatus is placed in a suitable heating

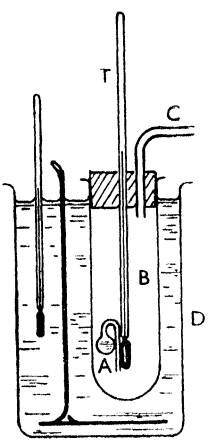


FIG. 25.

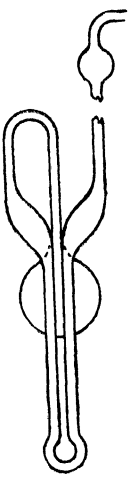


FIG. 26.

bath and is connected with a manometer and pressure-regulating bottle (Fig. 24). When the temperature has been adjusted to a definite value, the pressure is reduced until the liquid in the bulb of the isoteniscope begins to boil. Air is then allowed to enter very slowly through the tap H (Fig. 24), until the level of liquid is the same in the two limbs of the U-tube. The pressure registered by the manometer is the vapour pressure of the liquid at the temperature of the bath.

The variation of the vapour pressure with temperature can be represented with considerable accuracy by the formula, $\log p = A - B/T + C \log T$, where A, B, and C are constants. For many purposes the simpler formula, $\log p = A - B/T$, the theoretical basis of which will become

[1] *J. Amer. Chem. Soc.*, 1910, **32**, 1412.

clear later, may be used. On plotting log p against the reciprocal of the absolute temperature, a nearly straight

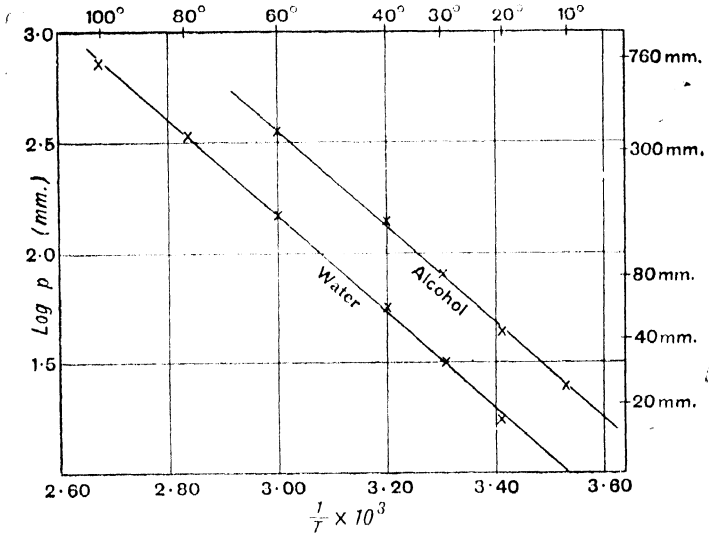


FIG. 27.

line is obtained (Fig. 27). This is useful for reading off intermediate values of the vapour pressure.

On comparing the vapour-pressure curves of different liquids, it was found by Ramsay and Young [1] that, for closely related substances, *e.g.*, the esters of fatty acids, the ratio $\frac{T_1}{T_2}$ of the absolute temperatures of the boiling-point under two different pressures, the same in all cases, is constant. The numbers in the following table illustrate this relation :—

Substance.	T_1 760 mm.	T_2 200 mm.	$\frac{T_1}{T_2}$
Methyl formate .	305·3°	273·7°	1·115
Methyl acetate .	330·5°	296·5°	1·115
Methyl propionate	352·9°	316·7°	1·114
Ethyl formate .	327·4°	293·1°	1·117
Ethyl acetate .	350·1°	314·4°	1·114
Ethyl propionate .	371·3°	333·7°	1·113
Ethyl butyrate .	392·9°	352·2°	1·116

In the case of substances not closely related, it is found that

$$\frac{T_a'}{T_b'} = \frac{T_a}{T_b} + c(T_a' - T_a),$$

[1] *Phil. Mag.*, 1885 (v), **20**, 515 ; 1886, **21**, 33 ; **22**, 37.

where T_a and T_a' are the absolute temperatures corresponding to two different values of the vapour pressure of substance a, and T_b and T_b' are the absolute temperatures at which substance b has the same two values of the vapour pressure; c is a constant.

These relations are of much value as giving a means of obtaining, with a fair degree of accuracy, the vapour-pressure curve of a liquid from determinations of the vapour pressure at two temperatures and a knowledge of the vapour-pressure curve of a comparison liquid.

Latent Heat of Vaporisation.—When a liquid is boiling freely, its temperature remains constant no matter how much heat is added to the liquid; and since the added heat brings about no rise of temperature, it is said to become *latent*. The amount of heat required to convert 1 g. of substance from liquid to vapour, without producing an alteration of temperature, is called the *latent heat of vaporisation*. This latent heat is the equivalent of the work done (1) in increasing the volume against the constant external pressure, and (2) in overcoming the mutual attraction of the molecules. In the case of associated liquids, the latent heat of vaporisation will also include the heat of dissociation of the complex molecules, and will therefore have a higher value than in the case of non-associated liquids.

Conversely, when vapour condenses to liquid, an amount of heat equal to the heat of vaporisation is given out.

When a liquid evaporates spontaneously, the heat of vaporisation is taken, in the first instance, from the liquid itself, and the temperature therefore falls. This effect is readily observed if one sprays ether, or other very volatile liquid, on the skin. Through the rapid evaporation of the liquid the temperature may fall to such a degree that local anæsthesia is produced. Similarly, by the rapid vaporation of water the temperature may be lowered to such an extent that the water freezes. (This is readily demonstrated by causing water in a Dewar vacuum tube to boil rapidly under reduced pressure.) From very early times, in fact, ice has been obtained by the natives of India by exposing water in shallow pans, embedded in straw to prevent access of heat. On a clear night, evaporation takes place so rapidly that the water freezes. The lowering of temperature produced by the evaporation of volatile liquids, *e.g.*, ammonia, sulphur dioxide, is made use of in various types of refrigerators.

This cooling by evaporation is readily explicable on the basis of the kinetic theory, for, during evaporation, the molecules which overcome the mutual attraction and pass

into free gas molecules are those which possess a relatively large amount of energy. The average kinetic energy of the remaining molecules, therefore, will be decreased, and the temperature, which is measured by the kinetic energy, will fall.

The latent heat of evaporation of water (or the heat of condensation of steam with reversed sign), which is of so great importance in connection with the use of the steam engine and with the transport of heat by means of steam, was first determined in 1764 by Joseph Black (1728-99), Lecturer in Chemistry in the University of Glasgow, who passed steam at a known temperature into water contained in a calorimeter. From the rise of temperature produced in a known weight of water by a known amount of steam the latent heat of vaporisation could be calculated. For water, the latent heat of vaporisation at 100° is 539·55 calories per gram.

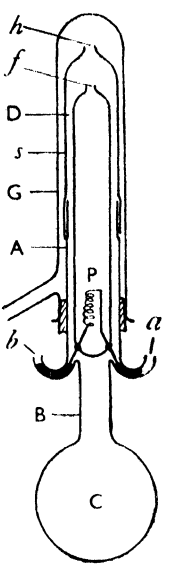


FIG. 28.
(Courtesy of Chemical Society.)

The latent heat of vaporisation may also be determined by adding a known amount of heat to a liquid and ascertaining how much of the liquid is thereby vaporised. The apparatus used by James Campbell Brown (1843-1910), Professor of Chemistry in the University of Liverpool, is very convenient for this purpose.[1]

The liquid under investigation is placed in a tube of thin glass P (Fig. 28), into which a spiral of platinum wire is sealed. This tube is then placed in the neck of the flask C so that the ends of the platinum wire dip into mercury contained in the side tubes *ab*. A cap *s* is placed over the neck of the flask, and a glass cover G fitted over all. The flask C also contains a quantity of the liquid under investigation. When the liquid in C is boiled, the vapour surrounds the tube P, passes out through the orifice *h*, and then through the exit tube to a condenser. By this means the liquid in P is heated to its boiling-point. Wires connected with a battery and an ammeter are inserted into the mercury in the tubes *ab*,

[1] *J. Chem. Soc.*, 1903, **83**, 987. See also Mathews, *J. Amer. Chem. Soc.* 1926, **48**, 562.

and a current of electricity passed through the platinum spiral. The liquid in P is thus caused to vaporise, and at the end of the experiment the loss of weight can be determined. The amount of heat required to effect the vaporisation of the known amount of liquid can be calculated from the amount of electrical energy passed through the platinum spiral, and this, in turn, is obtained from the current passed and the fall of potential in the platinum spiral. If E is the fall of potential in the spiral, I the strength of current in amperes, and t the time in seconds during which the current passes, the electrical energy is given by $I \times E \times t$, or, I^2Rt volt-coulombs, where R is the resistance of the spiral in ohms. From this, since 1 volt-coulomb = 0·239 calorie, the amount of heat passed through the liquid can be calculated.

Example.—A current of 0·615 amp. was passed for 20 mins. through a platinum spiral immersed in ethyl ether at its boiling-point. The fall of potential in the spiral was 3·38 volts, and 7·03 g. of ether were evaporated. From these data the latent heat of vaporisation per gram of ether is calculated to be

$$l = \frac{0{\cdot}615 \times 3{\cdot}38 \times 1200 \times 0{\cdot}239}{7{\cdot}03} = 84{\cdot}80 \text{ cal.}$$

The latent heat of vaporisation, it is found, varies not only from substance to substance but also with the temperature at which vaporisation takes place. As a rule, the latent heat of vaporisation decreases with rise of temperature, and at the critical temperature it is zero.

Vapour-pressure Curve and Heat of Vaporisation.—According to the THEOREM OF LE CHATELIER, when heat is added to a system in equilibrium a change takes place, if possible, which is accompanied by absorption of heat. Consequently, when heat is added to a liquid in equilibrium with its vapour, more vapour will be produced (because this is a change accompanied by absorption of heat), or the vapour pressure will be increased. The increase of vapour pressure with rise of temperature can in this way be predicted; but the prediction is only a qualitative one. The course of the vapour-pressure curve, however, can be predicted quantitatively by means of the thermodynamic relationship between the change of vapour pressure and the heat of vaporisation, expressed in what is known as the *Clausius-Clapeyron equation*,

$$\frac{dp}{dT} = \frac{l}{T(v_2 - v_1)},$$

where l is the latent heat of vaporisation, expressed in appropriate units, and v_1 and v_2 are the volumes of 1 g. of the substance in the liquid and vapour states respectively. The ratio dp/dT represents the rate of change of the pressure with the temperature at the absolute temperature T, or the ratio of the very small change of vapour pressure to the corresponding very small change of temperature. If one neglects the volume of the liquid in comparison with the volume of the vapour, and refers all quantities to 1 gram-molecule of the substance, one obtains the expression

$$\frac{dp}{dT} = \frac{L}{T.V},$$

where L is the latent heat of vaporisation per gram-molecule (equal to the latent heat of vaporisation l, multiplied by the molecular weight of the substance) and V is the volume of 1 gram-molecule of the vapour. *If it be assumed* that the vapour obeys the gas laws, one may write $V = \boldsymbol{R}T/p$, and, on substituting this value in the previous equation, one obtains the expression

$$\frac{1}{p} \cdot \frac{dp}{dT} = \frac{L}{\boldsymbol{R}T^2}; \text{ or, } \frac{d \log_e p}{dT} = \frac{L}{\boldsymbol{R}T^2}.$$

If it now be assumed that L as well as $\boldsymbol{R}$ is constant, integration of the latter equation yields the expression

$$\log_e p = -\frac{L}{\boldsymbol{R}} \cdot \frac{1}{T} + I; \text{ or, } \log_{10} p = -\frac{L}{2{\cdot}303\boldsymbol{R}} \cdot \frac{1}{T} + I$$

where I is the integration constant. When, therefore, $\log_{10} p$ is plotted against $1/T$, a straight line is obtained, the slope of which is $-L/2{\cdot}303\boldsymbol{R}$, or, $L = -(\text{slope} \times 2{\cdot}303 \times 1{\cdot}987)$ cal.

If the differential equation is integrated between the limits T_1 and T_2, at which the vapour pressures are p_1 and p_2, and *if it be assumed* that the latent heat of vaporisation remains constant over the temperature interval $(T_2 - T_1)$, one obtains the expression

$$L = 2{\cdot}303 \times 1{\cdot}987 \times \frac{T_1 \times T_2}{(T_2 - T_1)} \cdot \log_{10} \frac{p_2}{p_1}.$$

L is the mean molar heat of vaporisation in calories over the temperature range T_1 to T_2, and 2·303 is a factor for converting natural to decadic logarithms.

By means of this equation it is possible, from determinations of the vapour pressure, to calculate *approximately* the mean heat of vaporisation over a short range of temperature; or, conversely, if the heat of vaporisation is known, it is possible to calculate individual values of the vapour pressure, approximately, if any one is known.

The following example, given by Nernst, will illustrate the application of the above equations.

The vapour pressure of water at 99·5° is 746·52, and at 100·5°, 773·69 mm. of mercury. Since dT is equal to unity, the ratio dp/dT, therefore, has the value 773·69 − 746·52 = 27·17 mm. of mercury = 0·03570 atm. The specific volume of water vapour at 100° is 1·674 lit., and the specific volume of liquid water at the same temperature is 0·001 lit. Therefore, $v_2 - v_1 = 1·673$ lit., and

$$l = \frac{dp}{dT} \times T \times (v_2 - v_1)$$
$$= 0·03570 \times 373 \times 1·673$$
$$= 22·29 \text{ lit.-atm.}$$

But 1 lit.-atm. = 24·19 gram-cal., and therefore $l = 22·29 \times 24·19 = 539·12$ cal. The value found experimentally is 539·6 cal.

Again, in the case of benzene, at $T_1 = 273° + 20°$, $p_1 = 75·0$ mm., and at $T_2 = 273° + 30°$, $p_2 = 118·0$ mm. of mercury. Therefore,

$$L = 2·303 \times 1·987 \times \frac{293 \times 303}{10} \times \log \frac{118}{75}.$$
$$= 8000 \text{ cal.}$$

The value determined experimentally for 25° C. is 8040 cal.

Similarly, at $T_1 = 343°$, $p_1 = 546·5$ mm., and at $T_2 = 353°$, $p_2 = 750·0$ mm. of mercury. From these data one calculates $L = 7653$ cal., whereas the observed value is 7426 cal. The discordance here is mainly due to the fact that, at the higher pressures, benzene vapour deviates considerably from the simple gas laws. The assumptions made are no longer valid.

Trouton's Rule.—When one multiplies the latent heat of vaporisation, per gram, by the molecular weight of the substance in the state of vapour, the product is known as the *molecular* or *molar heat of vaporisation*; and, in 1884, it was discovered by F. T. Trouton [1] (1863-1922), while a student at Trinity College, Dublin, that, in the case of normal, non-associated liquids, the quotient obtained by dividing the molecular heat of vaporisation at the normal boiling-point by the absolute temperature of the boiling-point has nearly the same value for different normal liquids.[2] Some of these values are given in the table on p. 102 [3]:—

[1] Later, Professor of Physics, University College, London.

[2] Since the change of entropy on evaporation is given by $\Delta S = \frac{q_{\text{rev.}}}{T} = \frac{Ml}{T}$ (Chap. XVII.), one may also state that for normal, non-associated liquids, the entropy of vaporisation is equal to 21.

[3] See also Mathews, *J. Amer. Chem. Soc.*, 1926, **48**, 562.

Substance.	Molecular Weight.	Boiling-point, T° K.	Heat of Vaporisation per Gram (l).	$\frac{Ml}{T}$.
Benzene . . .	78	353·2°	94·4	20·85
Carbon tetrachloride .	154	249·7°	46·4	20·41
Ethyl formate . .	74	327·3°	94·4	21·33
Ethyl acetate . .	88	350·1°	88·1	21·93
Methyl iodide . .	142	316·8°	46·1	20·66
Ethyl alcohol . .	46	351·2°	216·5	28·4
Water . . .	18	373·0°	539·6	26·06
Acetic acid . .	60 (97)	391·5°	94·4	14·5 (23·4)

It will be seen that in the case of the first group of compounds, which are regarded as being non-associated, the Trouton quotient has an average value of about 21. It should be mentioned, however, that in the case of liquids of low boiling-point the value is much smaller ; for example, 12·2 for liquid hydrogen and 17·6 for liquid nitrogen.

In the case of substances such as ethyl alcohol and water, which have unusually great heats of vaporisation and are regarded as being associated in the liquid state, but which have normal molecular weights as vapours, the Trouton quotient has an abnormally high value. This behaviour may be taken as a criterion of association in the liquid state.

In the case of acetic acid the value of the Trouton quotient is found to be 14·5, if the molecular weight is taken as 60. Determinations of the vapour density, however, in the neighbourhood of the boiling-point, show that the molecular weight is about 97 ; and if this value is taken as the molecular weight, the Trouton quotient has the value 23·4, which indicates, as is to be expected, that the acid is rather more associated in the liquid state than in the state of vapour.

Many modifications of the Trouton rule have been put forward, and of these the modification suggested by J. H. Hildebrand, Professor of Chemistry in the University of California, may be specially mentioned.[1] If the heats of vaporisation of the different liquids are taken, not at the normal boiling-points but at such temperatures T_x that the saturated vapours have the same concentration or contain the same number of gram-molecules per litre, the value of the

[1] *J. Amer. Chem. Soc.*, 1915, **37**, 970. See also Cederberg, *Thermodynamische Berechnung chemischer Affinitäten* ; Byk, *Z. physikal. Chem.*, 1924, **110**, 291.

ratio $\frac{Ml}{T_x}$ is more nearly constant than is the Trouton quotient in the case of normal liquids. Associated liquids, again, give notably higher values.

B. Viscosity

One of the properties characteristic of liquids is that of flowing; but it is a well-known fact that some liquids flow much more readily, or are much more mobile, than others.

This can be demonstrated by sealing up ether, water, and glycerol in separate glass tubes, 35 to 40 cm. long and about 7 mm. in diameter. The tubes should be about four-fifths full of liquid. If all three tubes are inverted at the same time, it is found that the ether flows down the tube more rapidly than the water, and that, at the ordinary temperature, glycerol is so viscous that it flows with very great slowness. That the viscosity diminishes with rise of temperature is readily shown by heating the tube of glycerol in a bath of boiling water. The glycerol is now quite mobile.

When water, or other liquid, flows through a narrow tube, the velocity of flow will depend on the nature of the liquid and the force which produces the flow. All parts of the liquid, however, do not move through the tube with the same velocity. A very thin layer in contact with the wall of the tube remains stationary, and over a short distance the successive very thin layers of liquid move over one another with gradually increasing velocity, until a maximum is reached. There is thus a shearing or a movement of the different layers past one another in the direction of flow; and this displacement of the different layers relatively to one another is opposed by the *internal friction* or *viscosity* of the liquid. When the tube is a narrow one, therefore, one can regard the column of liquid as made up of a number of concentric tubes sliding past one another like the draw-tubes of a telescope; and the resistance to the flow is due to the friction between the different layers of liquid. In the case of a fairly mobile liquid the zone of variable rate of flow in the neighbourhood of the walls of the tube is a narrow one and outside this zone, in the middle of the tube, the liquid streams, without friction, at a constant rate.

When the liquid is moving through a narrow tube there will be a constant difference in velocity between the different tubes of which we have regarded the cylinder of liquid made up, and it has been found that the force per unit area which is necessary to maintain this condition is

proportional to the difference of velocity v of two adjacent tubes (or their relative velocity of displacement) and inversely proportional to their distance x apart, *i.e.*,

$$\text{Force} = \eta \times \frac{v}{x},$$

where η is a constant known as the *coefficient of viscosity*. When the velocity of displacement of two layers is numerically equal to the distance between the layers ($v = x$), the force in dynes per unit area becomes equal to the coefficient of viscosity. This gives the definition of the latter quantity. The reciprocal of the viscosity, or $1/\eta$, is called the *fluidity* (ϕ). The unit of viscosity in C.G.S. units is known as a *poise* (Poiseuille).

For the flow of a homogeneous liquid through a capillary tube the following expression (Poiseuille's formula) has been deduced :

$$\eta = \frac{\pi r^4 p t}{8 V l},$$

where p is the driving force, r is the radius of the tube, t is the time required for the volume V of liquid to flow through the tube of length l. This formula holds strictly, however, only when the velocity of the liquid on leaving the tube is zero ; and when this is not the case, a correction for the kinetic energy of the liquid must be introduced.

The apparatus now generally employed for the determination of the viscosity of liquids is the Ostwald modification of Poiseuille's apparatus, shown in Fig. 29. A definite volume of liquid is introduced into the larger bulb e and the liquid is then sucked up until its level rises above the mark at c. The liquid is then allowed to flow back through the capillary, and the time required for the surface of the liquid to pass from the mark c to the mark at d is noted.

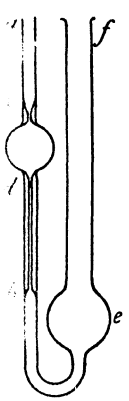


FIG. 29.

In the Ostwald viscosimeter the force driving the liquid through the capillary is equal to $h \times d_1 \times g$, where h is the mean difference of level of liquid in the two limbs of the tube, d_1 is the density of the liquid, and g is the gravitational constant. If the same volume of a second liquid is introduced into the tube, the mean difference of level of the two liquid surfaces will also be h, so that the driving force will now be $h \times d_2 \times g$; or the driving force is proportional to the

densities of the two liquids. According to Poiseuille's formula, however, the viscosity η is equal to $\frac{\pi r^4}{8Vl} \cdot pt$; *i.e.*, for a given apparatus and the same volume V of liquid, η is proportional to the driving force and to the time of outflow. Hence,

$$\frac{\eta_2}{\eta_1} = \frac{h \cdot d_2 \cdot g \cdot t_2}{h \cdot d_1 \cdot g \cdot t_1} = \frac{d_2 t_2}{d_1 t_1}.$$

This expression gives the viscosity of the second liquid relatively to the first. For many purposes only the relative viscosity of a liquid is required, and as comparison viscosity that of water at some particular temperature is generally chosen. It is, of course, easy to obtain the coefficient of viscosity of a liquid in absolute units by substituting, in the above equation, the value in absolute units of η_1, the coefficient of viscosity of the comparison liquid.

In the case of liquids of high viscosity, *e.g.*, glycerol, castor oil, etc., the viscosity can best be determined by the rate of fall of a sphere, in accordance with Stokes' law, namely, $v = \frac{2}{9} g r^2 \cdot \frac{d - d'}{\eta}$, where v is the velocity of fall in centimetres per second, g is the gravitational constant, r is the radius of the sphere, d is the density of the sphere, and d' is the density of the liquid. To this equation two corrections must be applied for the case of a small sphere falling axially through a viscous liquid in a cylindrical tube, a correction for "wall-effect" and a correction for "end-effect." Introducing these corrections one obtains the equation

$$9\eta v(1 + 2{\cdot}4r/R)(1 + 3{\cdot}3r/h) = 2gr^2(d - d'),$$

where R is the radius of the tube and h is the height of the liquid. If one measures the time of fall t through a distance s, the expression becomes

$$9\eta s(1 + 2{\cdot}4r/R)(1 + 3{\cdot}3r/h) = 2gr^2(d - d')t.$$

The apparatus devised by W. H. Gibson and L. M. Jacobs [1] is shown in Fig. 30. The fall-tube A has five rings etched round it at distances of 5 cm., and a small steel ball is dropped in through the tube C. The time of fall of the

[1] *J. Chem. Soc.*, 1920, **117**, 473.

ball between, say, the second and the fifth marks, is determined, and the viscosity calculated according to the above expressions. The tube A is placed in a cylinder of water at constant temperature.

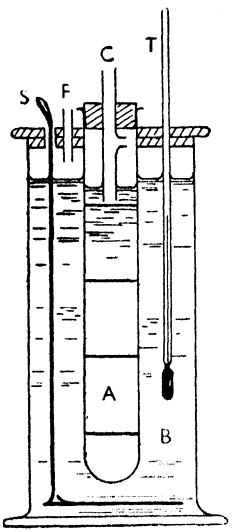


FIG. 30.

That liquids differ greatly in viscosity is shown by the values of the coefficients of viscosity given in the following table :—

	Viscosity in C.G.S. Units at	
	10°.	20°.
Ethyl ether . .	0·00258	0·00234
Chloroform . .	0·00625	0·00563
Methyl alcohol . .	0·00690	0·00593
Benzene . . .	0·00757	0·00647
Carbon tetrachloride .	0·01138	0·00975
Water . . .	0·01309	0·01008
Ethyl alcohol . .	0·10752	0·01716
Glycerol . . .	21·0	8·5

Influence of Temperature on Viscosity and Fluidity.—The viscosity of a liquid diminishes rapidly (about 2 per cent. per degree) with rise of temperature, and, in the case of a normal liquid, can be represented with fair accuracy by the expression,[1] $\log \eta = B/T - A$, where A and B are constants. On plotting $\log \eta$ against the reciprocal of the absolute temperature, therefore, a straight line is obtained.

Since the viscosities of gases have been shown to depend on the molecular weight and the molecular cross section, D. T. Lewis [2] suggested that any equation representing the variation of the viscosity of liquids must contain terms representing temperature, molecular weight, and molecular volume. On this basis there was derived, for chemically related series of compounds, the expression : $\log \eta = (A \log M - B)/T - \frac{2}{3} \log C[P]$, where A, B and C are constants, M is the molecular weight and $[P]$ is the parachor (p. 118), a molecular volume term. This equation is applicable to all members of an homologous series, and from it Andrade's expression follows directly.

[1] Andrade, *Nature*, 1930, **125**, 309, 582 ; *Phil. Mag.*, 1934, **17**, 497, 698.
[2] *J. Chem. Soc.*, **1938**, 1061 ; Lewis and Morgan, *ibid.*, **1939**, 1341.

In the case of non-associated liquids, the reciprocal of the viscosity, or the *fluidity*, varies much more nearly linearly with the temperature than does the viscosity; and the fluidity-temperature curves for members of an homologous series are, at not too low temperatures, nearly parallel.[1]

In recent years viscosity measurements have found application in many different directions: *e.g.*, to the detection of changes in the molecular complexity of liquid mixtures and of the formation of hydrates and of complex salts in solutions of electrolytes; to the study of colloid sols and changes which take place in these; and to the control of lubricants, tanning liquors, cellulose nitrate and acetate, and the molecular weights of high polymers.[2]

C. Surface Tension

When a liquid is withdrawn from the action of gravity, as, for example, when it is suspended in a medium of the same density, it assumes the form of a sphere [3]; and whenever a free surface is formed the liquid tends to form the smallest possible surface. This behaviour is due to the fact that an attractive force exists between the molecules of a liquid whereby an "internal pressure" is produced. A molecule in the body of a liquid is equally attracted in all directions, but a molecule in the surface layer is subject to an unbalanced force acting inwards at right angles to the surface. The surface of a liquid, therefore, may be regarded as being the seat of a special force, the action of which can be visualised by imagining the surface layer of liquid to act as an elastic skin which tends to contract. This force, acting perpendicularly to a section of the surface 1 cm. long, is called the *surface tension*, and is generally expressed in dynes per centimetre. Usually one thinks of the surface tension as the force existing at the interface between a liquid and its vapour or between a liquid and air, but a surface tension also exists

[1] Bingham and Miss J. P. Harrison, *Z. physikal. Chem.*, 1909, **66**, 1. See also Bingham and Spooner, *J. Rheology*, 1932, **3**, 221.

[2] Dunstan and Thole, *The Viscosity of Liquids* (Longmans); R. Linke, "Viscosity of Binary Mixtures and Associated Liquids," *Z. physikal. Chem.*, 1941, A, **188**, 191.

[3] To demonstrate this behaviour one may use olive oil suspended in a mixture of alcohol and water, or *o*-toluidine suspended in an aqueous solution of common salt.

at the boundary surface between two immiscible liquids, between a liquid and a solid, and, indeed, whenever a free surface is formed. The value of the surface tension will depend on the nature of the interface.[1]

When a liquid wets a solid the surface tension is able to do work, as when water rises in a glass tube or in a strip of blotting paper. If, however, the liquid does not wet the solid, the surface tension will resist the doing of work —or a certain amount of work must be done in order to break through the surface layer. Thus, when a glass tube is placed in mercury, a certain amount of work must be done in order to depress the tube through the surface of the mercury, and the level of the mercury inside the tube is lower than the level outside.

The existence of a surface tension and the fact that the surface layer of a liquid acts as if it were an elastic skin, afford an explanation of a number of familiar phenomena. If water or a water paint is brushed over a piece of greasy paper, it does not spread evenly as a film, but forms into drops owing to the action of surface tension, just as mercury forms drops or globules on a surface which it does not wet. If, however, the surface tension of the water is reduced, that is, if the imaginary surface skin is weakened, then the water will spread out as a film over the paper. The lowering of the surface tension of the water can be effected by the addition of various substances, *e.g.*, sodium soaps. Further, it is owing to the existence of a special surface layer that it is possible to float a steel needle or a boat of wire gauze on the surface of water, or to carry water in a vessel of wire gauze. If the needle or wire gauze be coated with a film of grease or of paraffin, so that it is not wetted by the water, the needle or gauze will merely form a depression, or series of depressions, on the surface of the water, as if resting on a thin elastic film (Fig. 31). As was pointed out, if a liquid does not wet a solid, a certain amount of work has to be done in order to break through the surface layer of the liquid.

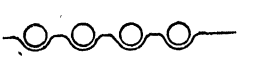


FIG. 31.

Determination of the Surface Tension.—For the measurement of the surface tension of a liquid various methods may be employed.

[1] For a full discussion of surface tension see N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press).

1. *Capillary Rise Method.*—When the end of a glass capillary tube is placed in water, or other liquid which wets the tube, a film of liquid spreads over the surface of the tube, and, since the surface tension tends to diminish the area of the liquid surface, the liquid is drawn up the capillary to a certain height h. At the same time the upper surface of the liquid becomes curved, thereby forming a *meniscus* (Greek, *mēniskos*, a little moon) which meets the surface of the glass tangentially, *i.e.*, at an angle of 0°. The column of liquid is supported by the surface tension acting along the circumference of the tube, that is, by the force $\gamma \cdot 2\pi r$, where γ is the surface tension; and the weight of the liquid which is thus supported is $\pi r^2 \cdot h \cdot d$, where r is the radius of the tube and d is the density of the liquid. We have, therefore, $\gamma \cdot 2\pi r = \pi r^2 \cdot h \cdot d$, or $\gamma = \frac{1}{2}h \cdot r \cdot d$, in grams per centimetre; or $\gamma = \frac{1}{2}h \cdot r \cdot d \cdot g$, in dynes per centimetre, where g is the acceleration due to gravity (say 981 cm./sec.^{2}). Consequently, in order to determine the value of γ, it is only necessary to determine the values of h, r, and d.

For the determination of the surface tension, the simple apparatus shown in Fig. 32 may be used.[1] The capillary tube B, having a bore of about 0·4 mm., dips into a liquid contained in the wider tube A. The height h may be determined by means of a cathetometer or by a scale attached to the capillary. Since the surface tension diminishes fairly rapidly as the temperature rises, the apparatus must be kept in a thermostat or constant-temperature bath.

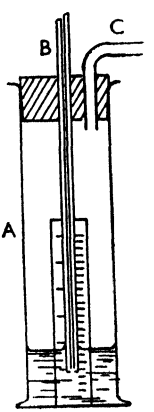


FIG. 32.

2. *Drop Method.*—The surface tension of a liquid may also be determined, very conveniently, by the so-called *drop method.*[2] When a liquid is allowed to flow very slowly from a tube a drop will form which increases in size up to a certain point and then falls. On the assumption that the surface tension

[1] For other forms of apparatus see Ramsay and Shields, *J. Chem. Soc.*, 1893, **63**, 1089; Walden and Swinne, *Z. physikal. Chem.*, 1912, **79**, 700; Richards and Coombs, *J. Amer. Chem. Soc.*, 1915, **37**, 1656; S. Sugden, *J. Chem. Soc.*, 1921, **119**, 1483.

[2] See J. Livingstone R. Morgan, *J. Amer. Chem. Soc.*, 1911, **33**, 349, and later volumes; Harkins and Brown, *ibid.*, 1916, **38**, 246; 1919, **41**, 499; Bircumshaw, *J. Chem. Soc.*, 1922, **131**, 887.

of the liquid, acting vertically round the rim of the tube, holds the drop up against the action of gravity, the simple formula, $\gamma \cdot 2\pi r = W$, where W is the maximum weight of the drop, is obtained; and it was thought that the value of γ could be calculated with the help of this expression from the weight of a drop and the radius of the dropping tube. The work, however, of Lohnstein [1] and of Harkins and Brown,[2] more especially, has shown that this simple expression is quite incorrect; and although there is no simple formula relating the weight of a falling drop to the surface tension of the liquid and the radius of the tip of the tube, it has been found that the surface tension, in dynes per centimetre, is given, with an accuracy of about 0·1 per cent. by the expression

$$\gamma = \frac{mg}{r} \times F,$$

where F is a function of v/r^3, v being the volume of a drop. The function is a somewhat complicated one, but values of F have been determined experimentally by Harkins and Brown for different values of v/r^3.

For relative measurements it is easier, instead of determining the weight of the drops, to determine the *number* of drops formed by a given volume of the liquids. If one uses the same dropping tube, and if the volumes of the drops are not very different, the correction term F will have practically the same value. Consequently, since $W = v \cdot d$, and since the number of drops, n, yielded by the same volume of liquid is inversely proportional to the volume of a single drop, it follows that

$$\frac{\gamma_1}{\gamma_2} = \frac{v_1 d_1}{v_2 d_2} = \frac{n_2 d_1}{n_1 d_2}.$$

If the surface tension of one of the liquids is known, that of the other can be calculated.

3. *Maximum Bubble-pressure Method.*—For the determination of the surface tension of liquids over a range of temperatures, especially when only small amounts of liquid are available, the method of maximum pressure in bubbles is very convenient and has been extensively used in connection with the calculation of the parachor (p. 118).

[1] *Z. physikal. Chem.*, 1908, **54**, 686; 1913, **84**, 410.
[2] *J. Amer. Chem. Soc.*, 1919, **41**, 499.

When a bubble is blown at the end of a tube which drips vertically into a liquid, the maximum pressure occurs when the bubble is a hemisphere, provided that the bubble is small enough to be taken as spherical. The relation between the pressure and the surface tension is a complicated one,[1] but the method may be simplified in practice by comparing the pressures, P_1 and P_2, required to liberate bubbles from

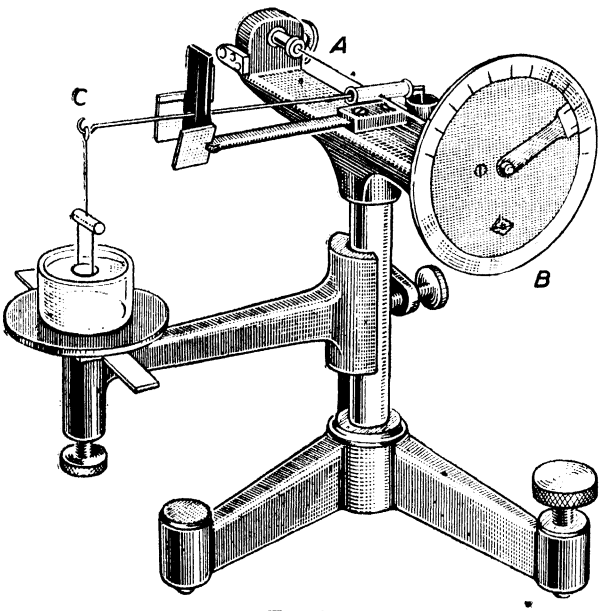


FIG. 33.
(Courtesy of Cambridge Scientific Instrument Co. Ltd.)

two tubes of different radii, immersed to the same depth in the liquid. In this case, it was found [2] that the surface tension could be calculated, with an accuracy of 0·1 per cent. by the empirical formula,

$$\gamma = \mathrm{A}(P_1 - P_2)\left(1 + 0{\cdot}69 r_2 \frac{gD}{P_1 - P_2}\right),$$

where A is a constant for the particular apparatus, r_2 is the radius of the larger tube, measured in centimetres, g is the acceleration due to gravity, and D is the density of the liquid.

[1] Adam, *Physics and Chemistry of Surfaces.*
[2] Sugden, *J. Chem. Soc.*, 1922, **121**, 864; 1924, **125**, 27.

4. In many cases the surface tension can be most satisfactorily determined by means of the tensiometric or *torsion-balance method*. In the apparatus (Fig. 33), as improved by Pierre Lecomte du Noüy [1] of the Rockefeller Institute of Medical Research, New York, a platinum ring, about 4 cm. in circumference, hangs from the end of the beam C of a torsion balance, and after the ring has been dipped under the surface of the liquid, one measures, by the torsion of the wire to which the beam C is attached, the force required to raise the ring out of the surface of the liquid. The amount of torsion is measured by the angle through which the pointer B moves over the scale engraved on the disc. Determinations can be carried out with small amounts of liquid (1 ml.), and the apparatus is much used in scientific and industrial laboratories for measuring, more especially, the surface tension of biological fluids, and for controlling the composition of solutions.

As the numbers in the following table show, the surface tension varies greatly with the nature of the liquid, and it diminishes fairly rapidly with rise of temperature.

	Surface Tension in Dynes per Centimetre at					
	0°.	10°.	20°.	30°.	40°.	50°.
Water . . .	75·64	74·22	72·75	71·18	69·56	67·91
Glycerol . . .	...	...	63·4	...	...	...
Benzene . . .	31·58	30·19	28·88	27·58	26·26	24·98
Ethyl acetate . .	26·5	...	23·9	...	...	20·2
Ethyl alcohol . .	24·05	23·14	22·27	21·43	20·60	19·80
Ethyl ether . .	...	...	17·01	...	...	13·47

Over short ranges of temperature the diminution of surface tension with rise of temperature may be regarded as linear; but over a greater range the change of surface tension with temperature can be expressed by the empirical expression [2] $\gamma = \gamma_0\left(1 - \frac{T}{T_c}\right)^{1.20}$, where γ is the surface tension at the absolute temperature T, and γ_0 is a constant having the signification of the surface tension at the absolute zero. T_c is the critical temperature. At the critical temperature the surface tension becomes zero.

Molecular Surface Energy.—If one imagines a gram-molecule of a liquid in the form of a sphere, the surface of the sphere may be called the *molecular surface*; and in the case of different liquids there will be the same number of molecules

[1] *J. Gen. Physiol.*, 1919, **1**, 521; 1925, **7**, 625. See also Lloyd and Scarth, *Science*, 1926, **64**, 253.

[2] S. Sugden, *J. Chem. Soc.*, 1924, **125**, 32.

distributed on the molecular surface, assuming the molecules to be spheres and unoriented. The product of surface tension and molecular surface should then be a quantity which is comparable for different liquids. Since the volumes (V) of different spheres are to one another as the cubes of the radii (r), and the surfaces (s) as the squares of the radii, it follows that

$$\frac{V_1}{V_2}=\frac{r_1^3}{r_2^3} \text{ or } \frac{r_1}{r_2}=\frac{V_1^{\frac{1}{3}}}{V_2^{\frac{1}{3}}},$$

and

$$\frac{s_1}{s_2}=\frac{r_1^2}{r_2^2}=\frac{V_1^{\frac{2}{3}}}{V_2^{\frac{2}{3}}}.$$

That is to say, the molecular surface is proportional to the two-thirds power of the molecular volume, Mv or M/D, where v is the specific volume and D is the density of the liquid. The product $\gamma . (Mv)^{\frac{2}{3}}$ or $\gamma . (M/D)^{\frac{2}{3}}$, was called by Ramsay and Shields the *molecular surface energy*, and is measured in ergs.

In 1886 it was deduced theoretically by Baron Roland von Eötvös [1] (1848-1919), Professor of Physics in the University of Budapest, and shown experimentally by Ramsay and Shields [2] in 1893, that the molecular surface energy decreases linearly with rise of temperature. It was, however, found that the straight line representing the decrease of molecular surface energy with temperature does not, in general, cut the temperature axis at the critical point, but at about 6° below this point. One has, therefore, the relation [3]

$$\gamma . (Mv)^{\frac{2}{3}}=k . (t_c-6-t).$$

Since the molecular surface energy is a linear function of the temperature, it follows that

$$\frac{\gamma_1(Mv)_1^{\frac{2}{3}}-\gamma_2(Mv)_2^{\frac{2}{3}}}{t_2-t_1}=k,$$

where k is a constant which gives the slope of the graph. Thus, in the case of carbon tetrachloride, the molecular

[1] *Ann. Physik*, 1886, (3), **27**, 452.

[2] *Phil. Trans.*, 1893, A, **189**, 647; *J. Chem. Soc.*, 1893, **63**, 1089.

[3] It has been shown by M. Katayama that a more correct relation is $\gamma \cdot \left(\frac{M}{D-D_g}\right)^{\frac{2}{3}}=a(T_c-T)$, where D and D_g are the densities of liquid and vapour at the temperature T, and a is a constant, the same for normal liquids, equal to 2·04.

weight of which is 153·8, γ_1 at 20° has the value 25·68 dynes per cm., and γ_2 at 80° has the value 18·71 dynes per cm. The density at 20° is 1·594, and at 80°, 1·470. Consequently,

$$k = \frac{25{\cdot}68\left(\frac{153{\cdot}8}{1{\cdot}594}\right)^{\frac{2}{3}} - 18{\cdot}71\left(\frac{153{\cdot}8}{1{\cdot}470}\right)^{\frac{2}{3}}}{80-20}$$

$$= \frac{(25{\cdot}68 \times 21{\cdot}04) - (18{\cdot}71 \times 22{\cdot}20)}{60} = 2{\cdot}08.$$

At 100°, γ has the value 16·48, the density being 1·420. On calculating the value of k from the values of the molecular surface energy at 80° and at 100°, one finds $k = 2{\cdot}06$. As the average value for a number of liquids (*e.g.*, benzene, carbon tetrachloride, ethyl ether, ethyl acetate, etc.), Ramsay and Shields found $k = 2{\cdot}12$, and it was therefore to be assumed that if one of these liquids has normal molecular weight, the other liquids also have normal molecular weight.

In the case of another group of liquids, however, it was found that k has a considerably smaller value : water, 1·04 ; methyl alcohol, 0·93 ; acetic acid, 0·98. This behaviour can be accounted for if one assumes that these liquids have a molecular weight greater than the normal value ; that is, the liquids are assumed to be associated. In order that the value 2·12 may be obtained for the Ramsay and Shields constant, the normal value of the molecular weight M must be replaced by the higher value xM, where x is the *association factor*, or the average number of normal molecules associated to form the more complex molecules. The association factor x is given by the expression

$$x = \left(\frac{2{\cdot}12}{k}\right)^{\frac{3}{2}},$$

where k is the Ramsay-Shields constant found experimentally. By this means the value of x was found to be 2·91 for water, 3·44 for methyl alcohol, and 3·18 for acetic acid. The assumption that these compounds are associated in the liquid state is supported by the high value of the latent heat of vaporisation.

It seemed from the work of Ramsay and Shields that the temperature coefficient of molecular surface energy was a colligative property and gave a means of determining

the molecular complexity of liquids, relatively to some standard liquid, *e.g.*, benzene, regarded as having normal molecular weight. Fuller investigation, however, has shown [1] that this is not a reliable method for determining the degree of association of a liquid, although it may be useful as giving a qualitative indication of molecular complexity.

Since, in the Ramsay-Shields equation, t_c is the critical temperature of the liquid having the same degree of association as at the temperature of measurement, it will vary with the temperature because the degree of association varies with the temperature. If the variation of the critical temperature with the degree of association is less than a certain value for the particular liquid, k will be abnormally small; but if the variation is greater than this value, k will be abnormally large, even if association occurs.[2] This is liable to be the case especially with liquids of high molecular weight, *e.g.*, glyceryl stearate, for which the value of k is 6·75. It may be also, that in the case of long-chain carbon compounds, orientation of the molecules takes place, leading to a greater crowding of the molecules at the surface than is assumed in the Ramsay-Shields equation, and giving an abnormally high value of the temperature coefficient of molecular surface energy.

An interesting application of surface tension measurements was made, in 1904, by Rudolf Schenk and E. Ellenberger,[3] of the University of Marburg, for the purpose of detecting the existence of tautomeric forms and of determining the range of temperature throughout which each form is stable. If each form were stable and had normal molecular weight, two parallel curves, $A_1A_2A_3A_4$ and $B_1B_2B_3B_4$ (Fig. 34), would be obtained on plotting molecular surface energy against temperature (Ramsay-Shields law). If, however, in a certain temperature range, change from one tautomeric form to another takes place, the curve will follow the course $A_1A_2B_3B_4$, or $B_1B_2A_3A_4$. Dibenzoylacetone gives the former, acetylacetone gives the latter type of curve.

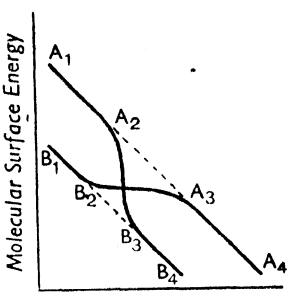


FIG. 34.

Surface Tension of Aqueous Solutions.—The surface tension of aqueous solutions, at a liquid-air interface, is in some cases greater, but, in general, is less than that of pure water; and the influence of different solutes on the surface tension varies greatly. Inorganic salts have only a slight effect on the surface tension, and frequently increase it slightly. The surface tension is scarcely affected by the sugars and the amino-acids, but a more or less well-marked decrease of surface tension is brought about by the addition

[1] See F. M. Jaeger, *Z. anorgan. Chem.*, 1917, **101**, 1.
[2] Masao Katayama, *Sci. Rep. Tohoku Univ.*, 1915, **4**, 373.
[3] *Ber.*, 1904, **37**, 3443.

of monohydric alcohols, aldehydes, ketones, many organic acids and esters of organic acids (Fig. 35). In the case of a given homologous series, further, it was found by Isidor

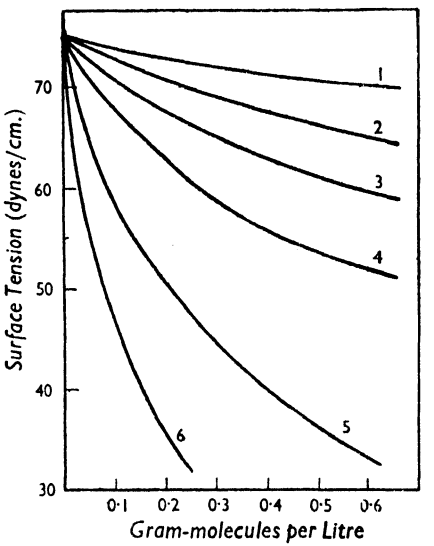


FIG. 35.

1, Cane sugar. 2, Acetic acid. 3, Allyl-amine. 4, Methyl acetate. 5, Iso-butyl alcohol. 6, Iso-amyl alcohol.

Traube [1] that as one ascends the series, *each member is three times more effective in reducing the surface tension than its immediate predecessor* (Traube's Rule). This is illustrated by the following table :—

Aqueous Solution of	Capillary Rise at 18°.
Methyl acetate, 1-normal . .	58·1 mm.
Ethyl acetate, $\frac{1}{2}$-normal . . .	58·0 „
Propyl acetate, $\frac{1}{5}$-normal . .	57·7 „
Iso-butyl acetate, $\frac{1}{27}$-normal . .	58·8 „
Iso-amyl acetate, $\frac{1}{81}$-normal . .	58·9 „

The surface tensions of the above solutions, as measured by the height to which the liquid rises in a capillary tube,

[1] *Annalen*, 1891, **265**, 27.

are practically the same, but the concentration of solute progressively diminishes.

When a solute lowers the surface tension of water, the relative lowering of the surface tension is greatest at low concentrations (Fig. 35), and is represented approximately by the expression

$$\Delta = \frac{\gamma_0 - \gamma}{\gamma_0} = k \cdot c^{\frac{1}{n}},$$

where c is the concentration and k and n are constants. That this expression is only approximately correct, however, is shown by the fact that if the values of log Δ are plotted against the values of log c, the curve is not quite rectilineal.

The Theorem of Gibbs.—Owing to the existence of surface tension, the concentration of solute molecules is not uniform throughout a solution, but is different at the surface from what it is in the body of the solution ; and the important theorem was deduced by Josiah Willard Gibbs (1839-1903), Professor of Mathematical Physics, Yale University, that *those substances which lower the surface tension become concentrated in the surface layer, whereas the concentration of those substances which raise the surface tension becomes less in the surface layer than in the body of the solution.* If the *excess* of solute in the surface layer above that in the body of the solution is represented by S, and if C is the concentration of the solute, we have, for dilute solutions,

$$-S = \frac{C}{RT} \cdot \frac{d\gamma}{dC},$$

where R is the gas constant ($8{\cdot}315 \times 10^7$ ergs per degree), T is the absolute temperature, and $\frac{d\gamma}{dC}$ is the change of surface tension with the concentration.

To this change of concentration of a solute at a boundary surface the term *adsorption* is applied. Increase of concentration at a surface is termed positive adsorption ; decrease of concentration, negative adsorption.

The equation of Gibbs has been experimentally verified by J. W. McBain and his collaborators at Stanford University, California,[1] who, by a most ingenious and accurately

[1] McBain and Humphreys, *J. Physical Chem.*, 1932, **36**, 300 ; McBain and Swain, *Proc. Roy. Soc.*, 1936, A, **154**, 608.

constructed apparatus, succeeded in rapidly slicing off a thin layer, 0·05 to 0·1 mm. thick, from the surface of a solution. From the weight of solution removed from a known area of surface the concentration of the solute could be determined and compared with the concentration of the solute in the body of the solution.

The general truth of the theorem becomes most clearly evident in those cases where a solute, *e.g.*, albumin, peptone, etc., not only diminishes the surface tension of water but also increases its viscosity. In such cases the surface concentration of the solute will obviously lead to the formation of a viscous layer, and this may even develop into a visible skin. Moreover, if such solutions are shaken with air, the free surface is greatly increased and the formation of viscous layers or films facilitated, so that a foam or froth is produced. The production of foam or froth, therefore, is associated not merely with a decrease in the surface tension but also with an increase in the viscosity of a liquid, brought about by the dissolved material. The production of foam will be prevented by a substance which diminishes the viscosity of the liquid, even although it also diminishes the surface tension.

D. Molecular Volume and the Parachor

The molecular volume is the volume, in millilitres, occupied by 1 gram-molecule of the substance, and is equal to the specific volume v multiplied by the molecular weight. Since the specific volume or the volume in millilitres occupied by 1 g. of liquid is the reciprocal of the density or weight of 1 ml., the molecular volume is also given by the expression M/d ml.

Since the variation of density or of specific volume with temperature is different in the case of different liquids, one should, in investigating the relation between molecular volume and composition or constitution of compounds in the liquid state, compare the volumes at " corresponding temperatures," *i.e.*, at temperatures which are, in each case, the same fraction of the critical temperature (p. 74). Since it has been shown that the boiling-point of a liquid is, approximately, two-thirds of the critical temperature, one may compare the values of the molecular volume determined in each case at the boiling-point of the liquid.

The density of a liquid at its boiling-point can readily be determined by filling a pycnometer, of the form shown in Fig. 36, with the liquid and suspending it in a flask in the vapour of the boiling liquid. The volume of the pycnometer can be determined in the ordinary manner by filling and weighing with water at a known temperature.

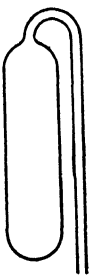


FIG. 36.

On comparing the molecular volumes of liquids at their boiling-points, it was found by Hermann Franz Moritz Kopp[1] (1817-92) in 1855, while Professor of Chemistry at the University of Giessen, that the molecular volume is essentially an *additive* property and is equal to the sum of the atomic volumes of the constituent elements. The property, however, is not purely additive, but is also *constitutive*, as shown by the fact that the atomic volume of oxygen and of certain other elements varies with the way in which the element is linked in the compound. The oxygen (O′) in the hydroxyl-group, for example, has a different atomic volume from the doubly linked oxygen (O″) present in aldehydes and ketones. Branched-chain compounds, also, have a lower molecular volume than straight-chain isomers, and other variations in the constitution exercise an influence on the molecular volume.

From a study of different compounds, the following values of the atomic volume have been calculated :—

Hydrogen . .	3·7	Iodine . . .	37·0
Carbon . .	14·8	Oxygen in >OH .	7·4
Chlorine . .	22·1	Oxygen in CO .	12·0
Bromine . .	27·0		

Thus the molecular volume of hexane, C_6H_{14}, is calculated to be $(6 \times 14{\cdot}8) + (14 \times 3{\cdot}7) = 88{\cdot}8 + 51{\cdot}8 = 140{\cdot}6$ ml. The observed value is 139·9 ml. Similarly, the value for acetic acid, $CH_3 \cdot COOH$ or $C_2H_4O''O'$, is calculated to be $29{\cdot}6 + 14{\cdot}8 + 12{\cdot}0 + 7{\cdot}4 = 63{\cdot}8$ ml. Value observed is 63·5 ml.

When one passes from the broad regularities to a more searching investigation of the relations, it is found that constitutional and structural influences are very widespread, and introduce more or less marked variations in the molecular volumes, so that the exact relations gain greatly in complexity.[2] The usefulness of molecular volume determinations

[1] *Ann. Physik.*, 1855, **96**, 153, 303.

[2] For a full discussion of molecular volumes of liquids, see Gervaise Le Bas, *The Molecular Volumes of Liquid Chemical Compounds* (Longmans).

in solving problems relating to the structure or constitution of compounds is thereby considerably reduced. Fortunately, another property, related to the molecular volume, has been discovered which exhibits fewer anomalies, and the relation of which to chemical structure and constitution is more clear-cut and simple. The use of this property, known as the *parachor*, was first suggested by Samuel Sugden, Professor of Physical Chemistry at University College, London.

In 1923 it had been found by D. B. Macleod, of Canterbury University College, New Zealand, that the relation

$$\frac{\gamma^{\frac{1}{4}}}{D-d}=C$$

holds, for non-associated liquids, over a wide range of temperature.[1] In this expression, γ is the surface tension of the liquid, D is the density of the liquid, and d the density of the vapour at the temperature of the experiment. C is a constant. Consequently, as Sugden pointed out,[2] the expression

$$\frac{M\gamma^{\frac{1}{4}}}{D-d}=MC=[P]$$

should also be valid. In this expression the constant $[P]$ is called the *parachor*, a name signifying a comparative volume. At not too high temperatures d will be negligible compared with D, and so one obtains the relation

$$[P]=\frac{M}{D}\cdot\gamma^{\frac{1}{4}},$$

where $\frac{M}{D}$ is the molecular volume. It is clear, therefore, that the parachor represents the molecular volume of a liquid at such a temperature that its surface tension is unity. Instead, therefore, of comparing the molecular volumes of liquids at their boiling-points as Kopp did, one compares the molecular volumes of liquids determined under such conditions that their surface tensions are the same. In the case of associated liquids the parachor varies with the temperature.

The above expressions for the surface tension and the parachor were originally put forward as empirical laws. It

[1] *Trans. Faraday Soc.*, 1923, **19**, 38.

[2] *J. Chem. Soc.*, 1924, **125**, 1185. See also Sugden, *The Parachor and Valency* (Routledge).

has, however, been shown that a theoretical basis can be obtained for them in the action of intermolecular forces.[1]

On comparing the parachors of different compounds in the liquid state, it is found that *the parachor is pre-eminently an additive property.* This is shown, for example, by the fact that the differences between the parachors of successive members of an homologous series are the same in different homologous series, and that isomeric compounds have parachors of the same value. This is illustrated by the following values for a series of isomeric esters, $C_6H_{12}O_2$:—

	[P].		[P].
Iso-amyl formate .	293·6	Ethyl butyrate .	293·6
Iso-butyl acetate .	295·1	Ethyl iso-butyrate	292·9
n-Propyl propionate .	295·3	Methyl valerate .	292·5

The parachor, however, depends not only on the elements present, but also, to some extent, on the manner in which the different atoms are linked together in the molecule. Thus, the formation of a ring structure increases the parachor by amounts which depend on the number of atoms in the ring ; and the effect of a double bond on the parachor depends on whether the double bond is of the ethylenic type (non-polar double bond) or is a semi-polar double bond. The parachor of a compound, therefore, can be expressed as the sum of a number of atomic and structural constants which are independent of the nature of the compounds.[2] Some of these constants, the values of which are obtained from a comparison of the parachors of different compounds of known composition and constitution, are given in the following table :—

ATOMIC AND STRUCTURAL PARACHORS

C . . .	7·2	Triple bond . . .	42·0
H . . .	16·2	Double bond . . .	20·0
N . . .	15·0	Semi-polar double bond .	0·0
O . . .	20·0	Singlet link . . .	−10·0
P . . .	37·0		
S . . .	48·5	3-membered ring . .	14·0
Cl . . .	53·5	4-membered ring . .	9·5
		5-membered ring . .	6·5
Ester group .	−2·0	6-membered ring . .	4·5
OH-group . .	−5·0		
NH_2 . . .	−2·5		

[1] See Lennard-Jones and Corner, *Trans. Faraday Soc.*, 1940, **36**, 1156 ; Fowler, *Proc. Roy. Soc.*, 1937, A, **159**, 229.

[2] The use of group-values in place of atomic values is to be preferred. See T. W. Gibling, *J. Chem. Soc.*, **1941**, 299.

With the help of these constants one can calculate the parachor of a compound and can also, in certain cases, draw conclusions regarding the structure of a molecule. In the help which it gives in solving problems of chemical constitution, the parachor has shown itself to be one of the most valuable of physical properties; but it must be borne in mind that definite conclusions as to structure can be drawn only when the alternative structures correspond with considerable differences in the parachor. A few illustrations of its application may be given.

The parachor of ethyl propionate, $C_5H_{10}O_2$, is calculated to be

$$(5 \times 7{\cdot}2) + (10 \times 16{\cdot}2) + (2 \times 20) + 20 - 2{\cdot}0 = 256{\cdot}0,$$

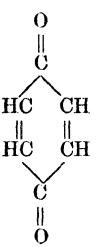
which agrees with the observed value, 255·2. In the case of benzene, C_6H_6, if one adopts the Kekulé formula, with alternate single and double bonds, the value of the parachor is calculated to be

$$(6 \times 7{\cdot}2) + (6 \times 16{\cdot}2) + (3 \times 20) + 4{\cdot}5 = 204{\cdot}9.$$

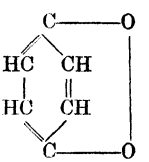
The observed value for benzine is 206·2. The value of the parachor, therefore, is in good agreement with the Kekulé formula.

In the case of quinone, two structures have been suggested, namely,

I.



II.



On calculating the parachor for structure I., one obtains

$$(6 \times 7{\cdot}2) + (4 \times 16{\cdot}2) + (2 \times 20) + (4 \times 20) + 4{\cdot}5 = 232{\cdot}5,$$

and the calculated value for the structure II. is, since there are now two 6-membered rings, 217·0. Since the observed value is 236·8, quinone must be regarded as having the diketonic structure.

The light which the parachor has thrown on the nature of the linkages in compounds of nitrogen, phosphorus, and sulphur is very valuable.

Thus phosphorus oxychloride, $POCl_3$, is shown to have the formula $Cl_2P{=}O$, the calculated value of the parachor, assuming the presence of a semi-polar double bond, being 217·5. The observed value is 217·6. If a non-polar double bond were present, the calculated value of the parachor would be 237·5.

From the evidence supplied by the parachor, much valuable information has been obtained regarding the constitution of compounds and the nature of the valency linkages.[1]

[1] See also Pearson and Robinson, *J. Chem. Soc.*, **1934**, 740; C. N. Copley, *Chem. and Ind.*, 1940, **59**, 675.

Various empirical expressions linking together viscosity and surface tension have been put forward. Thus, D. Silverman and W. E. Roseveare [1] derived the relation $\gamma^{-\frac{1}{4}} = A/\eta + B$, which is readily convertible into a parachor equation. The law has only a partial validity. C. A. Buehler,[2] similarly, has put forward the expression $\log(\log \eta) = 1{\cdot}2\gamma^{-\frac{1}{4}} - 2{\cdot}9$, where η, in millipoises, is measured at the same temperature as the surface tension. This relation appears to be valid in the case of compounds for which the parachor is independent of the temperature.

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[1] *J. Amer. Chem. Soc.*, 1932, **54**, 4460.
[2] *J. Physical Chem.*, 1938, **42**, 1207.

CHAPTER V

LIQUIDS AND THEIR PROPERTIES—continued

E. Refractive Power

Refractive Index.—When a ray of light passes from a less dense to a more dense medium, it is bent or refracted towards the normal. Thus, in Fig. 37, if I is the less dense and II the more dense medium, a ray of light passing from I to II will be bent so that the angle of refraction e will be less than the angle of incidence i; and, according to the law of refraction, the relation between these two angles will be such that

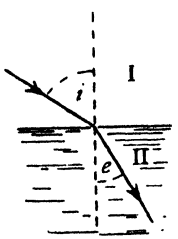


FIG. 37.

$$\frac{\sin i}{\sin e} = \frac{N}{n},$$

where n is the *index of refraction* of the less dense and N the index of refraction of the more dense medium. As the angle i increases, the angle e will also increase until, at the limit, when i becomes equal to a right angle, the incident ray will no longer pass into the more dense medium. At this limit, since $\sin 90° = 1$, the above equation becomes

$$\sin e = \frac{n}{N}.$$

Determination of the Refractive Index.—The methods now generally employed for the determination of the refractive index of a liquid are based on the relation just started. In determining the refractive index by the *Pulfrich refractometer*, the liquid, of which the refractive index is to be determined, is placed in a cell cemented to the top of

a right-angled glass prism (Fig. 38), the refractive index of which is known and must be greater than that of the liquid. A beam of monochromatic light entering the liquid will be refracted through the prism in the manner shown in the figure. If one considers the path of the last ray to enter the prism, the ray which enters at "grazing incidence" and which is represented by the thick line, then, as we have seen,

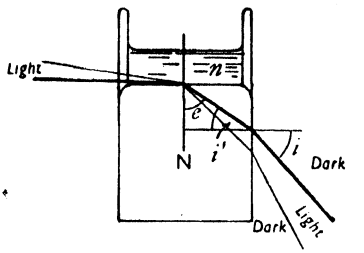


FIG. 38.

$\sin e = \frac{n}{N}$, or, $n = N \sin e$, where n is the index of refraction of the liquid and N that of the glass (referred to that of air equal to unity). But, $\sin e = \cos i'$, and therefore $n = N \cos i'$. Further, $\frac{\sin i}{\sin i'} = N$, or, $\sin i' = \frac{\sin i}{N}$. Since $\cos^2 i' = 1 - \sin^2 i'$, we have $\cos^2 i' = 1 - \frac{\sin^2 i}{N^2} = \frac{N^2 - \sin^2 i}{N^2}$; and since $n = N \cos i'$, it follows that

$$n^2 = N^2 \cos^2 i' = N^2 \times \frac{N^2 - \sin^2 i}{N^2} = N^2 - \sin^2 i.$$

or

$$n = \sqrt{N^2 - \sin^2 i}.$$

If, therefore, one knows the value of N, the refractive index of the prism, and the angle i at which the light emerges from the prism, the value of n, the refractive index of the liquid, can be calculated. A table of values of $\sqrt{N^2 - \sin^2 i}$ for different values of i is supplied by the makers of the instrument.

Since light is refracted in varying degree according to its wave-length, monochromatic light must be used; and since the index of refraction varies with the temperature, a heating arrangement is provided so that the temperature may be maintained constant. A view of the complete instrument is shown in Fig. 39.

Light, from a sodium vapour lamp, passes into the reflecting prism N, and is reflected into the liquid contained in the cell on the top of the prism L. The light, after

refraction, passes into the telescope F, and is reflected to the eye-piece E. The telescope is attached to a disc D, which is graduated into degrees and half degrees so that the angle through which the telescope is rotated can be readily determined. This is the angle of emergence from the prism. When it is desired to determine the index of refraction for light of different wave-length, *e.g.*, lines of the hydrogen spectrum, a discharge tube may be attached to the instrument.

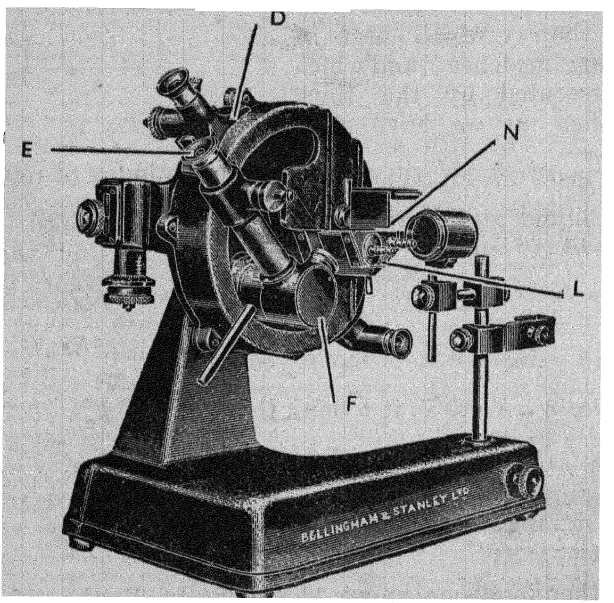


FIG. 39.

(Courtesy of Bellingham & Stanley Ltd.)

When it is not necessary to determine the index of refraction with the high degree of accuracy attainable with the Pulfrich refractometer, use is frequently made of the *Abbe refractometer*. In this instrument there is a fixed telescope, and the liquid under investigation is placed in contact with the *hypotenuse* face AB of a right-angled prism ABC (Fig. 40). According to the law of refraction, a ray of monochromatic light passing through the liquid and entering the prism at grazing incidence will emerge from the face AC along a path perpendicular to that face, provided $n = N \sin A$. This ray then passes through the centre of the focal plane of a telescope placed perpendicularly to the face of the prism.

When, however, the refractive index of the liquid n does not satisfy this condition, the emergent ray will no longer be at right angles to the face of the prism, but will make an angle α with the normal; and the prism must be rotated through an angle α, in order that this emergent ray may again pass through the centre of the focal plane of the fixed telescope. If this angle α is determined, the refractive index n is obtained from the relationships—

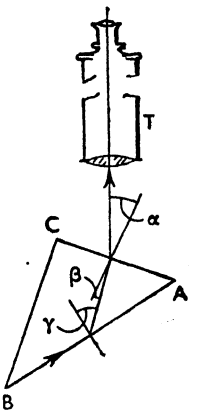


FIG. 40.

$$N = \frac{\sin \alpha}{\sin \beta},$$

$$\beta + r = A,$$

$$n = N \sin r.$$

By eliminating β and r, one obtains

$$n = \sin A \sqrt{N^2 - \sin^2 \alpha} - \cos A \sin \alpha$$

In the Abbe instrument the value of n for different values of α is engraved on the scale, so that the index of refraction can be read directly. The complete instrument is shown in Fig. 41.

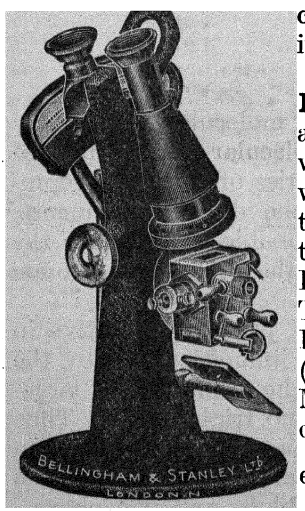


FIG. 41.
(Courtesy of Bellingham & Stanley Ltd.)

Specific and Molecular Refractive Powers.—The index of refraction of a liquid varies not only with the wave-length of the light but also with the temperature. In 1880, on the basis of the electro-magnetic theory of light, Hendrik Anton Lorentz (1853-1928), Professor of Theoretical Physics, University of Leyden, and Ludwig Valentin Lorenz (1829-91), Professor of Physics at the Military High School, Copenhagen, deduced independently that the expression $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$ should be independent of the temperature and constant for a given substance. This Lorentz-Lorenz expression for the *specific refractive power* (represented by r_L) is practically independent of the temperature and of the physical state.

To obtain values which shall be comparable for different substances, one employs the function of the refractive index known as the *molecular refractive power*, which is equal to the specific refractive power multiplied by the molecular weight of the substance. Thus one obtains the expression

$$[R]_L = Mr_L = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}.$$

On studying the relations between the molecular refractive power and chemical composition, it is found that the property is essentially additive in character, as is shown by the fact that the difference between the molecular refractive power of successive members of an homologous series is nearly constant. The following values will serve as illustration :—

	$[R]_L$ for D-line.	Difference.
Methyl alcohol . .	8·218	
		4·521
Ethyl alcohol . .	12·739	
		4·676
n-Propyl alcohol . .	17·515	
		4·615
n-Butyl alcohol . .	22·130	
		4·614
i-Amyl alcohol . .	26·744	
Hexane . . .	29·878	
		4·641 × 2
Octane . . .	39·160	
		4·670 × 2
Decane . . .	48·501	

Owing to the additive nature of molecular refractivity it is possible, from a study of the molecular refractivities of different compounds, to draw up a series of constants representing the *atomic refractivities* of the different elements. By means of these constants it is possible to calculate the molecular refractivity as the sum of the constituent atomic refractivities.

Although molecular refractivity is primarily additive in nature, investigation shows that it is influenced also by the constitution, by the arrangement of the atoms in the molecule, and by the presence of double and triple bonds. Thus the atomic refractivity of oxygen has different values in alcohols, ethers, and ketones, and varying values are also met with in the case of nitrogen, sulphur, and phosphorus. For this reason, however, determinations of the molecular refractivity may also be employed to solve problems in chemical constitution.

In the table on p. 129 are given the values of the atomic

refractivities for the sodium (D) line, and for the red and blue lines of the hydrogen spectrum (H_α and H_β).[1] By means of the constants in the table it is possible to calculate the molecular refractivity of a compound. Thus the molecular refractivity for the D-line of methylethyl ketone, $CH_3 . CO . C_2H_5$, or C_4H_8O, is calculated to be $(4 \times 2{\cdot}418) + (8 \times 1{\cdot}100) + 2{\cdot}211 = 20{\cdot}683$, while the

	H_α.	D.	H_β.
CH_2 . .	4·598	4·618	4·668
C . .	2·413	2·418	2·438
H . .	1·092	1·100	1·115
O″ (in CO) .	2·189	2·211	2·247
O< . .	1·639	1·643	1·649
O′ (in OH) .	1·522	1·525	1·531
Cl . .	5·933	5·967	6·043
Br . .	8·803	8·865	8·999
I . .	13·757	13·900	14·224
|= . .	1·686	1·733	1·824
|≡ . .	2·328	2·398	2·506

experimentally determined value is 20·674. Similarly, for isovaleric acid, $C_4H_9 . COOH$, or $C_5H_{10}O'O''$, one calculates $[R]_L = (5 \times 2{\cdot}418) + (10 \times 1{\cdot}100) + 2{\cdot}211 + 1{\cdot}525 = 26{\cdot}826$, which agrees exactly with the value obtained by experiment.

In the case of allyl alcohol, $CH_2{=}CH . CH_2OH$, or $C_3H_6O' + |{=}$, account must be taken of the presence of a double bond. Thus the molecular refractivity for the D-line is calculated to be 17·112, while the experimentally determined value is 16·973. This may be compared with the isomeric compound, propyl aldehyde, $CH_3 . CH_2 . CHO$, or C_3H_6O'', the molecular refractivity of which is calculated to be 16·065. The experimental value is 15·97. Determinations of the molecular refractivity may therefore be employed to detect differences in constitution in the case of isomeric compounds.

Optical Exaltation.—When a compound contains more than one double or triple bond, the molecular refractivity depends not only on the number of double or triple bonds but also on their relative position in the molecule. When the double or triple bonds are present in conjugated position, *e.g.*, $-CH{=}CH-CH{=}CH-$, the molecular refractive power

[1] F. Eisenlohr, *Z. physikal. Chem.*, 1910, **75**, 585. Values for the atomic constants differing somewhat from those given in the table, have been deduced by W. Swientoslawski, *J. Amer. Chem. Soc.*, 1920, **42**, 1945.

is higher than the value calculated from the atomic constants. This is known as *optical exaltation*. Thus, for hexatriene, $CH_2=CH-CH=CH-CH=CH_2$, one calculates $[R]_L=28{\cdot}52$ (for the D-line), whereas the experimental value is 30·58. There is here an optical exaltation of 2·06 units. A carbonyl group also, in conjugation with a double or triple bond, causes optical exaltation. Thus, for phorone, $(CH_3)_2-C=CH-CO-CH=C(CH_3)_2$, $[R]_L$ is calculated to be 42·73, while the experimental value is 45·39. There is thus an exaltation of 2·66 units. When double bonds are not conjugated no optical exaltation is found. This is illustrated by the compound diallyl, $CH_2=CH-CH_2-CH_2-CH=CH_2$, the molecular refractivity of which is 28·77. The calculated value is 28·89.

If the hydrogen atoms attached to the carbon atoms of the conjugated grouping, $CH_2=CH-CH=CH_2$, are substituted, the optical exaltation is diminished, more especially when substitution takes place at the middle carbon atoms. Thus, 2 : 4-hexadiene, $CH_3-CH=CH-CH=CH-CH_3$, with $[R]_L=30{\cdot}64$, shows an optical exaltation of $+1{\cdot}71$ units, whereas di-isopropenyl, $CH_2=C(CH_3)-C(CH_3)=CH_2$, with $[R]_L=29{\cdot}44$, shows an exaltation of only $+0{\cdot}47$ unit.

It is found also that conjugated double bonds in a ring compound do not give rise to optical exaltation. In the case of benzene, for example, assuming there are alternate single and double bonds (Kekulé formula), the calculated value of the molecular refractivity, $[R]_L$, for the D-line is 26·30, and the experimental value 26·19.

In the preceding discussion the molecular refraction has been regarded as made up additively of a series of *atomic* constants. The optical properties of substances, however, in the range of the visible spectrum probably depend on the outer rings of electrons in the atoms, and the values of the molecular refractivity, therefore, have been resolved into a series of constants which depend on the nature of the linkages in the compounds and on the distribution of the electrons between the atoms.[1] The variation of the atomic constants with the manner in which the atoms are linked in a compound is thus taken into account, and the method gives a more refined means of studying chemical structure.

[1] See, for example, A. L. von Steiger, *Ber.*, 1921, **54**, 1381; W. Hücke, *J. prakt. Chem.*, 1921, **211**, 241; K. Fajans and C. A. Knorr, *Ber.*, 1926, **59**, 249; C. P. Smyth, *Phil. Mag.*, 1925, **50**, 361, 715; R. Samuel, *Z. Physik*, 1928, **49**, 95; 1929, **53**, 380.

F. Optical Activity

When a ray of ordinary light is passed through a Nicol's prism, formed of Iceland spar, the emergent light is *plane polarised*, *i.e.*, the electric vibrations of the wave all take place in one plane. This polarised light does not affect the eye differently from ordinary light, in which the vibrations are taking place in all directions at right angles to the line of propagation ; but if a second Nicol's prism is inserted in the path of the beam it is found that when the crystalline axes of the two prisms are parallel to each other the field of view remains light, and when the axes are at right angles to each

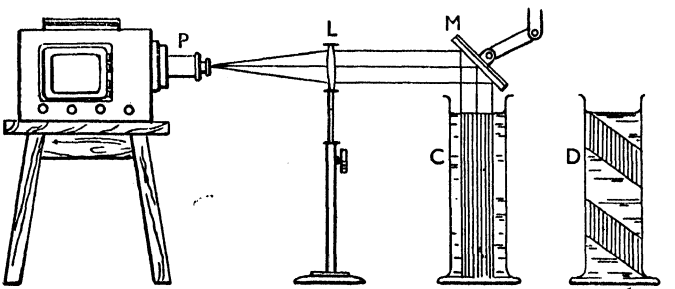


FIG. 42.

other the field of view is dark. If, when the prisms are in the latter position, or " crossed " as it is said, a piece of ordinary glass or a cell containing water is placed between the prisms, the field of view still remains dark ; but if a plate of quartz, or a cell containing turpentine or a solution of cane sugar is introduced, the field lights up, and one of the prisms must be rotated through a certain angle before " extinction " or darkness is produced. Substances such as quartz, sugar, etc., are said to have the power of rotating the plane of polarised light, or to be *optically active.*

The property of optical activity can be demonstrated by a modification of a very interesting experiment due to the English physicist, Sir George Gabriel Stokes [1] (1819-1903). When a beam of light from a projection lantern (Fig. 42) is reflected downwards by means of a mirror through a column of water rendered slightly turbid by the addition of a few drops of an alcoholic solution of rosin, the path of the beam

[1] Nicolai A. Umoff, *Z. physikal. Chem.*, 1899, **30**, 711.

is rendered visible by the fine suspension of rosin particles (Tyndall phenomenon), and the beam of light appears equally bright all round. If, however, the light from the lantern is first polarised by passage through a Nicol's prism or disc of Polaroid,[1] and then reflected downwards through the column of water, the appearance obtained is that of a band which is light *only on two* opposed sides, and dark on the other two opposed sides. On rotating the prism of Iceland spar, the band of light turns alternately its light and dark sides to the eye. The effect produced is as if the beam of light, on passing through the prism of Iceland spar, were given a flat form, like a book, from the two opposite edges of which light is emitted, while the sides remain dark. This experiment illustrates the phenomenon of polarisation of light.

If, now, the cylinder of water is replaced by a cylinder containing a solution of cane sugar (about 70 g. of sugar to 100 g. of water), also rendered turbid with rosin, the band of light is *twisted into a spiral form*; and on rotating the prism of Iceland spar or polaroid disc, this spiral band of light will appear to move with a screw-like motion. From the fact that the different rays of coloured light, which together constitute white light, are twisted or rotated to different extents (the blue rays being rotated more than the red), the spiral band of light shows the colours of the rainbow.

To explain the phenomenon of optical activity, Louis Pasteur (1823-95), by whom the study of this property was inaugurated, introduced the conception of *molecular asymmetry*, and this conception was developed independently in 1874 by the Dutch chemist, J. H. van't Hoff (1852-1911), and the French chemist, Joseph Achille Le Bel (1847-1930), into a consistent theory of molecular structure, by which it is possible to account for the occurrence of optical activity and the existence of optically active isomeric compounds.

According to this theory, the *theory of the asymmetric carbon atom*, the four valencies of a carbon atom are regarded as being directed, in space, towards the four corners of a regular tetrahedron, the centre of which is occupied by the carbon atom. So long as two at least of the atoms or groups attached to the carbon atom are the same, the molecule,

[1] Polaroid consists of a film of cellulose acetate mounted between two plane glass plates. The film is a matrix for sub-microscopic dichroic crystals accurately orientated in such a way that the entire film acts as a single polarising crystal.

represented as a tetrahedron, will be symmetrical, and its mirror image will be superposable on, and therefore identical with, the original. This will be clear from Fig. 43, which

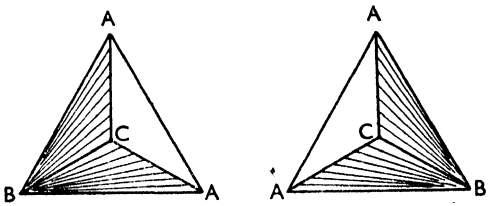


FIG. 43.

represents such a tetrahedron and its mirror image. The right-hand tetrahedron obviously only requires to be turned through an angle of rather more than 90°, on the corner B as a pivot, to become identical in disposition with the left-hand tetrahedron.

If, however, the four atoms or groups attached to the carbon atom are all different, the molecule becomes asymmetric, and gives a mirror image which is no longer superposable on the original. The two forms, indeed, are related to each other as a right hand is to a left hand ; they are, as it is said, *enantiomorphous*.[1] This will be understood from Fig. 44. Moreover, on viewing these tetrahedra from

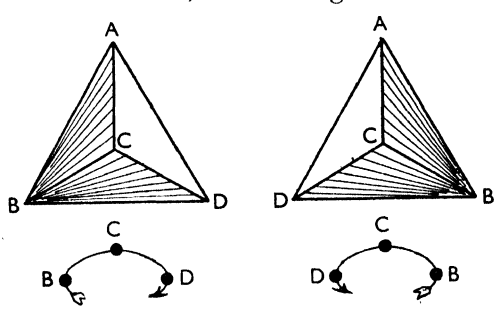


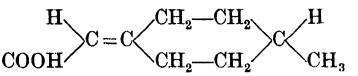
FIG. 44.

a similar position, it is seen that the groups BCD are in the one case arranged from left to right (clockwise) and in the other case from right to left (counter-clockwise). Two isomeric forms of the compound can, therefore, exist ; and if one of the molecules rotates the plane of polarised light

[1] From the Greek *enantios* = opposite and *morphē* = form.

to the right, the other will rotate the plane of polarised light to the left. The former is said to be *dextro-rotatory*, the latter *lævo-rotatory*.

Optical activity, however, is found not only in compounds which contain an asymmetric carbon atom but in compounds also which contain other asymmetric atoms, *e.g.*, nitrogen, silicon, tin, etc. ; and it is also found in the case of compounds of which the molecule *as a whole* is asymmetric, although an asymmetric carbon or other atom may not be present. Thus in the case of the compound 1-methylcyclohexylidene-4-acetic acid,



the molecule of which is represented by the model shown in Fig. 45, the groups H and CH_3 on the right lie in a different

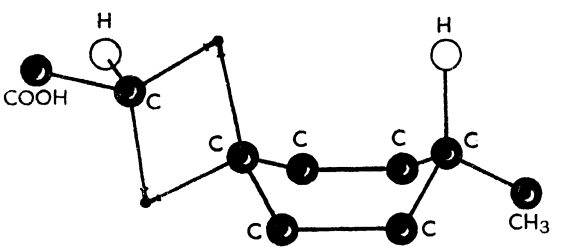


FIG. 45.

plane from the groups H and COOH on the left. The molecule has no plane of symmetry, and its mirror image, obtained by transposing the groups H and COOH on the left, is not superposable on, and therefore not identical with, the original molecule. These two optically active isomers have been obtained.[1] Similarly, as van't Hoff predicted, compounds of the allene type, $RR'C=C=CRR'$, which possess no plane of symmetry, can also occur in optically active forms.[2]

Specific and Molecular Rotation.—The angle through which a substance in the liquid state or in solution rotates the plane of polarised light depends (1) on the nature of the substance, (2) on the length of layer through which the light passes, (3) on the wave-length of the light employed, (4) on

[1] Perkin, Pope, and Wallach, *J. Chem. Soc.*, 1909, **95**, 1789.

[2] Maitland and Mills, *Nature*, 1935, **135**, 994 ; 1936, **137**, 542 ; *J. Chem. Soc.*, **1936**, 987.

the temperature. In order, therefore, to obtain a measure of the rotatory power of a substance, these factors must be taken into account. Thus the *specific rotation* is defined as the angle of rotation produced by a liquid which, in the volume of 1 ml. contains 1 g. of active substance, when the length of the column through which the light passes is 1 decimetre. If the observed angle of rotation is denoted by α, the specific rotation, $[\alpha]$, of a homogeneous active liquid is given by the expression,

$$[\alpha]=\frac{\alpha}{l \cdot d},$$

where l is the length of the column of liquid in decimetres and d is the density. If, further, account is taken of the other factors on which the rotation depends, viz., temperature and wave-length of light, one obtains a number which, for the particular conditions of experiment, is a constant, characteristic of the substance. Thus $[\alpha]_D^{25^\circ}$ represents the specific rotation for the D-line (sodium light) at the temperature of 25°.

When the active substance is examined in solution the concentration must be taken into account, in accordance with the expressions :

$$[\alpha]=\frac{100 \cdot \alpha}{l \cdot c} \text{ or, } [\alpha]=\frac{100 \cdot \alpha}{l \cdot p \cdot d},$$

where c is the number of grams of active substance in 100 ml. of solution, p is the number of grams of active substance in 100 g. of solution, and d is the density of the solution. In specifying the specific rotation of a substance in solution, the concentration and the solvent (which may have a marked influence on the rotation [1]) must also be stated.

The *molecular rotation* is given by the expression $[M]=\frac{M \cdot [\alpha]}{100}$, where M is the molecular weight.

In spite of the large amount of investigation which has been carried out in this field, comparatively few generalisations of a far-reaching character have been obtained. The property is almost wholly a constitutive one.

In the case of certain substances, *e.g.*, sugars, α-nitrocamphor, oxy-acids, etc., the rotation changes with time. This is known as *mutarotation*, and finds its explanation in

[1] See, for example, Rule, Smith, and Harrower, *J. Chem. Soc.*, **1933**, 376.

tautomeric change or change in the constitution of the substance, or in reaction between solvent and solute.

A physical theory of optical rotatory power has been developed on a mathematical basis by Max Born, of the University of Edinburgh,[1] which, when the necessary experimental data have been obtained with sufficient accuracy, will make it possible to predict the absolute rotatory powers of molecules of known configuration. Even if it may not be possible to make such absolute calculations with any great degree of accuracy, the theory of Born may be applied to the calculation of the relative magnitudes of the rotatory powers of related compounds.

G. Magnetic Rotation of Polarised Light.—Whereas only those substances the molecules of which are asymmetric have the power, under normal conditions, of rotating the plane of polarised light, it was discovered by Michael Faraday in 1845 that any transparent substance possesses this property when placed in a magnetic field. In this case the angle of rotation is proportional to the intensity of the magnetic field and to the length of column of liquid; and it depends on the nature of the substance and on the temperature.

The *specific magnetic rotation* is the ratio of the angles of rotation given by the substance in question and by a column of water in the same magnetic field, when the lengths of the columns are inversely proportional to the densities. If r is the rotation of a column of substance of length l and density d; and if r_0, l_0, d_0 are the corresponding values for water, at the same temperature and in the same magnetic field, then the specific magnetic rotation, $(\omega)=\frac{rl_0d_0}{r_0ld}$, and the *molecular magnetic rotation*, $(\Omega)=\frac{Mrl_0d_0}{18r_0ld}$, where 18 is the molecular weight of water.

The relations between the molecular magnetic rotation and chemical constitution were the subject of a long series of investigations carried out last century by Sir William Perkin (1838-1907), the discoverer of the first aniline dye, mauve, and it was established that while the property is, like the molecular refractive power, largely an additive one, it is also markedly affected by changes in chemical constitution.[2]

H. Absorption of Light by Liquids.—When a beam of white light emitted by an incandescent solid is passed through a prism, a continuous spectrum or band of colour, passing from red through orange, yellow, green, and blue to violet is formed. When a vessel containing a liquid is interposed in the path of the beam of light, which is then passed through a prism so as to form a spectrum, it may be found that the visible spectrum is unaltered thereby; or it may be found that certain wave-lengths are absorbed more strongly than others, so that certain parts of the spectrum may disappear. In the former case the liquid is said to be colourless, and in the latter case it is said to be coloured. In the case of a coloured substance, therefore, the *absorption spectrum* will show dark areas or bands occupying positions in the spectrum

[1] *Proc. Roy. Soc.*, 1935, A, **150**, 84. See also Lowry, *Optical Rotatory Power* (Longmans).

[2] See W. H. Perkin, *J. Chem. Soc.*, 1884, **45**, 465, and later volumes.

corresponding to definite wave-lengths of light; and by reading off, on a scale of wave-lengths, the position of the absorption band or bands, the coloured substance can be identified. The absorption spectrum of solutions of the coloured substance may also be examined and its variation with concentration, or thickness of the absorbing layer of solution, determined. In this case the solvent must not itself show colour or selective absorption in the spectral region under investigation. It must also be borne in mind that the solvent may cause a shift in the position or a change in the character of the absorption bands of the solute.

In considering the problem of absorption in relation to chemical constitution it is necessary to take into account absorption not only in the visible region of light waves ($\lambda = 4000 - 8000$ A.)[1] but also in the invisible regions of the ultra-violet ($\lambda < 4000$ A.) and the infra-red ($\lambda > 8000$ A.). While it is possible to use the eye for the detection and mapping of the spectrum in the visible region, a photographic plate or photo-electric cell must be used in the ultra-violet and a thermopile, or a specially sensitised photographic plate, up 11,000 A. in the infra-red region. Prisms and lenses of fused quartz and of rock salt respectively must be employed.

From the special point of view of colour in organic compounds, the investigation of the relation between chemical constitution and selective absorption of ultra-violet light has shown that saturated compounds usually show a general absorption while unsaturated and aromatic compounds show selective absorption. Strictly speaking, therefore, such compounds are coloured, but the colour is not visible to the human eye. The position of the absorption bands, however, can be altered by changes in the structure or constitution, or by the introduction of different groups, and the shift of the absorption bands may be such as to bring them into the region of the visible spectrum. The compound then appears visibly coloured. The introduction of the quinonoid structure, for example, into a molecule has a powerful influence in shifting the absorption bands towards longer wave-lengths and so in producing visible colour. This is clearly shown by

[1] The wave-length of light (λ) is generally expressed in Ångström units (1 A. $= 1 \times 10^{-8}$ cm.). Instead of the wave-length one may also use the *wave number*, $\bar{\nu}$, which is equal to the reciprocal of the wave-length, measured in centimetres. Thus if the wave-length is 5000 A. or $5{\cdot}0 \times 10^{-5}$ cm., the wave number will be $1/5{\cdot}0 \times 10^{-5} = 20{,}000$ reciprocal centimetres.

the shift of the absorption bands of phenolphthalein (colourless) into the visible region (red) when the quinonoid structure is brought about by alkali. Similarly, the azo group and certain other groups bring about a shift of the absorption bands, although the shift may not in all cases suffice to produce a visible colour.[1]

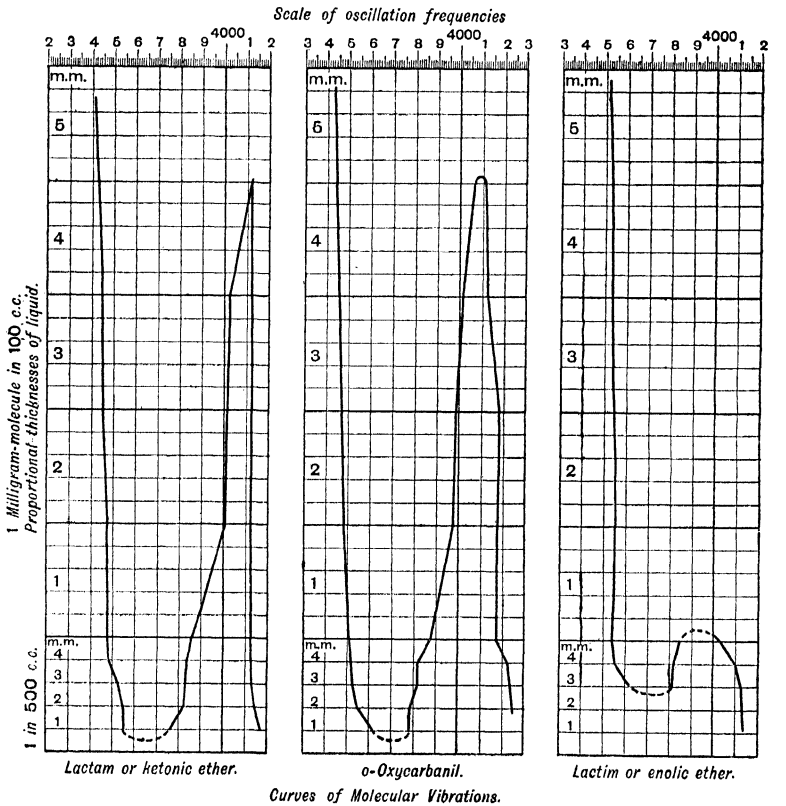


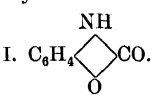
FIG. 46.

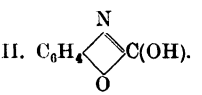
From the more general point of view the investigation of ultra-violet absorption spectra has shown that in the case of related substances similarity in the absorption spectrum goes hand in hand with similarity in chemical constitution. For this reason the determination of ultra-violet absorption

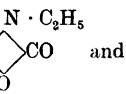
[1] A new theory of colour has been developed by G. N. Lewis and M. Calvin (*Chem. Rev.*, 1939, **25**, 273).

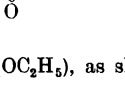
spectra has been frequently used for the purpose of obtaining light on problems of chemical constitution; but the results must be interpreted with caution.

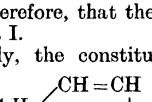
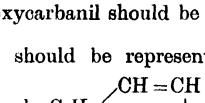
For example, the constitution of the compound *o*-oxycarbanil must be represented by one of the two alternative formulæ:

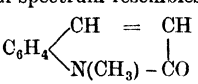




Since it has been shown that the introduction of a methyl or ethyl group does not alter the character of the absorption spectrum, one may compare the absorption spectrum of *o*-oxycarbanil with that of the ethyl derivatives, the constitution of which is known. The absorption spectrum is found to resemble that of the derivative  and to be quite different from that

of the compound  , as shown in Fig. 46. It must be concluded,[1] therefore, that the constitution of *o*-oxycarbanil should be represented by formula I.

Similarly, the constitution of carbostyril should be represented by the formula[2]  and not by the formula  , because its ultra-violet absorption spectrum resembles that of the compound



Although saturated aliphatic compounds do not show selective absorption in the ultra-violet they may do so in the infra-red; and the position of the absorption bands may be shifted into the visible region by variation of the molecular structure, more especially by the introduction of conjugate double bonds.

Whereas the absorption spectra in the ultra-violet and visible regions involve displacements of the valency electrons, absorption in the infra-red involves displacement (vibration and rotation) of atoms in the molecule. The study of infra-red absorption spectra throws light on the subtler problems of molecular structure, internuclear distances, etc.

Quantitative Determination of Absorption.—While for certain purposes the determination of the position of

[1] Hartley, Dobbie, and Paliatseas, *J. Chem. Soc.*, 1900, **77**, 839.
[2] Hartley and Dobbie, *J. Chem. Soc.*, 1899, **75**, 640.

absorption bands in the spectrum may suffice, the quantitative measurement of the amount of absorption may, in other cases, be a matter of importance This can be done by means of a spectrophotometer.

As light-source one may use an arc between tungsten-steel electrodes, which gives a large number of lines well spaced throughout the spectrum. From this source one beam of light passes through the absorbing liquid of thickness d and another beam through an adjustable diaphragm by means of which the intensity can be varied. By reducing the opening of the diaphragm the intensity of the unabsorbed beam can be reduced to that of the absorbed beam at any given wave-length. The ratio of the two intensities, I_0/I, can then be obtained from the aperture of the diaphragm.

The law of the absorption of light was first stated in 1760 by Johann Heinrich Lambert (1728-77), who found that layers of equal thickness of a homogeneous absorbing medium absorb equal proportions of the light. This is expressed by the equation $k=\frac{1}{d}\cdot\log_e\frac{I_0}{I}$, where k is a constant known as the *absorption coefficient* and d is the thickness of the absorbing layer. This law, known as *Lambert's law*, was extended in 1852 by Beer, who showed that the degree of absorption of light is proportional to the thickness of the layer of absorbing medium and to the molar concentration in the latter. That is, $\log_e(I_0/I)=k'\,.\,c\,.\,d$, where k' is the *molecular absorption coefficient*, c is the concentration in gram-molecules per litre, and d is the thickness of the absorbing layer in centimetres. In practice it is usual to make use of the *molecular extinction coefficient* ϵ, which is defined by the expression,

$$\epsilon=\frac{1}{c\,.\,d}\,.\,\log_{10}\frac{I_0}{I},$$

in which decadic take the place of natural logarithms. That is, the molecular extinction coefficient is the reciprocal of the thickness of a layer of a molar solution which will reduce the intensity of the transmitted light to one-tenth of its original value. It serves, therefore, as a quantitative measure of absorption. Absorption curves may then be drawn by plotting log ϵ against the wave-length in Ångström units or against the wave-number

I. Dielectric Constant.—When two metal plates, charged

respectively, positively and negatively, are brought near each other, the force of attraction between the plates will depend on the charge, on the distance between the plates, and on the nature of the substance between them. Or, putting the matter in another way, if the two plates, separated by air, are oppositely charged by imparting to them a certain amount of electricity, they will assume a certain potential. If, instead of air, one introduces sulphur, rubber, etc., between the plates, the potential of the plates will fall. That is to say, the capacity of the *condenser*, as the arrangement of two metal plates separated by an insulator is called, is increased; and a further amount of electricity can be imparted to the plates before their potential rises to its former value. The ratio of the capacity of a condenser, when a given substance is between the plates, to the capacity when the plates are separated by air (or, more correctly, vacuum) is called the *dielectric constant* of the substance. The higher the dielectric constant of a substance, the more will that substance reduce the attraction between two opposite charges when interposed between them.

The reduction of the strength of field between two charged plates, brought about by a dielectric, may be regarded as due (1) to the production of induced charges on neutral molecules with consequent polarisation of the molecules (distortion polarisation, P_D) and (2) to the orientation of permanent dipoles (orientation polarisation, P_μ). The polarised molecules orientate themselves with their positive charges towards the negatively charged plate, and their negative charges towards the positively charged plate, so that they oppose and reduce the strength of the electric field.

The dielectric constant varies greatly for different substances. Hydrocarbons have a very low dielectric constant, while alcohols, nitriles, etc., have relatively high dielectric constants, as is seen from the numbers in the following table :—

	Dielectric Constant.		Dielectric Constant.
Hydrogen cyanide (liq.)	95·0	Methyl alcohol	33·0
Hydrogen peroxide	93·0	Benzonitrile	25·1
Water	81·0	Ethyl alcohol	25·0
Acetonitrile	39·0	Ethyl ether	4·3
Nitrobenzene	36·0	Benzene	2·3

Liquids with high dielectric constant are generally associated to a considerable extent; and there is also a

certain parallelism between the dielectric constant of a liquid and its ionising power when used as a solvent, as was first pointed out by J. J. Thomson and W. Nernst (*Nernst-Thomson rule.*)

Determinations of the dielectric constant have in recent years gained in importance, owing to the development of the Debye-Hückel theory of strong electrolytes (Chap. XIV), and owing to the relation between the dielectric constant and the polar nature of molecules which is due to the non-coincidence of the mean electrical centres of positive and negative charges. From the values of the dielectric constant it is possible to calculate dipole moments and to obtain an insight into the structure of molecules.

The total molar polarisation P of a gas or vapour is given, as Debye showed, by the expression

$$P=\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M}{d}=P_D+P_\mu=\frac{4\pi N}{3}\cdot\alpha+\frac{4\pi N}{3}\cdot\frac{\mu^2}{3k\,.\,T},$$

where ϵ is the dielectric constant, α is a constant, characteristic of the medium, due to induced dipoles, μ is the dipole moment of the permanent dipoles, and k is the gas constant per molecule (the so-called Boltzmann constant) and is equal to R/N, where N is the Avogadro number. $k=1{\cdot}37\times10^{-16}$ erg per degree. The Debye equation has the form $P=a+b/T$, and on plotting P against $1/T$ a straight line is obtained. For a non-polar molecule μ is zero and therefore b is zero, and the straight line graph will be parallel to the $1/T$ axis. If, however, the molecule has a permanent dipole, the straight line will be inclined to the $1/T$ axis and the slope b will be related to μ as indicated by the above equation or $\mu^2=9kb/4\pi N$. Consequently, $\mu=0{\cdot}01276\times10^{-18}\cdot\sqrt{b}$, expressed in e.s.u. $\times$ cm., if the density is expressed in grams per millilitre. The greater the dipole moment, the steeper will be the slope. From measurements of the dielectric constant of a gas at different temperatures, therefore, the dipole moment, which is of importance in the study of molecular constitution, can be determined.

Further, from the relation $PT=aT+b$, it is seen that if PT is plotted against T, a straight line will be obtained, the slope of which is equal to a and the ordinate of which, at $T=0$, is equal to b.

Since, according to the electro-magnetic theory of light, $\epsilon=n^2$, where n is the refractive index for light of long wave-

length, the molar polarisation is approximately equal to the molecular refractivity determined with visible light.

Physical Properties and Chemical Constitution.—In the preceding pages various physical properties have been discussed which, like molecular volume, parachor, molecular refractivity, etc., are functions of the molecular weight and vary in an additive manner with the composition and constitution of a compound. It becomes possible, therefore, to calculate, at least approximately, the value of the property by adding together various atomic and structural constants, and these may be compared with the experimentally determined value. It should be borne in mind, however, that the structural or constitutional constants have been derived on the basis of structures deduced from the chemical behaviour of compounds, and their validity, therefore, is dependent on the validity of the chemically deduced structures. Consequently, the values of the physical properties cannot be used as absolute or independent criteria for deciding problems of chemical constitution, but only to confirm or supplement chemical methods, and more especially to decide between chemically possible alternative formulæ.

In recent years the application of various physical methods has also made it possible to obtain an insight into the finer structure of molecules, of which a brief discussion will be given in Chapter VII.

Molecular Association.—Attention has already been drawn to the fact that in the case of a number of the molar physical properties which have been discussed in the preceding pages, certain liquids behave "abnormally"; and the abnormal behaviour (deviation from the Trouton Rule, low value for the temperature coefficient of molecular surface energy, etc.) was attributed to *molecular association*, or union of simple molecules, into groups or aggregates of larger molecules. Moreover, it was sought, *e.g.*, by Ramsay and Shields, to determine the extent of this association, or the apparent molecular weight of the molecules in a liquid, from the extent to which the liquid deviated in its behaviour from that of liquids which were regarded as normal, or non-associated. Although these determinations can no longer be accepted as quantitatively valid, there can be no doubt that molecular association does, in fact, take place.

The idea of molecular association has long been accepted. Vapour density determinations, for example, have shown

that even in the gaseous state association may take place. Thus the vapour density of hydrogen fluoride at 25° corresponds to a molecular weight more than twice that represented by the formula HF, and the vapour density of acetic acid, in the neighbourhood of its boiling-point, shows that the molecule is dimeric, corresponding to the formula $(CH_3.COOH)_2$. In solution, also, as Nernst showed in 1891, in the case of benzoic acid dissolved in benzene, association of solute molecules may occur ; and modern views regarding the electronic constitution of matter and the modern physical methods of investigating molecular constitution not only support the conception of association but help one also to understand how this association is brought about.

Liquids which behave " normally " in respect of molar heat of vaporisation, additive molar volumes, etc., are found to consist of molecules which are electrically symmetrical and non-polar, and which are held together in the liquid state by the so-called van der Waals forces ; forces which may be due to interaction between electronic systems. Such liquids show, more or less completely, the behaviour of " ideal " liquids. Polar molecules, however, which have a dipole moment, or molecules which are electrically unsymmetrical, will tend to form themselves into groups of molecules owing to the attractions between opposite dipoles. Moreover, it has become clear that association or polymerisation of molecules may take place in certain cases, and notably in the case of hydroxylic compounds, owing to chemical co-ordination through the action of a " hydrogen bond."

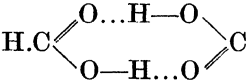
Although one has been accustomed to regard the hydrogen atom as being univalent and as capable of being attached to only one other atom, the view was expressed by W. M. Latimer and W. H. Rodebush [1] that, under suitable conditions, a proton can form a bond between two atoms, this bond being known as a " hydrogen bond." [2] In other words, it came to be realised that a hydrogen atom which was already united by a covalent bond to another atom could, in special circumstances, exercise a further bonding action, the strength of this so-called " hydrogen bond "

[1] *J. Amer. Chem. Soc.*, 1920, **42**, 1419. The occurrence of a hydrogen bond was first noted by Moore and Winmill, *J. Chem. Soc.*, 1912, **101**, 1635.

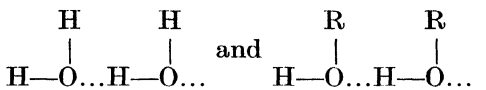
[2] See H. W. Melville, *Science Progress*, 1939, **34**, 100 ; Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press) ; *Trans. Faraday Soc.*, 1940, **36**, 871.

being, however, weaker than the normal covalent bond. The nature of this bond, due it may be to an attraction between dipoles, is not yet fully understood, and acceptance of its reality rests largely on physical evidence, about which, however, there can be little doubt. The bond is formed only between the most electronegative atoms, *e.g.*, fluorine > oxygen > nitrogen > chlorine.[1] Increasing the electronegativity of an atom increases its power of forming hydrogen bonds. Thus the phenols form stronger hydrogen bonds than the aliphatic alcohols.

From the chemical point of view, the association which is so frequently observed in the case of hydroxy compounds can be regarded as due to the bonding action of the hydrogen of the hydroxyl group, the dimer of formic acid, for example, being formulated as



The dotted line represents the hydrogen bond. The associated molecules of water and of alcohols, similarly, can be represented by the formulæ :



It is the hydrogen bond which, in the main, determines the magnitude and nature of the mutual interactions of water molecules and to which are due the abnormal physical properties of water, *e.g.*, high boiling-point, high heat of vaporisation, etc., compared with the hydrogen compounds of sulphur, selenium, and tellurium.

[1] The association of hydrogen fluoride, even in the gaseous state, is due to the strong hydrogen bond.

CHAPTER VI

PROPERTIES OF CRYSTALLINE SOLIDS

If one were asked for a definition of the solid state, one would probably quickly answer that a solid is a rigid body which does not flow and which possesses a definite shape and volume. Such a definition, however, is soon found to be unsatisfactory, for the property of flowing is shown by many bodies, *e.g.*, sealing wax, which one would certainly class as solids. Moreover, even although, generally speaking, a solid differs from a liquid in possessing the property of *elasticity*, *i.e.*, of recovering from a deformation when the deforming force is removed, this property also is found to be too indefinite to separate sharply solids from liquids. The classification, indeed, of bodies into solids and liquids is itself not a satisfactory one, for *amorphous solids*, on being heated, gradually lose their rigidity and elasticity and pass *continuously*, without any sudden change of properties, into liquids. Amorphous solids, therefore, cannot be sharply differentiated from liquids.

Between *crystalline* solids and liquids, however, a sharper distinction can be drawn. In the case of crystals, the structural units (atoms, molecules, or ions) exist in definite and orderly array *in a space lattice* (p. 160); and the orderliness of internal arrangement makes itself manifest in an external orderliness of geometrical forms which are bounded by faces inclined to one another at definite angles. In the case of liquids, however, even when the atomic or molecular units are not distributed entirely at random, there is a breaking down of the space lattice and a loosening of the intermolecular forces which maintain the rigidity of a crystal. There is, moreover, no continuous change from the crystalline to the liquid state, for a crystalline solid has a sharply defined *melting-point* at which it undergoes an abrupt change into a liquid.

In an amorphous solid the physical properties (*e.g.*, thermal expansion, elasticity, solubility) have the same values in all directions. Amorphous solids are *isotropic.* In crystals, however, except in the case of those belonging to the cubic system (p. 156), the physical properties have different values according to the direction. Such crystals are said to be *anisotropic.* If a sphere of glass, for example, is heated, expansion takes place equally in all directions and the spherical form persists ; but if a sphere of, say, rock crystal, is heated, expansion is not the same in all directions and an ellipsoid is obtained.

If the polished surface of a section through a crystalline substance is treated for a short time with a solvent, a pattern may be produced owing to the unequal rate of solution in different directions. The etch figures, as they are called, are all alike on similar faces but unlike on dissimilar faces. They conform to the symmetry of the class to which the crystal belongs, and by examining them by means of a microscope the crystal form of the substance may be determined. The production of such etch figures is of great importance in the investigation of metals and their alloys.

Formation of Crystals.—As the temperature of a liquid is lowered, the forces of attraction between the molecules gain more and more the upper hand over the disrupting and separating action of molecular motion ; and under favourable conditions molecule joins itself to molecule, not vaguely and uncertainly in loose attachment but in a firm linking together at definite points under the action of van der Waals forces. Molecular motion still exists but is restricted to a vibration or oscillation about certain fixed points. In this way, out of the general welter, small groups of molecules are formed in definite array. Around each such invisible group of molecules other molecules marshal themselves, and the structure grows into the visible crystal.

Crystallisation also may take place from solution. In an ordinary solution the molecules of the solute are kept apart by the molecules of the solvent ; but as the solution is concentrated by evaporation, or as the temperature of a concentrated solution falls, the molecules of the solute become more crowded, or their kinetic energy diminishes to such an extent that the molecules are able to join up into crystal units, to which more and more molecules attach

themselves in orderly array and so build up the visible crystal.

The structural units of crystals may not only be *molecules*, bound together by van der Waals' forces, but also *atoms* (*e.g.*, diamond), linked by covalent bonds, or *ions* (*e.g.*, sodium chloride), held together by electrostatic forces. In the case of metals, the structural units are positive ions with free electrons. The number of free electrons in unit volume varies with the temperature. For the most part, metals are close-packed assemblages of cubic, body-centred cubic, or hexagonal unit cells, and the bonds between the atoms are spatially undirected. Deformation by gliding can thus readily take place giving rise to the properties of malleability and ductility.

The production of a perfectly formed crystal, however, requires the exercise of great care and the existence of favourable conditions. Thus the growth of the crystal must be slow in order that the molecules may have time to arrange themselves properly ; and the crystal must also be allowed to grow freely in all directions. When these conditions do not exist the crystal becomes distorted in various ways, and great divergence from the form of the perfect crystal may be observed. The external " habit " of the crystal may vary greatly. Thus when a thin layer of liquid crystallises on a flat plate, growth can take place practically in only two dimensions, and flat fan-like or fern-like crystals are formed. This is observed, for example, when moisture freezes on the window-pane. Such distorted crystals are called *dendrites*,[1] or dendritic crystals, from their resemblance to tree growths. The beautiful leaf-like or lace-like crystals seen in snow-flakes have been formed owing to crystalline growth having been more rapid in certain directions than in others. It may, however, be noted that although the " habit " of a crystal may vary, the crystallographic system to which the crystal belongs remains the same.

Presence of impurities also may produce a variation in the habit of a crystal. Thus sodium chloride forms " hopper crystals " when allowed to crystallise from a solution con-

[1] From the Greek *dendron* = a tree. The formation of dendritic crystals can be beautifully illustrated by placing a small rod of zinc on a piece of filter paper soaked in lead acetate solution. A tree-like growth of lead is formed (Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 812).

taining a small amount of impurity (alum). This behaviour finds an important practical application in industry for the production of needle-shaped crystals of ammonium sulphate which do not cake together.

Not only may molecules link themselves together into a crystalline structure but they may sometimes link themselves into two or more different kinds of structure. This is the phenomenon of *polymorphism*. Thus sulphur forms not only the well-known rhombic crystals but also needle-shaped monoclinic crystals; and mercuric iodide crystallises in two different forms, one of which is scarlet and the other yellow in colour. These different crystalline forms of a substance, however, are not equally stable throughout the same range of temperature, and the conditions for their stable existence will be discussed later (Chap. XVII).

Melting-point and Freezing-point.—When a crystalline solid is heated it passes at a certain definite temperature into a liquid; it melts or fuses. The temperature of the mixture of solid and liquid, moreover, remains constant, on further addition of heat, until all the solid has melted, owing to the fact that heat becomes latent when a crystalline solid melts. This is known as the *latent heat of fusion*. *At the melting-point the solid and liquid are in equilibrium.*

Since a crystalline solid melts at a definite temperature, it might also be expected that when a liquid is cooled down to the melting-point of the solid the liquid would begin to crystallise. In most cases, however, this does not happen. One finds, on the contrary, that it is frequently, and indeed generally, possible to cool a liquid considerably below the temperature at which the solid melts without any crystallisation taking place. The liquid is then said to be *supercooled*. In order that crystallisation shall take place a "centre of growth" or a crystalline "nucleus" must first be formed round which the molecules may arrange themselves. In most cases, if the cooling is carried out sufficiently slowly, nuclei or stable crystal units are formed spontaneously by the accidental meeting, it may be, of the molecules in a suitable way; and vigorous stirring assists these favourable encounters. The number of nuclei formed increases with the degree of supercooling, passes through a maximum, and then decreases. In some cases, however, spontaneous formation of nuclei may not take place, and it may be necessary to introduce a small crystal from the outside in order to start

the process of crystallisation. For this purpose the tiniest particle (say, one-millionth of a gram) is sufficient. It would appear, therefore, that the *freezing-point* of a liquid, unlike the melting-point of a crystalline solid, is rather indefinite. If, however, one defines the freezing-point as the *temperature at which the liquid is in equilibrium with the crystalline solid*, the temperature becomes quite definite and identical with the melting-point.

It should be noted that crystallisation in a supercooled liquid or in a supersaturated solution cannot be initiated by any chance solid but only by a crystal of the fused or dissolved substance or by a crystal of an isomorphous substance. Thus a crystal of sodium acetate will not initiate crystallisation in fused sodium thiosulphate, but if a crystal of chrome alum is introduced into a supersaturated solution of potash alum the latter will crystallise out on the former, since the two substances are isomorphous.

Influence of Pressure on the Melting-point.—The melting-point of a crystalline solid varies with the pressure, and the change of melting-point with the pressure can be calculated by means of the Clausius-Clapeyron equation,

$$\frac{dT}{dp} = \frac{T(v_2 - v_1)}{l},$$

where T is the absolute temperature of the melting-point; v_1 and v_2 are the specific volumes of the solid and liquid respectively; l is the latent heat of fusion per gram; dT gives the change in the melting-point for a given change of pressure dp.

If the pressure is expressed in grams per square centimetre and the volume in millilitres, the latent heat must be expressed in gram-centimetres.

In the case of ice and water we have the following data: $T = 273°$; specific volume of ice (v_1) = 1·091 ml.; specific volume of water (v_2) = 1·00 ml.; l = 79·8 calories = 79·8 × 42670 g.-cm. If dp is equal to 1 atm. = 1033·3 g. per sq. cm., we obtain,

$$dT = \frac{273 \times (-0{\cdot}091) \times 1033{\cdot}3}{79{\cdot}8 \times 42670} = -0{\cdot}00752°.$$

Increase of pressure by 1 atm., therefore, *lowers* the melting-point of ice by about 0·0075°. The value found experimentally is 0·0072°.

In the following table are given the relevant data for a number of other substances :—

	Melting-point under Atmospheric Pressure. $t°$ C.	$v_2 - v_1$ ml.	Latent Heat of Fusion (Cals. per Gram).
Benzene . .	5·4°	0·1317	30·18
Benzophenone .	47·8°	0·0904	23·90
Sodium . . .	97·6°	0·02787	30·23
Phosphorus . .	43·94°	0·0191	5·03
Lead . . .	327·4°	0·003076	5·37

In the case of water, as we have seen, the melting-point is lowered by increase of pressure because contraction takes place on fusion ($v_2 < v_1$). In most cases, however, expansion takes place when a crystalline solid melts, and the melting-point, therefore, is raised by increase of pressure. The effect of pressure on the melting-point is also exceptionally small in the case of ice, because the change of volume on melting is small and the latent heat of fusion is large. The effect of pressure on the melting-point can be predicted qualitatively by the *theorem of Le Chatelier* (Chap. XII.).

Velocity of Crystallisation.—When crystallisation is started in a supercooled liquid by "inoculation" with the appropriate solid, the process extends throughout the liquid, not instantaneously but with a certain finite velocity, which depends not only on the nature and purity of the substance but also on the degree of supercooling. It has been found, in fact, that as the degree of supercooling is increased, the velocity of crystallisation increases to a maximum, remains constant through a certain range of temperature, and then falls off rapidly until it becomes practically zero. The supercooled liquid now has the appearance of a solid glass and does not crystallise even when brought into contact with the crystalline solid. Formerly, it was considered that *glasses* and *amorphous solids* were merely greatly supercooled liquids of high viscosity in which the molecules have a chaotic and random distribution. Recent investigation, however, indicates that this view should now be modified. Thus X-ray examination has shown that in silica glass, for example, there may be a building up of a silicon-oxygen network in much the same way as in a crystalline form of silica, but the scheme of co-ordination is a flexible one and the unit of structure need not repeat itself identically at regular intervals.[1] A certain amount of truly amorphous material may also be present.

[1] B. E. Warren, *Z. Krystallogr.*, 1933, **86**, 349; *Phys. Rev.*, 1934, **45**, 657.

When a "glass" is maintained for some time at a temperature in the neighbourhood of the softening point spontaneous crystallisation may set in, and the glass thereby loses its transparent vitreous or glassy character. The glass is said to undergo *devitrification*.

The velocity of crystallisation in a supercooled liquid can be readily demonstrated by the following experiment. A glass tube 20-30 cm. in length and 8-10 mm. in diameter is sealed at one end and filled with crystallised sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$). The open end of the tube is closed by a plug of cotton-wool. The salt is fused by suspending the tube in a long-necked flask in which water is kept boiling vigorously. When the thiosulphate has been completely fused the tube is removed from the heating jacket and allowed to cool to the ordinary temperature. If a small crystal of sodium thiosulphate is now dropped into the supercooled liquid, crystallisation begins at once and advances down the tube at a definite rate.

One may also prepare a tube in which the lower half contains supercooled sodium thiosulphate and the upper half supercooled sodium acetate ($NaC_2H_3O_2$, $3H_2O$). If a crystal of sodium thiosulphate is dropped into the tube it will fall through the layer of fused sodium acetate and will initiate crystallisation in the layer of supercooled thiosulphate. The supercooled sodium acetate, however, does not crystallise until a crystal of this salt is introduced.

The production of a glass and its devitrification can be illustrated in a very simple manner by the use of hippuric acid. A quantity of this compound is introduced into a thin-walled glass capillary tube (melting-point tube), and after the solid has been melted at as low a temperature as possible (m.p. = 188°) the open end of the tube is sealed up. The tube is then re-heated in order to melt the acid again if necessary, care being taken that no crystalline particles remain. The tube is then cooled rapidly by plunging it into cold water. A clear, rigid "glass" is thus obtained. If the tube is now carefully heated by passing it quickly through a small flame or by dipping it in boiling water, crystalline nuclei will form and grow until the whole glassy mass has become crystalline.

Atomic and Molecular Heat.—On studying the values of the specific heats of the solid elements it was found, in 1819, by the French physicists, Pierre Louis Dulong (1785-1838) and Alexis Thérèse Petit (1791-1823), that, with a few marked exceptions, *the product of specific heat and atomic weight* (the so-called *atomic heat*) *is nearly constant*, and has an average value of about 6·2 calories. This means that approximately the same amount of heat is required to raise the temperature of 1 gram-atom of lithium (6·94 g.) as to raise the temperature of 1 gram-atom of uranium (238·07 g.) by 1°. This remarkable regularity, known as DULONG AND PETIT'S LAW, proved of much value in former times in deciding doubtful atomic weights ; a service, however, which it is now no longer required to render. This law is illustrated by the numbers in the table on page 153.

Element.	Atomic Weight.	Specific Heat at 300° in Calories.	Atomic Heat. C_p.
Carbon (graphite) . .	12·0	0·171	2·1
Sulphur (rhombic) . .	32·06	0·174	5·6
Aluminium . . .	26·98	0·217	5·9
Copper	63·54	0·0925	5·9
Iron	55·85	0·108	6·0
Magnesium . . .	24·32	0·248	6·0
Silver	107·88	0·0562	6·1
Zinc	65·38	0·0929	6·1
Lead	207·21	0·0305	6·3
Tin	118·7	0·0543	6·4
Lithium	6·94	0·941	6·5
Uranium . . .	238·07	0·028	6·6

In considering the variations in the value of the atomic heat one has to bear in mind that the specific heat, and therefore the atomic heat, varies in all cases with the temperature, as is indicated by the curves in Fig. 47, in

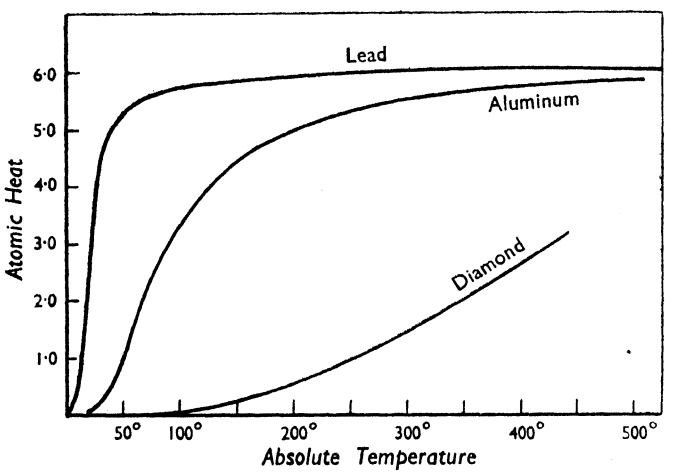


FIG. 47.

which the values of the atomic heat at constant volume are plotted against the temperature. As this diagram shows, the atomic heat increases with rise of temperature and approaches a value in the neighbourhood of 6 calories ; but whereas in most cases the atomic heat increases so rapidly with rise of temperature that this value is attained, or nearly so, at the ordinary temperature, the atomic heat curve in the case of

carbon, boron, etc., rises much more slowly. It is therefore only at temperatures much above the ordinary that in these cases the atomic heat approaches the value 6 calories.

A theoretical basis for the empirical law of Dulong and Petit has been obtained, more especially by Debye.[1]

In order to avoid complications due to thermal expansion and compressibility one may consider the atomic heat at constant volume, C_v, in place of the more commonly determined atomic heat at constant pressure.[2] If it is assumed that the N atoms or molecules present in a gram-atom or gram-molecule of a crystalline solid oscillate in three dimensions about their mean positions in the crystal, then, on the basis of the theory of the equipartition of energy $C_v = 3R = 5{\cdot}96$. To the average kinetic energy of the oscillating atoms, which would give $C_v = 3R/2$, one must add the potential energy gained by the displacement of the atoms. This is equal to the kinetic energy. Consequently, $C_v = 2 \times (3R/2) = 3R$. This is in harmony with the law of Dulong and Petit, bearing in mind that this law refers to the atomic heat at constant pressure.

As the temperature is lowered the atomic or molecular oscillations will become smaller and will cease altogether, it may be assumed, at the absolute zero.[3] The crystal will now act as a perfectly elastic body and any small addition of heat will cause a vibration of the crystal as a whole instead of an oscillation of the units. On the basis of this assumption and the laws of elasticity, Debye was able to express the relation between the atomic heat and the absolute temperature in the form,

$$C_v = \frac{12\pi^4 R}{5} \cdot \frac{T^3}{\theta^3} = 465 \cdot \frac{T^3}{\theta^3},$$

where T is the absolute temperature and θ is a constant (known as the Debye temperature) which is characteristic of the substance, and has the following values :—

	Pb.	Ag.	Cu.	Al.	Fe.	C (diamond).
$\theta =$	88	215	315	398	453	1860

[1] *Ann. Physik*, 1912, **39**, 789. See also Schrödinger, *Physikal. Z.*, 1919, **20**, 420.

[2] The difference of atomic heats, $C_p - C_v$, will depend on the atomic volume at the absolute zero, the coefficient of thermal expansion and the compressibility. For copper, the calculated value of $(C_p - C_v)$ at room temperature is $6{\cdot}7 \times 10^6$ ergs $= 0{\cdot}15$ cal.

[3] All crystalline solids at temperatures approaching 0° C. possess residual or zero point energy of vibration.

This equation has been found to hold up to a temperature of $T = \theta/12$.

As the temperature is raised, the assumption that the crystal as a whole acts as a vibrating body and that the structural units are fixed must break down. As heat energy is added to the solid the oscillation of the units about their mean positions must increase more and more; and the temperature at which this becomes appreciable and at which, therefore, the Debye relation begins to break down, will depend on the strength of the crystal forces and also on the mass of the structural units. Diamond, for example, which has an extremely low compressibility (indicative of powerful interatomic forces), has a very high Debye temperature, while lead, with a high compressibility, has a very low Debye temperature. In the case of lead, therefore, the atomic heat will attain the value $3R$ at a comparatively low temperature, whereas diamond will attain this value only at a high temperature. Moreover, the lighter the atoms, the higher must the temperature be raised before the energy absorbed by the vibrating units becomes appreciable and before the limiting value of $3R$ is reached.

In the case of good electrical conductors, the electrons within the solid also are capable of translatory motion in the internuclear space, and, consequently, they also will contribute to the specific heat. The value $3R$ will thus be exceeded at high temperatures.

Molecular Heat of Compounds.—The law, stated by Franz Ernst Neumann (1798-1895) in 1831 and by Hermann Kopp in 1864, that the molecular heat of a solid compound is equal to the sum of the atomic heats of the constituent elements has been found to be, at best, only a very rough approximation to the truth. Considerable deviations from the law may be found.

The Elements of Crystallography.—Since the physical properties of a crystal depend on the orderly arrangement of the structural units, a knowledge of, at least, the elements of crystallography is important.

From the orderliness of geometrical structure observed in crystals one can infer an orderliness in the arrangement of the atoms or groups of atoms of which the crystal is built up. If one considers any plane, parallel to a face of the crystal, the atoms or groups of atoms must be regarded as arranged in such a way that if they are joined together by straight lines a definite self-repeating pattern or *network* is obtained. But the orderliness of atomic arrangement must exist not only

in one plane but in space ; and, therefore, on joining by straight lines the corresponding atoms in the networks of different planes, a regular self-repeating *space lattice* or crystal unit will be formed, the unit cell being the least volume which contains the pattern. Throughout the whole crystal, therefore, there will be a regular repetition of this fundamental crystal unit, the structure of which determines the angles at which the crystal faces meet, the position of the cleavage planes, and the general properties of the crystal. Although different crystals of a substance may show differences in the growth or development of different faces, the *angle between corresponding faces is constant.*

In crystals, certain elements of symmetry—a centre of symmetry, planes of symmetry, and axes of symmetry—exist, and crystals differ in the number and nature of the elements of symmetry they possess. A crystal is said to have a *centre of symmetry* when the faces are arranged in pairs so that to each face there is a corresponding parallel face at the opposite side of the crystal. A *plane of symmetry* divides a crystal into two geometrically identical parts, of which the one is the mirror image of the other ; and an *axis of symmetry* is such that during a rotation of the crystal about the axis, the aspect of the crystal is repeated two, three, four, or six times during one complete revolution. Thus the crystals drawn in cross-section in Fig. 48 are said to have a dyad, triad, tetrad, or hexad axis of symmetry, respectively, because on rotation through 360° round the axis, represented by the black dot, the original aspect of the crystal is repeated twice, thrice, four, and six times.



FIG. 48.

The Seven Systems of Crystal Structure.—Crystals can be classified into seven systems according to the relative length and the mutual inclinations of the crystal axes (Fig. 49). The elements of symmetry indicated in the table on page 158 will be shown completely only by ideal or perfect crystals.

Miller Indices.—The position of a crystal face may be defined by its intercepts on the crystallographic axes, the *ratios* of the intercepts being the same for all parallel faces. The form of a crystal depends, also, on the angles at which

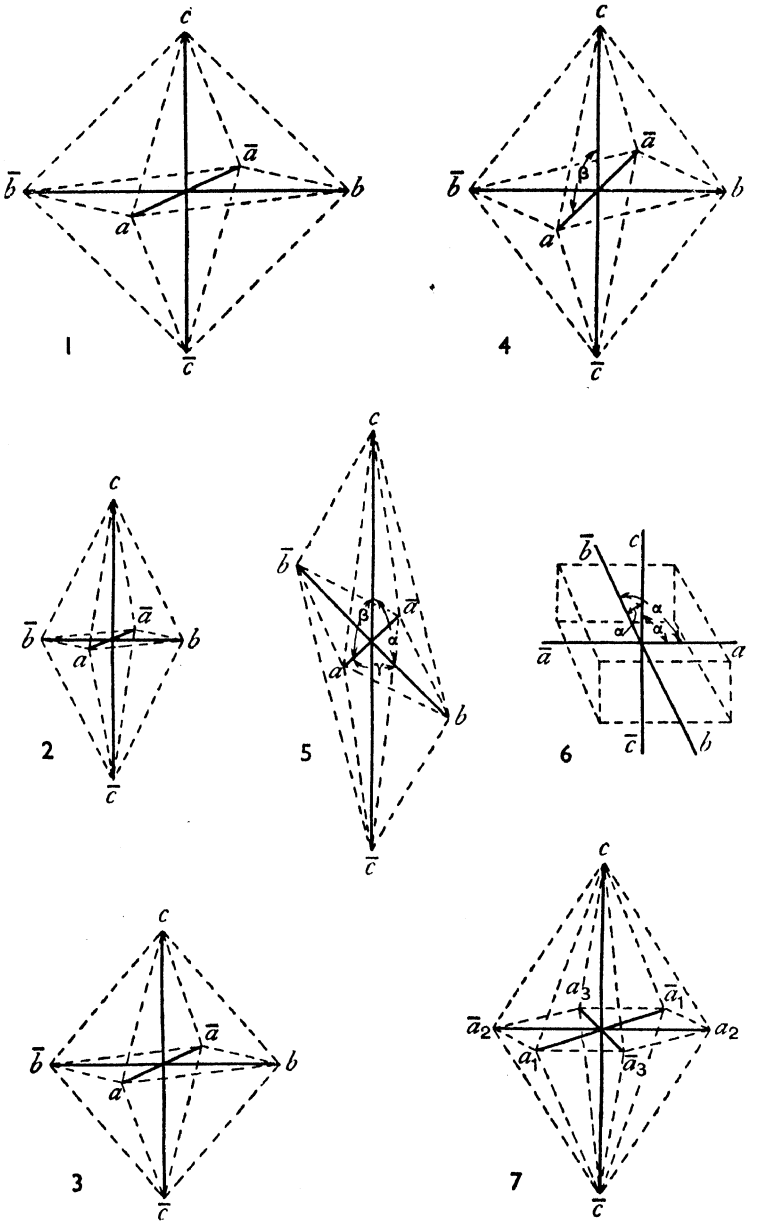


FIG. 49.

SEVEN SYSTEMS OF CRYSTAL STRUCTURE

System.	Characteristics.		Examples.
	Axial.	Symmetry.	
1. Cubic . .	Three equal axes intersecting at right angles.	Nine planes. Thirteen axes.	Diamond. Sodium chloride. Alum.
2. Tetragonal .	Three axes intersecting at right angles, two only being of equal length.	Five planes. Five axes.	Tin. Potassium ferrocyanide.
3. Rhombic (Orthorhombic)	Three axes intersecting at right angles; all unequal.	Three planes. Three axes.	Rhombic sulphur. Potassium nitrate.
4. Monoclinic (or Oblique)	Three unequal axes, one at right angles to other two which are obliquely inclined to each other.	One plane. One axis.	Monoclinic sulphur. Sodium sulphate decahydrate. Ferrous sulphate heptahydrate.
5. Triclinic (or Anorthic)	Three unequal axes intersecting obliquely.	No plane. No axis.	Copper sulphate pentahydrate.
6. Trigonal (or Rhombohedral)	Three equal axes intersecting obliquely at angles which are equal but not right angles.	Three planes. Four axes.	Sodium nitrate.
7. Hexagonal .	Three equal axes in the same plane and intersecting at angles of 60°, and a fourth axis, unequal in length and perpendicular to the plane of the other three.	Seven planes. Seven axes.	Magnesium. Beryl. Quartz.

the axes cut, and these *axial angles* must therefore be specified.

If one considers the three axes AA′, BB′, CC′, intersecting at the point O (Fig. 50), intercepts on these axes towards the front, the right, and upwards are regarded as positive; and intercepts towards the back, the left, and downwards are regarded as negative, and indicated by a bar. The intercepts which a characteristic face makes on these three axes are known as *parameters* and are represented by a, b, and c. It is now customary to define a crystal face in terms of these parameters divided by the intercepts made by the face on the axes. These are known as the *Miller indices*, and were introduced by the crystallographer, William Hallowes Miller (1801-80), of the University of Cambridge, in 1829.

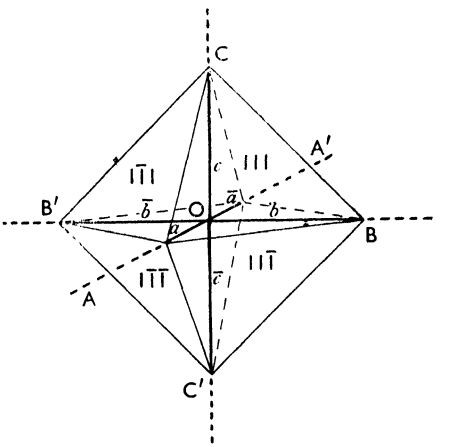


FIG. 50.

Thus if a crystal face is parallel to the A and B axes, its intercepts on these will be ∞a and ∞b respectively, and if it makes intercept c on the O axis, its Miller indices will be: $\frac{a}{\infty a} : \frac{b}{\infty b} : \frac{c}{c}$, or, 0 : 0 : 1, written (001). That is, a crystal face which is parallel to a given axis will have the Miller Index 0 with reference to that axis.

Again, if a crystal face makes intercepts $a : 2b : 2c$ its indices will be: $\frac{a}{a} : \frac{b}{2b} : \frac{c}{2c}$, or, $1 : \frac{1}{2} : \frac{1}{2}$, or, 2 : 1 : 1, written (211); and, similarly, a face with intercepts $3a : b : \infty c$ will have indices $\frac{a}{3a} : \frac{b}{b} : \frac{c}{\infty c}$, or, $\frac{1}{3} : 1 : 0$, or, (130).

In crystals of the cubic system the axes are at right angles and $a = b = c$. The faces of a regular octahedron (Fig. 50) will have the indices: (111), ($11\bar{1}$), ($1\bar{1}1$), ($1\bar{1}\bar{1}$), ($\bar{1}\bar{1}1$), ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}11$), ($\bar{1}1\bar{1}$).

Internal Structure of Crystals.—Since the structural units of a crystal are built up in a space lattice, the important questions at once arise: What are the dimensions of this space lattice and how are the structural units (atoms, ions, or molecules) arranged within it? How is the space lattice built up? The methods by which answers to these questions can be obtained were first indicated by experiments which were suggested in 1912 by Max von Laue in order to prove that X-rays are of the same nature as ordinary light.

When a beam of white light falls on a glass or metal plate on which a regular series of closely spaced parallel lines has been ruled, each line acts as a centre from which a secondary train of diffracted waves proceeds; and spectra are produced owing to the fact that the angle of diffraction varies with the wave-length of the light. It is to diffraction that the play of colour in mother-of-pearl is due. Diffraction effects are similarly produced by a regular arrangement of small particles, like the minute globules of moisture on a bedewed glass plate.

If X-rays are of the same nature as ordinary light, then diffraction effects should also be obtained; but as the wave-lengths of X-rays were estimated to be some ten thousand times shorter than the waves of ordinary light,[1] a diffraction grating with structural units ten thousand times smaller than those suitable for ordinary light would be necessary to produce the effect. Such a grating, von Laue thought, might be formed by the regular arrangement of atoms or atomic groups in a crystal; and the expectation was confirmed experimentally by the German physicists Walter Friedrich and Paul Knipping, of the University of Munich. A fine pencil of X-rays was passed through a crystal and then allowed to fall on a photographic plate. On developing the plate a symmetrical arrangement of spots (*Laue's spots*) appeared around the central spot due to the action of the direct pencil of rays. The patterns so obtained depend on the degree of symmetry of the crystal, and may be comparatively simple, as in the case of rock-salt (Fig. 51), or exceedingly complicated, as in the case of kaliophilite, $KAlSiO_4$ (Fig. 52). While the production of these diffraction patterns proved that X-rays are of the same nature as

[1] The wave-length of the D-line (sodium light) is 5896×10^{-8} cm., or 5896 Ångström units. The wave-length of the characteristic X-rays from palladium, for example, is 0·58 A.

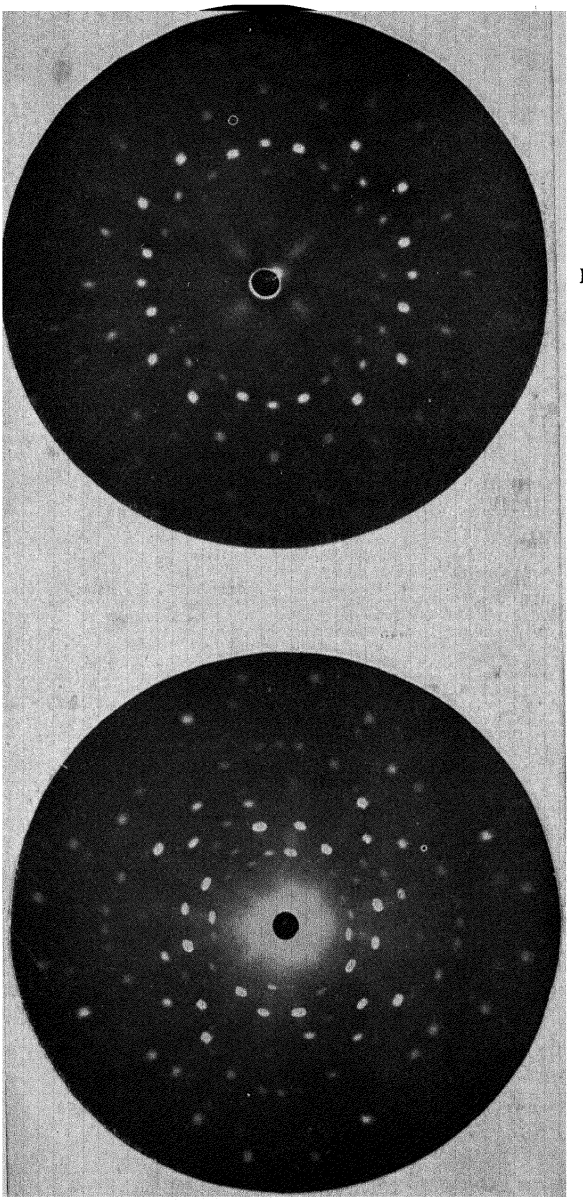


FIG. 51.

FIG. 52.

(Reproduced from Bunn, Chemical Crystallography, by permission of the author and the Oxford University Press)

ordinary light, it also suggested a means whereby the atoms or groups in crystals might be located in space and the dimensions of the space lattice be determined. From a study of the Laue patterns, information regarding crystal structure could be obtained.

Another and simpler method for the determination of the internal structure of crystals was introduced in 1912 by Sir William H. Bragg (1862-1942), at that time Professor of Physics in the University of Leeds, and his son, (Sir) William Lawrence Bragg, now Cavendish Professor of Physics

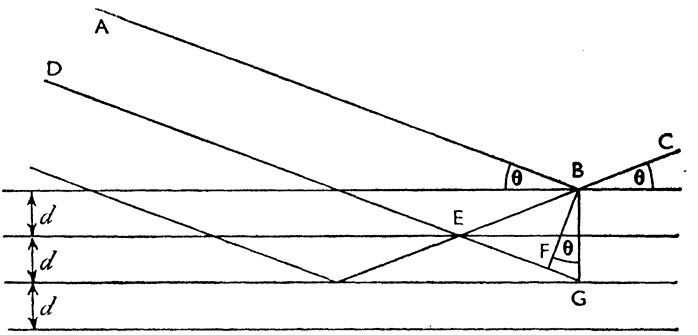


FIG. 53.

in the University of Cambridge.[1] When a beam of X-rays of definite wave-length is thrown on the face of a crystal the successive layers of atoms, lying in planes parallel to the crystal face and equidistant from one another, reflect the rays. The rays reflected from the different parallel layers will be out of phase and will therefore interfere with one another, unless the path differences are equal to an integral number of wave-lengths ; in which case, reinforcement will take place. The condition necessary for such reinforcement can be obtained as follows :—

If d is the distance between the parallel reflecting planes of a crystal, and if AB, DE (Fig. 53) represent a beam of X-rays falling on the crystal face at the angle θ, EBC will represent the path of the reflected rays. In order that the ray reflected at E may reinforce the ray reflected at B, the path DE + EB must be longer than AB by $n\lambda$, where n is a whole number and λ is the wave-length of the X-rays. Since BG is drawn perpendicular

[1] See W. H. Bragg, *An Introduction to Crystal Analysis* (Bell).

to the reflecting planes, and BF is perpendicular to EG, it follows that thepath difference (DE + EB − AB) will be equal to (DE + EF + FG − AB) = FG = $2d$ sin θ. The condition for reinforcement of the reflected rays is therefore

$$n\lambda = 2d \sin \theta.$$

A first order reflection will be obtained when $n = 1$, a second order reflection when $n = 2$, and so on, the intensity of the reflection decreasing as the order increases. If the wavelength of the X-rays is known, the distance d between the successive layers of atoms in the crystals can be determined in different directions, and so the dimensions of the crystal lattice can be measured. In the case of the more complex crystals, the Bragg method may have to be supplemented by the method of von Laue.

When crystals of sufficient size are not available the method due to Debye and Sherrer [1] and to A. W. Hull [2] may be used. A narrow pencil of X-rays is passed through a layer of powdered crystals and the diffracted rays allowed to fall on a photographic plate. A series of rings is obtained and from the spacing of the rings the distances between the atoms in the crystals can be calculated.

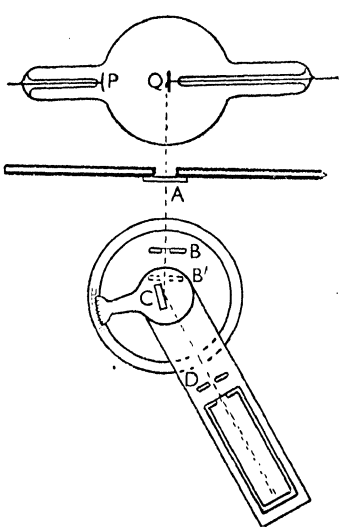


FIG. 54.
(From Bragg's *An Introduction to Crystal Analysis* (G. Bell & Sons Ltd.).)

Since the human eye is not constructed so as to be able to detect X-rays, a photographic plate or the property of X-rays of ionising gases must be utilised in order to detect the path of the reflected beam. A diagram of the arrangement is shown in Fig. 54. X-rays produced at the target Q pass through a slit A in the wall of the lead box in which the X-ray tube is contained, and further definition is given to the rays by passage through the slit B. The narrow

[1] *Physikal. Z.*, 1916, **17**, 277
[2] *Proc. Nat. Acad. Sci.*, 1917, **3**, 470.

pencil of X-rays is then reflected from the face of a crystal C, mounted on a rotating table, furnished with scale and vernier, and the reflected ray passes through the slit D into the ionisation chamber, filled with a readily ionisable gas (*e.g.*, vapour of methyl bromide). The ionisation chamber revolves about the same axis as the crystal. An electroscope connected with a metal plate placed in the ionisation chamber out of the path of the X-rays indicates the amount of ionisation and therefore the strength of the reflected beam. By rotating the crystal, the angle of incidence θ is varied, and the ionisation is determined at each setting. A sudden increase in the ionisation is shown when the law of reflection $n\lambda = 2 \cdot d \cdot \sin\theta$ is fulfilled.

By means of the above X-ray spectrometer one can determine the angles of incidence at which maxima of ionisation, corresponding to the first and higher order reflections, are produced. In the case of reflections from the planes (100) of rock-salt, for example, maxima of ionisation were observed for $\theta = 5{\cdot}9°$, $11{\cdot}85°$, and $18{\cdot}15°$. The sines of these angles are 0·103, 0·205, and 0·312, numbers which are, very approximately, in the ratio 1 : 2 : 3, in accordance with the law, $\sin\theta = n \cdot (\lambda/2d)$. From the relation, $d = \lambda/2 \cdot \sin\theta = \lambda/2 \times 0{\cdot}103$, the interplanar distance, $d_{(100)}$ is found equal to $4{\cdot}85\lambda$.

Determination of the Space Lattice.—In determining the space lattice, the system to which the crystal belongs is first ascertained by crystallographic measurements. The relative interplanar distances in the different possible types of lattice are then calculated, and by comparison of these calculated values with the results obtained by X-ray analysis the lattice type is determined. To illustrate this, the determination of the lattice type occurring in crystals of rock-salt may be described.

Rock-salt crystallises in the cubic system. For this system, three lattice types are possible, called the *simple cubic*, *face-centred cubic*, and *body-centred cubic* lattices (Fig. 55). In the simple cubic lattice there is one structural unit at each corner of the cubic cell. In the face-centred lattice, which can be thought of as four interpenetrating simple cubic lattices, there is a structural unit at each corner of the cubic cell and one unit in the centre of each face. In the body-centred lattice, which one may regard as being formed by the interpenetration of two simple cubic lattices in such

a way that the corner of one unit lies at the centre of the other, there is a structural unit at each corner and one unit at the centre of the cubic cell. In these crystals the possible crystal faces are (1) parallel to the faces of the cube : plane

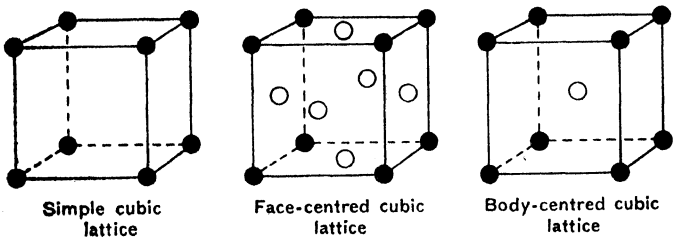


FIG. 55.

(100); (2) perpendicular to the diagonal of a face: plane (110); (3) perpendicular to the diagonal of the cube: plane (111). These are shown in Fig. 56.

If, in the simple cubic lattice, the distance between the (100) planes is put equal to 1, the distance between the (110) planes will be equal to half the diagonal of a face, or $\sqrt{2}/2$;

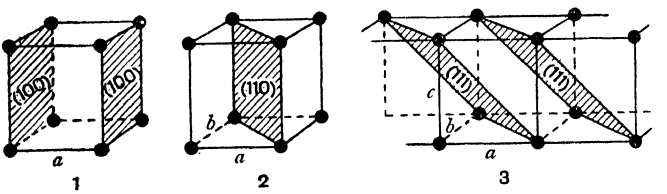


FIG. 56.

and the distance between the (111) planes will be one-third of the diagonal of the cube, or $\sqrt{3}/3$. These interplanar distances are therefore in the ratio

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : 0{\cdot}707 : 0{\cdot}577.$$

In the case of the face-centred cubic lattice, (100) planes pass through the structural units in the centre of the face of the simple cube and so divide the cube into two equal parts. The interplanar distance will therefore now be half that for the simple cubic lattice. Similarly, new (110) planes pass through the structural units in the faces of the cube (Fig. 57), and so divide the diagonal of the face into four parts. The interplanar distance will therefore be $\sqrt{2}/4$.

The number of (111) planes is the same as in the simple cubic lattice, and the interplanar distance will therefore be $\sqrt{3}/3$. In the face-centred cubic lattice the interplanar distances are in the ratio

$$d_{(100)} : d_{(110)} : d_{(111)} = \tfrac{1}{2} : \sqrt{2}/4 : \sqrt{3}/3 = 1 : \sqrt{2}/2 : 2\sqrt{3}/3$$
$$= 1 : 0{\cdot}707 : 1{\cdot}154.$$

Lastly, in the case of the body-centred cubic lattice, (100) planes will pass through the structural unit in the centre of the cube and the interplanar distance will again, therefore, be half that for the simple cubic lattice. New (111) planes, passing through the central structural unit, will lie midway between the (111) planes of the simple cubic lattice. The interplanar distance will therefore be $\sqrt{3}/6$. The number of (110) planes is the same as in the simple cubic lattice. The ratio of interplanar distances will therefore be

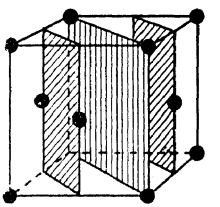


FIG. 57.

$$d_{(100)} : d_{(110)} : d_{(111)} = \tfrac{1}{2} : \sqrt{2}/2 : \sqrt{3}/6 = 1 : \sqrt{2} : \sqrt{3}/3$$
$$= 1 : 1{\cdot}414 : 0{\cdot}577.$$

On determining the intensity of X-ray reflections from the faces of rock-salt crystals (Fig. 58),[1] first order reflections

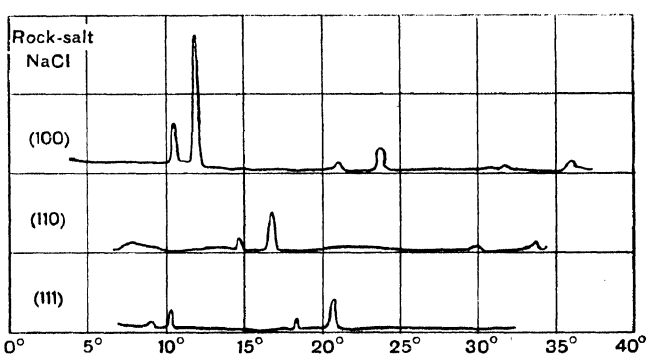


FIG. 58.

are found at the angles[2] $\theta = 5{\cdot}9°$, $8{\cdot}4°$, and $5{\cdot}2°$ for the planes (100), (110), and (111) respectively. The sines of these

[1] W. H. Bragg and W. L. Bragg, *X-rays and Crystal Structure* (Bell).

[2] In Fig. 58 the abscissæ represent the angles through which the rotating table of the apparatus shown in Fig. 54 (p. 162) is turned. These angles must be divided by 2 in order to obtain the angle of reflection θ.

angles are 0·103, 0·146, and 0·0906; and on calculating the interplanar distances by means of the expression

$$d = \frac{\lambda}{2 \cdot \sin \theta},$$

the values 4·855λ, 3·425λ, and 5·518λ respectively are obtained. These numbers are in the ratios 1 : 0·706 : 1·137, which correspond to the ratios for a face-centred cubic lattice. It must be concluded, therefore, that in crystals of rock-salt the structural units are arranged in a face-centred cubic lattice.

The structural units in the crystal may be molecules, atoms, or ions, and in the case of rock-salt the accepted view is that the units are sodium and chloride ions and that the sodium ions alternate with chloride ions in the crystal, as shown in Fig. 59. Each sodium ion is surrounded by six chloride ions, and each chloride ion is similarly surrounded by six sodium ions. The sodium chloride molecule, as such, has disappeared. This view with regard to the nature and arrangement of the structural units is in harmony with the X-ray reflection spectra.

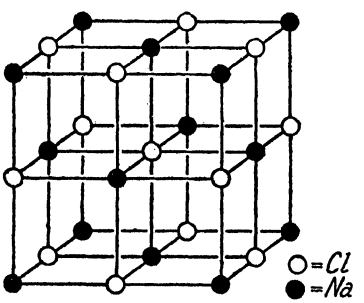


FIG. 59.

From Fig. 59 it will be seen that the (100) and the (110) planes contain an equal number of sodium and chloride ions and it is therefore to be expected that the nature of the X-ray reflection spectra for these two planes will be similar. That is, the first order reflection should be greater than the second, and the second greater than the third. This is in harmony with experiment Fig. 58. In the case of the (111) planes, however, the alternate planes contain only sodium ions or only chloride ions (Fig. 60, shaded planes) and the reflections from these alternate planes will differ, because the intensity of reflection increases with the mass of the reflecting unit. The intensity of the reflections from the planes containing only chloride ions will be greater than the intensity of the reflections from the planes containing only sodium ions. In the case of a first order reflection

from two chloride ion planes, reinforcement takes place when the path difference is equal to one wave-length. There is, however, another plane containing only sodium ions midway between the chloride ion planes, and for rays reflected from this plane the path difference will be half a wave-length. Interference with the ray reflected from the chloride ion plane will therefore take place, and if the intensity of the two reflected rays were equal the one would neutralise the other. The intensity of reflection from the sodium ion plane, however, is less than that from the chloride ion plane, so that the first order reflection, although present, is reduced in intensity. In the case of the second order reflection, the path difference between the sodium ion plane and the chloride ion plane is equal to one wave-length, and there will therefore be a strengthening of the reflection. In the case of the third order reflection, interference again occurs and the intensity of this reflection, in any case weak, is weakened still further, and practically disappears. These predictions are in harmony with the results of experiment (Fig. 58).

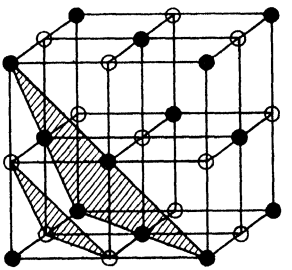


FIG. 60.

Whereas potassium chloride shows the same type of crystal lattice as sodium chloride, cæsium chloride has a body-centred cubic lattice in which a cæsium ion is at the centre of a cube of *eight* chloride ions, and a chloride ion is at the centre of a cube of *eight* cæsium ions.

Another type of cubic lattice is shown by diamond (Fig. 62), in which one atom is attached to *four* other atoms. The same structural type is found in the case of zinc sulphide.

No fewer than 230 different groups of crystals are known, and the particular crystal structure depends on various factors, such as the nature of the structural units and atomic or ionic radii.

Determination of the Wave-length of X-rays.—In the elementary cubic cell of rock-salt shown in Fig. 59, it will be recognised that each corner ion is common to eight adjacent cubes, so that only one-eighth of its mass can be regarded as contributing to the mass of a unit cell; or all eight corner ions contribute the mass of only one ion.

Similarly, each face-centred ion is common to two adjacent cubes, and the six face-centred ions of the unit cube contribute the mass of three ions. The total mass of chlorine, therefore, associated with a unit cell is equal to the mass of four chloride ions. Similarly, the total mass of sodium will be equal to the mass of four sodium ions; and the unit cube may therefore be regarded as having a mass equal to four molecules of sodium chloride. Since the density of rock-salt is 2·17 g. per ml., the mass of the unit cube will be $2{\cdot}17a^3$, if a is the length of one side of the cube. The mass of four molecules of sodium chloride is equal to $4 \times 58{\cdot}454/6{\cdot}031 \times 10^{23}$, where $6{\cdot}031 \times 10^{23}$ is the number of molecules in a gram-molecule. Consequently, $2{\cdot}17a^3 = 4 \times 58{\cdot}454/6{\cdot}031 \times 10^{23}$, or

$$a^3 = \frac{4 \times 58{\cdot}454}{2{\cdot}17 \times 6{\cdot}031 \times 10^{23}} = 178{\cdot}7 \times 10^{-24} \text{ ml.}$$

and $a = 5{\cdot}632 \times 10^{-8}$ cm. $= 5{\cdot}632$ A.

The distance $d_{(100)}$ between the planes parallel to the (100) face will therefore be 2·816 A., and since it has already been found that $d_{(100)} = 4{\cdot}85\lambda$, it follows that the wave-length of X-rays from the particular target used (palladium) is

$$\lambda = 2{\cdot}816 \times 10^{-8}/4{\cdot}85 = 0{\cdot}581 \times 10^{-8} \text{ cm.} = 0{\cdot}581 \text{ A.}$$

Applications of X-ray Analysis.—The method of X-ray analysis, the use of which has been illustrated by a discussion of the investigation of crystals of rock-salt, has been very widely applied in investigating the nature and arrangement of the structural units of crystalline substances. Since many of the physical properties of crystals are largely dependent on the nature of the crystal lattices, the method of X-ray analysis gives a means of interpreting these properties in terms of the crystalline structure. By this means, for example, light is thrown on the marked differences in the properties of the two allotropic modifications of carbon, diamond and graphite.

The X-ray examination of diamond has shown that its structure is based on a faced-centred cubic lattice, with an additional atom situated in the centre of alternate cubes of the sodium chloride lattice. The structure is that given by two interpenetrating face-centred lattices, arranged so that an atom of one lattice is surrounded by four atoms of the

other. Each carbon atom, then, is at the centre of a regular tetrahedron and is joined to four other atoms which lie at the corners of a regular tetrahedron, as represented in Fig. 61.[1] The atoms are all spaced at equal distances from one another, the distances between the centres of adjacent atoms being 1·54 A. The atoms are thus bound with equal strength by covalence forces to four symmetrically arranged atoms, an arrangement which serves to account for the hardness and non-volatility of the diamond. The whole crystal forms, as it were, a "giant molecule." Moreover, the linking of the atoms in the manner described leads to the formation of a network of regular hexagons (Fig. 62), but the six carbon atoms forming a hexagon are not all in one plane.

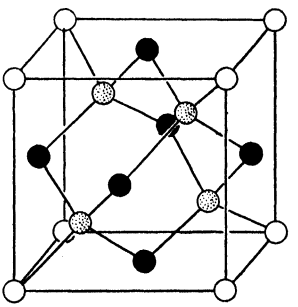


FIG. 61.

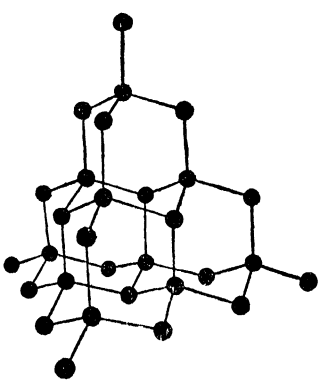


FIG. 62.

In the case of graphite (Fig. 63)[2] the crystal consists of layers of co-planar carbon atoms held together by covalence forces and forming a network of hexagons with interatomic distances of 1·42 A. The layers constitute, as it were, giant molecules in two dimensions. The carbon atoms of *alternate* networks lie exactly above and below one another, but in adjacent networks the atoms are arranged so that half of them lie directly above half of the atoms in the lower network and the other half lie above the centres of the lower network. The four valencies, moreover, are not of equal strength. The distance between the layers is not the same as the distance between the atoms in the hexagonal networks,

[1] The carbon atoms at the corners of the cube are shown as circles, those at the centre of the cube faces are shown as black discs, and those on the diagonals of the cube as stippled discs.

[2] R. C. Evans, *An Introduction to Crystal Chemistry* (Cambridge University Press).

but is much greater, namely, 3·41 A. The force acting between the different layers of carbon atoms is therefore much less than between the atoms of a given layer ; and the soft, flaky nature of graphite thus finds an explanation.

Thermal expansion, also, it is found, is greater in a direction normal to the layers of hexagons than in their plane.

By the X-ray examination of hexamethyl-benzene, the presence of a ring of six carbon atoms, inferred on chemical grounds by Kekulé, has been confirmed ; and the distance

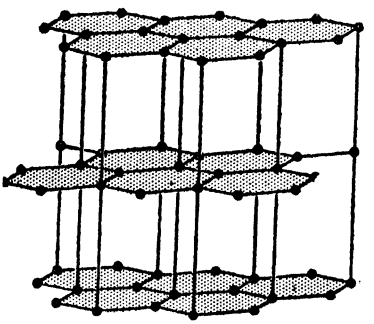


FIG. 63.

between the carbon atoms in the ring has been found to be 1·42 A., as in the case of graphite.[1] This applies also in the case of naphthalene and anthracene. It has thus been shown that the crystal structures of benzene derivatives are more closely related to that of graphite than to that of diamond, and that the benzene ring is to be regarded as a *flat* ring of six carbon atoms. In the case of long-chain aliphatic compounds, X-ray analysis indicates that the carbon atoms have a zigzag arrangement in the chain, in harmony with the tetrahedral arrangement in space of the four valencies. X-ray analysis of organic compounds has thus yielded a verification of the structural formulæ which had been adopted on purely chemical grounds ; and these formulæ have gained a degree of reality which they did not formerly possess, owing to the introduction of exact metrical representation.

The methods of X-ray analysis have also been widely applied to the investigation of metals and their alloys, and

[1] The C—C bond lengths in benzene have been found, by electron diffraction methods to be 1·39 A.

of the changes in crystalline structure which take place as the result of polishing, mechanical working, and thermal treatment. By means of X-ray examination, also, much light is being shed on molecular arrangement in apparently non-crystalline or amorphous substances. Unstretched rubber, for example, is apparently entirely amorphous ; in stretched rubber there is evidence of definite "fibre structure." So-called amorphous carbons all appear to contain small crystallites of graphite, the average size depending on the source and method of preparation.[1]

Electron Diffraction.—According to a theory put forward in 1923 by the French physicist Prince Louis de Broglie, a moving electron is associated with waves [2] which can show interference, diffraction effects, etc. ; and the predictions from this theory were realised experimentally in 1927 by (Sir) G. P. Thomson, and by C. Davisson and L. H. Germer.[3] Electron beams can therefore be used in place of X-rays for the investigation of the arrangement of the structural units in a crystal. Electron beams, however, are very much less penetrating than X-rays, and for that reason are not so suitable for the study of solids. They are, however, most suitable for the study of surface layers and films and for the study of molecular dimensions and configurations in gases ; and to their use for this purpose reference will be made in the following chapter.

[1] See J. T. Randall, *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids, and Gases* (Chapman and Hall) ; C. W. Stillwell, *Crystal Chemistry* (M'Graw-Hill) ; R. C. Evans, *An Introduction to Crystal Chemistry* (Cambridge University Press) ; Rooksby, *J. Roy. Soc. Arts*, 1940, **88**, 308.

[2] The wave-length associated with the electrons may be calculated from the relationship.

[3] Bell Telephone Laboratories, New Jersey.

CHAPTER VII

MOLECULAR DIMENSIONS AND CONFIGURATIONS

IT has just been learned how, by means of X-rays, it is possible to ascertain the spatial arrangement of the structural units of a substance in the crystalline state, and one is thereby led, quite naturally, to inquire whether the spatial arrangement of the atoms in a molecule and the interatomic distances may not also be capable of determination. Experiment has shown that such determinations can, in fact, be made, and that information can thereby be obtained regarding molecular dimensions and configurations.

We shall be concerned here only with molecules formed by a covalent linking of the atoms, a linking which was claimed by G. N. Lewis to be the only true linking in chemistry and which is dependent mainly on the nature of the atoms linked together. Such a link has a definite length and strength (measured by the energy given out in its formation), and has a certain spatial direction with respect to other links. The covalent link, moreover, is formed by the sharing of electrons, and the question of the proportion in which the electrons are shared between the two linked atoms is of interest.

For the determination of the length of the covalent link, or the interatomic distance (distance between the centres of adjacent atoms), various methods may be employed.

(*a*) *X-ray Analysis.* — By a technique similar to that used in the examination of crystalline powders (p. 160), Debye, in 1929, found that X-ray interference patterns could be obtained with liquids and with gases, although in the case of the former the results, owing to the scattering of the rays by the molecules as well as by the atoms, could not easily be interpreted. With gases, however, it has been found possible, from the interference patterns obtained, to

determine interatomic distances, as in the case of crystals. The experimental difficulties, however, are great, as the amount of material in a given volume of gas is small, and the scattering power therefore minute compared with that of a solid.

It may be noted that the scattering of X-rays is not caused by the atomic nuclei but by the surrounding electrons, and the interatomic distances which are measured are not the distances between the atomic nuclei but between the centres of action of the electronic orbits. In the case of gases the difference between these two distances is appreciable, and a correction must therefore be applied to the results obtained by means of X-rays.

(*b*) *Electron Diffraction.*—It has already been pointed out that a beam of electrons or cathode rays behaves as if the electrons consisted of, or were associated with, waves of very short wave-length [1] and can be used in place of X-rays for the determination of the spatial arrangement of the structural units in a crystal. In 1930 R. Wierl showed that electron beams are of especial value for the investigation of gases and vapours. When a narrow pencil of electrons passes through a gas or vapour, the electrons are scattered and the interference patterns which are produced by their waves (as in the X-ray examination of powders) can be recorded on a photographic plate. The method can be applied even to gases and vapours under reduced pressure and, owing to the greater intensity of the electron beam, the period of exposure necessary to obtain the photographic image is reduced from a few hours (required for the X-ray method) to a fraction of a second.[2]

(*c*) *Spectroscopic Methods.*—Information regarding interatomic distances and molecular configuration can also be obtained from a study of molecular spectra. Whereas comparatively simple line spectra, due to energy transitions, brought about by the drop of an electron from an orbital of higher to one of lower energy, are emitted by atoms, molecules yield band spectra, a band being formed by a large number of fine lines crowded together. Although lines due to electronic transitions are found, spectra are also observed in the

[1] The wave-length is given by the expression $\lambda = h/mv$, where h is Planck's constant, m is the mass, and v the velocity of the electron.

[2] See J. T. Randall, *Diffraction of X-rays and Electrons by Amorphous Solids, Liquids, and Gases*; N. V. Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press).

infra-red region due, on the one hand, to changes in the energy of rotation of the molecule and, on the other hand, to changes in the energy of vibration of the constituent atomic nuclei. Of these, the rotation-vibration spectrum is the most important and has been most widely studied—generally as an absorption spectrum—owing to the fact that it lies mainly in that part of the infra-red which is nearest to the visible spectrum, while the pure rotation spectrum lies in the far infra-red. By the use of specially sensitised plates some of these rotation-vibration absorption spectra can be studied photographically up to about 11,000 A.

While it is not possible to discuss here the detailed theory of these molecular spectra, it may be said that the difference in frequency, $\Delta\nu$, of two successive rotational lines in the vibration spectrum is equal to $h/4\pi^2 I$, where h is Planck's constant and I is the moment of inertia of a diatomic molecule. If, therefore, the moment of inertia of the molecule is determined spectroscopically, the internuclear distance can be calculated, because the value of I depends on the masses of the atoms (which are known) and on the distance between them. Owing to difficulties in interpreting the band spectra the method has been applied, so far, only to the simpler molecules.

The spectroscopic method has been supplemented more especially by Sir Chandrasekhara Venkata Raman. In 1923 the German physicist Adolf Smekal predicted, on theoretical grounds, that if a beam of monochromatic light is passed through a transparent substance, a scattering of the light by the molecules of the substance will take place, and that in the scattered light there will be radiations of different frequencies from those of the incident light. These frequency differences are characteristic of the scattering medium. This alteration of frequency was verified experimentally by Raman in 1928, and is generally known as the *Smekal-Raman effect.* From a study of the Raman spectra valuable information regarding molecular structure can be obtained.[1]

From the results of spectroscopic investigations it is possible, in the case of the simpler molecules, not only to determine interatomic distances but also to get information

[1] See J. H. Hibben, *The Raman Effect and its Chemical Applications* (*Amer. Chem. Soc. Monographs*); G. B. B. M. Sutherland, *Infra-red and Raman Spectra* (Methuen).

about the shape of the molecules. In the case of a simple molecule of three or four atoms it is possible, theoretically, to calculate interatomic distances and valency angles, provided all the moments of inertia are known. Thus it is found that the molecule of carbon dioxide is rectilinear, that the molecules of water and of sulphur dioxide are triangular, the molecule of ammonia is pyramidal, and the molecule of carbonyl chloride is Y-shaped.

Dipole Moments and Molecular Structure.—If in the formation of a covalent link between two atoms the two electrons are shared equally between the two atoms, the resulting molecule will be electrically symmetrical, neutral, and non-polar. If, however, the two shared electrons constituting the single covalent linkage are not shared equally between the two atoms, then one atom will have an excess of positive electricity associated with it and the other an excess of negative electricity. The molecule will be polar and will possess a dipole moment equal to the charge on one of the atoms multiplied by the distance between the atoms. The existence of a dipole moment is evidence of an unequal sharing of the electrons, and the magnitude of the dipole moment will be a measure of the electrical asymmetry or of the degree of polarity of the molecule. Since unit electric charge is equal to $4{\cdot}8 \times 10^{-10}$ e.s.u., and since the molecular diameter is of the order 10^{-8} cm., the dipole moments will be of the order 1×10^{-18} e.s.u. $= 1$ Debye unit (D.).

Dipole moments, as has been pointed out, can be calculated from determinations of the dielectric constant of the substance as well as by other methods; and since dipole moments are a measure of the electrical asymmetry of molecules, valuable information concerning the shape of molecules and the directions of the valencies relatively to one another can be obtained from their study.[1]

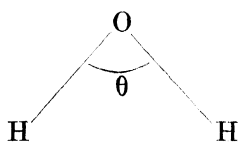
Molecular Dimensions and Configurations.—A few illustrations may now be given of the application of the physical measurements just discussed to the elucidation of molecular dimensions and configurations.

Elementary molecules, *e.g.*, H_2, O_2, are found to have no dipole moment and, consequently, there is, as one would expect, a uniform sharing of the electrons. The molecules,

[1] See C. P. Smyth, *Dielectric Constants and Molecular Structure* (Chem. Catalog Co.); R. J. W. Le Fèvre, *Dipole Moments* (Methuen).

however, of diatomic compounds such as carbon monoxide, hydrogen chloride, etc., have dipole moments. For hydrogen chloride the dipole moment is 1·04 D., the distance between the atoms, calculated from the band spectrum, being 1·28 A.

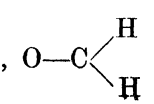
In the case of a triatomic molecule of the type AB_2, one may conclude that if the molecule is linear, the electric moments of the two bonds will be equal in magnitude and opposite in direction, and will thus neutralise each other. The molecule will have no dipole moment. This is found to be the case with carbon dioxide, for the molecule of which, therefore, one must assume a linear structure, O—C—O. The distance between the carbon atom and each of the oxygen atoms is 1·15 A. Unlike carbon dioxide, the molecule of water is found to have a dipole moment of 1·84 D. The molecule, therefore, cannot be linear but the two valency bonds must be inclined, as shown by band spectra, at an angle to each other, thus :



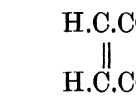
The dipole moment will be equal to $2m \cos \frac{1}{2}\theta$ where m is the moment of a single O—H link. For water, the angle $\theta = 105°\ 6'$ and the O—H link is 0·970 A. A similar configuration is found in the case of hydrogen sulphide.

The tetratomic molecule, BCl_3, is found to be non-polar, and it must be presumed, therefore, that all four atoms lie in a plane and that the angles between the three valencies of boron are equal. Ammonia, NH_3, however, has a dipole moment of 1·46 D., and the molecule, therefore, forms a triangular pyramid with the nitrogen atom at the apex. The height of the pyramid is 0·52 A.

Methane and carbon tetrachloride are non-polar, in harmony with the tetrahedral grouping of the four hydrogen atoms or the four chlorine atoms round the carbon atom. From electron diffraction measurements the interatomic C—Cl distance is 1·83 A. and the Cl—Cl distance 2·98 A.

Lastly, the molecule of formaldehyde, H.CHO, is found to have a Y-shape, 

In the field of stereochemistry great advances have been made during the present century through the application of the physical methods described in the preceding pages. Thus, from a study of the dipole moment, for example, it is possible to distinguish between *cis*- and *trans*-isomerides (*e.g.*, maleic and fumaric acids), since the *cis*-form,



will have a dipole moment, whereas the *trans*-form,



will not.[1]

Further, determinations of atomic size and of valency angles are of much importance in the study of an optical activity which is dependent on restricted rotation within the molecule. Thus by means of the physical methods already discussed, diphenyl, $C_6H_5.C_6H_5$, is shown to consist of two flat benzene nuclei joined coaxially, and capable of free rotation about the common axis. Such a molecule is symmetrical and cannot be obtained in different optically active forms. If, however, the hydrogen atoms of the two benzene rings are substituted in the ortho-positions to the connecting bond, optically active molecules can be obtained if the dimensions (atomic radii) of the substituting groups are sufficiently large to interfere with one another and prevent free rotation about the common axis. In this case the molecule cannot be wholly planar, and it therefore becomes asymmetric and capable of existing in optically active forms. These spatial or steric effects are of much importance.[2]

Resonance.—The development during the present century of wave mechanics[3] has proved of great importance in chemistry, for on the basis of that concept (which cannot be discussed here) it is possible to calculate the properties of some of the simpler molecules at least. Of importance for organic chemistry, more particularly, is a principle of structure which has been deduced on the basis of wave

[1] J. Errera, *Physikal. Z.*, 1926, **27**, 764.
[2] E. E. Turner, *Science Progress*, 1936, **31**, 29.
[3] See L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics with Applications to Chemistry.*

mechanics, the principle of *resonance* (or *mesomerism* as it has also been called). On the basis of wave mechanics it can be shown that if two electronic structures of almost equal energy are possible for the same molecule, the normal state of the molecule is neither the one nor the other of the two separate states but a linear combination of the two. The molecule is to be regarded as having a structure intermediate between the two, and not expressible by the ordinary structural formulæ. The molecule, therefore, exhibits some of the properties of each of the two possible electronic structures.

The occurrence of resonance produces a characteristic shortening of linkages, or a reduction of the "atomic radius" [1]; and it may be that the shortening of the C—C link in benzene, 1·39 A. as compared with 1·42 A. in graphite, may be due to resonance. The fact that the benzene molecule has no dipole moment indicates that it consists of a flat ring of carbon atoms with the electrons regularly distributed as a result of resonance. The theory of resonance, therefore, leads to the view that in benzene the bonds between adjacent carbon atoms are identical and not alternately double and single.[2]

[1] Since the interatomic distance is the distance between the centres of two linked atoms, the "atomic radius" of an atom may be taken as half the interatomic distance between two like atoms.

[2] See L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press).

CHAPTER VIII

DILUTE SOLUTIONS AND THEIR COLLIGATIVE PROPERTIES. OSMOSIS AND OSMOTIC PRESSURE

Osmosis and Osmotic Pressure.—One of the most notable properties of gases, it was learned, is the property of diffusion, owing to which a gas can distribute itself uniformly throughout the whole space offered to it. The molecules of a liquid, or of a substance in solution, also possess this property ; but the process of diffusion in liquids takes place much more slowly than in the case of a gas, for the molecules of a liquid are crowded more closely together, and the mutual collisions are therefore more frequent.

That diffusion does take place in liquids can be demonstrated by carefully bringing a layer of water on the top of a concentrated solution of copper sulphate or of potassium permanganate standing at the bottom of a cylinder. In the course of time it will be found that the coloured solute has diffused upwards into the water, while at the same time water has diffused downwards into the solution. The same process can be illustrated by pouring the deep-blue coloured solution, obtained by adding excess of ammonium hydroxide to a solution of copper sulphate, into a test-tube containing a 3 per cent. gelatine jelly. After a time the coloured solute will have diffused some distance into the jelly.

When solvent and solution are brought together diffusion takes place, because the concentration of the solvent and solute molecules is not the same in the two layers ; the solvent and solution are not in equilibrium. In carrying out the experiment as described above, however, one cannot distinguish between the diffusion of the solvent and the diffusion of the solute. The following experiment, therefore, may be carried out. A parchment paper " thimble " is firmly attached to a glass tube, as shown in Fig. 64, and a

moderately concentrated solution of cane sugar in water is passed into the apparatus through the side tube *a* until the level rises to a certain point in the narrow glass tube. The parchment paper tube is then immersed in pure water. Since the parchment-paper membrane is permeable to both the solvent and the solute, diffusion can still take place; and after some time it is found that the level of the solution in the apparatus has *risen*, thereby producing a hydrostatic pressure.



FIG. 64.

The production of such a pressure, first observed in 1748 by the French *Abbé*, Jean Antoine Nollet (1700-70), a Professor of Physics in Paris, indicates that water molecules diffuse through the parchment-paper membrane more rapidly than the solute molecules do; and as the hydrostatic pressure is produced by a process of *osmosis*, a term which we owe to the French physiologist René Joachim Henri Dutrochet[1] (1776-1847), it was called an *osmotic pressure*. Since the membrane of parchment paper is permeable to the sugar molecules as well as to the molecules of water, the hydrostatic pressure cannot be permanent, and the level of the liquid in the osmometer—as the apparatus may be called—after rising to a certain height, will fall until the level of liquid outside and inside the osmometer is the same. This will occur when, through osmosis, uniform concentration of solution has been established throughout the liquids inside and outside the osmometer.

Since the osmotic pressure produced in the experiment just described is due to a difference in the *relative* velocity of osmosis of solvent and solute molecules, it is clear that in proportion as the membrane becomes relatively less and less readily permeable to the solute, the observed pressure will increase. It is, however, possible to imagine a membrane which, while still permeable to water molecules, is quite impermeable to solute molecules; and with such a membrane —called by van't Hoff a *semipermeable membrane*—osmosis

[1] Dutrochet applied the terms *endosmose* and *exosmose* to the oppositely directed diffusion currents. The single term osmosis is now generally employed to denote the process of diffusion of a liquid through a membrane or permeable septum. The term is derived from the Greek *ōsmos* = a push.

can, of course, take place only on one direction, namely, inflow of water into the solution. The process of osmosis, however, cannot go on indefinitely, for, as the hydrostatic pressure inside the osmometer increases, or as the pressure on the solution increases, it tends to force the solvent back again through the membrane. That is to say, the mechanical or hydrostatic pressure produced by the osmosis of water into the solution opposes the force causing the osmosis, and when the two become equal, osmosis will stop. The hydrostatic or osmotic pressure produced with such a membrane as has been postulated here is an *equilibrium pressure*, and is no longer temporary but permanent. The pressure so produced is, moreover, the *maximum* pressure which can be attained with the given solution. It is to this maximum pressure that the term *osmotic pressure of a solution* is now applied.[1]

The osmotic pressure of a solution, therefore, may be defined as *the equivalent of the hydrostatic pressure which is produced when the solution is separated from the solvent by a semipermeable membrane*, or, as *the equivalent of the excess pressure which must be applied to the solution in order to prevent the passage into it of solvent through a semipermeable membrane.* It is a measure of the difference which exists between the *free energy* (Chap. XIII) or the *activity* of the solvent in the pure state and in the solution. It is to this difference of activity, which manifests itself also, as we shall learn, in a difference of vapour pressure, that osmosis is due; and in the case of dilute solutions the initial rate of osmosis is proportional to the osmotic pressure of the solution. Similarly, if solutions of the same substance but of different concentration are separated by a semipermeable membrane, solvent will flow from the less concentrated to the more concentrated solution, until the concentration of the two solutions becomes the same, or until a hydrostatic pressure is produced equal to the difference between the osmotic pressures of the two solutions. When solutions of different substances are separated by a semipermeable membrane (*i.e.*, a membrane impermeable to the solutes in both solutions), solvent will

[1] It may be mentioned that the term "osmotic pressure of a solution" is not strictly correct. A solution does not, in itself, have any osmotic pressure, for this is a hydrostatic or mechanical pressure produced by osmosis under the conditions described above—that is, *it is osmosis that produces osmotic pressure and not the osmotic pressure which produces osmosis.* The osmotic pressure is a measure of the force producing osmosis.

flow from the solution of lower osmotic pressure to the solution of higher osmotic pressure, until the solutions become *isosmotic* or have an equal osmotic pressure.

The conception of the osmotic pressure of a solution, it is clear, will have no real value—for one will not be able to measure it—unless it is possible to obtain a semipermeable membrane. Fortunately such a membrane can be obtained which is semipermeable for certain solutions at least.

The first membranes found to possess the property of semipermeability are those surrounding animal and vegetable cells; and with such membranes experiments were made by the Dutch botanist Hugo de Vries.[1] When the epidermal cells of the leaf of certain plants, *e.g.*, *Tradescantia discolor*, are examined under a microscope, it is seen that the cells are normally pressed against the cellulose sheath by which they are surrounded, so as to produce a certain tenseness or *turgor* (Fig. 65, A). If the cell is now placed in a solution of sucrose, containing 7·5 per cent. or more of sugar (a solution the osmotic pressure of which is greater than that of the cell sap), water will pass out from the cell, which will then contract away from the sheath of cellulose (Fig. 65, B and C). This is the phenomenon of *plasmolysis*. By bringing cells of the same kind into solutions of different concentration one can determine the concentration at which plasmolysis ceases or is just detectable. Such solutions are then said to be *isotonic* with or capable of producing the same pressure or turgor in the cell as the cell sap. If the plasmatic membrane surrounding the cell is impermeable to the dissolved substances, isotonic solutions will also be isosmotic.[2] It was by such measurements that the osmotic pressure of solutions was first studied.

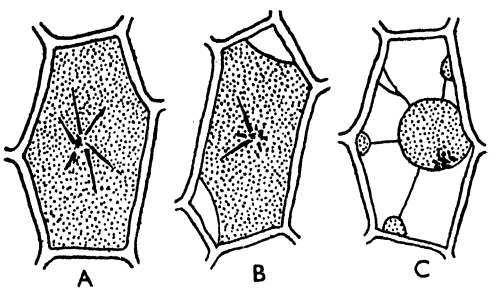


FIG. 65.

Red blood corpuscles, similarly, have been used for this

[1] *Z. physikal. Chem.*, 1888, **2**, 415.

[2] The term *isotonic* was used by de Vries as synonymous with *isosmotic*, but it is better now that a distinction should be drawn between the two terms.

purpose. When introduced into pure water or into a solution containing less than 0·9 per cent. of sodium chloride, human red blood corpuscles swell, and in some cases burst, owing to the diffusion into them of water, but if introduced into a solution containing more than 0·9 per cent. of sodium chloride they lose water, shrink, and become " crenated." A 0·91 per cent. solution of sodium chloride is isotonic with human red blood corpuscles.

Measurement of Osmotic Pressure.—While the osmotic experiments with animal or vegetable cells were of much importance in biology they were of little value for a general study of the osmotic properties of solutions ; but in 1866 Moritz Traube (1826-94), in Breslau, showed that the precipitation membrane of copper ferrocyanide, formed when solutions of copper sulphate and potassium ferrocyanide are brought together, is semipermeable to solutions of cane sugar and of certain other substances. It is with such a membrane that most direct measurements of the osmotic pressure of solutions have been carried out.

In order to obtain a membrane sufficiently strong to withstand a pressure of several atmospheres, the German botanist Wilhelm Pfeffer (1845-1920), in 1877, produced a precipitate of copper ferrocyanide in the walls of a porous battery-pot by filling the pot with a solution of copper sulphate and standing it in a solution of potassium ferrocyanide. Diffusion of the salts took place, and where the two salts met in the walls of the pot a gelatinous precipitate of copper ferrocyanide was formed: and this precipitate, being supported by the material of the pot, was found capable of sustaining considerable pressures.

A sketch of Pfeffer's apparatus is shown in Fig. 66. The porous pot z, containing the solution of which the osmotic pressure is to be measured, is connected with a closed manometer m by means of the tube t and the collars v and r. The pot is then placed in pure water kept at a constant temperature. In the course of a short time the pressure inside the pot is shown by the manometer to increase, and ultimately to become constant. The constant pressure thus produced represents the osmotic pressure of the solution.

The osmotic pressure of a solution depends on the total molar concentration of the dissolved substances (see later), whereas the tonicity depends on the molar concentration of those solutes which do not pass through the particular plasmatic membrane. Substances to which the membrane is permeable do not produce plasmolysis.

The measurements carried out by Pfeffer, although of no great accuracy, indicated that the osmotic pressure is proportional to the concentration and that it increases with rise of temperature. As experimental support for a theory of solutions these measurements became of the greatest importance.

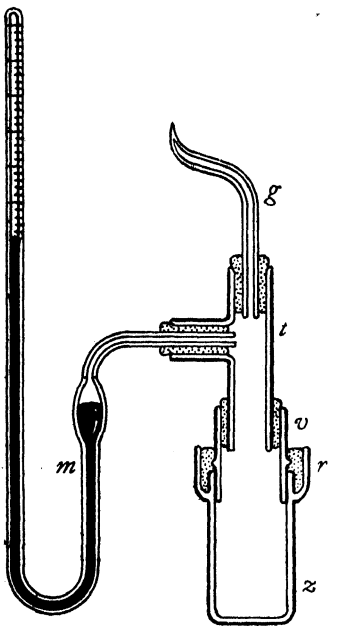


FIG. 66.

The van't Hoff Theory of Dilute Solutions.—In the course of an investigation of the laws of chemical equilibrium in solutions, the Dutch chemist Jacobus Henricus van't Hoff (1852-1911), in 1885, became impressed by the profound analogy which exists between gases and solutions, provided that for the ordinary pressure of gases one substitutes, in the case of solutions, the so-called osmotic pressure.[1] Moreover, his attention having been drawn to the osmotic experiments of Pfeffer, van't Hoff recognised that the conception of osmotic pressure and of semipermeable membranes allows of the second law of thermodynamics being applied with ease and clearness to the theoretical investigation of the *quantitative* relations between the properties of solutions and their concentration.

The experiments of Pfeffer having indicated that the osmotic pressure of a solution is proportional to the concentration, van't Hoff pointed out that if one regards a dissolved substance as analogous to a gas and the osmotic pressure as produced by the bombardment of the semipermeable membrane by the molecules of the solute, the proportionality between pressure and concentration follows, as in the case of a gas. Even if osmotic pressure be regarded as due to an attraction between solvent and solute molecules, its value will also be proportional to the number of attracting molecules in unit volume, provided that the solution is so

[1] See *Z. physikal. Chem.*, 1887, **1**, 481; *Phil. Mag.*, 1888, **26**, 81.

dilute that the dissolved molecules exercise no attraction on one another and that each one exerts its own special attractive action, uninfluenced by its neighbours. This law of proportionality between osmotic pressure and concentration is analogous to Boyle's law for gases, and is known as the BOYLE-VAN'T HOFF LAW for solutions. It is illustrated by the values of the osmotic pressure of solutions of cane sugar at 0°, determined at Oxford by the Earl of Berkeley and E. G. J. Hartley,[1] and shown in the following table :—

Concentration (Grams per Litre). C.	Volume in Litres in which 1 Gram-molecule is Dissolved. V.	Pressure in Atmospheres. P.	$\frac{P}{C}$	PV.
10·00	34·2	0·65	0·065	22·2
20·00	17·1	1·27	0·064	21·7
45·00	7·60	2·91	0·065	22·1
93·75	3·65	6·23	0·067	22·7

As is clear, the ratio $\frac{P}{C}$ is constant.

By the method of Carnot's thermodynamic cycle (Chap. XVII), and by employing the conception of a semipermeable membrane, van't Hoff deduced that *the osmotic pressure must be proportional to the absolute temperature*; but in making this deduction *the important assumption was introduced that the solution is so dilute that the heat effect on further dilution* is negligible. This theoretical deduction is also borne out by the experiments of Pfeffer as well as by the more recent and exact determinations of H. N. Morse (1848-1920) and his collaborators at Johns Hopkins University.[2] This is shown by the numbers in the following table, which refer to a solution of cane sugar containing 32·6 g. per litre.

	Temperature (Cent.).					
	0°	5°	10°	15°	20°	25°
Osmotic pressure (P) . .	2·43	2·45	2·50	2·54	2·59	2·63
$\frac{P}{T} \times 1000$	8·90	8·81	8·83	8·82	8·84	8·83

[1] *Proc. Roy. Soc.*, 1909, A, **82**, 271.

[2] *Amer. Chem. J.*, 1901, **26**, 80, *et seq.*; *The Osmotic Pressure of Aqueous Solutions* (Carnegie Institution, Washington); Findlay, *Osmotic Pressure* (Longmans).

The above numbers show that the osmotic pressure is proportional to the absolute temperature, and that the law of variation of the osmotic pressure with the temperature is therefore analogous to Gay-Lussac's law for gases. It is known as the GAY-LUSSAC-VAN'T HOFF LAW.

Since the osmotic pressure of dilute solutions is proportional to the concentration, or inversely proportional to the volume in which a given amount of substance is dissolved, and since, also, the pressure is proportional to the absolute temperature, van't Hoff was able to write $PV = (i\boldsymbol{R}) \, . \, T$, *an expression which is analogous to that which is found to express the behaviour of a perfect gas.* In this expression $(i\boldsymbol{R})$ is a constant characteristic of the dissolved substance.

But a further step was taken by van't Hoff. By the application of thermodynamics to the case of a gaseous solute which obeys Henry's law, and by postulating the existence of semipermeable membranes, one of which is permeable only to the solvent while the other is permeable only to the gaseous solute, van't Hoff deduced the important generalisation that *the osmotic pressure of a solution is equal to the pressure which the dissolved substance would exercise in the gaseous state if it occupied a volume equal to the volume of the solution.* In other words, the law of Avogadro applies also to dilute solutions. This deduction, however, is valid, in the first instance, only in the case of infinitely dilute solutions and in the case of gaseous solutes which obey Henry's law (Chap. XVII), *i.e.*, which exist in the same molecular state as a gas as in solution; and it involves, also, the assumption that the vapour of the solvent obeys the gas laws. By reason, however, of the fact that the analogy between dilute solutions and gases extends to the laws of Boyle and of Gay-Lussac, the possibility immediately suggested itself that Avogadro's law would apply not only in the case of gaseous but also in the case of other solutes, and that therefore the value of the factor $(i\boldsymbol{R})$ in the equation $PV = i\boldsymbol{R} \, . \, T$ would have the same numerical value per gram-molecule as the constant $\boldsymbol{R}$ of the gas equation. That is to say, i would be equal to unity. This remarkable suggestion was shown to be valid not only by the osmotic pressure measurements carried out by Pfeffer but also by determinations of the freezing-point and boiling-point of solutions, to which reference will be made in the next chapter. Confirmation of the validity of the van't Hoff

suggestion is afforded also by the more recent determinations of osmotic pressure by Lord Berkeley and E. G. J. Hartley. From the table on page 185 it is seen that the mean value of the product PV is 22·2 litre-atmospheres, and if one divides this by the absolute temperature 273°, one finds $iR = 0{\cdot}0813$, a number agreeing to within 1 per cent. with the value of the constant R ($=0{\cdot}0821$).

The Avogadro theorem applied to solutions can also be tested in the following way. In the case of gases, it was learned that at a temperature of 0°, 1 gram-molecule of a gas exerts a pressure of 76 cm. of mercury when it occupies a volume of 22,400 ml. The analogous law applied to solutions would be: At a temperature of 0° the osmotic pressure of a solution would be 76 cm. of mercury (1 atm.) when it contains 1 gram-molecule of solute in 22,400 ml. of solution. From the table on page 185 one finds that a solution of cane sugar containing 1 gram-molecule in 34,200 ml. has, at 0°, an osmotic pressure of 0·65 atm. or 49·4 cm. of mercury. Therefore if 1 gram-molecule were dissolved 22,400 ml., the osmotic pressure would be $\frac{49{\cdot}4 \times 34200}{22400} = 75{\cdot}4$ cm., a number in sufficiently close agreement with the theoretical value 76 cm.

Determination of Molecular Weights.—According to the laws of van't Hoff for dilute solutions, the osmotic pressure depends on the *molar* concentration, or the number of gram-molecules of solute in a litre of the solution, and is represented by the expression $P = \frac{nRT}{V}$, where n is the number of gram-molecules of solute in volume V of solution. *Equimolecular solutions of all substances, therefore, have the same osmotic pressure.*[1] The osmotic pressure, clearly, is a colligative property, and from determinations of the osmotic pressure of a solution of known concentration one can calculate the molecular weight of a substance in solution.

Thus a solution of cane sugar containing 10·0 g. in 1 litre or 224 g. in 22,400 ml. was found to have, at 0°, an osmotic pressure of 49·4 cm. of mercury. How many grams of cane sugar would have to be dissolved in 22,400 ml. in order to give a pressure of 76 cm. ? This is given by

$$\frac{224 \times 76}{49{\cdot}4} = 345 \text{ g.}$$

The molecular weight, therefore, is approximately 345. The correct value is 342.

The molecular weight may, of course, also be calculated by means of the expression $P = \frac{nRT}{V} = \frac{w}{m} \cdot \frac{RT}{V}$, where w is the weight in grams of the solute in the volume V of solution and m is its molecular weight. If P is expressed in atmospheres and V in litres, R will have the value 0·0821. Thus from the previous example we have

$$m = \frac{w \cdot RT}{PV} = \frac{10 \times 0{\cdot}0821 \times 273}{0{\cdot}65 \times 1} = 345.$$

[1] This law, however, is not valid in the case of electrolytes. The behaviour of these will be discussed later.

Owing to manipulative difficulties and to the difficulty of obtaining truly semipermeable membranes, measurements of osmotic pressure are not a generally practicable means of determining molecular weight values, although the method is used for determining the molecular weight of high polymer molecules.

The Osmotic Pressure of Concentrated Solutions.—Although the earlier experiments of Pfeffer were in harmony with the theoretical laws deduced by van't Hoff for dilute solutions, they were too few in number and insufficient in accuracy to yield a satisfactory control of the deductive theory, or to define the limits of concentration within which such theory could claim validity. During the earlier part of the present century, however, direct measurements of the osmotic pressure of solutions over a wide range of concentration were carried out with great care and with a high degree of accuracy by various workers, more especially by H. N. Morse, J. C. W. Frazer, and their collaborators in America, and by the Earl of Berkeley and E. G. J. Hartley in England.

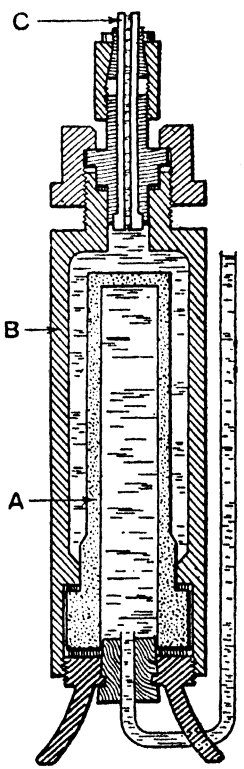


FIG. 67.

Morse and his collaborators employed essentially the method of Pfeffer, but they very greatly improved both the apparatus and the method of working. For the highest pressures the apparatus was given the form shown in Fig. 67. The semipermeable membrane was deposited on the outside of the porous pot A, which was firmly clamped inside a bronze cylinder B, into which, also, the manometer tube C was securely fixed. The solution was placed outside the porous pot, in the bronze cylinder, and the pot was kept full of water. Although a glass manometer could be used for pressures up to 100 atm., higher pressures were measured by means of an electrical resistance gauge based on the principle that the resistance of certain conductors

to an electric current increases with pressure in a nearly linear manner.

The method employed by Lord Berkeley and E. G. J. Hartley, however, is essentially different from that of Morse. Instead of measuring the pressure developed in a cell by the passage inwards of the solvent, Lord Berkeley and E. G. J. Hartley subjected the solution, separated from the solvent by a semipermeable membrane, to a gradually increasing pressure, until the solvent, which at first flows into the

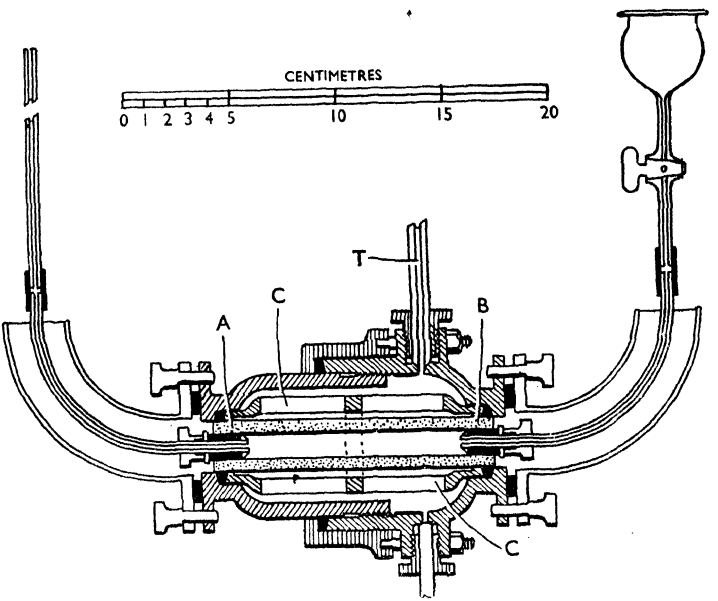


FIG. 68.

solution, reverses its direction and is squeezed out. The turning-point at which the pressure on the solution is just sufficient to prevent the inflow of solvent is taken as the equivalent of the osmotic pressure of the solution.

The apparatus is represented in section in Fig. 68. The porcelain tube AB, on the outside of which the semipermeable membrane is deposited, is firmly fixed in a gun-metal cage CC, which contains the solution. The tube T connects the solution with a pressure pump and manometer. The inside of the tube AB is filled with water and is connected with an open gauge tube on the left by which the direction of flow of water through the semipermeable membrane is indicated.

In the tables below are given the values of the osmotic pressure of cane-sugar solutions at 20° and at 0°, determined by Morse and his collaborators and by Lord Berkeley and E. G. J. Hartley respectively.

In the top table the numbers in the first column give

OSMOTIC PRESSURE OF SOLUTIONS OF CANE SUGAR AT 20°

Weight Normal Concentration.	Volume Normal Concentration.	Osmotic Pressure Observed. (Atmospheres.)	Osmotic Pressure in Atmospheres, 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
0·4	0·369	10·14	8·82	9·56
0·6	0·533	15·39	12·72	14·34
0·8	0·684	20·91	16·36	19·12
1·0	0·835	26·64	19·73	23·90

the number of gram-molecules of solute dissolved in 1000 g. of solvent, and the values given in the last column are calculated on the assumption that the osmotic pressure is equal to the pressure which the solute would exercise if it existed as a gas in the volume occupied by the *solvent* at 4°, not by the solution as according to the van't Hoff theory.

OSMOTIC PRESSURE OF SOLUTIONS OF CANE SUGAR AT 0°

(Lord Berkeley and E. G. J. Hartley)

Volume Concentration (Grams of Sugar in 1 Litre of Solution).	Osmotic Pressure in Atmospheres	
	Observed.	Calculated according to van't Hoff.
32·6	2·23	2·13
90·1	6·85	6·2
176·8	14·21	12·0
256·7	21·87	18·0
540·6	67·74	40·5
659·6	100·13	46·0
751·4	134·84	52·8

Besides the high pressure osmometers there is a low pressure type specially designed for measuring the molecular weights of high polymeric substances (see Chap. XIX) where the value may rise to one million or even more. Here there are two difficulties to be overcome. The osmotic pressures

are extremely small, *e.g.*, of the order of 1 mm. of mercury; diffusion of dissolved molecules is very slow. A general design is shown in Fig. 69. Here the membrane is clamped

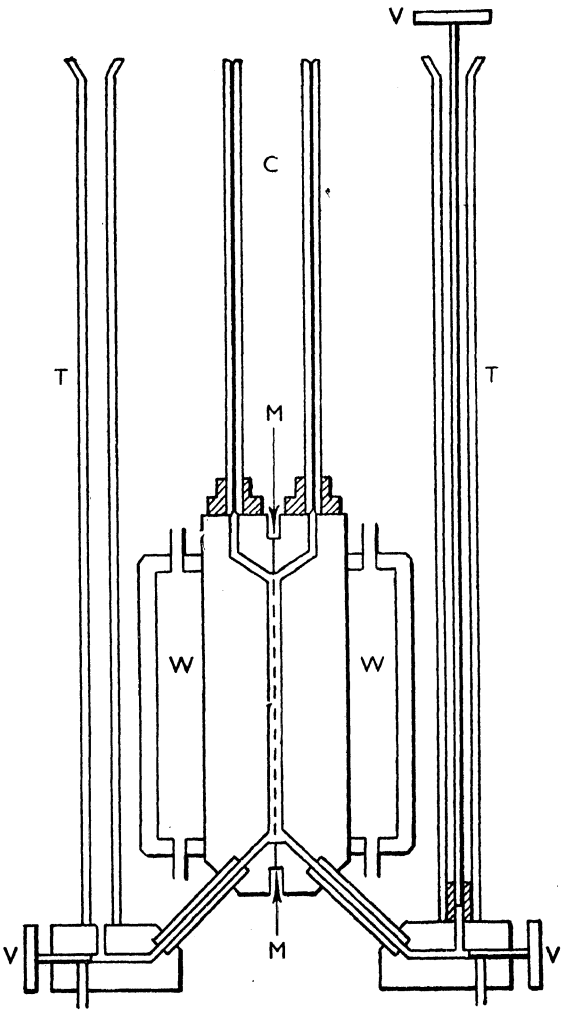


FIG. 69.

between two metal blocks, each of which is suitably grooved. The blocks carry glass capillary tubes to enable the pressure to be observed. Also connected to the blocks is a system of

valves so that the osmometer may be filled with liquid without introducing air bubbles. For organic solvents it is customary to use diaphragms of cellulose, suitably swollen and prepared, so that the solvent diffuses through rapidly but the high molecular weight substance is prevented from passing through. The action of such membranes does not appear to be selective, for the more highly swollen the cellulose the more readily the solute passes through. In fact the molecular weight limit lies around 10,000. With smaller molecules appreciable penetration occurs. This kind of construction allows of a high membrane area-volume ratio so that equilibrium is attained in a reasonable time. Even so this may take as long as twenty-four hours. A dynamic method has thus been employed. From preliminary experiments the approximate value of the osmotic pressure is known. By means of the valve system the levels of the meniscus in the capillaries are adjusted first above and second below the equilibrium value. At each setting the *velocity* of movement of the meniscus is measured, and the results plotted as shown in Fig. 70. The mean position of the points at given time intervals is then plotted as a function of time and it will be seen that this time approaches the equilibrium value very soon. The time required for obtaining results is thus cut down. In addition the diffusion of solute through the membrane is kept at a minimum.

It has been pointed out that the van't Hoff laws of solutions were deduced only for very dilute solutions, and the numbers given in the preceding tables show that these laws have a very restricted validity. Even when the concentration is not greater than about deci-molar, the calculated value of the osmotic pressure is appreciably lower than the observed value. As the concentration increases, the divergence between the observed and calculated values becomes increasingly greater.

With regard to the validity of the Gay-Lussac-van't Hoff law, it is found in the case of sucrose solutions, that while the osmotic pressure increases proportionally with the absolute temperature up to about 25°, this simple proportionality is no longer found at temperatures above 25°.

General Theory of Ideal Solutions.—Since the van't Hoff theory of solutions was put forward as applying only to dilute solutions, and has been found to have only a very restricted validity, many attempts to formulate a more

general theory of solutions have been made. Owing to the analogy between dilute solutions and gases, it was thought by many that the osmotic pressure is, like the gas pressure, kinetic in its origin and due to the bombardment of the semipermeable membrane by the solute molecules. It was

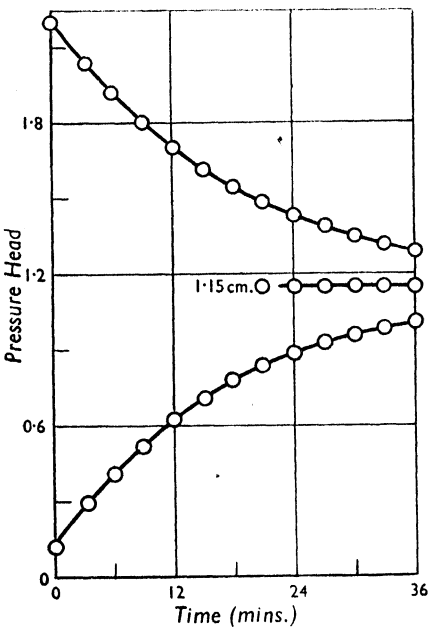


FIG. 70.

sought, therefore, to correct the simple van't Hoff equation very much as van der Waals corrected the simple gas equation. But this must be regarded as a very illogical method of procedure. The osmotic pressure, it seems certain, is not a bombardment pressure but is due to the inflow of solvent into the solution, and this inflow takes place because there is a difference between the " activity " of the solvent in the pure state and in the solution. This difference of activity can be measured not only by the osmotic pressure but also by the diminution of the vapour pressure (see later), and the laws of concentrated solutions (variation of activity with temperature and concentration) can be deduced independently of the concept of osmotic pressure. So far as a general theory of solutions is concerned, therefore, the concept

of osmotic pressure is now largely of historic interest, and any importance which it may possess is due mainly to the fact that it is a concept, the meaning of which can be readily grasped. The quantitative laws of solutions, however, deduced thermodynamically, *i.e.*, on the basis of energy changes, are quite independent of the phenomena of osmosis altogether.

In his deduction of a theory of solutions, van't Hoff introduced the simplifying assumption that the solutions were very dilute. One may, however, while retaining the concept of osmotic pressure, introduce the assumption that the solutions are *ideal.* By ideal solutions one understands solutions which are formed when the constituents have normal molecular weight [1] and *mix without any change of the total volume and without any heat effect or chemical interaction.*

Introducing the assumption that the solution is ideal and the further, only approximately valid, assumption that the vapour of the solvent follows the laws of a perfect gas, one can deduce the following general expression for the osmotic pressure of a solution [2]:—

$$P = \frac{RT}{V_0}[-\log_e(1-x)].$$

In this expression, V_0 is the molecular volume of the solvent under normal pressure and x is the *molar fraction* of the solute, or the ratio n_2/n_1+n_2. where n_2 and n_1 are the number of gram-molecules of solute and of solvent respectively in the solution.[3] In deriving the above expression, the compressibility of the solution was neglected.

On expanding the logarithmic expression one obtains—

$$P = \frac{RT}{V_0}(x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 \ldots),$$

or

$$P = \frac{RT}{V_0}\left[\left(\frac{n_2}{n_1+n_2}\right) + \tfrac{1}{2}\left(\frac{n_2}{n_1+n_2}\right)^2 + \ldots\right].$$

This expression has been found to hold fairly closely in the case of mixtures of hydrocarbons and of other closely

[1] That is, the same molecular weight as in the state of vapour.

[2] See also E. A. Guggenheim, *Modern Thermodynamics by the Methods of Willard Gibbs* (Methuen).

[3] It should be noted that the value of n_1 is given by $\frac{W}{M}$, where W is the weight of solvent in grams and M is the molecular weight of the solvent *in the state of vapour.*

related and non-associated liquids, the properties of which approximate to those of ideal solutions. Marked discrepancies, however, are found between the values of the osmotic pressure of aqueous sucrose solutions calculated by means of the above expression and the observed values; and these discrepancies are not surprising, for the solutions of sucrose possess none of the properties of ideal solutions. From the discrepancies, indeed, one may infer that chemical action, *e.g.*, formation of hydrates, takes place between the solvent and the solute, or that other changes occur which betray themselves in heat effects and alteration of volume.

A comparison of the above equation with that of van't Hoff will show clearly the nature of the simplifying assumptions introduced, and will explain the inadequacy of the van't Hoff equation when applied to concentrated solutions.

When one assumes that the solution is very dilute, then the expression $\frac{n_2}{n_1+n_2}$ becomes practically equal to $\frac{n_2}{n_1}$, n_2 being negligible in comparison with n_1. In this case, moreover, the fraction $\frac{n_2}{n_1+n_2}$ becomes small, and consequently $\left(\frac{n_2}{n_1+n_2}\right)^2$ and higher powers of the fraction become negligible. For very dilute solutions, therefore, the expression given above reduces to $P=\frac{RT}{V_0}\cdot\frac{n_2}{n_1}$. But n_1V_0 represents the volume of *water* in the solution,[1] and this, in the case of dilute solutions, can be put equal to the volume of the solution itself. For the limiting case of very dilute solutions, therefore, one obtains the van't Hoff equation $P=\frac{n_2RT}{V}$, where V is the volume of the solution.

Action of the Semipermeable Membrane.—Various views have been expressed regarding the mode of action of a semipermeable membrane. According to the oldest view, put forward by Moritz Traube, a semipermeable membrane acts as an "atomic sieve" allowing molecules of certain dimensions to pass through but preventing the passage of larger molecules. Except with reference to high polymer

[1] This affords some explanation, at least, of the somewhat closer agreement between the observed osmotic pressures and the values calculated by Morse on page 190.

solutions, however, this view may be said to have passed completely out of favour.

According to another view, the membrane is regarded as consisting of fine capillary tubes, the pore diameter of which is so small that the whole capillary is under the influence of surface forces. The adsorption effects shown by colloidal membranes are selective in nature, and a copper ferrocyanide film takes up water rather than sucrose from aqueous solutions of the latter. One thus finds an explanation of the permeability of the membrane to water but not to sugar.[1]

The explanation of semipermeability which is most widely accepted, however, is that of selective or preferential solubility. The membrane is permeable to those substances which dissolve in it and is impermeable to those substances which are insoluble in it. This explanation was first suggested in 1855 by Michel Lhermite (1817-57).

It is most probable that the different views of the action of semipermeable membranes are not mutually exclusive. Each explanation may be correct within limits. In some cases the membrane may act through capillarity and by selective adsorption or the formation of slightly stable compounds ; in other cases the explanation may best be found in selective solubility.

[1] This explanation is favoured by S. Fordham and J. T. Tyson who have shown, by electron diffraction experiments, that membranes of copper ferrocyanide are crystalline (*J. Chem. Soc.*, **1937**, 483).

CHAPTER IX

DILUTE SOLUTIONS AND THEIR COLLIGATIVE PROPERTIES. LOWERING OF THE VAPOUR PRESSURE

It has already been pointed out that the osmotic pressure of a solution is a measure of the difference of the free energy or activity of the solvent in the pure state and in the solution; and the osmotic work PV represents the energy required to separate, isothermally and reversibly, a volume V of solvent from a dilute solution having the osmotic pressure P by means of a perfectly semipermeable membrane. The same volume of solvent can, however, be separated from the solution in other ways, *e.g.*, by evaporation; and in this case the free surface layer of the solution acts as a semipermeable membrane when one is dealing with a non-volatile solute. There must, therefore, be a definite relationship between the osmotic pressure and the vapour pressure of a solution, so that if one determines the vapour pressure of a solution relatively to that of the pure solvent one can calculate the osmotic pressure of the solution. It follows from this that *the lowering of the vapour pressure is a colligative property* by means of which the molecular weight of a solute can be determined. This deduction, which is supported, as we shall learn, by experimental evidence, is of very great importance, for it makes it possible to study the quantitative properties of solutions in the case of a great variety of solvents and over a wide range of concentration and temperature, by means of measurements which can be carried out with greater accuracy than can the direct measurements of osmotic pressure.

The Vapour Pressure of Solutions.—That the vapour pressure of a liquid is always lowered by the solution in it of another substance has been known for a very long time; and in the case of non-volatile solutes, the investigations of

Lambert von Babo in 1847, and Adolf Wüllner (1835-1908) in 1856, indicated that *the lowering of the vapour pressure is proportional to the amount of dissolved substance in the solution* (Wüllner's law); and that, *for one and the same solution, the lowering of the vapour pressure at each temperature is the same fraction of the vapour pressure of the pure liquid* (Babo's law).[1] Algebraically these laws can be expressed in the form

$$\frac{p-p'}{p}=k \,.\, w,$$

where p and p' are the vapour pressures of the solvent and solution respectively, and w is the weight of solute in grams.

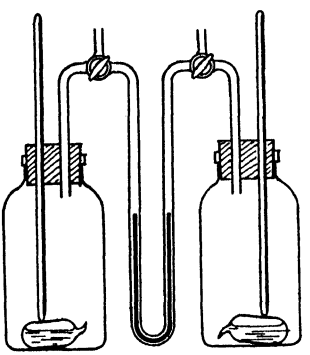


FIG. 71.

That a solution has a lower vapour pressure than the pure solvent can be demonstrated by a simple experiment. Ether and a saturated solution of salicylic acid in ether are sealed up in two thin-walled glass bulbs which are placed in small bottles, closed by rubber stoppers (Fig. 71). Through these stoppers pass a brass rod and the end of a U-tube containing coloured water. By opening the three-way taps to the air, it is ensured that the pressure in the two bottles is the same and that the water stands at the same level in the two limbs of the U-tube. The taps are then closed, and the bulbs are broken by means of the brass rods. On turning the taps so as to make connection between the bottles and the U-tube, a difference in the level of the water in the two limbs of the U-tube will indicate the difference of vapour pressure of the solvent and the solution.

The earliest investigations of the lowering of vapour pressure were carried out with aqueous solutions of salts (electrolytes), and complications, due, as will be explained later, to ionisation, were introduced, so that clear-cut laws could not be established. In 1886, however, François Marie Raoult (1832-1901), Professor of Chemistry in the University of Grenoble, by investigating the properties of

[1] This law will hold only when the heat of dilution is zero.

solutions of non-electrolytes and also by employing solvents other than water, was able to establish general laws of a simple character.[1] Expressing concentration not in terms of grams but of *gram-molecules* of solute, Raoult found that *the relative lowering of vapour pressure of a given solvent is proportional to the molecular concentration of the solute*, or

$$\frac{p-p'}{p}=K\,.\,\frac{w}{m},$$

where w is the weight in grams of solute in a given weight of solvent and m is its molecular weight. The following values, obtained with solutions formed by dissolving w grams of solute in 100 g. of ether, will illustrate the law :—

Solute.	m.	$K=\frac{p-p'}{p}\,.\,\frac{m}{w}$.
Cyanamide . .	42·0	0·74
Aniline . . .	93·0	0·71
Benzoic acid . .	122·0	0·71
Trichloracetic acid .	163·5	0·71

The value of K in the above expression represents the relative lowering of the vapour pressure produced when 1 gram-molecule of solute is dissolved in 100 g. of ether. For each solvent, K has a characteristic value. It follows from the above law that, for any given solvent, *the relative lowering of the vapour pressure produced by equimolecular quantities of different solutes is the same.* The relative lowering of the vapour pressure is thus a colligative property, and can be employed for the determination of molecular weights.

A second and more general law was also established by Raoult, namely : *The relative lowering of the vapour pressure is equal to the ratio of the number of gram-molecules of solute to the total number of gram-molecules in the solution*, i.e., *is equal to the molar fraction of the solute.* Thus we have

$$\frac{p-p'}{p}=\frac{n_2}{n_1+n_2}=N_2,$$

or

$$\frac{p-p'}{p}=\frac{wM}{wM+Wm},$$

[1] *Compt. rend.*, 1886, **103**, 1125 *et seq.*; *Z. physikal. Chem.*, 1888, **2**, 353; *Annales chim. phys.*, 1888 (6), **15**, 375; 1890, **20**, 297.

where w and W are the weights of solute and solvent respectively, m is the molecular weight of the solute in the solution, and M is the molecular weight of the solvent *in the state of vapour*. N_2 is the molar fraction of the solute. For very dilute solutions, when n_2 is negligible compared with n_1, the above expressions reduce to

$$\frac{p-p'}{p}=\frac{n_2}{n_1}=\frac{wM}{Wm}.$$

By means of this expression the molecular weight of a substance can be calculated.

Thus, on dissolving 1 g. of cyanamide (M.W. = 42) in 100 g. of ether (M.W. = 74), the relative lowering of the vapour pressure was found to be 0·0176. Hence, $m=\frac{1\times 74}{0{\cdot}0176\times 100}=42$.

Similarly, when 108·24 g. of mannitol (M.W. = 182·1) were dissolved in 1000 g. of water at 20°, the lowering of the vapour pressure $(p-p')$ was equal to 0·1860 mm. of mercury.[1] Since, at 20°, $p=17{\cdot}54$ mm., $\frac{p-p'}{p}=\frac{0{\cdot}1860}{17{\cdot}54}=0{\cdot}01060$, and therefore $m=\frac{108{\cdot}24\times 18}{0{\cdot}01060\times 1000}=183{\cdot}7$.

Ideal Solutions.—In the case of an ideal solution of two components it can be shown that, if it is assumed that the vapours of the constituents follow Boyle's law, the vapour pressure of each constituent is, at constant temperature, proportional to the molar fraction of that constituent. Consequently, in the case of a solution of a non-volatile solute, the relative vapour pressure of the solvent will be equal to the molar fraction of the *solvent* in the solution; that is, $\frac{p'}{p}=\frac{n_1}{n_1+n_2}$, or $p'=p\,.\,N_1$, where N_1 is the molar fraction of the solvent. From this, Raoult's law can be deduced, for we have $1-\frac{p'}{p}=1-\frac{n_1}{n_1+n_2}$, or $\frac{p-p'}{p}=\frac{n_2}{n_1+n_2}$.

This law will be valid, therefore, only in the case of an ideal solution, or in the case of very dilute solutions, the behaviour of which approaches to that of an ideal solution. *The law may, in fact, be taken as giving a definition of an ideal solution.*[2]

The Relation between Vapour Pressure and Osmotic Pressure.—The simplified Raoult law for dilute solutions,

[1] Frazer, Lovelace, and Rogers, *J. Amer. Chem. Soc.*, 1920, **42**, 1801.

[2] For a discussion of the theoretical basis of Raoult's law, see Guggenheim, *Trans. Faraday Soc.*, 1937, **33**, 151.

$\frac{p-p'}{p}=\frac{n_2}{n_1}$, can be derived from the van't Hoff law of osmotic pressure in the following manner :—

A solution, we shall suppose, is placed in the osmometer A, which is closed by a semipermeable membrane, and is immersed in pure water (Fig. 72). The solution rises to such a height h in the tube that the hydrostatic pressure is equal to the osmotic pressure. The whole apparatus is supposed to be covered by a bell-jar B, from which the air has been removed, so that only vapour of the solvent is present. It is assumed also that constant temperature is maintained. When equilibrium has been established the vapour pressure of the solution p' at its surface x must be equal to the pressure of the water vapour in the surrounding space at the same level, otherwise processes of distillation or condensation would occur. These would produce concentration or dilution of the solution and so lead to osmosis through the semipermeable membrane. Since equilibrium is assumed, however, this cannot take place.

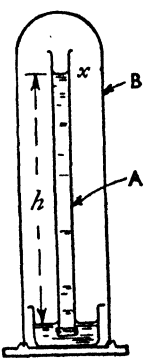


FIG. 72.

The pressure of the water vapour at x, which is equal to the vapour pressure of the solution p', must be less than the vapour pressure p at the surface of the solvent by the pressure of the column of vapour of height h. If, therefore, d is the density or weight in grams per millilitre of the vapour, the pressure of the column of vapour will be $h \cdot d$, and, consequently, $p-p'=h \cdot d$.

If it be assumed that the vapour obeys the gas laws, the volume v, occupied by 1 gram-molecule of the vapour under a pressure p and at the absolute temperature T, will be $v=\frac{RT}{p}$, and the density of the vapour will therefore be

$$d=\frac{M}{v}=\frac{M \cdot p}{RT},$$

where M is the molecular weight of the solvent in the state of vapour. It has, however, been found that $d=\frac{p-p'}{h}$, and therefore $p-p'=h \cdot \frac{M \cdot p}{RT}$, or $\frac{p-p'}{p}=h \cdot \frac{M}{RT}$.

Since the osmotic pressure of the solution is equal to the hydrostatic pressure of the column of solution of height h, we have $P = h \cdot s$, where s is the density of the solution ; or, since the solution is supposed to be very dilute, s may also be taken as the density of the pure solvent. Substituting the value of $h = \frac{P}{s}$ in the preceding equation, one obtains the relation

$$\frac{p - p'}{p} = \frac{P \cdot M}{s \cdot RT},$$

or

$$P = \frac{p - p'}{p} \cdot \frac{s \cdot RT}{M}.$$

Since, in the above deduction, the volume has been expressed in millilitres, the value of R expressed in millilitre-atmospheres will be $0{\cdot}0821 \times 1000$ (p. 46).

The following example will illustrate the application of the above relation.[1] At 20° the lowering of the vapour pressure in the case of a solution containing 0·0984 gram-molecule of mannitol in 1000 g. of water was found to be 0·0307 mm., the vapour pressure of pure water being 17·539 mm. The density of water at 20° is 0·9982. The osmotic pressure of this solution is therefore calculated to be $P = \frac{0{\cdot}0307}{17{\cdot}54} \cdot \frac{0{\cdot}0821 \times 1000 \times 293 \times 0{\cdot}9982}{18} = 2{\cdot}33$ atmospheres.

The osmotic pressure of a solution containing 0·1 gram-molecule in 1000 g. of water was found by direct measurement to be 2·395 atmospheres.

For a given solvent at constant temperature, the quantity $\frac{sRT}{M}$ is constant. Consequently, the relative lowering of the vapour pressure is proportional to the osmotic pressure, and is independent of the nature of the solute.[2]

Experimental Determination of the Lowering of the Vapour Pressure.—In recent years the most accurate measurements of the lowering of the vapour pressure of a solvent have been made either by a static or by an air-saturation method. The former method, which consists in measuring directly, by means of a suitable pressure gauge, the difference of vapour pressure of pure solvent and solution, has been highly perfected by the German physicist, Conrad Dieterici,[3] by J. C. W. Frazer and B. F. Lovelace,[4] of Johns Hopkins University, and by others. The air-saturation

[1] Frazer, Lovelace, and Rogers, *J. Amer. Chem. Soc.*, 1920, **42**, 1801.

[2] For a fuller discussion of the relation between osmotic pressure and the lowering of the vapour pressure, see Findlay, *Osmotic Pressure* (Longmans).

[3] *Ann. Physik*, 1893, **50**, 47.

[4] *J. Amer. Chem. Soc.*, 1914, **36**, 2439. A static method has also been developed by A. W. C. Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1615.

method, first suggested by Wilhelm Ostwald (1853-1932), Professor of Physical Chemistry, University of Leipzig, and worked out by James Walker,[1] has been perfected by Lord Berkeley and E. G. J. Hartley,[2] by E. W. Washburn and E. W. Heuse,[3] and by others, and has found application, to a greater extent perhaps than any other method, for the accurate determination of the lowering of the vapour pressure of a solvent by a non-volatile solute. In this method air is passed over or through first the solution and then the pure solvent at such a rate that it becomes saturated with the vapour. When the air is passed over or through the solution it takes up vapour in an amount which is proportional to the vapour pressure of the solution at the temperature of the experiment; and on then being passed through the solvent it takes up a further amount of vapour which is proportional to the *difference* of the vapour pressures of solvent and solution. Thus, if the vessels containing the solvent and the solution respectively are weighed, one obtains the relation

$$\frac{\text{Loss in weight of solution}}{\text{Loss in weight of solvent}} = \frac{p'}{p-p'}.$$

In accurate work a number of precautions must be taken and corrections introduced which cannot, however, be discussed here.

As in the case of a pure liquid, the vapour pressure p' of a solution can also be determined by the gas-saturation method by applying Dalton's law of partial pressures (p. 46). This method has been successfully employed by J. N. Pearce and R. D. Snow to determine the vapour pressure of solutions of mannitol.[4]

Determination of Molecular Weights.—The method may be applied in a simple form for the determination of the approximate molecular weight of a non-volatile substance in solution. Thus, we have

$$\frac{p'}{p-p'} = \frac{p}{p-p'} - 1 = \frac{n_1+n_2}{n_2} - 1 = \frac{n_1}{n_2},$$

where n_2 and n_1 are the number of gram-molecules of solute and solvent respectively. Since $n_2 = \frac{w}{m}$ and $n_1 = \frac{W}{M}$, where w and W are the weights, and m and M are the molecular

[1] *Z. physikal. Chem.*, 1888, **2**, 602.
[2] *Proc. Roy. Soc.*, 1906, A, **77**, 156.
[3] *J. Amer. Chem. Soc.*, 1915, **37**, 309.
[4] *J. Physical Chem.*, 1927, **31**, 231.

weights of the solute and solvent respectively, one obtains the expression

$$m = \frac{wM}{W} \times \frac{\text{loss in weight of solution}}{\text{loss in weight of solvent}}.$$

When working with aqueous solutions, the moisture present in the air after passage through the pure solvent may be absorbed in a calcium chloride drying tube and its weight determined. This will be proportional to the vapour pressure of the solvent. One then has the relation

$$\frac{\text{Loss in weight of solvent}}{\text{Gain in weight of drying tube}} = \frac{p - p'}{p} = \frac{n_2}{n_1} = \frac{wM}{Wm},$$

or

$$m = \frac{w \,.\, M}{W} \times \frac{\text{gain in weight of drying tube}}{\text{loss in weight of solvent}}.$$

Dew-point Method.—The lowering of the vapour pressure of water by a non-volatile solute may also be determined by the dew-point method.[1]

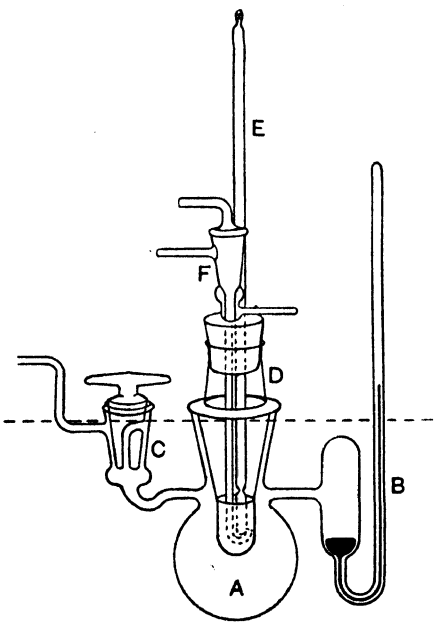


FIG. 73.

The tube D (Fig. 73), ground to fit into the neck of the flask A, is formed, at its lower end, of thin, soft glass well silvered on its outer surface. Through a stopper in the tube D there pass a thermometer E and the narrow tube F. The solution under investigation is placed in the flask A, which is then partially exhausted; and the apparatus is immersed in a constant temperature bath. By drawing a current of air through a quantity of ether contained in tube D, evaporation of the ether and a lowering of

[1] J. R. I. Hepburn, *Proc. Physical Soc.*, 1928, **40**, 249; *J. Chem. Soc.*, 1932, 550.

temperature are produced. The temperature at which dew appears on the silvered tube is noted. Since the vapour is in equilibrium with pure water at the dew-point temperature, and in equilibrium with the solution at the temperature of the bath, the vapour pressure of water at the dew-point, which can be obtained from tables, is equal to the vapour pressure of the solution at the temperature of the bath.

Elevation of the Boiling-point.—Since the vapour pressure of a solution is lower than the vapour pressure of the pure solvent, it follows that the boiling-point of the solution, or the temperature at which its vapour pressure is equal to the atmospheric pressure, must be higher than that of the solvent. There will therefore be a certain relation between the lowering of the vapour pressure and the elevation of the boiling-point which can be deduced in the following manner :—

In Fig. 74 the curves *cf* and *be* represent the vapour pressure curves of the pure solvent and of the solution respectively, and *ce* is a line of constant pressure equal, say, to the atmospheric pressure. The boiling-point of the solution is therefore represented by point *d*, and that of the solvent by *a*. Since we are concerned here only with dilute solutions and with small elevations of the boiling-point, the vapour-pressure curves may be assumed to be straight lines.

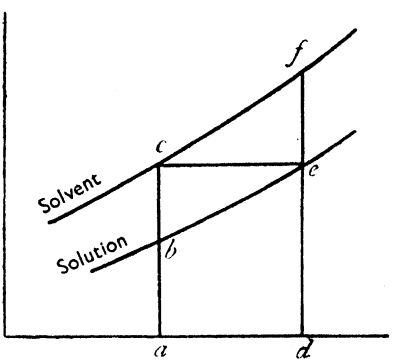


FIG. 74

In Fig. 74, *ac* represents the vapour pressure (p) of the solvent at its boiling-point and *ab* that of the solution (p') at the same temperature. Therefore, $\frac{bc}{ac}=\frac{p-p'}{p}$. Further, the ratio $\frac{bc}{ce}$ represents the relation between the lowering of the vapour pressure and the elevation of the boiling-point, and if this is known it is clear that the molecular weight of

a solute can be calculated from the elevation of the boiling-point. Thus,

$$\frac{p-p'}{p}=\frac{bc}{p}=\frac{bc}{ce}\times\frac{ce}{p}=x\times\frac{ce}{p},$$

where x is put equal to the ratio $\frac{bc}{ce}$. It, has, however, already been shown (p. 200) that $m=\frac{w\,.\,M}{W}\,.\,\frac{p}{p-p'}$, and therefore $m=\frac{w\,.\,M}{W}\,.\,\frac{p}{x\,.\,ce}$. For a given solvent, x is a constant; and since M and p are also constant, it follows that

$$m=K\,.\,\frac{w}{e\,.\,W}$$

where e, the elevation of the boiling-point, is put in place of ce. In this expression K, the molecular elevation of the boiling-point, represents the elevation of the boiling-point which would, theoretically, be produced if 1 gram-molecule of non-volatile solute $\left(\frac{m}{w}=1\right)$ were dissolved in 1 g. of solvent ($W=1$). The value of K varies from solvent to solvent, as shown in the following table [1]:—

Solvent.	Boiling-point (760 mm.).	K	Heat of Vaporisation (calories).
Acetone . .	56·2°	1720	124·5
Benzene . .	80·2°	2570	94·4
Chloroform .	61·2°	3860	59·0
Ethyl alcohol .	78·5°	1150	204·4
Ethyl ether .	34·6°	2110	83·9
Water . .	100·0°	513	539·5

It is clear from the above discussion that, for a given solvent, the elevation of the boiling-point is proportional to the molecular concentration of the solute, and that *equi-molecular solutions have the same boiling-point.*

Relation between the Molecular Elevation of the Boiling-point and the Latent Heat of Vaporisation. — When the lowering of the vapour pressure and the consequent elevation

[1] Raoult defined the molecular elevation constant as the elevation obtained on dissolving 1 gram-molecule of solute in 100 g. of solvent. Other authors define it with reference to 1000 g. of solvent. The constants so defined are therefore 100 or 1000 times smaller than those in the table.

of the boiling-point are small, the vapour-pressure curves for solvent and solution may be regarded as being parallel straight lines, and *bc* will therefore be equal to *ef* (Fig. 74). Hence,

$$x=\frac{bc}{ce}=\frac{ef}{ce}=\frac{\text{increase in vapour pressure}}{\text{rise of temperature}}=\frac{\Delta p}{\Delta t}.$$

From this, one obtains the relation

$$K=\frac{M\,.\,p}{x}=\frac{M\,.\,p}{dp/dt}.$$

It has, however, already been pointed out that $\frac{dp}{dt}=\frac{l}{T(v_2-v_1)}$, where l is the latent heat of vaporisation, v_2 is the specific volume of the vapour, and v_1 the specific volume of the liquid; and if one neglects the volume of the liquid as small compared with that of the vapour, then $\frac{dp}{dt}=\frac{l}{T\,.\,v}$, where v is the specific volume of the vapour. Assuming that the vapour obeys the gas laws, one obtains the relations

$$\frac{M\,.\,p}{x}=\frac{M\,.\,p}{dp/dt}=\frac{M\,.\,p\,.\,v\,.\,T}{l}.$$

But, $M\,.\,p\,.\,v=RT$, and therefore

$$\frac{M\,.\,p}{x}=\frac{R\,.\,T^2}{l}=K,$$

where T is the absolute temperature of the boiling-point and R has the value of 1·987 calories per degree.

On calculating, by means of this relationship, the molecular elevation of the boiling-point of water, one obtains

$$K=\frac{1{\cdot}987\times 373{\cdot}2^2}{539{\cdot}5}=513{\cdot}0.$$

Experimental Determination of the Elevation of the Boiling-point.—Various forms of apparatus have been devised for the determination, by the boiling-point or ebullioscopic method, of the molecular weight of substances in solution, the method being applicable, however, only if the solute is not appreciably volatile at the temperature of the boiling solvent.

The older forms of apparatus introduced by Ernst

Beckmann (1853-1923), Professor of Applied Chemistry in the University of Leipzig, which were designed for heating by gas, have been largely superseded by apparatus designed for electrical heating. These apparatus, first suggested by S. L. Bigelow,[1] of the University of Michigan, possess a number of advantages and permit of results being obtained more rapidly and with greater accuracy. One form of the apparatus is shown in Fig. 75.

The boiling-point tube A is fitted with a cork through which pass a Beckmann thermometer T and two stout copper wires WW, connecting with a spiral of platinum wire. The platinum spiral should be placed near the bottom of the boiling-point tube, which, when in use, is supported by means of a cork in a silvered Dewar vacuum vessel V. A condenser C inserted in the side-tube B serves to condense the vapour of the boiling solvent. A weighed amount of solvent placed in the tube B is raised to its boiling-point by the passage of an electric current through the heating spiral, and when the temperature has become constant, the thermometer reading is noted. This represents the boiling-point of the solvent. A weighed amount of solute is then introduced into the solvent, the heating current again passed and the boiling-point of the solution determined. Further quantities of the substance may be introduced and the boiling-point of the solution determined after each addition of solute. The molecular weight of the solute can then be calculated by means of the equation,

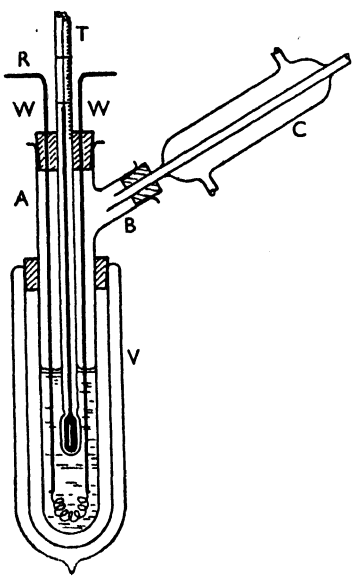


FIG. 75.

$$m = K \cdot \frac{w}{e \cdot W}.$$

[1] *Amer. Chem. J.*, 1899, **22**, 280.

An improved boiling-point apparatus was designed by the American chemist, F. G. Cottrell,[1] for the purpose of securing a more perfect equilibrium between the solution and the vapour, and of enabling the temperature of equilibrium to be accurately determined when both liquid and vapour are under the same external pressure. With this apparatus, which has been modified in various ways, fluctuations of temperature and errors of temperature determination due to superheating, etc., are avoided.

The apparatus (Fig. 76) consists of a boiling-tube A, into the neck of which fits the hollow stopper B. The walls of the neck are prolonged downwards so as to form a cylinder enclosing the bulb of the Beckmann thermometer[2] T, and the branches of the "pump" tube C. The cylinder serves as a jacket for the thermometer and prevents the liquid, flowing from the condenser D, coming into contact with the thermometer. The pump tube divides into two or three branches arranged symmetrically around the lower end of the thermometer.

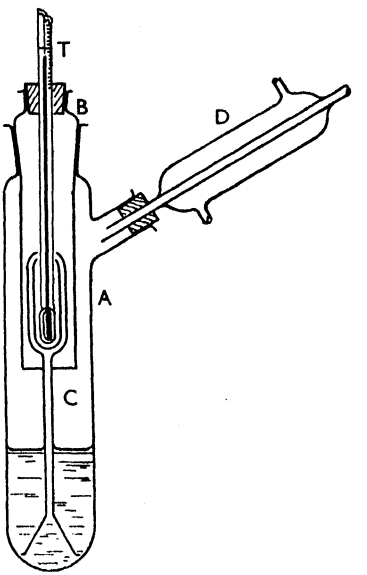


FIG. 76.

In using this apparatus, the solvent, in known amount, is caused to boil by means of a gas flame protected from draughts. When the liquid boils, the bubbles of vapour which form under the funnel rise up in the narrow tube, carrying with them liquid which is then projected against the stem of the thermometer. The bulb of the thermometer is in this way kept bathed in the boiling liquid which is pumped up by the vapour bubbles and which is in equilibrium with the vapour in the apparatus. By this means a constant temperature (boiling-point) is soon attained, and the temperature remains very steady. After determining the boiling-point of the pure solvent, a weighed amount of the solute is introduced and the boiling-point of the solution is then determined in the same way as for the solvent.

Sakurai-Landsberger Method.—According to the Sakurai-Landsberger method,[3] the solution is heated by means of the vapour of the boiling solvent, the amount of which is determined not by weight but by volume. This makes no

[1] *J. Amer. Chem. Soc.*, 1919, **41**, 721.

[2] A differential thermometer for use with this apparatus has been described by A. W. C. Menzies and S. L. Wright, jun. (*J. Amer. Chem. Soc.*, 1921, **43**, 2314).

[3] *J. Chem. Soc.*, 1892, **61**, 989; *Ber.*, 1898, **31**, 461.

difference in the expression for the calculation of the molecular weight, except that a different constant K' is employed, which is equal to the ordinary boiling-point constant divided by the density of the solvent at its boiling-point. The value of some of these constants is given in the following table :—

Solvent.	Boiling-point.	K'.	Solvent.	Boiling-point.	K'.
Acetone .	56·5°	2220	Chloroform	61·2°	2600
Alcohol .	78·3°	1560	Ether .	34·6°	3030
Benzene .	80·2°	3280	Water .	100·0°	540

The molecular weight of the solute is given by the expression $m = K' \cdot \frac{w}{e \cdot v}$, where v is the volume of the solution in millilitres.

Of the various forms of apparatus which have been devised for this method one of the most convenient for ordinary laboratory work is that due to H. N. McCoy.[1] This apparatus (Fig. 77) consists of a tube B, which serves both as a boiling-tube and as a vapour jacket. Inside this there passes the narrower tube A, which is graduated from the volume 10 ml. to the volume 35 ml., from the closed end of the tube. Sealed into the wall of A is the narrow tube *ab*, the lower (closed) end of which is perforated with a number of small holes. The graduated tube A is fitted with a cork carrying a Beckmann thermometer, and a side-tube connected it with a condenser C.

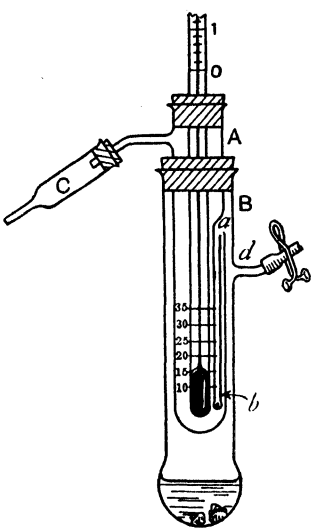


Fig. 77.

In carrying out a determination, pure solvent is placed in B and about 12 to 15 ml. of the solvent are also placed in the graduated tube A. When the solvent in B is boiled, vapour rises, heats the solvent in A, and then forces its way through the narrow tube *ab* into the liquid and so raises its temperature to the boiling point. This temperature is noted. The clip on the side tube *d* is now opened and the heating interrupted. A weighed amount of substance is introduced into the inner tube and the boiling-point of the solution determined in the manner described above. After opening the clip on *d* and interrupting the heating, the thermometer is carefully raised out of the solution and the volume of the solution noted. Further quantities of substance can be added to the solution and the boiling-point determined after each addition.

[1] *Amer. Chem. J.*, 1900, **23**, 353

Depression of the Freezing-point.—It has long been known that the freezing-point of a solution, or the temperature at which the solution is in equilibrium with the pure crystalline solvent, is lower than the freezing-point of the pure solvent; and, in 1788, the English physician, Sir Charles Blagden (1748-1820), found that the lowering of the freezing-point of the solvent is proportional to the amount of the dissolved substance. The same law was rediscovered by later investigators, but as most of the investigations were carried out with aqueous solutions of electrolytes, complications were met with. It was not till 1882, therefore, that Raoult,[1] who investigated the effect of organic non-electrolytes on the freezing-point of water and of other solvents, was able to establish the important law that *the depression of the freezing-point of a given solvent is proportional to the molecular concentration of the solute*, and that *equimolecular solutions, therefore, have the same freezing-point.* We thus obtain the relation

$$\Delta = K \cdot \frac{n}{W},$$

where Δ (delta) is the lowering of the freezing-point produced when n gram-molecules of solute are dissolved in W g. of solvent. K is a constant which depends only on the solvent and is equal to $\frac{RT^2}{l}$, where l is the latent heat of fusion of the crystalline solvent, and T the absolute temperature of the freezing-point. In the case of water, therefore, we have

$$K = \frac{1{\cdot}987 \times 273{\cdot}2^2}{79{\cdot}77} = 1859.$$

The above law, established experimentally and deduced on the basis of thermodynamics, *is valid only when the solvent crystallises pure from the solution.*

The freezing-point or cryoscopic constant K, it will be clear, represents the depression of the freezing-point which would, theoretically, be produced when 1 gram-molecule of solute is dissolved in 1 g. of solvent. It represents, therefore, the *molecular depression of the freezing-point.*[2]

[1] *Comptes rend.*, 1882, **94**, 1517.

[2] Owing to the fact that one cannot, in general, dissolve 1 gram-molecule of substance in 1 g. of solvent, it is not unusual to define the molecular depression as the depression produced when 1 gram-molecule of substance is dissolved in 100 or in 1000 g. of solvent.

The value of K for some of the most frequently used solvents is given in the table below :—

Solvent.	Freezing-point.	K.	Latent Heat of Fusion (cal.).
Acetic acid .	16·6°	3900	44·7
Benzene .	5·4°	5120	30·4
Water . .	0·0°	1858	79·8
Nitrobenzene .	5·72°	6870	22·5

The **relation between the depression of the freezing-point and the lowering of the vapour pressure** can be derived in an approximate manner as follows. In Fig. 78, ad is the vapour-pressure curve of ice and de the vapour-pressure curve of water At the point of intersection d the liquid and crystalline solvent co-exist in equilibrium. The corresponding temperature t is the freezing-point of the solvent. Similarly, if bb' and cc' are the vapour-pressure curves of the two solutions—which must, of course, lie below the curve for the pure solvent—the points of intersection b and c represent the conditions under which the two solutions, respectively, have the same vapour pressure as ice, and the corresponding temperatures t' and t'' at which equilibrium exists are the freezing-points of the respective solutions. Since the vapour-pressure curve of a solution lies below the vapour-pressure curve of the solvent, the freezing-point of the solution must, it is clear, lie below the freezing-point of the solvent. If the solutions are dilute and the depression of the freezing-point small, the curves may be regarded as being straight lines, and therefore

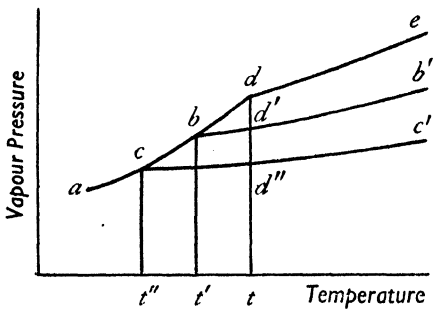


FIG. 78.

$$\frac{dd'}{dd''}=\frac{p-p'}{p-p''}=\frac{bd'}{cd''}=\frac{tt'}{tt''}=\frac{\Delta_1}{\Delta_2},$$

where Δ_1 and Δ_2 are the depressions of the freezing-point, and p' and p'' are the vapour pressures of the two solutions.

The vapour pressure of the solvent is represented by p. From the above relationships it follows that

$$\Delta_1 : \Delta_2 = \frac{p - p'}{p} : \frac{p - p''}{p}.$$

That is to say, *the depression of the freezing-point is proportional to the relative lowering of the vapour pressure*, and, consequently, *it is also proportional to the osmotic pressure of the solution.*

From the general relation

$$\Delta = K \cdot \frac{n}{W} = K \cdot \frac{w}{m \cdot W},$$

one obtains the expression

$$m = K \cdot \frac{w}{\Delta \cdot W},$$

where m is the molecular weight of the solute in the solution and w and W are the weights of solute and of solvent respectively.

Experimental Determination of the Depression of the Freezing-point.—The depression of the freezing-point of a solvent can be carried out with the apparatus represented in Fig. 79. A cooling bath A of glass or stoneware is covered by a brass lid through which pass a wide glass tube B and a stirrer E. A third opening in the lid allows of the passage of a thermometer. The freezing-point tube C, which is furnished with the side tube D, is supported in the neck of the tube B by means of a cork or asbestos ring, so that the freezing-point tube is surrounded by an air-mantle. This ensures a slower and more uniform rate of cooling of the liquid. Through a cork in the neck of C there pass a thermometer T, graduated in hundredths of a degree, and a stirrer S. A known amount of solvent having been placed in the freezing-point tube, the apparatus is fitted together as shown in the figure, the bath A being filled with a suitable cooling material—water, a mixture of water and ice, or a mixture of

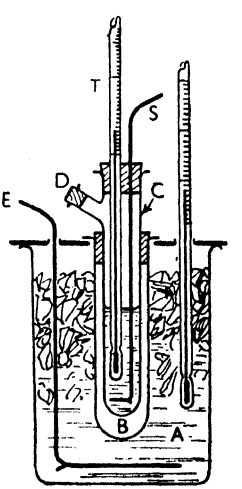


FIG. 79.

ice and salt, according to the temperature required. The solvent generally undergoes a slight degree of supercooling before crystallisation takes place, so that when freezing occurs there is a sudden rise of temperature to the freezing-point. The temperature then remains constant.

The freezing-point of the solvent having been determined, a weighed amount of solute is added to the solvent, and the freezing-point of the solution determined in the same way as that of the solvent. In this way the depression of the freezing-point for a solution of known concentration is determined. Further additions of the solute may be made and the freezing-point of the solution determined after each addition. The molecular weight of the solute may then be calculated by means of the expression given above.

More accurate determinations of the freezing-points of solutions can be made by adding ice to the well-insulated solution and, when the equilibrium temperature has been attained, finding the concentration of the solution.[1]

From the values of the depression of the freezing-point one may also calculate the osmotic pressure of the solution, which, as we have seen, is proportional to the depression. A solution containing 0·1 gram-molecule of solute dissolved in 1000 g. of water gives a depression of the freezing-point $\Delta = 0{\cdot}186°$. Such a solution has, at 0°, an osmotic pressure equal to 2·24 atmospheres. A depression Δ of 0·100° would therefore correspond to an osmotic pressure of 1·205 atmospheres, or 915 mm. of mercury.[2]

Micro-cryoscopic Method.—From the table on page 212 it is seen that the cryoscopic constant for ordinary solvents has a value of about 2000-7000. In the case of camphor, however, the value is 40,000. That is, 1 gram-molecule of substance dissolved in 1000 g. of camphor lowers the freezing-point of the latter by no less than 40°. For this reason, as was pointed out by the French chemist, A. Jouniaux, and by Karl Rast, of the University of Würzburg,[3] one can determine the molecular weights of many substances which dissolve in molten camphor, in a very simple manner

[1] Adams, *J. Amer. Chem. Soc.*, 1915, **37**, 381. See also Scatchard, Jones, and Prentiss, *ibid.*, 1932, **54**, 2676.

[2] Osmotic pressures calculated in this way are only approximate. For the exact relationship between osmotic pressure and the depression of the freezing-point, see Findlay, *Osmotic Pressure*.

[3] *Bull. Soc. Chim.*, 1912, **11**, 722; *Ber.*, 1922, **55**, 1051. See also Böhme and Schneider, *Z. angew. Chem.*, 1939, **52**, 58.

and with the aid of an ordinary thermometer graduated in whole degrees. The method has a practical importance only for the determination of approximate molecular weights.

To carry out a determination, a few milligrams of substance are mixed with 10 to 20 mg. of camphor, and the mixture melted completely in a small, clean glass tube. After solidification, the mixture is ground in an agate mortar and introduced, in small amount, into a thin-walled tube, such as is used for determining the melting-point of organic substances. The tube is then attached to a thermometer which is placed in a bulb-tube containing sulphuric acid; and by carefully heating the latter, the temperature is determined at which the last crystals of camphor disappear. This is taken as the freezing-point of the solution. The freezing-point of camphor is 178°. The molecular weight of the substance can then be calculated, using $K=40{,}000$. Thus, a mixture of 6·4 mg. of acetanilide and 61·0 mg. of camphor was found to have a freezing-point of 147° ($\Delta=31°$). Therefore, $m=40{,}000\times\frac{6\cdot4}{31\times61\cdot0}=135$. The molecular weight of acetanilide is 139.

Abnormal Freezing-points.—The depression of the freezing-point is proportional to the molecular concentration of the solute only when the solvent crystallises out pure from the solution. If, however, the solute separates out along with the solvent, forming with the latter what are known as mixed crystals, the depression of the freezing-point will be abnormally small.

If x per cent. of the solute remains in the liquid solution and y per cent. goes into the crystalline solid, it is found that

$$\Delta=\Delta_0\left(1-\frac{y}{x}\right),$$

where Δ is the observed depression and Δ_0 is the normal depression of the freezing-point. This behaviour is illustrated by the following numbers which refer to solutions of iodine in benzene :—

Grams of Iodine.	Gram-molecules.	$\frac{y}{x}$.	Δ_0.	Δ.	$\Delta_{calc.}$
0·914	0·00360	0·34	0·184°	0·129°	0·121°
2·24	0·00882	0·36	0·450°	0·313°	0·288°

In the case of a number of substances (very commonly in the case of organic acids and hydroxy-compounds dissolved in benzene) it is found that the molecular weight, determined by the cryoscopic method, is greater than that calculated from the usual chemical formula of the substance, by an

amount greatly exceeding the experimental error. One is therefore led to assume that these substances undergo *association*, *i.e.*, two or more molecules combine to form a larger molecule. Thus, in the case of acetic acid in benzene solution, one obtains the following numbers :—

Grams of Acid in 100 g. of Benzene.	Δ.	Molecular Weight (Calculated).
0·465	0·208°	110
2·321	0·970°	117
8·159	3·105°	129

The molecular weight corresponding to the formula, $CH_3 . COOH$, is 60.

From the depression of the freezing-point one can calculate the *degree of association*, or the fraction of the total number of molecules which combine to form larger molecules. Thus, if x is the degree of association and if n is the number of simple molecules which combine to form a complex molecule, then there will be $(1-x)$ unassociated molecules and $\frac{x}{n}$ associated molecules. The number of solute molecules will therefore be less than if no association took place in the ratio $1 : 1-x1-\left(\frac{1}{n}\right)$. But the depression of the freezing-point is proportional to the number of molecules, and therefore

$$\frac{\Delta}{\Delta_0}=\frac{1-x\left(1-\frac{1}{n}\right)}{1}, \text{ and } x=\frac{\Delta_0-\Delta}{\Delta_0\left(1-\frac{1}{n}\right)}.$$

If no association took place, a solution containing 0·465 g. of acetic acid in 100 g. of benzene should give $\Delta_0=0{\cdot}397°$. One calculates, therefore, that in this solution the acetic acid is associated to the extent of 95·3 per cent., assuming that $n=2$.

In the case of aqueous solutions of salts, acids, and alkalis, abnormally *great* depressions are obtained. These cases will be discussed later.

CHAPTER X

THE BEHAVIOUR OF ELECTROLYTES IN SOLUTION

WHEN discussing the laws of osmotic pressure, it was stated that equimolecular solutions of different substances have the same osmotic pressure ; and also, since the depression of the freezing-point of a solvent is proportional to the osmotic pressure of the solution, it was found that equimolecular solutions of different substances in water have the same freezing-point. These rules, however, cannot be applied directly to solutions of acids, alkalis, and salts.

It has already been pointed out that, according to van't Hoff, the osmotic pressure of a solution can be represented by the expression $PV = iRT$; and that, whereas i was found, in the case of many substances, to be equal to unity, for acids, alkalis, and salts it was found to be greater than unity. That is to say, the osmotic pressure of solutions of acids, alkalis, and salts, determined, more especially, by means of freezing-point depressions, is greater than the osmotic pressure of equimolecular solutions of a normal substance (*e.g.*, cane sugar), or a substance which in dilute solution obeys the simple van't Hoff-Avogadro law,[1] $PV = RT$. The van't Hoff coefficient i, therefore, represents the ratio of the observed osmotic pressure to the normal osmotic pressure, or, $i = P_{\text{obs.}}/P_{\text{norm.}}$ Since, moreover, the lowering of the vapour pressure, the depression of the freezing-point and the elevation of the boiling-point of a solvent are proportional to the osmotic pressure, i will also represent the ratio of the observed values of these properties to the values which would be obtained with equimolecular solutions of, say, cane sugar.

[1] This abnormal osmotic activity of salt solutions was first observed by the Dutch botanist Hugo de Vries (1848–1935) in 1882, during his investigation of the plasmolysis of plant cells (p. 182).

Not only do salts, acids, and alkalis, when dissolved in water, give solutions which have an abnormally high osmotic pressure and an abnormally low freezing-point, but the behaviour is all the more abnormal the more dilute the solution ; that is, the van't Hoff coefficient i increases with dilution. This is amply borne out by the determinations of the depression of the freezing-point given in the following tables. The concentrations are expressed in gram-molecules per litre.

Sodium Chloride.			Sodium Sulphate.		
Concentration.	Δ.	i.	Concentration.	Δ.	i.
0·0467	0·117°	2·0	0·0280	0·141°	2·66
0·117	0·424°	1·93	0·0701	0·326°	2·46
0·194	0·687°	1·87	0·117	0·515°	2·33
0·324	1·135°	1·86	0·195	0·817°	2·21
0·539	1·894	1·85	...	...	...

Magnesium Sulphate.

Concentration.	Δ.	i.
0·0638	0·165°	1·37
0·159	0·366°	1·22
0·398	0·802°	1·07
0·663	1·303°	1·04

From the above numbers it is seen that the van't Hoff coefficient may have very different values in the case of different salts, and in the case of the same salt at different concentrations. In the case of sodium chloride the coefficient reaches a value of 2 at high dilution, whereas in the case of sodium sulphate the value tends towards 3. In all the above cases, then, the solutions behave as if they contained an abnormally large number of molecules or dissolved particles in solution ; they behave, in other words, as if the molecules of the salt broke up in solution so as to yield a larger number of molecules or particles, each of which behaves as a separate solute molecule.

It is worthy of note that in the case of certain substances in the gaseous state a closely analogous phenomenon is observed. It is well known, for example, that when ammonium chloride is vaporised by heat, the molecules of the compound, in the vapour state, undergo dissociation with production of molecules

of ammonia and of hydrogen chloride. In the vapour, therefore, there are present not only molecules of NH_4Cl, but also molecules of NH_3 and HCl. One would find, therefore, that if a given quantity of ammonium chloride were vaporised in an exhausted vessel, the pressure produced would be greater than would be produced in the same vessel by an equimolecular amount of hydrogen at the same temperature. In other words, the behaviour of ammonium chloride in the vapour state does not appear to be in harmony with Avogadro's law.

Just as the apparently abnormal behaviour of ammonium chloride in the vapour state found its explanation in the dissociation of the molecules, so it appears a not unnatural assumption to make that when salts, acids, and alkalis are dissolved in water they also dissociate; for their solutions behave as if the number of dissolved molecules were greater than that calculated from the molecular weight of the dissolved salt. If, however, one makes this assumption, the question at once arises: What, then, are the products of dissociation? In the case of sodium chloride, for example, one must ask: Into what substances does this salt dissociate when it is dissolved in water? Clearly, not into sodium and chlorine; for sodium is a metal which decomposes water with evolution of hydrogen, and chlorine is a gas which dissolves in water, imparting to it a characteristic odour and bleaching properties.

The Theory of Electrolytic Dissociation.—To obtain an answer to the above question, one must consider another property of the apparently abnormal solutions, the property of conducting an electric current.

When one places in a vessel containing pure distilled water the ends of two wires which are connected through a lamp with a source of electricity, the lamp remains dark. The electrical circuit is broken by the water which is a non-conductor of electricity. If to the water one adds cane sugar, glycerol or alcohol, the lamp still gives forth no light, for the solutions of these substances do not conduct the electric current. If, however, one dissolves in the water even a very little common salt, or caustic soda, or hydrochloric acid, the lamp at once lights up, showing that the flow of electricity is no longer interrupted by the liquid. In this way it is found that certain substances yield solutions which do not conduct the electric current, while others yield solutions which are electrically conducting. Substances belonging to the latter class are called *electrolytes*; substances belonging to the former class, *non-electrolytes*. Substances which yield solutions

having a normal [1] osmotic pressure, freezing-point, etc., are found to be non-electrolytes, whereas salts, acids, and alkalis, those substances, in short, which yield solutions having an abnormally high osmotic pressure, an abnormally low freezing-point, etc., are found to be electrolytes. The electrical conductivity of pure water is very small.

This relationship between the conducting power of solutions for electricity and their abnormal osmotic behaviour was first clearly pointed out by the Swedish physicist, Svante August Arrhenius [2] (1859-1927), who, in 1887, propounded the view that when an electrolyte is dissolved in water the solute molecules undergo, to a greater or less extent, dissociation (electrolytic dissociation) into positively and negatively charged particles or ions.[3] The ions, according to this theory, lead an independent existence in the solution, have their specific properties (*e.g.*, colour) and reactions, and behave, therefore, as independent molecules. It is, then, this production of new solute particles in solution which, according to the theory of Arrhenius, causes the solutions of electrolytes to exhibit an abnormally great osmotic pressure, etc.

With regard to the nature of the different ions, one can say that when a salt undergoes electrolytic dissociation, or ionises, in solution, the metal part forms the positively charged ion, the *cation*, and the acid part forms the negatively charged ion, the *anion*. Thus, for example, sodium chloride, NaCl, ionises into the positively charged cation Na^+ (sodium ion), and the negatively charged anion Cl^- (chloride ion). In the case of acids, hydrogen ion forms the cation, so that hydrochloric acid, for example, gives the ions $H^{\cdot}$ and Cl' (where a dot and a dash are used in place of the plus and minus sign respectively). Nitric acid, similarly, gives the ions $H^{\cdot}$ and NO_3' (nitrate ion).[4] One sees, then, that the only property which acids have in common is that of giving rise to hydrogen ion, and it is to the presence of hydrogen ion in solution that the so-called acid properties are to be ascribed. *Acid properties are the properties of hydrogen ion.*

[1] By "normal" is meant the value calculated in accordance with van't Hoff's laws from the molecular weight of the dissolved substance, when i is equal to unity.

[2] *Z. physikal. Chem.*, 1888, **2**, 491.

[3] This term was introduced many years previously by Faraday.

[4] The ions are represented here as anhydrous, but it will be found later that the ions may be associated with larger or smaller amounts of water or other solvent.

(We shall learn later that an extended meaning must be given to the term " acid " (Chap. XIX.).)

In the case of alkalis, *e.g.*, sodium hydroxide, NaOH, the anion is formed by the hydroxyl group, giving the ion OH' or hydroxide ion. Thus, NaOH ionises with formation of $Na^{\cdot}$ and OH'. *It is to the presence of hydroxide ion in solution that the general properties of alkalis are due.*

So far, mention has been made only of binary electrolytes, *i.e.*, electrolytes which are capable of yielding only two ions. A molecule, however, of sodium sulphate (Na_2SO_4), for example, is capable of giving rise to three ions, namely, two sodium ions and one sulphate ion ; and since the solution of sodium sulphate, as a whole, is neither positively nor negatively charged, the amount of electricity associated with one sulphate ion must be equal to that associated with two sodium ions. The amount of electricity associated with 1 gram-ion (atomic or molecular weight of ion in grams), or 22·997 g. of sodium ion, is 96,494 coulombs, and this is the smallest amount of electricity associated with the gram-ionic weight of any substance, it is regarded as the unit gram-ionic charge and called a *faraday* (*F*). Hence the symbol for sodium ion is written $Na^{\cdot}$ with only one plus sign, or with one dot, to represent one unit charge or one faraday, whereas the symbol for sulphate ion is written with two negative signs, or with two dashes, to represent two units of charge or two faradays—thus, SO_4^{--} or SO_4''. Similarly, since 1 gram-ion of cupric ion (from cupric salts) carries two units of positive electricity, it is written $Cu^{\cdot\cdot}$. In general, the number of unit charges or faradays which a gram-ion carries is given by the valency of the ion. Thus we have the cations $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, etc., and the anions CO_3'', of carbonates, and PO_4''', of phosphates (*e.g.*, Na_3PO_4).

From the above discussion it will be clear that in the case of the solution of a binary electrolyte, one molecule of which can give rise to two ions, the osmotic pressure, depression of the freezing-point, etc., will be greater than, but cannot be more than twice as great as, that which would be given by an equimolecular solution of a non-electrolyte. On the other hand, a solution of sodium sulphate or of calcium chloride, $CaCl_2$, can have, at most, an osmotic pressure three times greater than that of an equimolecular solution of a non-electrolyte. This conclusion is also borne out by the numbers given in the tables on page 218, the maximum value which

the coefficient i tends to assume being equal to the number of ions into which the electrolyte dissociates.

The electrolytic dissociation or ionic hypothesis has proved of the greatest value in connection with the study of electrolytic solutions. Not only does it enable one to give an explanation of the process of electrolysis but, as will be made clear later, it may also be applied to the quantitative treatment of the properties of conducting solutions, the generation of voltaic electricity, and the relations between chemical and electrical energy. As will be pointed out more fully later, however, the original theory developed by Arrhenius has had to undergo certain modifications (Chap. XIV.).

Theory of Ionisation and Electrolysis.—When two electrodes, connected with the poles of a galvanic cell, and therefore positively and negatively charged, are introduced into the solution of an electrolyte, decomposition of the electrolyte, or *electrolysis*, occurs, and a current passes through the solution, provided the potential of the electrodes is sufficiently high. The products of electrolysis appear at the electrodes. Thus, when an electric current is passed through a solution of copper sulphate, metallic copper is deposited on the *cathode* or negatively charged plate; and if dilute sulphuric acid is electrolysed, gases are evolved at both electrodes—hydrogen at the cathode and oxygen at the positive plate or *anode*. Faraday saw that these reactions —which occur at the electrodes only, and not in the body of the solution—imply a flow in opposite directions of positively and negatively charged particles, which he called *ions*[1] or wanderers. Those ions, which move in the direction of flow of positive electricity, downstream as it were, were called *cations* (from *kata* = downwards); those moving in the opposite direction, upstream, were called *anions* (from *ana* = upwards).

Theodor von Grotthuss[2] (1785-1822) attempted, in 1805, to explain the occurrence of these reactions at the electrodes by imagining that the salt molecules AB are oriented by the attraction of the poles so that the A's are directed towards the positive pole and the B's towards the negative pole. The molecules in the vicinity of the poles are decomposed by this attraction, A being deposited on the anode and B on the

[1] Participle of the Greek verb εἶμι (eimi), to go, or travel.

[2] Christian Johann Dietrich von Grotthuss assumed the name of Theodor.

cathode. This leaves a B and an A without partners; the B takes an A from the adjacent molecule, while the A similarly takes a B, thus forming two molecules BA, which then, in turn, undergo decomposition at the electrodes.

According to Grotthuss, decomposition is brought about by the action of the electric current on the electrolyte; but Clausius in 1857 pointed out that since the conductivity of electrolytic solutions obeys Ohm's law, none of the electrical energy of the current could be used up in decomposing the molecules of the electrolyte. Clausius assumed, therefore, that the molecules of electrolytes in solution decompose *spontaneously* into ions, as a result, possibly, of collisions between the molecules. According to this hypothesis there is always a certain small but unknown fraction of the ions free, and these, during electrolysis, show a steady drift towards the electrically charged poles or electrodes.

The hypothesis of the spontaneous dissociation of the molecule of an electrolyte into ions, which forms the basis of the Arrhenius theory, was therefore no new idea; but instead of the very small degree of ionisation which Clausius assumed, Arrhenius was led by the osmotic and cryoscopic behaviour of electrolytic solutions to assume that, in the case of salts, for example, the degree of dissociation is large and tends to become complete in dilute solution.

According to the theory of Arrhenius, the attraction of the electrodes does no work in decomposing the molecules of an electrolyte but only directs the flow through the solution of the spontaneously produced charged particles or ions; and this flow of positively and negatively charged ions constitutes the current in the solution.[1] When the ions reach the electrodes their charges are neutralised. Thus, when a solution of copper sulphate is electrolysed, copper ions, $Cu^{\cdot\cdot}$, move to the cathode and combine with electrons which flow from the battery to the cathode. The copper ions, therefore, lose their charge and form atomic copper which is deposited on the electrode. Sulphate ions, SO_4'', move to the anode and give up their charge. Electrons flow from the anode to the battery. Discharge of the sulphate ion, however, under certain conditions, yields a

[1] The current in a solution can be detected by passing a current through a solution contained in a narrow glass tube supported horizontally above a magnet. The magnet will be deflected in the same way as when the current is carried by a metallic conductor.

group of atoms which is incapable of independent existence; and it reacts with water with evolution of oxygen:

$$SO_4 + H_2O \longrightarrow H_2SO_4 + O.$$

If a solution of sodium chloride is electrolysed, sodium ions move to the cathode and chloride ions to the anode. The former, on being discharged, give rise to sodium which reacts with water with production of hydrogen. Chlorine is evolved at the anode.

The nature of the ions discharged at an electrode may depend on the applied potential and on the decomposition potential of the ions (Chap. XV.). Secondary reactions also may take place and are sometimes of great practical importance. Thus, from concentrated solutions of ammonium sulphate, and with a high current density (current per unit area), SO_4'' may be discharged, and the discharged ions may combine to form S_2O_8'', and this in presence of $NH_4^{\cdot}$ yields the slightly soluble ammonium persulphate.

In the electrolysis of organic acids also various secondary products may be obtained.

The theory of ionisation in solution enables one not only to understand the mechanism of electrolysis but also the laws of electrolysis discovered experimentally by Faraday, and generally known as Faraday's laws. *Faraday's First Law* states: *When an electrolyte is decomposed by the electric current, the amount of decomposition is proportional to the quantity of electricity which flows through the solution.* This law follows at once from the fact that, according to the theory of Arrhenius, each ion carries a certain definite charge or amount of electricity, and a given weight of the ion is therefore associated with a definite amount of electricity. Double the weight of that ion will therefore be associated with double the amount of electricity, and, consequently, the amount of electricity which is conveyed by the ions through the solution will be proportional to the weight of ions discharged at the electrode; or the amount of electricity will be proportional to the amount of electrolyte decomposed.

On the basis of this law one can determine the amount of current which flows through a circuit by determining the weight, say, of copper or of silver deposited on the cathode, or the volume of hydrogen liberated at the cathode, by the given current of electricity. In this way one obtains *voltameters* or *coulommeters, i.e.*, instruments for measuring

the amount of electricity or the number of units, *coulombs*, of electricity which pass through a circuit. These are exact, since there are no electrolytic side reactions, for the First Law holds strictly, as can be seen from the weight of silver obtained on passing the same current through a silver nitrate solution in water at 20° and a silver nitrate solution in molten potassium nitrate at 260°. The silver deposited was 1·14916 g. and 1·14919 g. respectively—a difference of only 0·003 per cent.

Faraday's Second Law states : *When the same current (or the same amount of electricity) is passed through solutions of different electrolytes, the weights of ions discharged are in the ratio of their chemical equivalents* ; the equivalent being given by the ionic weight divided by the valency of the ion. Thus, if the same current of electricity be passed through solutions of sulphuric acid, silver nitrate, and copper sulphate, the weights of hydrogen, silver, and copper respectively which will be liberated at the cathodes of the electrolytic cells will be in the ratio $1 : 108 : \frac{63{\cdot}6}{2}$. (The atomic weights of hydrogen, silver, and copper are here taken as 1, 108, and 63·6 respectively.) One can therefore say : One gram-equivalent of any ion is associated with a definite amount of electricity. This amount is known as 1 faraday (*F*) and is equal to 96,500 coulombs. In order that 1 gram-equivalent of an ion (any ion) may be discharged at an electrode, this unit amount of electricity, 1 faraday, must be passed through the solution. When, therefore, one writes the symbols of the ions, each positive or negative sign (or each dot and each dash) represents 1 faraday of electricity. Thus, $Na^{\cdot}$ means that 22·997 g., or 1 gram-equivalent, of sodium ion, are associated with 96,500 coulombs of electricity ; and SO_4'' means that 96·06 g. of sulphate ion are associated with $2 \times 96{,}500 = 193{,}000$ coulombs. On the basis of Faraday's Second Law, therefore, one can at once calculate the weight of an ion which will be deposited by a given amount of electricity. The weight of an ion deposited by unit quantity of electricity, 1 coulomb, is known as the *electrochemical equivalent* of the ion.

Conductivity of Solutions.—When a metallic conductor forms part of an electrical circuit, it opposes a certain resistance to the passage of the current, and this resistance depends on the material of the conductor, on its length, and on its

cross-section. The resistance offered by a cube of the substance having a side equal to 1 cm. is called the *specific resistance* or *resistivity* of the material, and is generally measured in ohms.[1] The reciprocal of this, or $\frac{1}{R}$, is called the *specific conductance* or the *conductivity*, and is generally represented by the Greek letter kappa (κ). The conductivity is measured in "reciprocal ohms" or in *mhos* (mho being formed by writing ohm backwards).

Although the specific conductance is a suitable property by which to characterise a metallic conductor, it is not so suitable in the case of electrolytic solutions; for in the case of conducting solutions the conductance does not depend on the whole of the material between the electrodes but only on the ions formed by the solute. When, therefore, it is desired to compare different substances with respect to the conductivity which they exhibit in solution, one should compare solutions of equivalent concentration, or solutions which contain such amounts of solute as are capable of yielding ions bearing the same total charge of electricity.[2] In this way one obtains what is known as the *equivalent conductivity* (represented by the Greek letter capital lambda, Λ). By equivalent conductivity is meant the conductance of a solution which contains 1 gram-equivalent of the solute when placed between two electrodes of indefinite size, 1 cm. apart.

The connection between the specific and the equivalent conductivity can be obtained in the following way. If 1 cm. or 1 ml.[3] of a solution is placed in a rectangular vessel, two opposite sides of which are of metal (forming the electrodes) and 1 cm. apart, the measured conductance will, of course, be the specific conductance, because the distance between the electrodes is 1 cm. and the cross-section of the conducting solution is therefore 1 sq. cm. Further, if 1 gram-equivalent, of dissolved electrolyte is contained in 1 ml. of the solution

[1] An ohm is the resistance at 0° of a column of mercury 106·3 cm. in length and weighing 14·4521 g.

[2] Since Na_2SO_4 ionises into $2Na^{\cdot}$ and SO_4'', 1 gram-molecule of sodium sulphate can yield ions bearing, in all, a charge of four faradays; NaCl, on the other hand, ionises into $Na^{\cdot}$ and Cl', so that 1 gram-molecule of sodium chloride can yield ions bearing a total charge of only two faradays. One gram-molecule of sodium chloride, therefore, is equivalent to $\frac{1}{2}$ gram-molecule of sodium sulphate.

[3] The error introduced by taking millilitres as equal to cubic centimetres is negligible.

then, according to the definition given above, the conductance measured will also represent the equivalent conductivity. If, now, the solution is diluted by pouring pure water into the conductivity cell until the volume is, say, 1000 ml., then the conductance of this solution will be 1000 times the specific conductance, because there are, so to speak, 1000 cubes of solution of 1 cm. side between the electrodes. Since, however, there is still only 1 gram-equivalent of electrolyte between the electrodes, the measured conductance is also the equivalent conductivity. In this case, therefore, the equivalent conductivity is 1000 times the specific conductance. In general, then, one can say that the equivalent conductivity of a solution is equal to the specific conductance multiplied by the volume (ϕ) in cubic centimetres or millilitres in which 1 gram-equivalent of the electrolyte is dissolved, or $\Lambda = \kappa \cdot \phi$. If η represents the number of gram-equivalents of electrolyte in 1 ml. of solution, then one has the relation $\Lambda = \frac{\kappa}{\eta}$.

The term " molecular conductivity " is also sometimes employed, by which is meant the conductivity of a solution containing 1 gram-molecule of electrolyte when placed between electrodes of indefinite size 1 cm. apart. It is represented by μ.

Experimental Determination of the Conductivity of Solutions.—For the purpose of measuring the resistance of a solution, one usually employs the Wheatstone bridge method, the arrangement of which is shown diagrammatically in Fig. 80.

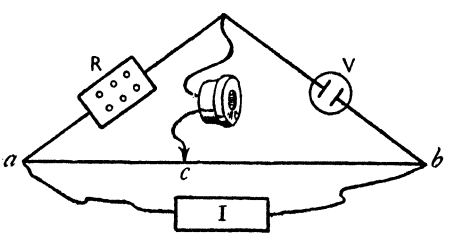


Fig. 80.

Since, during the electrolysis of an aqueous solution between platinum electrodes gases are evolved, and a back electromotive force (polarisation e.m.f.) therefore produced, one cannot readily measure the resistance of a liquid conductor by means of a direct current, but one must employ an alternating current such as is given by audio-frequency oscillation from an oscillating circuit driven by a thermionic valve or other similar device. The output from the source of alternating current is connected with the ends of the resistance

wire *ab*, which is stretched above a scale divided into millimetres. R is a resistance box, and V is a conductivity vessel containing the solution to be investigated. In order to determine the position of balance, a telephone receiver T is inserted between the sliding contact *c* and the junction of the resistance box with the conductivity vessel. A resistance is inserted in R of the same order as that in the conductivity vessel, and the sliding contact *c* is moved along the wire *ab* until there is minimum sound in the telephone. When this is the case, the resistance of V is given by the expression

$$R : V = ac : cb \; ; \quad \text{or } V = R \cdot \frac{cb}{ac}.$$

Knowing the value of the resistance R and the lengths *ac* and *cb*, which can be read off on the millimetre scale, the value of the resistance V can be calculated.

The conductivity vessel may have various forms, according to the solution for which it is to be used. Two very commonly used forms for routine work are shown in Fig. 81. They consist of cylindrical glass vessels, either of uniform diameter or narrowed at the foot, for use with solutions of greater conductivity. The electrodes are circular platinum plates sealed into glass tubes, and electrical connection is made by means of mercury. These two tubes pass through an ebonite cover, and their relative positions are fixed either by means of a glass tie or by cementing the tubes to the cover. Before use, the electrodes are coated electrolytically with a layer of platinum black, whereby the sharpness of the sound minimum is improved.

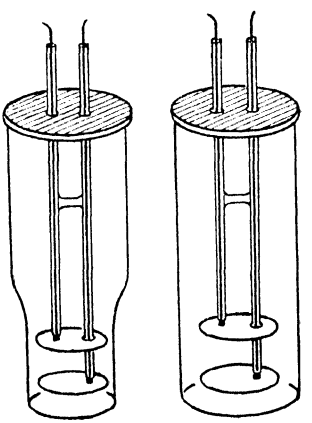


Fig. 81.

The specific conductance or conductivity, we have seen, is the conductance of 1 cm. cube (not 1 c.c.) of the material. If, therefore, the electrodes of the conductivity vessel are not exactly 1 sq. cm. in area and 1 cm. apart, the measured resistance or conductance of a solution placed between them will have to be multiplied by a factor in order to reduce the value to that which would be obtained if the electrodes enclosed between them 1 cm. cube of the liquid. This factor, which depends on the size and shape of the electrodes, and on their distance apart, is known as the *resistance capacity of the cell*, or the *cell constant*. If κ represents the specific conductance, and c the measured conductance of the solution, then $\kappa = K \cdot c$, where K is the cell constant. This cell constant is best determined by measuring in the given cell the conductance of a solution of known specific conductance, such as a solution of potassium chloride.

The specific conductance of solutions of this salt of various concentrations and at different temperatures is known from the work of Kohlrausch and others.

In conductance measurements it is necessary to control the temperature, for the conductivity of electrolytic solutions is markedly affected by temperature changes; and consideration must also be given to the conductivity of the solvent, though this is of importance chiefly in the case of very dilute solutions. To apply a correction for the medium the above experiment must be repeated, using water instead of the solution. The conductivity due to the electrolyte is then obtained from the expression

$$\kappa = K(c - c_o),$$

where c_o is the measured conductance of the solvent. Solvents should be used in as pure a state as possible, since impurities may react with the solutes and render experiments useless for purposes of comparison. The purest "conductivity water" obtained by Kohlrausch and Heydweiller had the very small specific conductance of $0{\cdot}043 \times 10^{-6}$ mho at 18°.

Equivalent Conductivity and Concentration.—When one investigates the conductivity of different solutions it is found that the equivalent conductivity of all electrolytic solutions increases with dilution. This is shown very clearly by the numbers in the following table :—

EQUIVALENT CONDUCTIVITIES AT 18°

Dilution in Litres.	KCl.	$NaNO_3$.	CH_3COOH.
1	98·27	65·86	1·32
10	112·03	87·24	4·6
100	122·43	98·16	14·3
1,000	127·34	102·85	41·0
5,000	128·77	104·19	50·0
10,000	129·07	104·55	107·0
∞	130·10	105·33	350

In the above table the numbers given in the first column are the volumes in litres (v), in which 1 gram-equivalent of the electrolyte (*i.e.*, 74·56 g. of KCl or 85·01 g. of $NaNO_3$) is dissolved. The conductivity values are expressed in reciprocal ohms.

In the case of electrolytes such as potassium chloride and sodium nitrate, so-called strong electrolytes, the value of the equivalent conductivity at infinite dilution can be obtained by means of an extrapolation formula put forward by the

German physicist, Friedrich Wilhelm Kohlrausch (1840-1910). This has the form

$$\Lambda_c = \Lambda_o - b\sqrt{c}$$

and is found applicable to dilute solutions (c = N/200 and less).[1] Λ_c is the equivalent conductivity when the concentration is c gram-equivalents per litre, and Λ_o is the equivalent conductivity at zero concentration (infinite dilution).

In the case of electrolytes like acetic acid, so-called weak electrolytes, the value of the equivalent conductivity at infinite dilution must be obtained indirectly from the sum of the ionic conductivities (p. 231).

It will be clear from the numbers contained in the above table not only that the equivalent conductivity increases with dilution, but that, as the dilution increases, the change in the conductivity becomes less and less. One can therefore conclude that a point will be reached at which further dilution will cause no increase in the equivalent conductivity ; or in other words, *the equivalent conductivity tends with dilution towards a maximum.* The dilution at which the maximum value of the equivalent conductivity is attained, and beyond which, therefore, no increase of equivalent conductivity occurs, is spoken of as *infinite dilution*, and the equivalent conductivity at infinite dilution is represented by the symbol Λ_∞ or Λ_o.

Ionic Conductivities.—When one examines the Λ_∞ values for salts containing the same cation, or for salts containing the same anion, an important relation is observed which may be illustrated by means of the salts KCl, NaCl, KNO_3, and $NaNO_3$. At 18° the Λ_∞ values for these four salts are 130·1, 109·0, 126·3, and 105·2 respectively, the conductivities being measured in mhos. From these values one sees that

$$\Lambda_{KCl} - \Lambda_{NaCl} = 130{\cdot}1 - 109{\cdot}0 = 21{\cdot}1$$
$$\Lambda_{KNO_3} - \Lambda_{NaNO_3} = 126{\cdot}3 - 105{\cdot}2 = 21{\cdot}1$$
$$\Lambda_{KCl} - \Lambda_{KNO_3} = 130{\cdot}1 - 126{\cdot}3 = 3{\cdot}8$$
$$\Lambda_{NaCl} - \Lambda_{NaNO_3} = 109{\cdot}0 - 105{\cdot}2 = 3{\cdot}8$$

It is clear, therefore, that when the potassium ion is replaced by the sodium ion a certain constant difference, equal to 21·1 units, is produced in the equivalent conductivity at infinite dilution, no matter what the anion may be ; and,

[1] *Ann. Physik*, 1885, **26**, 161 ; 1893, **50**, 385 ; *Z. Elektrochem.*, 1907, **13**, 333. See also *Trans. Faraday Soc.*, 1927, **23** 404.

similarly, when the chloride ion is replaced by the nitrate ion, a certain constant difference equal to 3·8 units is produced, no matter what may be the cation. In other words, each ion makes a certain definite contribution to the conductivity of a solution, or *the equivalent conductivity at infinite dilution is the sum of two values (the ionic conductivities), one depending on the cation and one on the anion.* If, therefore, one represents the conductivity due to the cation by l_c and the conductivity due to the anion by l_a, one obtains the relationship $\Lambda_\infty = l_c + l_a$. This is known as the *law of the independent migration of ions,* and was established in 1876-78 by Kohlrausch. From the values of the ionic conductivity, therefore, one can calculate the Λ_∞ values of different electrolytes.

The ionic conductivity increases with rise of temperature in accordance with the empirical equation

$$l_t = l_{18}[1 + c(t - 18)].$$

In the following table are given the values of the equivalent conductivity at infinite dilution of some of the more important ions at 18°, and of the temperature coefficients c :—

IONIC CONDUCTIVITIES AT 18°

	l_c.	c.		l_a.	c.
$H^{\cdot}$	315·0	0·01573	Cl'	65·5	0·0216
$Li^{\cdot}$	33·4	0·0265	Br'	67·6	0·0215
$Na^{\cdot}$	43·5	0·0244	I'	66·5	0·0213
$K^{\cdot}$	64·6	0·0217	NO_3'	61·7	0·0205
$NH_4^{\cdot}$	64·3	0·0222	OH'	174·0	0·018
$Ag^{\cdot}$	54·3	0·0229	$\overline{Ac'}$	35·0	0·0238
$\frac{1}{2}Ca^{\cdot\cdot}$	51·0	0·0247	$\frac{1}{2}\overline{Ox''}$	61·0	0·0231
$\frac{1}{2}Mg^{\cdot\cdot}$	45·0	0·0256	$\frac{1}{2}SO_4''$	68·3	0·0227

For most ions, the temperature coefficient has a value of about 0·024, but for the ions of high mobility the value is less.

An illustration of the use of the Kohlrausch law may be given in the case of acetic acid. The values of the equivalent conductivity at 18° and at different dilutions (in litres) are shown in the table on page 229. Owing to the very high dilution at which the equivalent conductivity attains its maximum value, it is not possible to determine this value experimentally; and it must be calculated from the values of the ionic conductivities of hydrogen ion and acetate ion. In this way one obtains the value

$$\Lambda_\infty = l_{H^{\cdot}} + l_{Ac'} = 315 + 35 = 350.$$

Influence of Temperature on the Equivalent Conductivity.—Since the ionic conductivity increases with rise of temperature, it is also found that the equivalent conductivity similarly increases. In the case of weak electrolytes, however, which may undergo ionisation with evolution of heat, the degree of ionisation will diminish as the temperature is raised, in accordance with the theorem of Le Chatelier (Chap. XII.); and it may happen that this decrease of ionisation more than counterbalances the increase of conductance due to increased mobility of the ions. The equivalent conductivity will therefore pass through a maximum. Such maxima have been observed.

The variation of conductivity with temperature is a complex of effects, and depends not only on the change of ionisation of the electrolyte but also on the influence of temperature on the dielectric constant and the viscosity of the solvent. At ordinary temperatures the conductivity increases by about 2 per cent. per degree.

Degree of Dissociation. Complete and Partial (Reversible) Dissociation.—Two factors may be involved in the increase of the equivalent conductivity with dilution, the occurrence of which is evident from the numbers in the table on page 229, namely, change in the velocity of movement or mobility of the ions and change in the number of conducting particles or ions. According to the classical theory of Arrhenius, only the second factor was supposed to be involved. According to Arrhenius, an electrolyte in solution undergoes a partial dissociation or ionisation, the extent or degree of which depends on the concentration. As the dilution is increased, more and more of the neutral electrolyte molecules undergo dissociation, and the number of conducting particles or ions therefore increases. At length, when the dilution is sufficiently great, the electrolyte is completely dissociated; no further increase in the number of ions can occur, and the equivalent conductivity, therefore, must have its maximum value.

According to this classical theory the equivalent conductivity of an electrolytic solution is a measure of the degree of dissociation of the dissolved electrolyte. If Λ_∞ represents the equivalent conductivity when dissociation is complete, or when the degree of dissociation is unity, and if Λ_v represents the equivalent conductivity at a dilution of 1 gram-equivalent in v litres, then the degree of dissociation

α will be given by the expression $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$. This conductivity ratio we may call the *Arrhenius coefficient.*

If one calculates the value of α from the values of the equivalent conductivities of potassium chloride and acetic acid given in the table on page 229, one obtains the following numbers :—

Dilution.	1 Litre.	10 Litres.	100 Litres.	1000 Litres.	10,000 Litres.
α_{KCl} . .	0·755	0·861	0·941	0·979	0·992
α_{HAc} . .	0·00377	0·0131	0·0409	0·117	0·306

The behaviour in these two cases is very different. In the case of potassium chloride the values of α are high and show comparatively small increase with dilution; in the case of acetic acid, however, the values of α are small, even in the most dilute solutions, but there is a very great increase in the value with dilution. These two series of values for α illustrate in a typical manner the difference in behaviour of what are known as "strong" electrolytes (for which the value of α is high), and "weak" electrolytes (for which the value of α is small). Between such typically strong and weak electrolytes are others for which α has intermediate values.

If one accepts the theory of Arrhenius that in the solution of an electrolyte one has an equilibrium between free and mutually independent particles, the molecules and the ions of the electrolyte, one should also be able to calculate the degree of dissociation from the osmotic behaviour of the solution : for example, from the depression of the freezing-point. If 1 gram-molecule of a binary electrolyte is dissolved in 1 litre, and if the fraction α of the molecules is ionised, there will then be in the solution $(1-\alpha)$ gram-molecule of the un-ionised electrolyte and 2α gram-molecule of ions. In all, therefore, there will be $(1-\alpha)+2\alpha = 1+\alpha$ gram-molecules of solute. The observed depression of the freezing-point will therefore be greater than the theoretical depression (on the assumption of no dissociation) in the ratio $1+\alpha : 1$. That is to say, $\frac{\Delta_{observed}}{\Delta_{theoretical}} = i = \frac{1+\alpha}{1}$, or $\alpha = i-1$. Similarly, if a molecule of the electrolyte gives rise, on dissociation, to n ions,

the increase in the number of solute particles will be in the ratio of $1+(n-1)\alpha : 1$; and $\alpha=\frac{i-1}{n-1}$. When $i=n$, $\alpha=1$; that is, dissociation is complete.

The numbers in the following table enable one to compare the values of α obtained from osmotic measurements (α_o) and from conductivity measurements (α_Λ) respectively [1] :—

SOLUTIONS OF SODIUM CHLORIDE AND POTASSIUM NITRATE

Gram-molecules per 1000 g. of Water.	KNO_3.		NaCl.	
	α_o.	α_Λ.	α_o.	α_Λ.
0·1	0·787	0·824	0·861	0·860
0·05	0·848	0·867	0·888	0·889
0·02	0·908	0·911	0·922	0·922
0·01	0·937	0·935	0·943	0·941
0·005	0·958	0·953	0·961	0·956
0·002	0·967	0·970	0·969	0·971

It is clear from the numbers in this table that the values of α_o and α_Λ show a large measure of agreement ; but in other cases marked divergences are found. Thus in the case of a 0·5-molar solution of potassium sulphate, $\alpha_o=0{\cdot}728$ and $\alpha_\Lambda=0{\cdot}714$; and in the case of a similar solution of magnesium sulphate, $\alpha_o=0{\cdot}322$ and $\alpha_\Lambda=0{\cdot}438$.

The approximate agreement between the values of α_o and α would seem to support, in a qualitative manner at least, the hypothesis of Arrhenius, that one is dealing here merely with a dissociation equilibrium between un-ionised molecules and free and independent ions. This support, however, is illusory, because, as can be shown on thermodynamic grounds, the inter-ionic forces which, according to modern theory, influence the electrical conductivity will also affect the osmotic properties ; and the approximate parallelism between the values of the conductivity and the osmotic pressure cannot therefore be taken as confirmation of the Arrhenius hypothesis. Moreover, the marked divergences which are met with in some cases show that there are certain factors involved of which Arrhenius took no account ; and when one comes to test the hypothesis *quantitatively*, it is found (see Chap. XIV.) that although the hypothesis is justified in

[1] Leason H. Adams, *J. Amer. Chem. Soc.*, 1915, **37**, 481.

the case of weak electrolytes, it is not justified in the case of salts and other strong electrolytes. In the case of weak electrolytes, it is true, the conductivity ratio or Arrhenius coefficient can be taken as representing the degree of dissociation of the electrolyte in solution, but in the case of strong electrolytes the conductivity ratio is not a measure of degree of dissociation. In these cases, other factors enter (Chap. XIV.).

When the electrolytic dissociation theory was put forward by Arrhenius in 1887, no satisfactory explanation could be given of the process of ionisation which, in the case of salts, was supposed to take place to a large extent, At first the objection was raised that since the heat of formation of, say, sodium chloride from its elements amounts to 98,400 calories, a decomposition of the salt, merely by dissolving it in water, was unthinkable. Even when it was pointed out that this objection rested on a misunderstanding, and that the products of electrolytic dissociation are not the atoms sodium and chlorine, but the electrically charged ions, sodium ion and chlorine (or chloride) ion, the difficulty still remained of accounting for the formation and stable existence of these ions. By some the formation of ions was attributed to a process of hydration, an idea first suggested by Arrhenius, and the assumption was made that the affinity between the solvent (water) and the ions is greater than that between the solvent and the salt molecules, or that the " residual affinity " of the solvent molecules deflected or weakened the Faraday tubes of force by which the atoms were supposed to be held together in the molecule. Ostwald, on the other hand, postulated that a large amount of energy is liberated when an atom combines with an electric charge to form an ion, and that this combination, therefore, takes place. The growth of knowledge has justified this postulate.

It was not until after the electronic constitution of the atom had been established and an explanation of valency, based on this theory, had been given, that a satisfactory account of the high degree of dissociation of salts in aqueous solution could be offered. According to modern views, the sodium atom can part with an electron and so pass into the positively charged sodium ion in which the electronic configuration is that of the very stable neon atom. Similarly, the chlorine atom can take up an electron to form the negatively charged chlorine ion, and so assumes the electronic

configuration of the very stable argon atom. These ions, then, are very stable entities. The molecules of sodium chloride, NaCl, consist of sodium ions and chlorine ions in the form of electrically neutral "doublets," held together by electrostatic attraction, and thus potentially free. Even in the crystal of sodium chloride, as X-ray examination shows, these ions exist, and when the salt is fused the ions become free to move, and an electrically conducting liquid is obtained.[1]

Modern views regarding atomic structure and the constitution of salts or polar compounds have led to a modification of the theory of Arrhenius and the setting-up of a *theory of complete ionisation* in aqueous solutions of such compounds. According to this theory, the quantitative aspects of which will be discussed later (Chap. XIV.), it is concluded that when a salt is dissolved in water there is merely a breaking-up or separation of the groups of *pre-existing* ions. In such cases, then, ionisation is complete, and increase of the value of the van't Hoff coefficient i, or increase of the osmotic activity and of the equivalent conductivity with dilution is to be ascribed not to increase in the number of ions, as was suggested by Arrhenius, but to an increase of ionic activity produced by a decrease of the interionic forces and to a change in the mobility of the ions.[2]

Further, since the work necessary to separate two opposite electrical charges is inversely proportional to the *dielectric constant* of the medium, it follows that the interionic attractions will be less and the extent to which free ions exist will be all the greater the higher the dielectric constant of the medium. This is the so-called Nernst-Thomson Rule, enunciated by Walter Nernst [3] and by J. J. Thomson.[4] In accordance with this rule, the ions of a salt may be completely free in aqueous solution (water having a high dielectric constant), but only incompletely free in a solvent of low dielectric constant. In the latter case, not only free ions but also incompletely separated ionic doublets or ion pairs may exist. The conductivity

[1] Even in the solid state, salts or polar compounds have been found to conduct the electric current when heated to a suitable temperature. See C. Tubandt and S. Eggert, *Z. anorgan. Chem.*, 1920, **110**, 196.

[2] To a certain relatively small extent, there may be a dissociation of "ionic doublets."

[3] *Z. physikal. Chem.*, 1894, **13**, 531.

[4] *Phil. Mag.*, 1893, **36**, 320.

ratio is thus found to vary considerably in solutions of a salt in solvents of different dielectric constant.[1] The dielectric constant, however, is only one of the factors operative, the property of the solvent of combining with the ions exercising a powerful and, in some cases, a preponderating influence.

Although complete ionisation is to be assumed in the case of polar compounds, such as the salts of metals (with a few exceptions, *e.g.*, mercuric chloride) and the metal hydroxides, partial and reversible electrolytic dissociation, as assumed by Arrhenius, is found in the case of non-polar compounds, such as the acids, ammonium hydroxide, and other nitrogenous bases, in which the ion radicals are bound by a covalent bond. In such cases the compounds in the liquid state, *e.g.*, liquid hydrogen chloride, are non-conductors. When such substances are dissolved in water, we may assume the occurrence of such reactions as $HCl + H_2O = H_3O^{\cdot} + Cl'$, the hydrated hydrogen ion or oxonium ion being formed. That the hydrogen ion exists in the hydrated form is borne out by the fact that X-ray examination of crystals of the monohydrate of perchloric acid,[2] $HClO_4 . H_2O$, shows that the components of the polar lattice are $H_3O^{\cdot}$ and ClO_4'. (While bearing the fact of the hydration of hydrogen ion in mind, we shall, in general, use the symbol of the anhydrous ion, $H^{\cdot}$.) Similarly, when ammonia is dissolved in water the reaction $NH_3 + H_2O = NH_4^{\cdot} + OH'$ takes place.

Osmotic Coefficient of Salts. Since, according to the theory of complete ionisation of salts in solution, the osmotic activity may be interfered with by interionic attraction, one may introduce, in place of the van't Hoff factor i, the *osmotic coefficient* g, defined by the equation,

$$g = \frac{i}{\nu} = \frac{P}{\nu P_0},$$

where ν is the number of ions into which a molecule of the salt dissociates. The osmotic coefficient, therefore, is the ratio of the actual or observed osmotic pressure (or depression of the freezing-point, etc.), P, to the ideal osmotic pressure, P_o, which would be obtained if the salt were completely ionised and if there were no interionic attraction. The osmotic coefficient, g, is always less than unity and the

[1] P. Walden, *Z. physikal. Chem.*, 1906, **54**, 131.
[2] M. Volmer, *Annalen*, 1924, **440**, 200.

quantity, $1-g$, is a measure of the deviation of the solution from the ideal, assuming the salt to be completely ionised. In other words, the quantity, $1-g$, is a measure of the influence of interionic attraction in such solutions. Since, according to modern theory (Chap. XIV.), interionic attraction increases with the number and the valency of the ions, the quantity, $1-g$, is greater for, say, binary electrolytes with polyvalent ions (*e.g.*, $MgSO_4$) than for binary electrolytes with univalent ions (*e.g.*, NaCl). This is shown, for example, by the fact that the value of i for solutions of magnesium sulphate is less than for solutions of sodium chloride of the same molecular concentration (p. 218). The influence of the valency of the ions on the value of $(1-g)$ becomes very clear on plotting the values of $(1-g)$ for different electrolytes against vc or $\sqrt{vc}$, where c is the concentration (Fig. 82).[1] As the interionic attraction decreases with dilution, the quantity $(1-g)$ approaches zero, or the value of g approaches unity, as the concentration of the salt approaches zero.

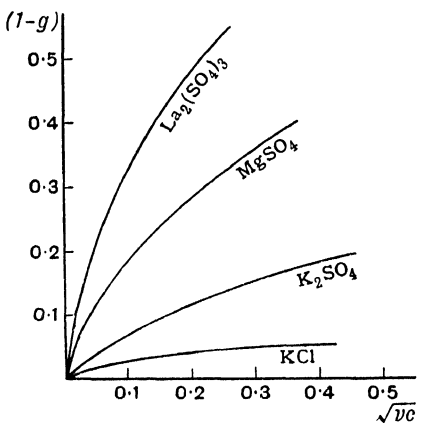


FIG. 82.

Ionisation of Water.—Hitherto the conductivity of a solution, even the most dilute, has been regarded as depending solely on the ions of the dissolved electrolyte, but this is not correct. Water has itself a certain, though very small, conductivity, and it must therefore be concluded that it is ionised into hydrogen ions and hydroxide ions. The purest water which has been investigated electrically was obtained by F. W. G. Kohlrausch and Adolf Heydweiller[2] by repeated and slow distillation of water *in vacuo*, and was found to have a specific conductance, at 18°, of $0{\cdot}043 \times 10^{-6}$ mhos. When such water is exposed to the air, the conductivity rapidly rises owing to absorption of carbon dioxide, and if ammonia or other soluble impurities are

[1] Ulich and Birr, *Z. angew. Chem.*, 1928, **41**, 467.
[2] *Z. physikal. Chem.*, 1894, **14**, 317.

present in the air, the conductivity acquires a still higher value. Ordinary distilled water may have a specific conductance at 18° of $3-6\times10^{-6}$ mhos. How feeble is the conductivity of pure water compared with that of a salt solution will be more fully realised when it is recalled that at 18° the specific conductance of a solution of potassium chloride containing 1 gram-equivalent in 50 litres is $2{\cdot}4\times10^{-3}$ mhos. At 0° the specific conductance of water is $0{\cdot}01\times10^{-6}$, and at 25°, $0{\cdot}17\times10^{-6}$ mhos.

From the value of the specific conductance of pure water the degree of ionisation can be calculated. The specific conductance, or the conductance of a cube of water of 1 cm. side, at 18°, is $0{\cdot}043\times10^{-6}$ mhos. The conductance of 1000 ml.[1] when placed between electrodes 1 cm. apart would be 1000 times as great, namely, $0{\cdot}043\times10^{-3}$. If 1 litre of water contained 1 gram-equivalent of hydrogen ion and hydroxide ion, the equivalent conductivity would be 489, that is, equal to the sum of the ionic conductivities (315 + 174). The actual conductivity, however, is only $0{\cdot}043\times10^{-3}$, and the water, therefore, contains only $\frac{0{\cdot}043\times10^{-3}}{489}=0{\cdot}88\times10^{-7}$ gram-equivalent per litre. In other words, 1 gram-equivalent of hydrogen ion and of hydroxide ion is contained in about eleven and a half million litres of water. This value has been confirmed by measurements of an entirely different kind, as will be described later.

Amphoteric Electrolytes.—Since water undergoes ionisation with production of hydrogen ion and hydroxide ion, it will act both as an acid and as an alkali. This property is also met with in the case of a number of other compounds when dissolved in water, and which are therefore spoken of as *amphoteric electrolytes* or *ampholytes*. Some of the most important of these are the amino-acids.

Acetic acid, CH_3 . COOH, when dissolved in water undergoes ionisation to a small extent with production of hydrogen ion ; and it therefore acts as an acid. If the amino-group is introduced into the molecule, amino-acetic acid or glycocoll, CH_2 (NH_2) . COOH, is obtained ; and this compound, in solution, can not only yield hydrogen ion but, in virtue of the presence of the NH_2-group, can also, through reaction with water ($-NH_2+H_2O=-NH_3OH$), give rise to hydroxide

[1] Strictly, 1000 cm.^{3}

ion. Amino-acetic acid, therefore, behaves as an amphoteric electrolyte and can act both as an acid (giving salts with alkalis, *e.g.*, $CH_2 . NH_2 . COONa$) and as a base (giving salts with acids, *e.g.*, $CH_2 . NH_2 . COOH$, HCl). As in the case of all amphoteric electrolytes, however, ionisation takes place only to a slight extent, so that amino-acetic acid behaves as a very weak acid and a very weak alkali (see Chap. XIV.).

Applications of Conductivity Measurements.—(a) *Solubility of Sparingly Soluble Salts.*—As Kohlrausch showed, conductivity measurements may be used in order to determine the solubility of salts which are so sparingly soluble that chemical analytical methods cannot be employed (cf. *the electromotive force method*, Chap. XV.). In order that this method may be satisfactorily applied, the salt must be obtainable uncontaminated by other electrolytes ; it must not be a salt of a weak acid or base, because hydrolysis at high dilutions and consequent formation of hydrogen ion and hydroxide ion would then give too high values for the conductivity. Since the salt is only sparingly soluble, it is generally assumed that it is completely ionised, and that the ions are without action on one another.[1]

For example, a saturated aqueous solution of silver chloride has at 18° a specific conductivity of $1{\cdot}12 \times 10^{-6}$ reciprocal ohms (after deducting the specific conductivity of the water). The conductivities of $Ag^{\cdot}$ and Cl' are 54·3 and 65·5 respectively ; therefore, $\Lambda_\infty = 119{\cdot}8$. If 1 ml. of saturated solution contained 1 gram-equivalent of silver chloride, the conductivity would be 119·8, but as the conductivity is only $1{\cdot}12 \times 10^{-6}$, the concentration will be

$$\frac{1000\kappa}{\Lambda_\infty} = \frac{1000 \times 1{\cdot}12 \times 10^{-6}}{119{\cdot}8} = 0{\cdot}93 \times 10^{-5} \text{ gram-equivalent per litre.}$$

(b) *Conductimetric Titrations.*—In the titration of an alkali by an acid, the addition of the acid from the burette reduces at first the concentration of the fast-moving hydroxide ions, their place being taken by the less mobile acid anion, *e.g.*,

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' \longrightarrow Na^{\cdot} + Cl' + H_2O.$$

The conductance of the titrated solution, therefore, falls until the neutral point is reached ; and thereafter the addition of acid causes a marked increase of conductance owing to the presence of the rapidly moving hydrogen ion.

If the number of millilitres of acid added is plotted

[1] In some cases, however, the assumption of complete ionisation is not correct. See Böttger, *Z. physikal. Chem.*, 1903, **46**, 521 ; Johnson and Hulett, *J. Amer. Chem. Soc.*, 1933, **55**, 2258.

against the conductance (or against the resistance as given by the bridge readings), the graph which is obtained consists of two intersecting straight lines, the point of intersection being the neutralisation point (Fig. 83, A). The lines will not be straight, however, if a dilute solution of the acid is used, for the consequent change in dilution of the titrated solution will cause the conductance to vary, apart from the effect of the chemical reaction. The solution of the acid should be 10-20 times more concentrated than the alkali solution to be titrated.[1]

It is better, when dealing with a weak acid, to add the acid to the alkali, and, in this case, a strong alkali must be chosen. The conductance of the solution decreases as the acid is added, for the hydroxide ion is replaced by the slower anion of the acid. As the acid is only slightly ionised, and its ionisation is reduced by the presence of a salt of the acid (Chap. XIV.), excess of acid does not give an increased conductance. The neutral point can, however, be obtained, because there is a sharp change in the direction of the conductance curve (Fig. 83, B).

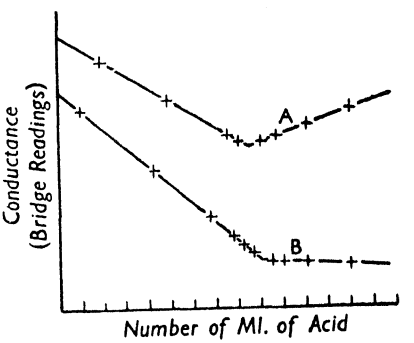


FIG. 83.

Conductimetric titrations of acids and alkalis are very useful when coloured or turbid solutions are to be titrated, for then indicators cannot be employed.

Other reactions which cause a sharp change in the conductivity of a solution can also be followed by measurements of the conductance.[2] Such reactions are those which result in the formation of a precipitate. Thus, one can determine the concentration of barium by means of lithium sulphate:

$$BaCl_2 + Li_2SO_4 \longrightarrow BaSO_4 + 2LiCl.$$

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[1] See Harned and Laird, *J. Amer. Chem. Soc.*, 1918, **40**, 1213; Eastman *ibid.*, 1925, **47**, 332; Rae, *J. Chem. Soc.*, **1931**, 876.

[2] See, for example, P. Dutoit, *J. Chim. Phys.*, 1910, **8**, 12; H. S. Harned, *J. Amer. Chem. Soc.*, 1917, **39**, 252; G. Edgar, *ibid.*, 914; Britton, *Conductometric Analysis*; Harms and Jahr, *Z. Elektrochem.*, 1935, **41**, 130.

Since lithium ion has one of the lowest, and the sulphate ion one of the highest mobilities, the replacement of barium ions by lithium ions, and, after the end point, the addition of sulphate ions, result in a sharp change in the conductivity curve; and thus one gets an accurate determination. Or, again, one may estimate magnesium sulphate by the addition of baryta. In this case two precipitates are formed, as shown by the equation:

$$MgSO_4 + Ba(OH)_2 \longrightarrow Mg(OH)_2 + BaSO_4,$$

and the end point is again sharply defined on the graph. Magnesium sulphate can be determined in the presence of calcium by this method.

If the precipitates formed during the titration are slightly soluble, the angle of intersection of the two lines of the graph is rounded off. In this case the straight sections of the curves are produced, and the point of intersection is taken as the end point of the titration.

As will be shown later (Chap. XIV.), conductivity measurements may also be applied to determine the degree of hydrolysis of a salt.

The Mobilities of Ions.—The equivalent conductivity of an electrolyte at infinite dilution is, as has been pointed out, made up additively of the equivalent conductivities of its ions, l_c and l_a; and when one examines the values given on page 231, considerable differences are observed. It is found, more especially, that the conductivities of hydrogen ion and hydroxide ion are markedly greater than those of the other ions. Since the equivalent conductivity represents the amount of electricity carried in unit time by 1 gram-equivalent of the ion under unit driving force or fall of potential, these differences might be due either to the ions carrying different amounts of electricity or to differences in the rate of motion or mobility of the ions. One gram-equivalent of an ion, however, carries the same amount of electricity no matter what may be the nature of the ion, and it follows, therefore, that the differences in the values of the ionic conductivities must be due to differences in the mobilities of the ions. Under the same driving force, therefore, or under the same potential gradient (*i.e.*, fall of potential per centimetre), different ions move with different velocities.

The following very instructive experiment, due to the American chemists A. A. Noyes and A. A. Blanchard,[1] will serve to demonstrate not only the migration but also the differences in the velocity of migration of ions. The bend and about three-quarters of one limb (A) of a U-tube (Fig. 84) are filled with a 5 per cent. gelatin solution containing potassium chloride (4 ml. of saturated potassium chloride solution to 15 ml. of 5 per cent. gelatin solution), and phenolphthalein rendered pink by the addition of a few drops of caustic potash solution. When this has set, a quantity of the same solution, but without the alkali, is filled into the other limb (*B*) of the U-tube and the solution allowed to set. Immediately before the experiment is started a solution of cupric chloride and hydrochloric acid is poured into the limb A, and a solution of caustic potash and potassium chloride into the limb B, and platinum electrodes, connected with a battery, are then placed in these solutions, the positive electrode in A and the negative electrode in B. On allowing the current to pass, hydrogen ion migrates towards the cathode, passing downwards into the gelatin solution in limb A and decolorising the phenolphthalein; and, on the other hand, hydroxide ion migrates towards the anode, passing downwards into the colourless gelatin solution in limb B and colouring the phenolphthalein pink. A colourless zone C will thus extend downwards in limb A, and a coloured zone D in limb B; and it will be found that the former zone is much wider than the latter, showing that the velocity of migration of hydrogen ion is much greater than that of hydroxide ion. After a time it will also be observed that the blue-coloured copper ions, which migrate towards the cathode, penetrate into the colourless zone produced by the hydrogen ions, but as the copper ion migrates much more slowly than hydrogen ion, the blue zone E is comparatively narrow.

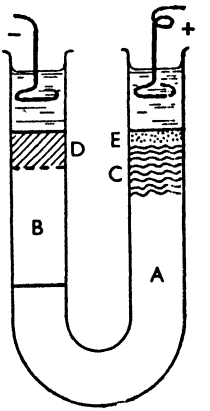


FIG. 84.

If in a solution containing 1 gram-equivalent of electrolyte the latter is completely ionised (infinite dilution), then there will be present in the solution 1 gram-equivalent of cation and 1 gram-equivalent of anion; and if this solution be placed between electrodes 1 cm. apart, and if the difference of potential between the two electrodes be 1 volt, then the amount of electricity which passes in 1 sec. between the electrodes will be 96,500 u_c coulombs in one direction, and 96,500 u_a coulombs in the opposite direction,[2] where u_c and u_a are the velocities of the cation and anion in centimetres per second under a fall of potential of 1 volt per cm. The total amount of electricity passing in 1 sec. will therefore be 96,500 $(u_c + u_a)$ coulombs. According to Ohm's law,

Current in amperes = electromotive force × conductance,

and since the strength of current in amperes is equal to the number of coulombs passing per second, one has (since the

[1] *Z. physikal. Chem.*, 1901, **36**, 1; *J. Amer. Chem. Soc.*, 1900, **22**, 726.
[2] Because 1 gram-equivalent of an ion carries 96,500 coulombs.

e.m.f. is equal to 1), conductance $= 96{,}500(u_c + u_a)$. This conductance, however, must be equal to the equivalent conductivity at infinite dilution, because there is 1 gram-equivalent of completely ionised electrolyte between the electrodes. Consequently,

$$\Lambda_\infty = 96{,}500(u_c + u_a),$$

or

$$\Lambda_\infty = 96{,}500u_c + 96{,}500u_a = l_c + l_a.$$

The quantity, 96,500 u_c, therefore, represents the contribution to the total conductivity made by the cation, and 96,500 u_a the contribution made by the anion. Since, as has been found, these contributions are not equal, it follows that u_c cannot be equal to u_a.

Although from determinations of Λ_∞ one is able to calculate the value of the sum of the mobilities of the ions, another relationship between these quantities must be known in order to obtain the individual values of u_c and u_a. Such a relationship is the ratio $\frac{u_c}{u_a}$, a ratio which can be determined by a method due to Johann Wilhelm Hittorf (1824-1914), Professor of Physics and Chemistry in the University of Münster.

As has already been pointed out, Faraday showed that when a solution is electrolysed, equivalent quantities of ions are discharged at the cathode and at the anode. It might therefore be thought that the decrease of concentration of electrolyte at the two electrodes would be the same. This, however, is in general not the case; in fact, the fall of concentration at the two electrodes during electrolysis may vary greatly, owing, as Hittorf pointed out in 1853, to the difference in mobility of the ions. This will be readily understood from the diagram (Fig. 85).

Let us suppose that the solution between the electrodes is divided up by a number of imaginary parallel partitions, equidistant apart, and let us suppose that the ions of the electrolyte, one positive and one negative, lie in the cells so formed (Fig. 85). During electrolysis, the positive ions will move towards the cathode, and the negative ions towards the anode, and will there be discharged. If the electrolysis is not continued too long, it is clear that change of concentration of solution can take place only in the neighbourhood of the cathode and of the anode, in what we may call the cathode

compartment and anode compartment respectively, whereas, in the body of the solution, represented in the diagram as lying between the wavy lines, the concentration will remain unchanged. Only the changes of concentration, therefore, which take place in the cathode and anode compartments need be considered.

Since, at the commencement of the electrolysis, the concentration is uniform, the number of positive and negative ions in the cathode and anode compartments respectively will be the same, as indicated in the diagram, where six equivalents of electrolyte are shown. Let an electric current be now

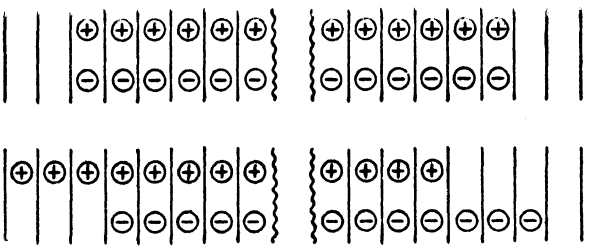


FIG. 85.

passed through the solution for a certain unit of time, and let us suppose that the cation moves twice as fast as the anion ; then, at the end of the unit of time the positive ions, we shall suppose, will have moved over two spaces, while the negative ions will have moved over only one space. Moreover, at the end of the unit of time, three positive ions and, similarly, three negative ions will have been discharged. In the cathode compartment there are now left only five complete molecules, in the anode compartment only four. Since there were initially six molecules in each compartment, the fall of concentration in the cathode compartment will be represented by 1, while the fall of concentration in the anode compartment is 2. Similarly, if the electrolysis were continued for another unit of time the concentration in the cathode compartment would fall from 5 to 4, representing a total fall of concentration of 2 ; while the concentration in the anode compartment would fall from 4 to 2, representing a total fall of concentration of 4. We see, therefore, that the fall of concentration in the anode compartment is twice as great as the fall of concentration in the cathode compartment ; but, according to our assumption, the mobility of the cation

is twice as great as the mobility of the anion, and we therefore obtain the relation

$$\frac{\text{Velocity of cation}}{\text{Velocity of anion}} = \frac{u_c}{u_a} = \frac{\text{decrease of concentration round anode}}{\text{decrease of concentration round cathode}}.$$

Transport Numbers.—Since the velocities with which the cations and anions move are, in general, not the same, it follows that in a given time more electricity must be transported in one direction than in the other, the amount transported in either direction being proportional to the velocity of the ion transporting it. As the total amount of electricity passing in unit time is proportional to $u_c + u_a$ or to $l_c + l_a$, the fraction of the total current transported by the cation will be proportional to $\frac{u_c}{u_c + u_a}$ or to $\frac{l_c}{l_c + l_a}$, and the fraction transported by anion will be proportional to $\frac{u_a}{u_c + u_a}$ or to $\frac{l_a}{l_c + l_a}$. *These fractions are known as the* TRANSPORT NUMBER *or* TRANSFERENCE NUMBER *of the cation and anion respectively.* If, as is usual, one represents the transport number of the anion by n_a, one has

$$n_a = \frac{u_a}{u_c + u_a} = \frac{1}{1 + (u_c/u_a)}.$$

A relation is thus obtained between n_a, which can be determined experimentally, and the relative velocities of migration of the ions. The transport number of the cation, n_c, is, of course, equal to $1 - n_a$.

The determination of the transport numbers and the ratio of the mobilities of the ions can be conveniently carried out in the apparatus shown diagrammatically in Fig. 86. This consists of three tubes, of which A represents the anode compartment and B represents the cathode compartment. The apparatus is filled with a solution of known concentration, and the electric current is allowed to pass for a certain time, which, however, must not be so long as to bring about a change of concentration in the middle portion of the solution contained in tube C. At the end of the experiment the solution is run from A and B into separate flasks, and the concentration determined by analysis. The decrease of concentration at the two electrodes is thus obtained. (The tube B′ is used when gas is evolved at the electrode.) [1]

In a particular case in which silver nitrate was electrolysed, the composition of the solution before electrolysis was such that in 10·058 g. of solution there were 9·973 g. of water and 0·0847 g. of silver nitrate. That is, for every 9·973 g. of water there is 0·000498 gram-equivalent of silver.

[1] See Findlay, *Practical Physical Chemistry.*

After electrolysis, 27·04 g. of solution were found to contain 0·2818 g. of silver nitrate; that is, for every 26·78 g. of water there is 0·2818 g. of silver nitrate, or 0·001658 gram-equivalent of silver.

If the solution had remained unchanged in composition, 26·76 g. of water would have been associated with $\frac{0{\cdot}000498 \times 26{\cdot}76}{9{\cdot}973} = 0{\cdot}001337$ gram-equivalent of silver. There has been an increase, therefore, of $0{\cdot}001658 - 0{\cdot}001337 = 0{\cdot}000321$ gram-equivalent of silver.

The weight of copper deposited in a voltameter in series amounted to 0·0194 g. or to 0·000610 gram-equivalent, and the total amount of electricity passed through the solution is proportional to this number.

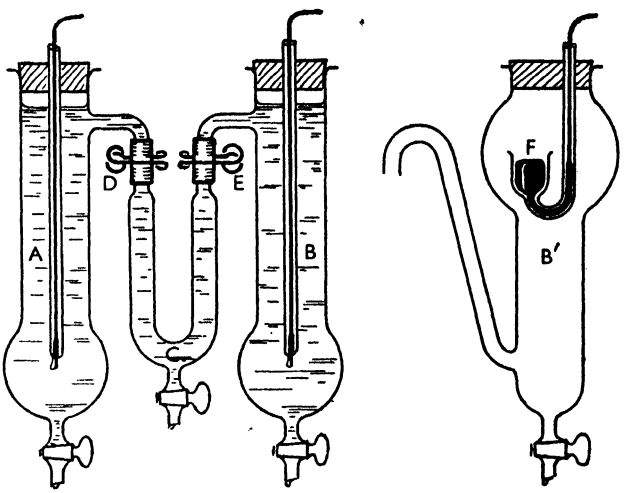


FIG. 86.

If none of the silver had wandered away from the anode, there ought, therefore, to have been an increase of 0·000610 gram-equivalent, because during electrolysis the liberated nitrate ion reacts with the silver electrode to form silver nitrate. But the increase found amounted only to 0·000321 gram-equivalent. Hence there must have wandered away $0{\cdot}000610 - 0{\cdot}000321 = 0{\cdot}000289$ gram-equivalent of silver, and this number must be proportional to the velocity of the silver ion. Hence the fraction of the total current carried by the cation amounts to $\frac{0{\cdot}000289}{0{\cdot}000610} = 0{\cdot}474$. From this it follows that the fraction carried by the anion amounts to $1 - 0{\cdot}474 = 0{\cdot}526$. These two numbers, 0·526 and 0·474, are called the transport numbers of the nitrate ion and silver ion respectively in a solution of silver nitrate.

The relative mobility and the transport numbers of ions may also be determined by the *moving-boundary* method, first employed by Sir Oliver Lodge,[1] and later by W. C. D. Whetham [2] and by J. I. Orme Masson,[3] in the

[1] *Brit. Assoc. Reports*, 1886, 389.
[2] *Phil. Trans.*, 1893, **184**, A, 337; 1895, **186**, A, 507.
[3] *Phil. Trans.*, 1899, **192**, A, 331.

case of electrolytes with coloured ions. It is, however, also possible to make use of the method even when the ions are not coloured, the moving boundary being made evident by the difference in refractice index.[1]

The transport number of an ion varies with the concentration, as is shown in the following table :—

TRANSPORT NUMBER OF CATIONS AT 18°

Electrolyte.	Concentration in Gram-equivalents per Litre.				
	0·01.	0·02.	0·05.	0·5.	1·0.
LiCl . . .	0·332	0·328	0·320	...	...
NaCl . . .	0·397	0·396	0·393	0·374	0·365
KCl . . .	0·496	0·496	0·496	0·492	0·490
HCl . . .	0·833	0·833	0·834	0·840	0·844
$AgNO_3$ . .	0·471	0·471	0·471	...	...
H_2SO_4 (at 20°) .	...	0·822	0·822	0·816	0·812
$CuSO_4$ . . .	...	0·375	0·375	0·327	...

The transport numbers vary also with the temperature, the values for the anion and cation, in the case of uni-univalent electrolytes, tending, at high temperatures, to approach 0·5.

It will be learned later that the transport number of an ion may also be determined by means of electromotive force measurements (Chap. XV.).

It may, perhaps, be emphasised here that since the transport number depends on the *relative* mobilities of the cation and anion the value for a given ion will depend on the nature of the other ion with which it is associated in solution. Thus the numbers in the above table show that the transport number of chloride ion in a solution of lithium chloride ($c = 0{\cdot}01$) is 0·668, whereas, in a solution of hydrochloric acid, it is 0·167.

Absolute Velocities of Ions.—It has been pointed out that $\Lambda_\infty = l_c + l_a$, and if one combines this with the relations given

[1] See R. B. Denison and B. D. Steele, *Phil. Trans.*, 1906, **205**, A, 449 ; E. R. Smith and D. A. MacInnes, *J. Amer. Chem. Soc.*, 1924, **46**, 1398 ; 1925, **47**, 1009 ; MacInnes and collaborators, *ibid.*, 1926, **48**, 1909 ; 1929, **51**, 267 ; H. P. Cady and L. G. Longsworth, *ibid.*, 1929, **51**, 1656. For a discussion of the moving-boundary method, see MacInnes and Longsworth, *Chem. Rev.*, 1932, **9**, 171. For more recent determinations, see also Hartley and Collie, *Trans. Faraday Soc.*, 1934, **30**, 648 ; Longsworth and MacInnes, *J. Amer. Chem Soc.*, 1938, **60**, 3070 ; R. Wright, *J. Chem. Soc.*, **1942**, 678.

above, $n_a = \frac{1}{1+(u_c/u_a)} = \frac{u_a}{u_c+u_a} = \frac{l_a}{l_c+l_a}$, one obtains the important results, $n_a = \frac{l_a}{l_c+l_a} = \frac{l_a}{\Lambda_\infty}$, or $l_a = n_a\Lambda_\infty$, and $l_c = n_c\Lambda_\infty$. It is therefore possible, from the experimentally determined values of n_a and of Λ_∞, to calculate the values of l_a and of l_c. Since, moreover, $l_c = 96{,}500\ u_c$ and $l_a = 96{,}500\ u_a$, one can, from the experimentally determined values, calculate the *absolute velocities* of the ions u_c and u_a, or the velocities of migration of the ions under a fall of potential of 1 volt per cm.[1] Some of these values are given in the following table :—

VELOCITIES OF IONS AT 18°.

$H^\cdot$	$Li^\cdot$	$Na^\cdot$	$K^\cdot$	OH'	Cl'	NO_3'	Ac'
33	3·5	4·6	6·7	18·2	6·8	6·5	$3{\cdot}6 \times 10^{-4}$ cm. per sec.

Complex Ions.—In discussing the transport numbers of ions the relative velocities of migration were deduced from the changes of concentration around the cathode and anode, on the assumption that when a salt is dissolved in water it gives rise to a positively charged metal ion and a negatively charged acid ion. In certain cases, however, an abnormal behaviour is observed. Thus, when a solution of potassium silver cyanide is electrolysed, it is found that the silver migrates not towards the cathode but towards the anode, and it must therefore be inferred that the silver is not present in solution as a cation. This conclusion is also borne out by the fact that no precipitate of silver chloride is obtained when a soluble chloride is added to the solution of potassium silver cyanide. The behaviour observed in this and in other cases led to the conception of *complex ions*, formed by the combination of an ion with a neutral molecule ; and in the solution of potassium silver cyanide one infers the presence of the ions $K^\cdot$ and $Ag(CN)_2'$, the latter ion being formed by the combination of AgCN with CN'.

The presence of silver as part of a complex anion in solutions of potassium silver cyanide can be demonstrated by the following experiment.[2] The bend of a U-tube (Fig. 87) is filled with a suspension (A) of precipitated and washed zinc sulphide in a 5 per cent. gelatin solution, to which, also, potassium nitrate is added to act as a conductor. When the gelatin has set, a thin layer (B) of

[1] Since the value of the transport number varies with dilution, one must, in the above calculations, use the value for very dilute solutions. The effect of dilution on transport numbers is seen in the table on page 248.

[2] A. A. Noyes and A. A. Blanchard, *Z. physikal. Chem.*, 1901, **36**, 1.

a gelatin solution, containing potassium nitrate only, is poured into one limb of the tube, and when this layer of gelatin has set, a gelatin solution (C) containing potassium nitrate and potassium silver cyanide is poured into the same limb of the tube. An aqueous solution of potassium nitrate (D) is then poured into each limb of the tube and a small current of electricity passed through the solutions in the direction indicated in the figure. After some time it will be found that the zinc sulphide under the layer (B) will begin to blacken, owing to the formation of silver sulphide, thus showing that silver is migrating towards the anode.

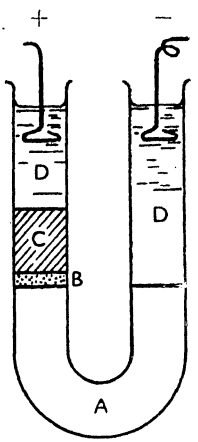


FIG. 87.

By a similar experiment [1] it can be shown that in Fehling's solution copper forms part of a complex copper tartrate anion.

A striking example of deviation from the ordinary behaviour of salt solutions is met with on electrolysing a solution of cadmium iodide. It has been pointed out that when a solution of silver nitrate is electrolysed, the concentration of silver round the anode is less than it would be if migration of silver ion were not assumed. In the case of solutions of cadmium iodide, however, it is found that there is an *increase* of concentration of cadmium at the anode. There must therefore take place an immigration of cadmium into the anode space more than sufficient to counterbalance the emigration of cadmium ions from the anode solution to the cathode space.

Since, as we have learned,

$$\frac{u_c}{u_a} = \frac{\text{decrease of concentration round anode}}{\text{decrease of concentration round cathode}},$$

and since there is an increase of concentration round the anode, *i.e.*, a fall of concentration with negative sign, it follows that the ratio u_c/u_a has a negative sign. On calculating the transport number of the anion, therefore, from the expression $n_a = \frac{1}{1-(u_c/u_a)}$, it is found that n_a must have a value greater than unity, as is shown by the following numbers :—

TRANSPORT NUMBER OF THE IODIDE ION IN SOLUTIONS OF CADMIUM IODIDE

Concentration in gram-molecules per litre	0·01	0·05	0·2	0·5	1·0	2·0
n_a	0·56	0·64	0·83	1·0	1·12	1·22

[1] J. I. O. Masson and B. D. Steele, *J. Chem. Soc.*, 1899, **75**, 725.

These numbers indicate that as the concentration increases complex ion formation also increases; and that as the solutions are made more and more dilute, the complex ions dissociate into the simple ions, and the solutions exhibit normal behaviour. By increasing the concentration of iodide ion (addition of potassium iodide to the solution), the concentration of complex ions can also be increased owing to the reaction

$$CdI_2 + 2I' = CdI_4''.$$

The formation of complex ions in solution is also borne out by determinations of the depression of the freezing-point. Thus, when one determines the freezing-point of a normal solution of hydrochloric acid to which varying amounts of mercuric chloride are added, the following numbers are obtained :—

Concentration of $HgCl_2$ (Gram-molecule per Litre).	Freezing-point.
0·0	−3·965
0·125	−3·785
0·25	−3·560
0·5	−3·350

It is seen that on adding mercuric chloride, the freezing-point *rises*, thus indicating that a decrease of the number of solute molecules has taken place. This can be explained by the assumption that complex ion formation occurs through the reaction $HgCl_2 + 2Cl' = HgCl_4''$.

Hydration (Solvation) of Ions.—In calculating the transport numbers of ions from the results obtained by the Hittorf method, it is assumed that the ions are "bare" or uncombined with water or other solvent; and when one examines the values, so calculated, of the transport numbers of the ions of the alkali metals in salts containing the same anion, it is found that the value increases with increase of the atomic weight of the metal. The mobilities, therefore, of the ions increase in the same way. This conclusion is contrary to what one would expect, for one would expect that, under a given potential gradient, the lighter lithium ion would have a greater velocity than the heavier cæsium ion. If, however, it is assumed that the ions are hydrated, or, speaking more generally, solvated, the behaviour observed could be explained on the assumption that the degree of ion-hydration decreases as the atomic weight increases.

Various attempts have been made, by means of migration and other experiments, to determine the extent to which ions

are solvated. Thus, in 1909, E. W. Washburn determined the transport numbers of ions in aqueous solutions containing a definite concentration of the non-electrolyte raffinose.[1] If, during electrolysis, the ions transport water, then the concentration of the raffinose at the electrodes will undergo change, and the relative hydration of the ions can be determined. In this way Washburn found that if the hydrogen ion is assumed to combine with only one molecule of water, the hydration of other ions is given by the values: $Cl' = 4$; $Li' = 14$; $Na' = 8{\cdot}4$; $K' = 5{\cdot}4$; $Cs' = 4{\cdot}7$.

Although it is now generally accepted that solvent is transported by the ions during electrolysis, opinion differs as to whether the solvent molecules are held by the ions by purely physical forces, or whether and to what extent chemical combination takes place between the ions and the solvent. In the case of the hydrogen ion, the view is increasingly held that, in aqueous solution, chemical hydration takes place, and that hydrogen ion exists as the hydrated ion $H(H_2O)'$ or H_3O'; and chemical hydration may also occur with other ions. Even, however, if chemical hydration or solvation occurs, through the formation of co-ordinate linkages or semipolar double bonds, it is accepted that molecules of the solvent are also held attached to the ions by electrostatic forces, depending on the extent to which the solvent molecules form "dipoles," and on the intensity of the electrical field at the surface of the ion. The extent to which a solvent can combine or associate with an ion will affect the extent to which ion doublets or undissociated molecules can exist in solution.

Non-aqueous Solutions.—It has been found that not only water but also many other liquids, both organic (*e.g.*, the alcohols, acetone, benzonitrile) and inorganic (*e.g.*, liquid hydrogen cyanide, sulphur dioxide, ammonia), may act as ionising media and yield solutions which conduct the electric current; and such solutions have formed the subject of many investigations. The behaviour of such solutions has been found to be much more complex than that of aqueous solutions.

[1] Washburn, *J. Amer. Chem. Soc.*, 1909, **31**, 322; Washburn and E. B. Millard, *ibid.*, 1915, **37**, 694. See also H. Remy, *Z. physikal. Chem.*, 1915, **89**, 467, 529; J. Baborovsky, *J. Physical Chem.*, 1928, **25**, 452; Millicent Taylor and E. W. Sawyer, *J. Chem. Soc.*, **1929**, 2095.

Although, in the case of a number of non-aqueous solutions, the equivalent conductivity increases with dilution, in other cases, especially when the dielectric constant of the solvent is small, the value of the equivalent conductivity may pass through a minimum; a behaviour which may be attributed to a change in the dielectric constant of the medium with concentration of the solution, or to chemical reaction between solute and solvent (solvation).

That solvation of ions takes place in a varying degree in different solvents is supported by the fact that the product of the equivalent conductivity and viscosity of the medium ($\Lambda_\infty \cdot \eta$), or the product of the ionic conductivity and viscosity, at infinite dilution, is not constant for different solvents, as it should be if the size and therefore the speed of the ion, under a given potential, were independent of the medium. In the following table[1] are given the values of the product of ionic conductivity and viscosity ($l_c \cdot \eta$) for a number of cations at 25° :—

Solvent.	100η.	$lc \times \eta$.							
		$H^{\cdot}$.	$Li^{\cdot}$.	$Na^{\cdot}$.	$K^{\cdot}$.	$N(C_2H_5)_4^{\cdot}$.	Cl'.	Br'.	NO_3'.
Water	0·894	3·14	0·347	0·459	0·668	0·295	0·682	0·698	0·634
Methyl alcohol	0·545	0·779	0·213	0·251	0·292	0·294	0·284	0·305	0·832
Ethyl alcohol	1·087	0·669	0·192	0·238	0·267	0·295	0·232	0·244	0·282
Acetone	0·3158	...	0·224	0·217	0·220	0·294	0·332	0·370	...
Acetonitrile	0·346	...	...	0·28	0·31	0·294	...	0·35	...

It will be observed that marked deviations from constancy occur, more especially in the case of aqueous solutions. Approximate constancy of the product is found only in the case of ions which have slight "residual affinity" or power of forming co-ordinate linkages, such as the ion $N(C_2H_5)_4^{\cdot}$, and which are therefore not markedly solvated.

In the case of a number of strong electrolytes in different solvents, it was found by Paul Walden, Professor of Physical Chemistry in the University of Rostock,[2] that for a given value of the Arrhenius coefficient (Λ_v/Λ_∞), the value of $\epsilon \cdot \sqrt[3]{v}$ is constant, where ϵ is the dielectric constant of the solvent and v is the dilution. There are, however, many exceptions. It is clear, therefore, that the dissociating power of a solvent does not depend only on its dielectric constant.[3]

[1] H. Ulich, *Trans. Faraday Soc.*, 1927, **23**, 388.
[2] *Z. physikal. Chem.*, 1920, **94**, 263.
[3] See C. A. Kraus, *Electrically Conducting Systems.*

The behaviour of electrolytic solutions, it is clear, is much more complex than would appear to be the case from a study only of aqueous solutions ; and it has become evident that the electrolytic dissociation of an electrolyte depends not only on physical factors, such as the dielectric constant of the medium, but also, and in some cases mainly, on chemical factors—the chemical nature of the solvent and of the ions. The greater the tendency of the ions to become solvated, the greater the degree of dissociation ; and the dissociating power of a solvent may be related to its power of forming co-ordinated linkages or semipolar double bonds, or to its power of acting as a donor and acceptor of electrons. Such solvents are very generally found to be associated liquids.

CHAPTER XI

THERMOCHEMISTRY AND THE FIRST LAW OF THERMODYNAMICS

WHEN a reaction is considered from the purely chemical point of view, interest is concentrated on the material substances involved, and the chemical and physical properties of the substances are those which attract attention. A chemical change or reaction, however, is in general accompanied by certain heat effects—evolution or absorption of heat—although in the case of certain intramolecular transformations these heat effects may be absent or negligible. Since heat is a form of energy, it is clear that a substance may be regarded as a carrier of so much energy, and we may then direct our attention not merely to the chemical properties of the substances involved in a reaction but also to the *changes of energy* which accompany the transformation of substances. In some cases, indeed, as is well known—in the case, for example, of the combustion of fuel—it is not the chemical nature of the substances which is of interest but the energy change, the evolution of heat, which accompanies the chemical process.

Similarly, chemical energy, or the energy associated with substances and due to the nature and arrangement of their structural units, may be converted into other forms of energy—*e.g.*, into electrical energy, as in the voltaic cell—and a study of the conditions under which and of the laws according to which these conversions take place is one of much importance. In the present chapter we shall be concerned only with the relations between heat energy and chemical energy, and the relations between chemical and electrical energy will be considered later.

First Law of Thermodynamics.—The study of the laws of transformation of one form of energy into another constitutes

a branch of science known as thermodynamics, the basis of which is the *law of conservation of energy.* This law was first enunciated in 1842 by the German physicist, Julius Robert Mayer (1814-78), and in 1847 it was more accurately defined and more fully illustrated by Hermann Ludwig Ferdinand von Helmholtz (1821-94). This great generalisation, constituting as it does the FIRST LAW OF THERMODYNAMICS, may be stated thus: *In an isolated system the sum total of energy remains unchanged no matter what chemical changes may take place in the system.*[1] In other words, *energy can be neither created nor destroyed.* This law may be inferred from the failure of every attempt made during the preceding centuries to construct what is called a perpetual motion machine of the first class, or a machine which would give out more work or energy than is put into it; and it may also be derived inductively from the experiments of James Prescott Joule and others. These experiments showed that whenever mechanical work or other form of energy is converted into heat, *the ratio of the amount of energy which disappears to the amount of heat which is produced is constant.* In actual practice, it is true, the condition of isolation postulated in the law cannot be completely realised, for it is not possible to obtain an insulator so perfect that no heat can pass into or out of a system; nevertheless, the more nearly complete isolation is attained, the more completely is the validity of the law proved experimentally.

Since, then, mechanical, electrical, and other forms of energy can be converted into an equivalent amount of heat energy, one may express a given amount of energy in units of the different forms of energy. Thus, in heat units, 1 calorie or 1 gram-calorie (cal. or g.-cal.) is the amount of heat which will raise the temperature of 1 g. of water from 15° to 16° C. It has, however, been found experimentally that when mechanical energy (*e.g.*, the fall of a certain weight through a certain distance) is converted by friction into heat, $4{\cdot}185 \times 10^7$ ergs of work must be expended in order to produce 1 calorie of heat. Therefore, 1 cal. $= 4{\cdot}185 \times 10^7$ ergs. This is known as the *mechanical equivalent of heat.*

A larger unit of energy than the erg has also been introduced, namely, the *joule* (j.), which is equal to 1×10^7 ergs.

[1] This generalisation does not hold in nuclear transformations, as has already been explained in Chapter I.

One has, therefore, the relation, 1 cal. = 4·185 j., or 1 j. = 0·2390 cal. Also, 1 cal. = 42,670 gram-centimetres.

When a gas expands against a certain pressure from volume v_1 to volume v_2, it does a certain amount of work, represented by the product $p(v_2 - v_1)$. If the pressure is measured in atmospheres and the volume in litres, the work done, or energy given out, is expressed in litre-atmospheres. It is found that 1 cal. = 0·0413 litre-atmosphere, or 1 litre-atmosphere = 24·21 cal.

Instead of the ordinary or gram-calorie, it is sometimes convenient, in thermochemistry, to use as unit of heat energy the kilogram-calorie (kg.-cal.), or the heat required to raise the temperature of 1 kg. of water from 15° to 16°. One has, then, 1 kg.-cal. = 1000 g.-cal.

Changes in the Total Energy of a System.—A chemical system (one substance or a group of substances) contains a definite amount of energy which depends on the mass, chemical nature, and physical conditions (temperature volume, etc.) of the system ; and this is constant so long as the system is unchanged. The absolute value of the *total energy*, or, as it is also called, the *internal energy* or *intrinsic energy* of a system, is unknown, and all that one can determine is the *change* of total or internal energy ($U_a - U_b$) when the system a undergoes change and passes into a new system b with a different total energy. When such a change takes place the *decrease* of internal energy ($-\Delta U$) of the system must, in accordance with the law of conservation of energy, be equal to the external work (w) done by the system minus the heat absorbed (q). That is,

$$-\Delta U = U_a - U_b = w - q.$$

When no external work is done by the system, *i.e.*, when no change of volume takes place, then $-\Delta U = -q_v$; or the decrease of internal energy is equal to the heat evolved at constant volume.[1]

In stating this first law of thermodynamics, one may also

[1] It may be noted here that in thermodynamics heat *absorbed* is given the positive sign, whereas heat evolved is negative. In thermochemistry, on the other hand, heat evolved is represented with the positive sign. In thermodynamics the matter is viewed from the standpoint of the system, so that heat absorbed is a gain to the system and therefore represented as positive; but in thermochemistry one is concerned with what one can get out of the system, and heat absorbed is regarded as a loss and therefore given a negative sign.

consider the *increase* of total or internal energy when heat is added to the system and when external work is done by the system. If one represents *increase* of internal energy by ΔU, one has

$$\Delta U = U_b - U_a = q - w,$$

where, again, q is the heat *absorbed* by the system and w is the external work done by the system during the process.

Another nomenclature is also employed. When, during a reaction, change of volume at constant pressure takes place, the increase of total energy is given by the expression

$$\Delta U = U_b - U_a = q_p - p(v_b - v_a),$$

where v_a is the volume of the initial system and v_b is the volume of the final system. This expression can also be written in the form :

$$(U_b + pv_b) - (U_a + pv_a) = q_p.$$

The quantity $(U + pv)$ is called the *heat content* or *enthalpy* of the system, and is represented by H. One obtains, therefore, the relation

$$H_b - H_a = \Delta H = q_p = \Delta U + p \,.\, \Delta v.$$

The quantity, ΔH, represents the *heat of reaction at constant pressure*, and has a positive sign when heat is absorbed and a negative sign when heat is evolved.

The heat of a reaction, it will be clear, is a measure of the change of total energy of a system only when no external work is done. When external work is done, as when a gas is formed in a reaction carried out under constant pressure, the decrease of the total energy is equal to the heat of reaction plus the work done. When a gas is formed under atmospheric pressure, the work done per gram-molecule of gas is given by $pv = RT = 1{\cdot}987T$ cal., so that for every gram-molecule of gas formed in a reaction, under atmospheric pressure, $1{\cdot}987T$ cal. must be added to the measured heat of reaction in order to give the change of total energy during the reaction or the heat of reaction at constant volume. Thus, in the reaction,

$$\mathrm{Zn} + \mathrm{H_2SO_4}, \text{ aq.} = \mathrm{ZnSO_4}, \text{ aq.} + \mathrm{H_2},$$

the heat of reaction measured is 34,200 cal. at 16°. At this temperature $1{\cdot}987T$ cal. = 575 cal., and therefore the heat of the above reaction at constant volume is 34,200 + 575 = 34,775 cal.

If, on the other hand, gases disappear during a reaction, then $1{\cdot}987T$ cal. must be subtracted from the measured heat of reaction in order to give the difference of total energy.

From what was said above, it will be seen that $-\Delta U$ represents the heat evolved in a reaction which takes place *at constant volume*; and $-\Delta H$ represents the heat evolved in a reaction which takes place *at constant pressure.*

THERMOCHEMISTRY

As has already been stated, chemical reactions are generally accompanied by some heat effect—evolution or absorption of heat—which, in accordance with the law of conservation of energy, shows that the total energy of the reactants is not the same as the total energy of the resultants. The heat effect produced in a chemical change, or the *heat of reaction*, has, for a given reaction, a constant value, provided the conditions under which the reaction takes place (pressure, temperature, physical state, crystalline form, etc., of the substances) remain the same; and it is usual to refer the heat of reaction to 1 gram-molecule of substance. The heat of reaction, moreover, is generally determined under constant pressure. Although the view, once held, that the heat which is evolved when two substances react together is a measure of the chemical affinity can no longer be regarded as generally valid, the study of heats of reaction and the relation between chemical energy and heat energy (a branch of science known as *thermochemistry*) is one which is of much importance.

The heat of reaction, as has been pointed out, depends on the physical state of the reacting substances, and in writing thermochemical equations this should be indicated. For the sake of simplicity, however, it is assumed, in the absence of special indication, that the substances are in the state in which they exist under normal conditions. When solid substances can react in different crystalline forms, the particular form must be indicated, *e.g.*, S_{rh} = rhombic sulphur.

Heat of Formation of Compounds.—One of the simplest cases of chemical reaction is the formation of a compound from its elements. Thus, when copper and rhombic sulphur are allowed to react copper sulphide is formed, and heat, amounting to 11·6 kg.-cal. (11,600 g.-cal.), is evolved for each gram-molecule of copper sulphide formed. This is represented by the equation,

$$Cu + S_{rh} = CuS + 11{\cdot}6 \text{ kg.-cal.},$$

or

$$Cu + S_{rh} = CuS\ ;\ \Delta H = -11{\cdot}6 \text{ kg.-cal.}$$

The quantity of heat, 11·6 kg.-cal., is known as the *heat of formation* of copper sulphide.

Since the heat of reaction depends on the physical condition of the substances involved, it is customary to define the heat of formation of a compound as *the heat evolved or absorbed at constant pressure when* 1 *gram-molecule of the compound is formed by the combination of the elements when in their normal state.*

When the elements can exist in different forms, amorphous or crystalline, the heat of formation of a compound will be different for the different forms. Thus, the heat of formation of carbon dioxide is 94·47 and 94·02 kg.-cal., according as the carbon is in the form of diamond or graphite. It follows, therefore, that the intrinsic energy of an element is different in its different crystalline forms, and that, when change from one form to another takes place, heat will be evolved or absorbed. This is known as the *heat of transition.* Thus :

$$C_{gr} = C_{d}\ ;\ \Delta H = 220 \text{ cal.}$$
$$S_{m} = S_{rh}\ ;\ \Delta H = -69 \text{ cal.}$$

The heat of formation of a compound will also necessarily depend on the final condition of the compound. Thus, when hydrogen and oxygen combine to form liquid water at just below 100°, the heat of reaction is 67,727 cal., but this includes the heat which is given out when vapour condenses to liquid, and which is equal to the latent heat of vaporisation. In the case of water vapour at 100°, this amounts to 9670 cal. per gram-molecule, so that the heat of formation of water vapour at 100° is $67{,}727 - 9670 = 58{,}057$ cal. The heat of formation of liquid water at 20° C. is 68,400 calories.

In the following table are given the values of the heat of formation of a number of typical compounds :—

Reaction.	ΔH at 20° c. in Kg.-cal. per G.-mol.
$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 = HCl$	-22·03
$\frac{1}{2}H_2 + \frac{1}{2}I_2 = HI$	+ 5·93
$H_2 + \frac{1}{2}O_2 = H_2O(l)$	-68·4
$H_2 + S_{rh} = H_2S$	- 5·26
$S + O_2 = SO_2$	-69·3
$C + 2S_{rh} = CS_2$	+22·0
$Pb + Cl_2 = PbCl_2$	-85·66
$\frac{1}{2}N_2 + \frac{3}{2}O_2 + \frac{1}{2}H_2 = HNO_3$	-42·4

Always bear in mind that when ΔH has a negative value, the reaction takes place with evolution of heat; and when ΔH has a positive value, the reaction takes place with absorption of heat.

Internal Energy of Compounds.—The thermochemical equation for the heat of formation of copper sulphide indicates that the internal energy of 1 gram-molecule of the compound is less than the sum of the internal energies of 1 gram-atom of copper and 1 gram-atom of sulphur by 11·6 kg.-cal. The absolute value of the energy of the elementary atoms is, however, unknown, and so the absolute value of the internal energy of 1 gram-molecule of copper sulphide is also unknown; but since the elements do not undergo change into one another, the absolute values of their internal energy are of no consequence when one is dealing with changes of energy. One may therefore regard the internal energy of the free elements under normal conditions as zero; and consequently, since the internal energy of a compound differs from the internal energy of the elements by the amount of heat of formation of the compound, *the internal energy of a compound becomes equal to the heat of formation with reversed sign.*

In the case of carbon dioxide and of copper sulphide, the internal energy of the compound is less than the sum of the internal energies of the elements; and formation of the compound from the elements, therefore, takes place with *evolution of heat.* Such a reaction is said to be an *exothermic* reaction, and the compounds are said to be *exothermic* compounds. Other compounds, however, are known which are formed from the elements with *absorption of heat,* and such compounds are said to be *endothermic* compounds. The internal energy of such compounds is *greater* than the sum of the internal energies of the elements.

A knowledge of the heat of formation of compounds is of importance because such knowledge enables one to calculate the heat of a reaction in which these compounds take part. Thus the heat of formation of $MgCl_2$ and of NaCl is 153·2 kg.-cal. and 98·4 kg.-cal. respectively; and the internal energies of the compounds are therefore −153·2 kg.-cal. and −98·4 kg.-cal. If, therefore, in the equation

$$\underset{-153\cdot2}{MgCl_2} + \underset{0}{2Na} = \underset{0}{Mg} + \underset{-(2\times98\cdot4)}{2NaCl}$$

one inserts the values of the energies, the internal energy of an element being regarded as zero, it is seen that the internal energy of the system on the left (the reactants) is greater than the internal energy of the system on the right (the resultants) by 43·6 kg.-cal., and therefore the above reaction will take place from left to right with evolution of 43·6 kg.-cal. of heat. Hence, one can write the thermochemical equation

$$MgCl_2 + 2Na = Mg + 2NaCl + 43\cdot6 \text{ kg.-cal.},$$

or $$MgCl_2 + 2Na = Mg + 2NaCl\,; \quad \Delta H = -43\cdot6 \text{ kg. cal.}$$

Similarly, the heats of formation of cupric chloride and of ferrous chloride in dilute solution are 62·5 kg.-cal. and 99·8 kg.-cal. respectively, and the internal energies of these compounds in solution are therefore −62·5 kg.-cal. and −99·8 kg.-cal. respectively. From the equation

$$\underset{0}{Fe} + \underset{-62\cdot5}{CuCl_2,\ aq.} = \underset{0}{Cu} + \underset{-99\cdot8}{FeCl_2,\ aq.},$$

in which the letters aq. (short for *aqua* = water) represent an indefinite amount of water and indicate that the salt exists in dilute solution, one sees that the internal energy of the reactants is greater than the internal energy of the resultants by 37·3 kg.-cal., and the thermochemical equation can therefore be written,

$$Fe + CuCl_2,\ aq. = Cu + FeCl_2,\ aq. + 37\cdot3 \text{ kg.-cal.}$$

Further, from the following heats of formation: Hg_2Cl_2 = 63·01, KOH, aq. = 114·85, KCl, aq. = 99·88, Hg_2O = 21·5, H_2O = 68·4 kg.-cal., one finds that in the case of the reaction,

$$\underbrace{\underset{-63\cdot01}{Hg_2Cl_2} + \underset{-229\cdot70}{2KOH,\ aq.}}_{-292\cdot71} = \underbrace{\underset{-199\cdot76}{2KCl} + \underset{-21\cdot5}{Hg_2O} + \underset{-68\cdot4}{H_2O}}_{-289\cdot66}$$

the energy of the reactants is *less* than the energy of the resultants by 3·05 kg.-cal. The above reaction, therefore, is an *endothermic* reaction and takes place with absorption of heat. The value of ΔH found experimentally is +3280 cal.

Hess's Law of Constant Heat Summation.—One of the most important laws of thermochemistry is that discovered in 1840 by the Swiss scientist, Germain Henri Hess (1802-50), Professor of Chemistry in the University of St. Petersburg (Leningrad). This law, known as the *law of constant heat summation*, states that *the total heat of a reaction is constant no matter whether the reaction is allowed to take place directly or in stages*; or, in other words, *the heat of reaction depends only on the initial and final systems.* This law, which was established experimentally by Hess before the enunciation of the law of conservation of energy, can be deduced from the first law of thermodynamics, for the total energy of a system depends only on the state (pressure, temperature, volume) of the system at the moment. The heat of reaction at constant volume, therefore, which measures the difference of total energy, $U_a - U_b$, must also depend only on the state of the systems at the moment and not on the process or processes by which system b is formed from system a.

The law is illustrated by the heat of production of a solution of ammonium chloride from ammonia, hydrogen chloride, and water. The process can be carried out in two ways :—

First Way

$$NH_3 + HCl = NH_4Cl + 42{\cdot}1 \text{ kg.-cal.}$$
$$NH_4Cl + aq. = NH_4Cl, aq. - 3{\cdot}9 \text{ kg.-cal.}$$

$$\therefore \quad NH_3 + HCl + aq. = NH_4Cl, aq. + 38{\cdot}2 \text{ kg.-cal.}$$

Second Way

$$NH_3 + aq. = NH_3, aq. + 8{\cdot}4 \text{ kg.-cal.}$$
$$HCl + aq. = HCl, aq. + 17{\cdot}3 \text{ kg.-cal.}$$
$$NH_3, aq. + HCl, aq. = NH_4Cl, aq. + 12{\cdot}3 \text{ kg.-cal.}$$

$$\therefore \quad NH_3 + HCl + aq. = NH_4Cl, aq. + 38{\cdot}0 \text{ kg.-cal.}$$

The total heat of a reaction which takes place in stages may be obtained, therefore, by adding together the heat effects with proper algebraic sign, of the different reaction stages.

Since thermochemical equations may be multiplied,

added, or subtracted like ordinary algebraic equations, Hess's law of constant heat summation is of the greatest importance in thermochemistry, because it enables one to calculate heats of reaction in cases where direct measurement is impossible. Thus the heat of formation of organic compounds cannot, as a rule, be determined directly ; but from the heat of combustion of a compound and of the elements forming it, it is possible to calculate the heat of formation of the compound. For example, the heat of formation of sucrose can be calculated from the following data :—

(1) $C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O + 1349{\cdot}4$ kg.-cal.
(2) $C + O_2 = CO_2 + 94{\cdot}4$ kg.-cal.
(3) $H_2 + \frac{1}{2}O_2 = H_2O + 68{\cdot}4$ kg.-cal.

From these equations one can eliminate CO_2 and H_2O as follows :—

$$C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O + 1349{\cdot}4 \text{ kg.-cal.}$$
$$11H_2 + 5\tfrac{1}{2}O_2 = 11H_2O + 752{\cdot}4 \text{ kg.-cal.}$$

$$\therefore \quad C_{12}H_{22}O_{11} - 11H_2 + 6\tfrac{1}{2}O_2 = 12CO_2 + 597{\cdot}0 \text{ kg.-cal.}$$
and $$12C + 12O_2 = 12CO_2 + 1132{\cdot}8 \text{ kg.-cal.}$$

$$\therefore \quad 12C + 11H_2 + 5\tfrac{1}{2}O_2 = C_{12}H_{22}O_{11} + 535{\cdot}8 \text{ kg.-cal.}$$

That is, the heat of formation of sucrose from its elements is 535·8 kg.-cal.

Similarly, one can calculate the heat of formation of carbon monoxide from the heats of combustion of carbon and of carbon monoxide. Thus,

$$C + O_2 = CO_2 + 94{\cdot}4 \text{ kg.-cal.}$$
$$CO + \tfrac{1}{2}O_2 = CO_2 + 67{\cdot}7 \text{ kg.-cal.}$$
Hence, $$C + \tfrac{1}{2}O_2 - CO = 26{\cdot}7 \text{ kg.-cal.}$$
or $$C + \tfrac{1}{2}O_2 = CO + 26{\cdot}7 \text{ kg.-cal.}$$

From the two cases considered, it will be seen that the heat of formation of a compound is equal to the sum of the heats of formation of the products of combustion minus the heat of combustion of the compound. It should, however, be noted that the heats of formation calculated in this way are subject to considerable error, owing to the fact that they are obtained as the difference of relatively large numbers. Although the percentage error in the experimental values may be fairly small, the percentage error in their difference

may be large. Attention, also, should be given to the fact that heats of combustion are very generally determined in closed vessels, and therefore at constant volume. If it is desired to convert these ΔU values into ΔH values, or values under constant pressure, a correction must be applied.

Since, as we shall learn later, the heat of reaction varies with the temperature, it is necessary, in applying Hess's law, that the heats of reaction should all refer to the same temperature.

Heats of Combustion of Organic Compounds.—Most hydrocarbons have a smaller heat of combustion than corresponds to the carbon and hydrogen which they contain, and their heat of formation is therefore positive; but in a number of cases, *e.g.*, acetylene, the heat of combustion of the compound is greater than the heat of combustion of the constituent carbon and hydrogen, and the heat of formation of such compounds is therefore negative (endothermic compounds). Although, in some cases, the heat of formation of hydrocarbons may be fairly large, *e.g.*, heat of formation of acetylene is $-54{,}300$ cal., in most cases it is comparatively small, so that an approximate value of the heat of combustion of a hydrocarbon can be obtained from the heats of combustion of the constituent carbon and hydrogen.

The heat of combustion of a hydrocarbon is, to a large extent, an additive property and, for a hydrocarbon, C_aH_{2b}, can be calculated by the additive formula [1]

$$q = ax + 2by - h_1 - h_2 - h_3,$$

where x and $2y$ represent, respectively, the heats of combustion of a gram-atom of carbon and of a gram-molecule of hydrogen in the compound, and h_1, h_2, and h_3 represent the heat of combustion due to each single, double, and triple bond respectively. From the heats of combustion of many hydrocarbons the following thermal constants, in kilogram-calories, have been obtained: $x = 135{\cdot}34$; $2y = 37{\cdot}69$; $h_1 = 14{\cdot}71$; $h_2 = 13{\cdot}27$; $h_3 = 0$. Making use of these values,

[1] See Julius Thomsen, *Thermochemistry*, trans. by Katherine A. Burke (Longmans); Thornton, *Phil. Mag.*, 1917, **33**, 196. M. S. Kharasch (*J. Research Nat. Bur. Stand.*, 1929, **2**, 359) has suggested a method of calculating heats of combustion on the basis of a displacement of electrons. (In this paper a list of heats of combustion is given.)

one calculates the heat of combustion of butene-2, $CH_3 . CH : CH . CH_3$, to be

$$q = 4 \times 135{\cdot}34 + 4 \times 37{\cdot}69 - 2 \times 14{\cdot}71 - 13{\cdot}27.$$
$$= 541{\cdot}36 + 150{\cdot}76 - 29{\cdot}42 - 13{\cdot}27.$$
$$= 649{\cdot}43 \text{ kg.-cal.}$$

The experimental value is 648·88 kg.-cal.

More accurate determinations of the heat of combustion of the saturated hydrocarbons and aliphatic alcohols, which have been carried out at the Bureau of Standards of the United States of America,[1] have shown that the increase in the heat of combustion at constant pressure for each addition of CH_2 to the composition is constant, and equal to 157·00 kg.-cal. per gram-molecule, only when the number of carbon atoms is greater than 5. Thus the increases in the heat of combustion for each addition of CH_2 on passing from methane to pentane are 162·02, 157·76, 157·37, 157·33 kg.-cal. The variations from constancy, although not large, are significant since the error of determination amounted to only 150 g.-cal. per carbon atom.

A similar behaviour is found in the case of saturated aliphatic compounds containing a normal alkyl group. When the alkyl group contains more than five carbon atoms, the heat of combustion of the compound at 25° and under a pressure of 1 atmosphere, increases by 157·00 kg.-cal. for each addition of CH_2.

From heats of combustion one may calculate the heats of formation of various linkages, C – C, C – H, etc.

In the following table are given the heats of combustion of a few compounds :—

HEATS OF COMBUSTION

Substance.	Heat of Combustion at Constant Volume (ΔU). Kg.-cal./mole.	Substance.	Heat of Combustion under Constant Pressure (ΔH). Kg.-cal./mole.
Benzene	– 783·4	Methane	– 212·8
Naphthalene	– 1232·5	Ethane	– 372·8
Methanol	– 173·6	Propane	– 530·6
Ethanol	– 326·7	Butane	– 687·9
Propanol	– 482·2	Hexane	– 1002·4
Butanol	– 638·1	Octane	– 1316·4
Benzoic acid	– 771·2	Decane	– 1630·4
Sucrose	– 1349·4		

[1] F. D. Rossini, *J. Research Nat. Bur. Stand.*, 1934, **12**, 735; **13**, 21, 189.

The heat of combustion of a compound containing oxygen is less than that of the carbon and hydrogen in the compound, and can be calculated approximately by making use of a modification of what is known as WELTER'S RULE. From the molecular formula of the compound one subtracts the oxygen atoms together with as many carbon atoms as are required to form carbon dioxide. The heat of combustion of the compound will then be approximately equal to the heat of combustion of the carbon and hydrogen remaining. Thus, in the case of sucrose, $C_{12}H_{22}O_{11}$, subtracting O_{11} and 5·5 C from the molecule, one is left with 6·5 C and 11 H_2, and the calculated heat of combustion is therefore $6{\cdot}5 \times 94{\cdot}0 + 11 \times 68{\cdot}4 = 611 + 752{\cdot}4 = 1363{\cdot}4$ kg.-cal. The experimental value is 1349·4 kg.-cal.

Determination of the Heat of Combustion.—The heat of combustion is best determined by the method of Berthelot, which consists in burning the substance in a bomb (Fig. 88) in an atmosphere of compressed oxygen.[1]

The bomb consists of a steel vessel which can be tightly closed by means of a lid screwed down on a lead washer. The substance to be burned is placed in the crucible T, and the bomb is filled with oxygen through the channel K_2, and the tube R under a pressure of 20-25 atmospheres. The bomb is placed in a polished metal calorimeter which contains a known weight of water.

In order to diminish loss of heat by radiation, the calorimeter is placed in a large water-jacketed vessel. When the temperature conditions have become adjusted, the substance is ignited by means of a spiral of platinum or iron wire a_1a_2 which is raised to incandescence by the passage of an electric current. By means of a thermometer, graduated in hundredths of a degree, the rise of temperature of the water in the calorimeter is determined. In this way the heat of combustion at constant volume is obtained.

The heat of combustion at constant volume per gram-molecule of substance can be calculated by means of the equation

$$-\Delta U = \frac{M}{m}(W + w)(t_2 - t_1),$$

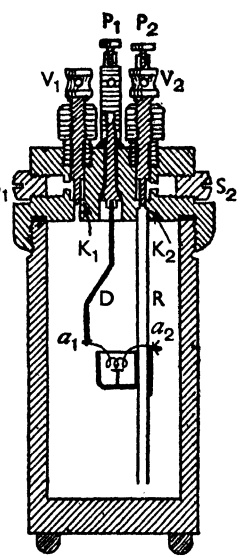


FIG. 88.

where m is the mass of substance burned, the molecular weight of which is M; W and w represent the weight of water and the water-equivalent of the apparatus

[1] For determinations of heats of combustion see T. W. Richards and F. Barry, *J. Amer. Chem. Soc.*, 1915, **37**, 993; Richards and H. S. Davis, *ibid.*, 1917, **39**, 341; F. D. Rossini, *J. Research Nat. Bur. Stand.*, 1934, **12**, 735.

respectively ; and $(t_2 - t_1)$ is the rise of temperature produced by the combustion. The water-equivalent of the apparatus can best be obtained by burning in the bomb a substance the heat of combustion of which is known.

Heat of Solution.—When a substance is dissolved in a solvent, heat is in general either absorbed or evolved.[1] Generally speaking, hydrated salts and salts which do not form hydrates dissolve in water with absorption of heat or with a very small evolution of heat ; but the solution of anhydrous salts which form hydrates is frequently accompanied by evolution of heat, the combination of salt with water being an exothermic process. Since, moreover, the process of dilution is generally accompanied by a heat effect, known as the *heat of dilution*, it follows that the *heat of solution*, or the amount of heat absorbed or evolved when 1 gram-molecule of substance is dissolved, depends on the amount of solvent used or on the final concentration of the solution produced. This is clearly shown by the numbers in the following table :—

Number of Gram-molecules of Water in which 1 Gram-molecule of $CuCl_2, 2H_2O$ is dissolved.	ΔH (Kg.-cal.).
8·0	+19·8
10·1	+ 3·1
10·5	+ 1·0
18·0	− 9·1
19·9	−11·7
47·7	−10·5
98·0	− 6·6
198·0	− 3·7

As dilution increases, the heat of dilution diminishes rather rapidly and becomes negligible when the solution consists of about 200-400 gram-molecules of water to 1 gram-molecule of solute. A solution of such dilution is represented by writing the symbol *aq.* after the formula of the solute. Thus the heat effect produced when potassium nitrate is dissolved in water so as to give a dilute solution (the so-called *integral* heat of solution) is represented by the equation

$$KNO_3 + \text{aq.} = KNO_3, \text{ aq.} - 8{\cdot}5 \text{ kg.-cal.}$$

[1] Considerable advances have been made in the calculation of heats of solution from a knowledge of intermolecular forces. A review of this work is given in *Chem. Soc. Annual Reports*, 1939, **36**, 34.

According to Hess's *law of thermoneutrality of salt solutions*, no heat effect is observed when two dilute salt solutions are mixed, provided no precipitate is formed. This law is valid, however, only when ionisation is complete and when no change in ionisation takes place.

Heat of Neutralisation.—The heat which is evolved when 1 gram-equivalent of an acid is neutralised in aqueous solution by 1 gram-equivalent of an alkali is called the *heat of neutralisation*. When the solutions are so dilute that the acid, alkali, and salt formed are completely ionised, the sole reaction which takes place on neutralisation is the combination of hydrogen ion and hydroxide ion to form un-ionised water and the thermochemical equation is therefore

$$H^{\cdot} + OH' = H_2O + 13{\cdot}8 \text{ kg.-cal.}$$

It follows, therefore, that the heat of neutralisation of all strong acids by strong alkalis in dilute solution should be practically the same, and this is borne out by the following values :—

Acid.	Alkali.	Heat of Neutralisation (Kg.-cal.).
HCl	NaOH	13·68
HNO_3	NaOH	13·69
HCl	KOH	13·93
HCl	LiOH	13·70

If, however, either the acid or the alkali is weak, or if both are weak and therefore only partially ionised, the heat of neutralisation will be different, because the heat of ionisation of acid or alkali must then be added to the heat of combination of hydrogen ion and hydroxide ion. The numbers in the following table may be taken in illustration :—

Acid.	Alkali.	Heat of Neutralisation (Kg.-cal.).
Acetic acid	NaOH	13·40
HCl	NH_4OH	12·27
HF	NaOH	16·40

Since, in the case of ammonium hydroxide, the heat of neutralisation is only 12·27 kg.-cal., whereas in the case of a completely ionised base it is 13·8 kg.-cal., it follows that

the heat of ionisation of ammonium hydroxide is approximately $-1{\cdot}5$ kg.-cal. In the case of hydrofluoric acid the heat of ionisation is approximately $+2{\cdot}6$ kg.-cal.

Experimental.—For the determination of the heat of solution or of neutralisation, one makes use of a polished metal vessel or of a silvered Dewar vacuum vessel as *calorimeter*. A known weight of water is placed in the calorimeter, which is then surrounded by protecting cylinders and water-jacketed vessel, in order to diminish loss or gain of heat by radiation. When the temperature has become adjusted, a known weight of salt, finely powdered and at the same temperature as the calorimeter, is added to the water, which is kept well stirred. From the change of temperature produced, the *heat of solution* per gram-molecule of salt can be calculated for the known concentration of solution.

In determining the *heat of neutralisation*, a known volume of alkali solution of definite concentration is placed in the calorimeter, and a known volume of acid solution, of the same concentration as the alkali, is contained in a separate vessel surrounded by several metal cylinders to minimise changes of temperature by radiation. The temperature of the acid and of the alkali must be noted. The acid is then added rapidly to the alkali, the solution is well stirred, and the rise of temperature $(t_2 - t_1)$ determined. One then has

$$\text{Heat evolved} = (m_1 s_1 + m_2 s_2 + m_3 s_3 + m_4 s_4)(t_2 - t_1),$$

where m_1, m_2, m_3, m_4 are the masses of the solution, calorimeter, thermometer, and stirrer respectively, and s_1, s_2, s_3, s_4 their specific heats. In this way the heat evolved in the neutralisation of a known amount of alkali by acid is obtained, and one can then calculate the heat which would be evolved in the neutralisation of 1 gram-equivalent of alkali.

Heat of Reaction and Temperature. Kirchhoff's Law.—The heat of reaction will, in general, vary with the temperature, and the manner of its variation can be deduced as follows :—

Let the reaction be carried out at the temperature T_1 and let the heat effect be ΔH_1. If, now, the reaction-products (resultants) are heated to the temperature T_2, an amount of heat will be taken up by the molar system equal to $C_2(T_2 - T_1)$, where C_2 is the mean molar heat capacity of the resultants, in the temperature range $T_2 - T_1$. As a second experiment, the reactants are heated from T_1 to T_2. During this process heat is taken up by the system equal to $C_1(T_2 - T_1)$, where C_1 is the mean molar heat capacity of the reactants. The reaction is then allowed to take place at the temperature T_2 with a heat change of ΔH_2. Then, by the First Law of Thermodynamics,

$$\Delta H_2 + C_1(T_2 - T_1) = \Delta H_1 + C_2(T_2 - T_1),$$

or

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Sigma C_2 - \Sigma C_1,$$

where ΣC_1 and ΣC_2 are the sum of the molar heats of the reactants and of the resultants respectively.

For small changes of temperature, one can write

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_p = \Delta C_p.$$

This relationship, which was first deduced in 1858 by Gustav Robert Kirchhoff (1824-87), Professor of Physics in the University of Heidelberg, is sometimes known as KIRCHHOFF'S LAW.

It follows from the above expression that if the molar heats C_1 and C_2 are the same, as is approximately the case with solid substances, the heat of reaction will not vary with the temperature.

In general, the specific (and molar) heat varies with the temperature, but when the temperature range is small, the specific heat may be taken as constant. Consequently, one may calculate the heat of formation of water vapour at, say, 413° K. as follows :—

At 373° K., the heat of formation is given by the equation

$$H_2 + \tfrac{1}{2}O_2 = H_2O + 58{,}057 \text{ cal.} \quad \Delta H_{373°} = -58{,}057 \text{ cal.}$$

The molar heats of hydrogen, oxygen, and water vapour are 6·818, 6·960, and 9·000 cal. respectively. Therefore,

$$C_2 - C_1 = 9{\cdot}000 - (6{\cdot}818 + 3{\cdot}480) = 9{\cdot}000 - 10{\cdot}298 = -1{\cdot}298 \text{ cal.},$$

and

$$\Delta H_{413°} - \Delta H_{373°} = -1{\cdot}298 \times 40 = -51{\cdot}92 \text{ cal.}$$

Hence, $\Delta H_{413°} = -58{,}057 - 51{\cdot}92 = -58{,}109$ cal.

One may also employ Kirchhoff's law in order to calculate, for example, the variation of the heat of fusion of ice with the temperature. The specific heat of ice at 0° (c_1) is 0·50, and the specific heat of water (c_2) is 1·00. Since the heat of fusion is negative, we have $-\left(\frac{\partial \Delta H}{\partial T}\right)_p = c_2 - c_1 = 0{\cdot}5$. That is, the heat absorbed in fusion increases by 0·5 cal. per gram for a rise of 1° C. This is borne out by experiment, which shows that the heat of fusion of ice per gram at −6·6° is −76·0 cal., and at 0° −79·5 cal. That is,

$$-\left(\frac{\partial \Delta H}{\partial T}\right)_p = \frac{3{\cdot}5}{6{\cdot}6} = 0{\cdot}53.$$

CHAPTER XII

HOMOGENEOUS EQUILIBRIA

THERE are, as is well known, many reactions which take place completely, or practically completely, in one direction and which are irreversible. Thus, when one mixes solutions containing equimolecular amounts of barium chloride and sodium sulphate, reaction takes place, and practically the whole of the barium is removed from the solution in the form of the very sparingly soluble barium sulphate. There are also many reactions which do not take place completely in one direction as represented by the usual chemical equation, but which cease before all the reacting substances have been used up. Thus, to employ the classical reaction as an illustration, if equimolecular amounts of ethyl alcohol and acetic acid are mixed together at the ordinary temperature ethyl acetate and water are formed, as represented by the equation

$$CH_3.COOH + C_2H_5.OH = CH_3.COO.C_2H_5 + H_2O.$$

In this case the reaction does not take place completely as represented by the equation, *i.e.*, the acid and alcohol do not entirely disappear, but only two-thirds of them. One-third of the alcohol and of the acid remains unchanged, no matter how long they are left in contact. This is due to the fact that water acts on ethyl acetate, converting it back again into ethyl alcohol and acetic acid. In other words, the reaction tends to be reversed. In the case under consideration, therefore, two opposed reactions are taking place, and there is produced, in consequence, a condition of *equilibrium* between the acid and alcohol on the one side and the ethyl acetate and water on the other. This reaction is therefore spoken of as a *balanced* or *reversible reaction*; and in order to represent this, the usual sign of equality is

replaced by two arrows, so that the interaction between acetic acid and ethyl alcohol should be written

$$CH_3.COOH + C_2H_5.OH \rightleftharpoons CH_3.COO.C_2H_5 + H_2O.$$

Law of Mass Action.—The condition of equilibrium, at a given temperature, in the case of a balanced or reversible reaction can be obtained by applying the *law of mass action*, which was first most clearly enunciated in 1867 by the two Norwegian scientists, Cato Maximilian Guldberg (1836-1902), Professor of Mathematics in the University of Christiania (Oslo), and his brother-in-law, Peter Waage (1833-1900), Professor of Chemistry in the same University. This law states that *the velocity of a reaction at constant temperature is proportional to the product of the concentrations of the reacting substances*, the concentrations being expressed in gram-molecules per litre. Since Guldberg and Waage applied the term "active mass" to what is now called concentration,[1] the law enunciated by them received the name of the *law of mass action*. It would now more properly be called the *law of concentration action*.

On applying the law of mass action to determine the condition of equilibrium in the case of a reversible reaction taking place in a homogeneous system at constant temperature, and represented by the general equation

$$A + B \rightleftharpoons C + D,$$

one finds that the velocity with which A and B react is proportional to their concentrations, or $v_1 = k_1 . [A] \times [B]$, where k_1 is a velocity coefficient and the square brackets indicate molecular concentrations. Similarly, the velocity with which the reverse reaction takes place is given by the expression $v_2 = k_2 . [C] \times [D]$. The state of equilibrium which is established is not a static equilibrium but a *dynamic equilibrium*, at which the velocity of the direct and of the reverse reactions is the same. At equilibrium, therefore, $v_1 = v_2$, and therefore in the case under consideration, $k_1 . [A] \times [B] = k_2 . [C] \times [D]$, from which it follows that

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = K.$$

This equation, then, gives the condition for equilibrium at constant temperature, K being known as the *equilibrium*

[1] We shall learn presently (p. 286) that a different meaning must be given to the term "active mass."

constant. Expressing this in words one can say: *At equilibrium the product of the concentrations of the substances on the right-hand side of the equation* (the resultants), *divided by the product of concentrations of the substances on the left-hand side of the equation* (the *reactants*), *is constant at a given temperature.*

The expression may be generalised. For any reversible reaction represented by the general equation

$$m_1A_1 + m_2A_2 + m_3A_3 \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3,$$

where m_1, m_2, m_3 and n_1, n_2, and n_3 are the number of molecules of the reacting substances, the condition for equilibrium is given by the expression

$$\frac{[B_1]^{n_1} \times [B_2]^{n_2} \times [B_3]^{n_3}}{[A_1]^{m_1} \times [A_2]^{m_2} \times [A_3]^{m_3}} = K,$$

where, as before, square brackets are used to denote molecular concentrations.

Although the equilibrium constant has been represented here as a ratio of velocity coefficients, it is important to bear in mind that it can also be calculated from the change of free energy involved in the reactions. Conversely, from determinations of the value of the equilibrium constant of a reaction, the free energy of the reaction can be calculated. These relations will be discussed more fully in Chap. XIII.

Decomposition of Hydrogen Iodide.—The simplest cases of homogeneous equilibria are those which occur in gaseous systems. Thus, when hydrogen and iodine vapour are heated together, reaction takes place with formation of hydrogen iodide; and similarly, when hydrogen iodide is heated at the same temperature, partial decomposition into hydrogen and iodine takes place, and ultimately the composition of the mixture will be the same as in the former case. This reversible reaction is represented by the equation

$$2HI \rightleftharpoons H_2 + I_2,$$

and therefore the condition of equilibrium at a given temperature is given by the expression

$$\frac{[H_2] \times [I_2]}{[HI]^2} = K_c.$$

That the same state of equilibrium is attained whether one starts with hydrogen iodide or with a mixture of hydrogen and iodine was confirmed by experiment,

If a gram-molecules of hydrogen and b gram-molecules of iodine are heated together until equilibrium is attained, the amount of hydrogen and of iodine respectively at equilibrium will be $(a-x)$ and $(b-x)$ gram-molecules, and the amount of hydrogen iodide will be $2x$ gram-molecules. If the volume of the mixture is v litres, then the concentration of hydrogen will be $\frac{a-x}{v}$, the concentration of iodine $\frac{b-x}{v}$, and the concentration of hydrogen iodide $\frac{2x}{v}$. At equilibrium, therefore,

$$K_c = \frac{[H_2] \times [I_2]}{[HI]^2} = \frac{\frac{a-x}{v} \times \frac{b-x}{v}}{\left(\frac{2x}{v}\right)^2} = \frac{(a-x)(b-x)}{4x^2}.$$

This equation was confirmed experimentally by Max Bodenstein, as is shown by the numbers in the following table.[1] Here, concentrations are expressed in millilitres reduced to N.T.P., these numbers being proportional to the number of gram-molecules of the gases.

DECOMPOSITION OF HYDROGEN IODIDE AT 444·5°.
$K_c = 0{\cdot}0198$.

Initial Concentration.		$\frac{[I_2]}{[H_2]} = r$.	Final Concentration at Equilibrium.			
H_2.	I_2.		H_2.	I_2.	HI ($2x$).	HI (Calculated) ($2x$).
8·10	2·94	0·363	5·27	0·13	5·66	5·64
7·94	5·30	0·668	3·18	0·54	9·52	9·49
8·07	9·27	1·149	1·40	2·60	13·34	13·47
8·12	14·44	1·780	0·72	7·03	14·82	14·93
8·02	27·53	3·433	0·32	19·83	15·40	15·54
7·89	33·10	4·195	0·33	25·54	15·12	15·40

The numbers in the last column are calculated by means of the equation $\frac{(1-x)(r-x)}{4x^2} = 0{\cdot}0198$, the initial concentration of hydrogen being, in all cases, put equal to unity. The concentration of iodine then becomes equal to r, and at equilibrium the amounts of hydrogen and of iodine will be

[1] *Z. physikal. Chem.*, 1897 **22**, 1.

$(1-x)$ and $(r-x)$ respectively. On solving the above equation for x one obtains the expression [1]

$$2x=\frac{r+1-\sqrt{r^2+1-r(2-16K_c)}}{1-4K_c}.$$

From the equation $K_c=\frac{[H_2]\times[I_2]}{[HI]^2}$, it follows that the higher the initial concentration of hydrogen, the lower will be the concentration of iodine at equilibrium ; or, the larger the excess of one reactant, the greater will be the extent to which the other reactant is used up. This is clear from the numbers in the table.

Since the presence of excess of hydrogen or of iodine increases the equilibrium concentration of hydrogen iodide, decomposition of the iodide on heating will be diminished by the presence of excess of hydrogen or of iodine vapour.

In deducing the expression for the equilibrium constant $K_c=\frac{(a-x)(b-x)}{4x^2}$, it is found that the volume v of the system cancels out. The equilibrium, therefore, is independent of the volume, and is consequently also independent of the pressure.

The following values of the degree of dissociation of hydrogen iodide under different pressures are in harmony with this conclusion :—

Total pressure (Atm.) .	0·5	1·0	1·5	2·0
Dissociation of HI . .	0·2019	0·2143	0·2225	0·2306

The small variations which are found are attributed to adsorption of hydrogen iodide on the walls of the reaction bulb.

From the preceding discussion and from the form of the equilibrium equation, it will be clear that a reversible reaction may be made to take place in one direction or the other by altering the concentrations of the substances involved. Increase of the concentration of the substances on the left side of the equation will cause the reaction to take place from left to right ; and increase of the concentration of the substances on the right side of the equation will cause the reaction to take place from right to left.

[1] The general solution of the equation $K_c=(a-x)(b-x)/4x^2$ is

$$2x=\frac{a+b-\sqrt{a^2+b^2-ab(2-16K_c)}}{1-4K_c}.$$

The following simple experiment [1] makes this very clear. When very dilute solutions of ferric chloride and ammonium thiocyanate are mixed, the reaction, $FeCl_3 + 3NH_4CNS \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl$, takes place, and a reddish colour is produced owing to the presence of ferric thiocyanate. If to a portion of this mixed solution one adds a small quantity of solid ammonium thiocyanate, the red colour deepens owing to the formation of a larger amount of ferric thiocyanate. On the other hand, if ammonium chloride is added to a second portion of the mixed solution the red colour disappears (or is weakened), the reaction now taking place from right to left with conversion of ferric thiocyanate into ferric chloride.

Influence of Pressure and Temperature on Equilibria.—The effect of pressure and of temperature on the condition of equilibrium can be predicted qualitatively by means of the theorem enunciated in 1884 by Henri Louis Le Chatelier (1850-1936), Professor of Chemistry in the University of Paris. This theorem may be stated in the form : *Whenever changes in the external conditions of a system in equilibrium are produced, changes occur (if possible) within the system which tend to counteract the effect of the external changes.* Thus, if the external pressure is increased, reactions will be favoured which are accompanied by a diminution of volume ; and if the pressure is reduced, or the volume increased, reactions will be favoured which are accompanied by increase of volume. The condition of equilibrium, therefore, will be altered by increase of pressure, according as the direct or reverse reaction takes place with diminution of volume. When no change of volume, or change in the number of molecules, accompanies either the direct or the reverse reaction, as in the case of the decomposition of hydrogen iodide or the combination of hydrogen and iodine, the equilibrium is unaltered by change of pressure. With regard to the influence of temperature, one may say that when heat is added to a system in equilibrium, a reaction will be favoured which is accompanied by absorption of heat ; and when heat is withdrawn from a system in equilibrium, a reaction will be favoured which is accompanied by evolution of heat. High temperatures, therefore, favour endothermic reactions ; low temperatures favour exothermic reactions. This general statement of the effect of temperature on equilibrium is also known as van't Hoff's *law of mobile equilibrium* (see Chap. XIII.).

The effect of pressure and temperature can be studied in the case of the equilibrium

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

[1] Lash Miller and Kenrick, *J. Amer. Chem. Soc.*, 1900, **22**, 292.

The production of ammonia from hydrogen and nitrogen is accompanied by diminution of volume, and, therefore, if the pressure is increased there will be an increase in the proportion of ammonia—that is to say, the formation of ammonia is favoured by increase of pressure. The formation of ammonia, further, is an exothermic reaction, the heat of formation being 10,950 cal., and will therefore be favoured by a lowering of the temperature. These predictions from the theorem of Le Chatelier are fully borne out by experiment, as the numbers in the table below show.[1] In this table, $K_p = \frac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}} \times p_{H_2}^{\frac{3}{2}}}$, the partial pressures p, being taken as proportional to the concentrations of the gases.[2]

It is seen that as the pressure is increased at each temperature, the percentage of ammonia increases. The "constant" does not vary much at the lower pressures, but varies considerably when the pressure is above 50 atmospheres, because the ideal gas laws do not hold at the higher pressures, especially in the case of ammonia, and the partial pressures can no longer be used to represent the concentrations of the gases.

EQUILIBRIUM BETWEEN NITROGEN, HYDROGEN, AND AMMONIA

$t°$ C.		Pressure in Atmospheres.					
		10.	30.	50.	100.	300.	600.
350°	$\%NH_3$	7·35	17·80	25·11	...	...	...
	K_p	0·0266	0·0273	0·0278	...	...	...
400°	$\%NH_3$	3·85	10·09	15·11	24·91	...	...
	K_p	0·0129	0·0129	0·0130	0·0137	...	...
450°	$\%NH_3$	2·04	5·80	9·17	16·35	35·5	53·6
	K_p	0·00659	0·00676	0·00690	0·00725	0·00884	0·01294
500°	$\%NH_3$	1·20	3·48	5·58	10·40	26·2	42·1
	K_p	0·00381	0·00386	0·00388	0·00402	0·00498	0·00651

From the table above, also, it is seen that as the temperature is raised the percentage of ammonia in the equilibrium

[1] A. T. Larson and R. L. Dodge, *J. Amer. Chem. Soc.*, 1923, **45**, 2918; Larson, *ibid.*, 1924, **46**, 367.

[2] It must be noted that the values of K_p given in the table above, refer to the ammonia equilibrium when written as $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$. These K_p values are therefore equal to the square root of the values when referred to the equilibrium written as $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

mixture diminishes, as predicted from the theorem of Le Chatelier.

In the case of the production of nitric oxide by the direct combination of nitrogen and oxygen, one is dealing with an *endothermic reaction*: $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$; $\Delta H = +21{\cdot}5$ kg.-cal. The production of nitric oxide, therefore, will be favoured by elevation of the temperature, but will be independent of the pressure.

As will be discussed more fully later (Chap. XIII.), the effect of temperature on equilibrium can be calculated *quantitatively* from the heat of reaction by means of the expression known as the van't Hoff isochore, $\frac{d \log_e K_c}{dT} = \frac{\Delta U}{RT^2} = -\frac{q_v}{RT^2}$, where q_v is the heat evolved at constant volume when the reaction goes completely from left to right. If it is assumed that q_v does not vary over the temperature interval $(T_2 - T_1)$, the van't Hoff equation yields, on integration, $\log_{10} \frac{K_1}{K_2} = \frac{q_v}{2{\cdot}303 \times 1{\cdot}987} \cdot \left(\frac{T_2 - T_1}{T_1 \times T_2}\right)$. If, therefore, the heat of reaction is known, one can calculate the value of K_2 when K_1 is known; and, conversely, if the values of K_1 and K_2 are known, the heat of reaction can be calculated. K_1 and K_2 are the values of the equilibrium constant K_c at the absolute temperatures T_1 and T_2.

When the equilibrium is expressed in terms of pressure, the variation of equilibrium with temperature is given by

$$\frac{d \log_e K_p}{dT} = \frac{\Delta H}{RT^2},$$

and

$$\log_{10} \frac{K_{p_1}}{K_{p_2}} = \frac{-\Delta H}{2{\cdot}303 \times 1{\cdot}987} \cdot \left(\frac{T_2 - T_1}{T_1 \times T_2}\right).$$

From the values of K_p at 450° and at 500° C. under a pressure of 10 atmospheres, the heat of formation of ammonia is calculated to be

$$-\Delta H = 12{,}170 \text{ cal.}$$

The heat of formation can also be obtained by a graphic method. From the expression, $d \log_e K_p / dT = \Delta H / RT^2$, one obtains, on integration, $\log_e K_p = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + C$, where C is the integration constant. On plotting the values of $\log_{10} K_p$, therefore, against $1/T$, a straight line will be

obtained, the slope of which will be equal to $-\Delta H/2{\cdot}303\boldsymbol{R}$, or $-\Delta H = \text{slope} \times 2{\cdot}303\boldsymbol{R}$.

The variation of equilibrium with pressure, also, can be taken account of quantitatively by expressing the concentrations of the constituent gases in terms of their partial pressures. Thus, in the case of the equilibrium,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3,$$

if the initial amounts of nitrogen and hydrogen are 1 gram-molecule and 3 gram-molecules respectively, then at equilibrium there will be $(1-x)$, $3(1-x)$, and $2x$ gram-molecules of nitrogen, hydrogen, and ammonia respectively. Since the partial pressure of each molecular species will be proportional to the ratio of the number of molecules of the particular substance to the total number of molecules, and since the total number of molecules is $(1-x)+3(1-x)+2x = 4-2x$, the partial pressures of the different gases at equilibrium will be

$$p_{N_2} = P \cdot \frac{1-x}{4-2x}; \quad p_{H_2} = P \cdot \frac{3(1-x)}{4-2x} \text{ and } p_{NH_3} = P \cdot \frac{2x}{4-2x}$$

where P is the total pressure. Since, further, the partial pressures are taken to be proportional to the concentrations, one can write

$$K_p = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3} = \frac{\left(P \cdot \frac{2x}{4-2x}\right)^2}{P \cdot \frac{1-x}{4-2x} \times \left[P \cdot \frac{3(1-x)}{4-2x}\right]}$$

$$= \frac{P^2 \cdot \frac{4x^2}{(4-2x)^2}}{P \cdot \frac{1-x}{4-2x} \times P^3 \cdot \frac{27(1-x)^3}{(4-2x)^3}}$$

or

$$K_p = \frac{4x^2(4-2x)^2}{P^2 \times 27(1-x)^4}.$$

When the concentration of ammonia is small, that is, when x is small compared with unity, the preceding expression can be simplified to $K_p.P^2 = \frac{64x^2}{27}$. That is, x is proportional to the pressure. It will be seen from the table that at the

higher temperatures, at which the percentage of ammonia is small, this percentage is approximately proportional to the pressure.

Relation between K_p and K_c.—The equilibrium constant may be expressed not only in terms of pressure but also in terms of concentration or moles per litre. Since $c = 1/v = p/RT$, one has, for the ammonia equilibrium,

$$K_c = \frac{(p/RT)^2_{NH_3}}{(p/RT)_{N_2} \times (p/RT)^3_{H_2}} = \left(\frac{1}{RT}\right)^{2-(1+3)} \times \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = (RT)^2 \,.\, K_p.$$

Generalising, one may say: If Δn represents the change in the number of molecules when a reaction takes place, one has the relation $K_c = (RT)^{-\Delta n} K_p$, or $K_p = K_c \,.\, (RT)^{\Delta n}$. In the case of gas reactions, therefore, which take place without change of volume (or without change in the number of molecules), $K_p = K_c$.

From the table on page 278 it is seen that at 673° K., $K_p = p_{NH_3}/p^{\frac{1}{2}}_{N_2} \times p^{\frac{3}{2}}_{H_2} = 0{\cdot}0129$. For the ratio $p^2_{NH_3}/p_{N_2} \times p^3_{H_2}$, K_p will have the value $(0{\cdot}0129)^2 = 1{\cdot}664 \times 10^{-4}$. The value of K_c, therefore, will be

$$K_c = (0{\cdot}0821 \times 673)^2 \times 1{\cdot}664 \times 10^{-4} = 0{\cdot}507.$$

(Since the pressures are measured in atmospheres and the volumes in litres, R must be expressed in litre-atmospheres.)

Dissociation Equilibria.—The law of mass action has been applied to the dissociation of a gaseous compound, *e.g.*, dissociation of nitrogen tetroxide, as shown by the equation

$$N_2O_4 \rightleftharpoons 2NO_2.$$

In this case the equilibrium condition or degree of dissociation of the N_2O_4 molecules can be calculated from the density of the gas mixture.[1]

If the initial amount of N_2O_4 is 1 gram-molecule, and if, at the given temperature, the fraction x undergoes dissociation, the total number of molecules at equilibrium will be $1 - x + 2x = 1 + x$, because each N_2O_4 molecule gives rise to two NO_2 molecules. There is therefore an increase in the number of molecules from 1 to $1 + x$. When dissociation takes place, the volume increases in proportion to the increase

[1] An investigation of the dissociation of nitrogen tetroxide was carried out by F. H. Verhoek and F. Daniels, *J. Amer. Chem. Soc.*, 1931, **53**, 1250. References to earlier determinations are given here.

in the number of molecules, and therefore, since the mass remains constant, the density will decrease in the same proportion. The observed density, d_o, will therefore be less than the theoretical density (density if no dissociation occurred) in the ratio $d_o/d_t = 1/1+x$. From this it follow that

$$x = \frac{d_t - d_o}{d_o}.$$

At 100·1° the density of nitrogen tetroxide, referred to that of hydrogen as unity, was found to be 25·7. Hence $x = 46 - 25{\cdot}7/25{\cdot}7 = 0{\cdot}79$.

The degree of dissociation, x, is also given by the ratio $P - p^{\circ}_{N_2O_4}/p^{\circ}_{N_2O_4}$, where P is the total pressure and $p^{\circ}_{N_2O_4}$ is the pressure which would be exerted if the nitrogen tetroxide were undissociated. Hence, $p^{\circ}_{N_2O_4} = \frac{w}{M} \cdot \frac{RT}{V}$, where w is the weight in grams, M is the molecular weight (92·02) and V is the volume in litres. ($R = 0{\cdot}0821$.)

Alternatively, one may calculate the value of x as follows: If there are w grams of nitrogen tetroxide in V litres under the pressure P and at temperature T, then the total number of gram-molecules ($N_2O_4 + NO_2$) at equilibrium will be $\frac{w}{M}(1+x)$, where M is the molecular weight of the undissociated oxide (92·02). Therefore, one can write: $PV = \frac{w}{M}(1+x) \cdot RT$, and $x = \frac{PVM}{w \cdot RT} - 1$.

From the values of x, so found, the equilibrium constant can be calculated. Thus, if $p_{N_2O_4}$ is the partial pressure of N_2O_4 molecules and p_{NO_2} the partial pressure of NO_2 molecules, one has

$$p_{N_2O_4} = \frac{1-x}{1+x} \cdot P \text{ and } p_{NO_2} = \frac{2x}{1+x} \cdot P,$$

where P is the total pressure. Hence, applying the law of mass action,

$$K_p = \left(\frac{2x}{1+x} \cdot P\right)^2 \Big/ \frac{1-x}{1+x} \cdot P = 4x^2P/(1-x^2).$$

For example: At 25° and under a pressure of 1 atmosphere, x was found equal to 0·185. One calculates, therefore,

$$K_p = 4 \times (0{\cdot}185)^2 \times 1/1 - (0{\cdot}185)^2 = 0{\cdot}142.$$

Moreover, from the expression, $K_p/P = 4x^2/1-x^2$, the value of x at other pressures, P, can be calculated. Thus, if P is reduced to 0·5 atmospheres, x becomes 0·257.

In the following table are given some of the values of K_p obtained by Verhoek and Daniels. In this table $C^\circ_{N_2O_4}$ is the concentration of N_2O_4 assuming no dissociation, and is equal to w/MV. Hence, $p^\circ_{N_2O_4} = C^\circ_{N_2O_4} \times RT$. From this and the total pressure P, the degree of dissociation x, and the equilibrium constant K_p, can be calculated.

DISSOCIATION OF NITROGEN TETROXIDE

$C^\circ_{N_2O_4}$ (Mols N_2O_4 per Litre) $\times 10^3$.	25°.		35°.		45°.	
	P (Atm.).	K_p.	P (Atm.).	K_p.	P (Atm.).	K_p.
6·28	0·2118	0·1419	0·2382	0·3174	0·2662	0·6771
10·15	0·3271	0·1470	0·3649	0·3163	0·4064	0·6491
19·84	0·5996	0·1412	0·6623	0·3032	0·7349	0·6280
29·68	0·8623	0·1261	0·9470	0·2792	1·0474	0·5934

Since the dissociation of N_2O_4 molecules is accompanied by an increase of volume (increase in the number of molecules), the degree of dissociation will be increased by decrease of pressure, as was shown above. Moreover, since dissociation is accompanied by absorption of heat, the degree of dissociation will increase with rise of temperature. Thus, from determinations of the density under atmospheric pressure by Deville and Troost, it is found that while the degree of dissociation at 26·7° is 0·201, at 60·2° it is 0·501, and at 100·1°, 0·790.

From the values of the equilibrium constants, $K_{p_1} = 1{\cdot}349$ at 328° K. and $K_{p_2} = 2{\cdot}607$ at 338° K., one calculates, $\Delta H = 14{,}500$ cal.

Other dissociation equilibria, *e.g.*, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; $Ni(CO)_4 \rightleftharpoons Ni + 4CO$, can be treated in a manner similar to that shown for nitrogen tetroxide. In general, in the case of the dissociation of gases, if one dissociating molecule can give rise to n molecules, the degree of dissociation x can be calculated from the expression $x = \dfrac{d_t - d_o}{(n-1)d_o}$.

For phosphorus pentachloride ($M = 208{\cdot}28$), the values of the density at different temperatures are shown in the table on page 284.

$T°$ K.	Density ($O_2=16$).	x.
473°	70·2	0·483
503°	62·2	0·674
523°	57·9	0·798
547°	55·6	0·872
573°	52·9	0·968

From these values of density the degree of dissociation is given by the expression: $x=d_t-d_o/d_o$, where $d_t=104{\cdot}1$. The values so calculated are shown in column 3 of the above table. From these values of x the equilibrium constants, under pressure, P, can be calculated from the equation:

$$K_p=x^2\,.\,P/(1-x^2).$$

At a temperature of 503° K., therefore, under atmospheric pressure ($P=1$),

$$K_p=0.674^2\times 1/1-0{\cdot}674^2=0{\cdot}833 \text{ (atmospheres)},$$

and $$K_c=K_p/RT=0{\cdot}833/0{\cdot}0821\times 503=0{\cdot}0202 \text{ (moles per litre)}.$$

It will be evident from the application of the law of mass action that addition of one of the products of dissociation will diminish the dissociation.

Homogeneous Equilibria in Solution.—The law of mass action can be applied not only to reactions which take place in the gaseous state, but also to reactions occurring in liquid solution. On applying the law, therefore, to the equilibrium

$$C_2H_5.OH+CH_3.COOH\rightleftharpoons CH_3.COO.C_2H_5+H_2O,$$

which was investigated as long ago as 1862 by Berthelot and L. Péan de St. Gilles, one obtains, as the expression for the condition of equilibrium,

$$\frac{[\text{ester}]\times[\text{water}]}{[\text{alcohol}]\times[\text{acid}]}=K_c.$$

As the result of experiment it was found that when 1 gram-molecule of alcohol is allowed to react at the ordinary temperature with 1 gram-molecule of acetic acid until equilibrium is established, 0·667 gram-molecule of ester and of water is formed. If, therefore, v is the volume of the solution, one has

$$K_c=\frac{\frac{0{\cdot}667}{v}\times\frac{0{\cdot}667}{v}}{\frac{0{\cdot}333}{v}\times\frac{0{\cdot}333}{v}}=\frac{0{\cdot}667^2}{0{\cdot}333^2}=4.$$

It will be observed that in this equation v cancels out, and, consequently, *dilution with an indifferent solvent has no*

influence on the condition of equilibrium. This will obviously always be the case when the number of molecules on either side of the chemical equation is the same.[1] When the number of molecules on the two sides of the reaction equation is not the same, the equilibrium will be altered by dilution.

The above equation holds, of course, no matter what may be the proportions in which the four substances concerned are mixed, provided time is given for the equilibrium to be attained. If, when equilibrium is reached, a further quantity of acetic acid is added the product of concentrations in the denominator of the equilibrium equation is increased. In order, therefore, that the above equation shall be satisfied, the product of concentrations in the numerator must also increase ; that is, more ester and water must be formed by the combination of acid and alcohol. By increasing the proportion of acid sufficiently, practically all the alcohol can be converted into ester.

By means of the above equilibrium equation it is easy to calculate the extent to which acid or alcohol is transformed to ester and water when the reactants are mixed together in any given proportion. Thus, if 1 gram-molecule of acid is mixed with a gram-molecules of alcohol, the amount of acid, x, transformed at equilibrium is given by the expression

$$\frac{x^2}{(1-x)(a-x)} = 4.$$

In the following table are given the values of x, in gram-molecules, for different proportions of acid and alcohol. The initial quantity of acid was in all cases 1 gram-molecule.[2]

Initial Quantity of Alcohol (a) (in Gram-molecules).	x Calculated.	x Found.
0·05	0·049	0·05
0·18	0·171	0·171
0·33	0·311	0·293
0·50	0·423	0·414
1·0	0·667	0·667
2·0	0·845	0·858
8·0	0·967	0·966

[1] Dilution with an indifferent solvent corresponds to an increase of volume or diminution of pressure in the case of a gaseous equilibrium.

[2] The value of x is calculated by means of the expression

$$x = \tfrac{2}{3}(1 + a - \sqrt{1 - a + a^2}).$$

From the above numbers it is seen that when the acid and alcohol are taken in equimolecular amounts, 66·7 per cent. of the acid is converted into ester; whereas if 8 molecular proportions of alcohol are taken to 1 molecular proportion of acid, 96·7 per cent. of the acid will be transformed.

From the above discussion it will be clear that if one varies the concentrations of the reactants or of the resultants (the substances appearing on the right-hand side of the chemical equation), one can cause one or other of the opposing reactions to take place to a greater extent. By increasing the concentration of one of the reactants (acid or alcohol), one will promote the transformation

$$C_2H_5OH + CH_3.COOH \longrightarrow CH_3.COOC_2H_5 + H_2O,$$

whereas if the concentration of one of the resultants (*e.g.*, water) is increased, the opposing reaction,

$$CH_3.COOC_2H_5 + H_2O \longrightarrow CH_3.COOH + C_2H_5OH,$$

will be favoured.

Activity.—In the application of the law of mass action to homogeneous equilibria the concentration in gram-molecules per litre has been used as a measure of what Guldberg and Waage called the "active mass." In gaseous reactions the partial pressure of the gas is taken as a measure of its concentration, but this can be justified only for a perfect gas which obeys the law $pv = RT$; and in any actual case the equation of state will not be as simple as this, although in dilute gases it can be taken as a close approximation. Similarly, in the case of solutions the active masses will be proportional to the concentrations only when the solutions are ideal; and, except in the case of such solutions, the condition of equilibrium in solution will not be correctly given by the law of mass action in which the concentration of the reactants is used as a measure of their "active mass." Instead, however, of altering the law of mass action it is better to replace concentrations by what G. N. Lewis, of the University of California, has called *activities*, or quantities which are proportional to the true active mass of the reacting substances, and by the use of which concordance with the law of mass action is obtained.[1] The activity will be given by the expression $a = f \cdot c$, where a is the activity, c is the concentration, and f is the *activity coefficient*, the value of which varies with the concentration; and it is this quantity a which must be used in the mass law equation.

[1] *Proc. Amer. Acad.*, 1901, **37**, 45; 1907, **43**, 259.

By the use of activities instead of molar concentrations the law of mass action will yield a constant value for the equilibrium constant of a reaction ; and the thermodynamic formulæ may then be applied with accuracy.

The activity of a substance in solution may be determined in various ways. (1) One may, for example, obtain the value of the activity from determinations of the lowering of the freezing-point. Thus, for solutions of concentration lower than about 3-molal (*i.e.*, 3 gram-molecules per 1000 *grams* of solvent), the activity of the solute can be calculated by means of the expression $2{\cdot}303 \log_{10}\frac{a}{m} = -2\left(1 - \frac{\theta}{\lambda m}\right)$, where a is the activity of the solute, m is the concentration expressed in gram-molecules per 1000 g. of solvent, θ is the depression of the freezing-point, and λ is the molecular lowering of the freezing-point (per 1000 g. of solvent). λ for water is $1{\cdot}858°$.

(2) In the case of a volatile substance one may take the vapour pressure or partial vapour pressure as a measure of its effective concentration or activity, and the law of mass action will then give a true expression of the condition of equilibrium if the partial pressures of the reactants and resultants are used instead of the molar concentrations.

(3) The departure of solutions from the ideal condition may be regarded as due to attraction between solvent and solute ; and when the solute is very soluble this attraction is more pronounced and the active mass of the solute is proportionally less. Since the active mass of a solid is constant, and since, as van't Hoff assumed, the active mass of a solid must be the same as the active mass of the substance in a saturated solution, independently of the nature of the solvent, van't Hoff suggested that the concentration of the solute in a saturated solution should be taken as standard. That is, if the concentration of a given constituent is measured, not in gram-molecules per litre but as a fraction of its concentration in a saturated solution in the given solvent, this fraction may be taken as a measure of its activity, for it must be a definite fraction of the constant activity of the solid. The activity of the solute, therefore, is represented by the expression $a = \frac{C}{S}$, where S is the

solubility, or the concentration in the saturated solution. Thus, as van't Hoff pointed out, if two isomeric forms of a substance, *e.g.*, formyl phenyl acetic ester, $C_6H_5.C:(CHOH).COOC_2H_5$ and $C_6H_5.CH.(CHO).COOC_2H_5$, are in equilibrium in two solvents, *a* and *b*, the conditions of equilibrium are given by the expressions $K_a = \log\frac{C_a}{c_a}$ and $K_b = \log\frac{C_b}{c_b}$, where C and c represent the concentration of the two isomers respectively. The two equilibria can be related by means of the partition law (Chap. XVI.), according to which, for slightly soluble substances, the partition of a substance between two solvents is in the ratio of the solubilities. If, then, the two solutions are shaken together, one has $\frac{C_a}{C_b} = \frac{S_a}{S_b}$, where S_a and S_b are the solubilities of the substance in the solvents *a* and *b*. Therefore,

$$K_a - K_b = \log\frac{C_a}{c_a} - \log\frac{C_b}{c_b} = \log\frac{C_a}{C_b} - \log\frac{c_a}{c_b} = \log\frac{S_a}{S_b} - \log\frac{s_a}{s_b}$$

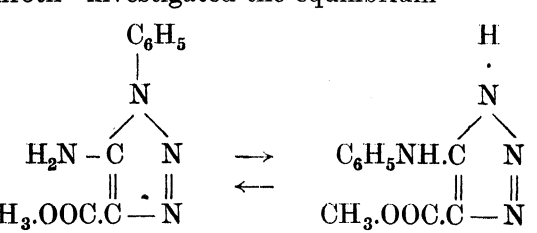
and consequently,

$$K_a - \log\frac{S_a}{s_a} = K_b - \log\frac{S_b}{s_b} = K,$$

K being a new constant which is independent of the solvent. This new constant can be expressed as

$$K = \log\frac{C_a/S_a}{c_a/s_a} = \log\frac{C_b/S_b}{c_b/s_b},$$

so that the influence of the solvent disappears if saturation is taken as the unit of concentration. In order to test this law, Otto Dimroth[1] investigated the equilibrium



1-phenyl-5-aminotriazol methyl-carbonic ester (neutral) ⟷ 5-aminotriazol carbonic ester (acid)

[1] *Annalen*, 1910, **377**, 127.

in several solvents. The attainment of equilibrium from either side was slow, even in the boiling solvents, and so the solubilities could be determined. In the following table are given the values of the equilibrium constant $K = \frac{C_{\text{acid}}}{C_{\text{neutral}}}$, and the ratio of the solubilities, $\frac{S_{\text{acid}}}{S_{\text{neutral}}}$, at 60°. In the last column are given the value of G, the ratio of the activities of the two isomers, or the ratio $\frac{C_{\text{acid}}}{S_{\text{acid}}} \Big/ \frac{C_{\text{neutral}}}{S_{\text{neutral}}}$. It will be observed that whereas K is very variable, G is approximately constant.

Solvent.	Dielectric Constant.	$K = \frac{C_a}{C_n}$.	$\frac{S_a}{S_n}$.	G.
Ether	4·6	21·7	53·0	0·4
Methyl alcohol . .	35·4	2·3	7·0	0·33
Toluene . . .	2·37	1·8	4·3	0·33
Benzene . . .	2·25	1·02	3·2	0·32
Nitrobenzene . .	34	0·8	2·2 (47°)	0·36
Chloroform . . .	5	0·32	1·1 (35°)	0·32

It is clear, from the above experimental results, that the van't Hoff method of deducing the activity of a substance in solution is, in the cases under discussion, fairly satisfactory. In all cases of equilibrium, however, the best method of deducing the activity of the substances concerned must be determined experimentally, the object being to obtain such functions of the concentrations that when these are inserted in the usual expression of the law of mass action this law is found in agreement with the results of experiment.

(4) Measurements of electromotive force (Chap. XV.).

CHAPTER XIII

THE SECOND LAW OF THERMODYNAMICS

THE first law of thermodynamics, it was learned, is concerned with the equivalence of different forms of energy, and states that the energy obtainable from an isolated system cannot exceed the energy put into the system. Moreover, the constancy of the ratio of mechanical, electrical, or other form of energy to the heat energy produced shows that these different forms of energy can be converted *completely and quantitatively* into heat. It might, therefore, be thought that the reverse transformation of heat energy into mechanical or other forms of energy could also be carried out quantitatively, but this is not the case. To employ a frequently used illustration, one might imagine a ship fitted with an engine which extracted heat energy from the ocean, converted the heat energy into the mechanical energy necessary to drive the ship, and returned the heat to the sea again through the friction of the screws or of the vessel. This arrangement would not contravene the first law of thermodynamics, but it would constitute a *perpetual motion machine of the second class* capable of converting continuously the heat of its surroundings into external mechanical work. Experience has shown that no such perpetual motion machine can be obtained, and the second law of thermodynamics is a statement of man's failure to produce such a machine. While, therefore, the first law of thermodynamics states the equivalence of different forms of energy, the second law, *which deals with the conditions under which transformation of heat energy into other forms of energy takes place,* proclaims that the extent to which such transformation can be effected is limited. The law, which is of fundamental importance in discussing the relation between heat and work in various processes, has been stated in different ways, two of which may be given here :—

1. *Heat cannot pass of itself* (i.e., *without some compensating transformation*) *from a colder to a warmer body.* (CLAUSIUS.)
2. *It is impossible, by inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.* (LORD KELVIN.)

Reversibility and Maximum Work.—Before one can calculate the extent to which heat can be converted into mechanical work one must first ascertain the conditions under which the maximum amount of external work can be obtained from any given process ; and for this purpose one may consider the work done when a perfect gas expands in a cylinder and so raises a piston. If one imagines that the piston is weightless and that it moves without friction, the maximum work is obtained on expansion when the external pressure on the piston is less than the pressure of the gas by an infinitely small amount. Thus, if the pressure of the gas is p, and if the external pressure on the piston is lowered to $p - dp$, where dp is an infinitely small pressure, the piston will be moved forward until the volume of the gas has increased by an infinitely small amount from v to $v + dv$. The work which is thereby done is $(p - dp) \,.\, dv = p \,.\, dv$, since one may neglect the product of two infinitely small quantities. Since the whole work of expansion is converted into external work, none being lost in friction or otherwise, the process can be completely reversed and the system obtained in its original state by increasing the pressure on the piston by an infinitely small amount. In order, therefore, that the maximum work may be obtained from a given process, that process must be carried out reversibly ; and the condition of reversibility is that at each moment the system shows only an infinitely small departure from a state of equilibrium, or that, at all points, action and reaction differ only by an infinitely small amount.

Bearing the condition of reversibility in mind, one can calculate the maximum work which can be obtained by the expansion of a perfect gas through a finite volume $(v_2 - v_1)$. Thus the work done in expanding 1 gram-molecule of a perfect gas from volume v_1 to volume v_2 must be equal to the sum of all the infinitesimal amounts of work represented by $p \,.\, dv$. That is to say, the work done, w, will be equal to

$\int_{v_1}^{v_2} p \,.\, dv$; and since one is dealing with 1 gram-molecule of gas, one has

$$w = \int_{v_1}^{v_2} p \,.\, dv = \int_{v_1}^{v_2} \frac{RT}{v} \,.\, dv = RT \log_e \frac{v_2}{v_1}.$$

Since, in the case of a perfect gas, $p_1 v_1 = p_2 v_2$, one may also write

$$w = RT \log_e \frac{p_1}{p_2}.$$

This, also, is the *maximum work* obtainable, since it is the sum of the work obtained in a series of reversible processes.

Conversion of Heat into Mechanical Work.—One may now calculate the extent to which heat can be converted into work by causing a perfect gas to pass through a cycle of reversible operations, in the course of which a certain amount of heat is transferred from a higher to a lower temperature, and a certain amount of work is done. At the conclusion of the operations the gas is restored to its initial state. Such a cycle of operations is known as a *Carnot cycle*, the method having been employed for the first time in 1824 by Nicolas Léonard Sadi Carnot (1796-1832), Officer of Engineers in the French Army.

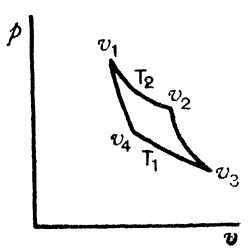


FIG. 89.

1. Let 1 gram-molecule of a perfect gas, enclosed in a cylinder with frictionless piston and occupying the volume v_1, be placed in contact with a large heat reservoir at constant absolute temperature T_2, and let the gas be allowed to expand isothermally to volume v_2 (Fig. 89). Work, w_2, is thereby done by the gas equal to $RT_2 \log_e \frac{v_2}{v_1}$; and, at the same time, an amount of heat, q_2, is taken up from the reservoir or "boiler" in order to keep the temperature of the gas unchanged. Since the energy of a perfect gas, at a given temperature, is independent of its volume,

$$q_2 = w_2 = RT_2 \log_e \frac{v_2}{v_1}.$$

2. The gas is now completely insulated, and expansion allowed to take place adiabatically until the temperature falls to T_1. The volume of the gas will now be v_3.

3. The gas is now placed in contact with a reservoir or " condenser " at the absolute temperature T_1, and compressed isothermally until the volume is v_4. Work has thereby to be done on the gas which is equal to $w_1 = RT_1 \log_e \frac{v_3}{v_4}$; and at the same time an amount of heat, $q_1 = w_1$, is given up to the condenser.

4. The gas is again insulated and compressed adiabatically until the volume is v_1 and the temperature has arisen to T_2. The system is now restored to its initial state.

For an adiabatic expansion from volume v_2 at the temperature T_2 to the volume v_3 at the temperature T_1, it can be shown that $\frac{T_2}{T_1} = \left(\frac{v_3}{v_2}\right)^{\gamma-1}$, where γ is the ratio of the specific heats of the gas at constant pressure and constant volume; and for the adiabatic compression from volume v_4 to volume v_1, one has $\frac{T_1}{T_2} = \left(\frac{v_1}{v_4}\right)^{\gamma-1}$. It follows, therefore, that $\frac{v_3}{v_2} = \frac{v_4}{v_1}$ or $\frac{v_3}{v_4} = \frac{v_2}{v_1}$; and for $w_1 = RT_1 \log_e \frac{v_3}{v_4}$, one may write $w_1 = RT_1 \log_e \frac{v_2}{v_1}$. Since, during the adiabatic processes, heat is neither taken up from nor given up to the outside, the net result of the Carnot cycle is that a certain amount of external work, $w_2 - w_1$, has been gained and a certain amount of heat, q_2, has been taken in at the temperature of the boiler T_2. The *efficiency* of the process, therefore, or the ratio of the work gained to the heat taken in from the boiler, is given by the expression

$$\frac{w_2 - w_1}{q_2} = \frac{T_2 - T_1}{T_2},$$

or, since all the operations have been carried out reversibly, one may write,

$$w_{max.} = q_2 \cdot \frac{T_2 - T_1}{T_2},$$

where $w_{max.}$ is the maximum external work done and q_2 is the heat absorbed at the higher temperature T_2, by the gas.

One sees from this that, of the heat taken up by the system, the theoretically maximum fraction which can be converted into work is $\frac{T_2 - T_1}{T_2}$. Further, the efficiency of a reversible heat engine depends only on the temperatures of the boiler and condenser T_2 and T_1, and does not depend on the medium by which the heat is transported ; or, *all reversible engines working in cycles between the same temperature limits are equally efficient.* This is known as *Carnot's theorem.* It will also be clear from the expressions given above that the efficiency becomes a maximum, equal to unity, when the temperature of the condenser is zero ($T_1 = 0$). One obtains in this way an absolute zero of temperature which is found to be the same as that derived from the gas laws applied to a perfect gas, namely, $-273{\cdot}16°$ C.

The above expression of the Second Law of Thermodynamics may be put in a different form. A system may be said to have a certain *work content,* which may be represented by A. When a system does external work on its surroundings the work content decreases, and if the process is carried out reversibly one may write, $-\Delta A = w_{\max.}$. In the case of a gram-molecule of a perfect gas expanding isothermally and reversibly under constant pressure,

$$-\Delta A = RT \log_e v_2/v_1 = w_{\max.}$$

Hence,

$$-\Delta A = q_2 \cdot \frac{T_2 - T_1}{T_2},$$

or, for a very small temperature difference,

$$d(-\Delta A) = q \cdot \frac{dT}{T}.$$

Clausius-Clapeyron Equation.—Since the efficiency of a reversible heat engine is independent of the medium by which the heat is transported, or of the nature of the process, the second law of thermodynamics can be applied to all physical and chemical processes which can be carried out reversibly. Thus, one may allow the given process, physical change or chemical reaction, to take place isothermally at the higher temperature $T + dT$, whereby a certain amount of work w is done by the system, and an amount of heat q is taken from the heat source. The reaction is then reversed at a lower temperature T by the expenditure of an amount of work

$w - dw$. The work gained is therefore dw, and the heat taken in from the heat source is q, so that one has

$$dw_{max.} = d(-\Delta A) = q \cdot \frac{dT}{T},$$

or

$$q = T\left(\frac{d(-\Delta A)}{dT}\right).$$

In this *maximum work equation*, as it may be called, it should be noted that dw or $-d \cdot \Delta A$ represents the excess of work obtained when the given process is carried out at a temperature $T + dT$, as compared with the work obtained when the process is carried out at a temperature T.

As an example of a reversible process, one may consider the vaporisation of a liquid. For 1 g. of liquid, heat equal to the latent heat of vaporisation l is taken in at the higher temperature, and work is done by the system which is represented by $(p + dp)(v_2 - v_1)$, where $(p + dp)$ is the vapour pressure, v_2 is the volume of the vapour, and v_1 is the volume of the liquid. At the lower temperature T and under the pressure p, 1 g. of vapour is condensed, the work expended being represented by $p(v_2 - v_1)$. The net gain of work, therefore, is $dp(v_2 - v_1)$ and the heat taken from the heat source is l. One has, therefore,

$$dp(v_2 - v_1) = l \cdot \frac{dT}{T}, \text{ or } \frac{dp}{dT} = \frac{l}{T(v_2 - v_1)}.$$

This is the *Clausius-Clapeyron* equation, and is another application of the second law of thermodynamics. Application of this equation has been made not only to the process of vaporisation (p. 296), but also to the process of fusion (p. 297). Other applications will be made later.

Relative Lowering of the Vapour Pressure.—The relation between the concentration of a solution and the relative lowering of the vapour pressure can be found by means of a cyclical process (*cf.* p. 201). If a dilute solution, consisting of n_1 gram-molecules of solute in n_2 gram-molecules of solvent, is contained in a cylinder fitted with a semi-permeable piston, one can remove pure solvent reversibly from the solution by exerting on the piston a pressure greater by an infinitely small amount than the osmotic pressure of the solution. By this means let an amount of solvent $\left(\frac{n_2}{n_1} \text{ gram-molecules}\right)$,

equal to that in which 1 gram-molecule of solute is contained, be expressed from the solution. Assuming that the gas laws hold for dilute solutions, the work which has to be done is equal to $pv = RT$. The volume of the solution is supposed to be so great that no change in its concentration is thereby caused. Let this amount of solvent be now vaporised reversibly at the constant temperature T and under a pressure p equal to the vapour pressure of the solvent. The work done will be equal to $\frac{n_2}{n_1} . pv$, where v is the volume of the vapour. (The volume of the liquid has been neglected as negligibly small.) The vapour is allowed to expand further to volume v', so that the pressure falls to p', the vapour pressure of the solution at the temperature T. Work is thereby done by the vapour equal to $\frac{n_2}{n_1} RT \log_e \frac{v'}{v} = \frac{n_2}{n_1} RT \log_e \frac{p}{p'}$. The vapour is brought in contact with the solution and condensed reversibly to liquid, the work done on the vapour being $\frac{n_2}{n_1} . p'v' = \frac{n_2}{n_1} . pv$. The system is now in its initial state, and since the series of changes has been carried out at constant temperature the work done on the system must be equal to the work done by the system. That is,

$$\frac{n_2}{n_1} . RT \log_e \frac{p}{p'} = RT, \text{ or } \log_e \frac{p}{p'} = \frac{n_1}{n_2}.$$

Further, one can write $\log_e \frac{p}{p'} = \log_e \left(1 + \frac{p - p'}{p'}\right)$, which, in the case of dilute solutions, can be put equal to $\frac{p - p'}{p'}$, the remainder of the terms of the expansion being neglected, since $p - p'/p'$ is small.[1] Also, if $(p - p')$ is small compared with p and p', one may write $\frac{p - p'}{p'} = \frac{p - p'}{p}$. In the case of very dilute solutions, therefore, one may write $\frac{p - p'}{p} = \frac{n_1}{n_2}$.

Elevation of the Boiling-point.—It has already been shown (p. 207), by applying the Clausius-Clapeyron equation, that

[1] The logarithmic expression, $\log_e \left(1 + \frac{p - p'}{p'}\right)$, when expanded in a series, takes the form $(y - \frac{1}{2}y^2 + \frac{1}{3}y^3 \ldots)$, where $y = p - p'/p'$.

the molecular elevation of the boiling-point of a solvent is given by the expression $K = \frac{RT^2}{l}$, where l is the latent heat of vaporisation per gram of the solvent and T is the absolute temperature of the boiling-point.

Depression of the Freezing-point.—The relation between the concentration of a solution and the depression of the freezing-point is given by the expression $\Delta T = K \cdot \frac{n}{W}$, where n $\left(=\frac{w}{m}\right)$ is the number of gram-molecules of solute and W is the weight of the solvent. The value of K, the freezing-point constant, can be calculated on the basis of the second law of thermodynamics.

At the temperature $T - \Delta T$, the freezing-point of the solution, let an amount of solvent $\left(\frac{W}{n}\text{ g.}\right)$, equal to that in which 1 gram-molecule of solute is dissolved, be allowed to freeze out reversibly from such a large amount of solution that no change of concentration is thereby produced. The solid solvent is now raised to the temperature T, the melting-point of the solvent, and allowed to melt. Heat is thereby taken up equal to $\frac{W}{n} \cdot l$ cal., where l is the latent heat of fusion of 1 g. of solid solvent. The melted solvent is now allowed to pass back into the solution reversibly through a semi-permeable membrane, whereby, assuming that the gas laws hold for the solution, work is done equal to $PV = RT$; P being the osmotic pressure of the solution and V the volume of the solvent in which 1 gram-molecule of solute was dissolved. The system is then cooled down to the initial temperature $T - \Delta T$. In this reversible cycle of operations the heat taken in at the higher temperature T is $\frac{W}{n} \cdot l$ cal., and the work which is done is RT.[1]

Hence $RT = \frac{W}{n} \cdot l \cdot \frac{\Delta T}{T}$, or $\Delta T = \frac{RT^2}{l} \cdot \frac{n}{W}$. Since, however,

[1] Change of volume on melting is neglected, and so also is the heat evolved or absorbed when the system is cooled or warmed through the temperature range ΔT. When ΔT is small, the specific heat of the system is negligible compared with the latent heat of fusion.

it has been shown that $\Delta T = K \cdot \frac{n}{W}$, one has

$$K = \frac{RT^2}{l} = \frac{1{\cdot}987 \times T^2}{l},$$

where T is the absolute temperature of the melting-point of the solid solvent and l is the latent heat of fusion.

The relation between the molecular depression of the freezing-point of a solvent and the latent heat of fusion is analogous to that between the molecular elevation of the boiling-point and the latent heat of vaporisation. The analogy depends on the fact that in both cases one is dealing with work done in separating pure solvent from solution, in the one case by freezing and in the other by vaporisation. Only the mechanism of the process differs in the two cases, and in thermodynamics one is not concerned with mechanism.

Chemical Affinity and Free Energy.—The term " affinity " was first used by Albertus Magnus (1193-1282) in the thirteenth century, and reflected the view, current at the time, that chemical action is due to a similarity or kinship between the reacting substances. Although this view was abandoned in the eighteenth century the term is still retained as signifying a force which acts between different kinds of matter and which, under certain conditions, brings about a chemical reaction between them. How, then, can this affinity, so important for chemical change, be quantitatively determined ?

The relative affinities of substances could, it was thought by the German chemist, Georg Ernst Stahl (1660-1734), be determined by the order in which substances expel one another from compounds ; and in 1718 Etienne François Geoffroy (1672-1731), Professor of Chemistry at the *Jardin du Roi* [1] in Paris, drew up a table of substances arranged in this way. Similar tables were also drawn up in 1775 by Torbern Bergman (1735-84), who, moreover, recognised that the affinity, as determined by mutual displacements, might alter with the temperature, especially when a substance is volatile. Thus, in solution, sulphuric acid expels phosphoric acid from calcium phosphate, with production of calcium sulphate ; but, at a high temperature, phosphoric acid expels sulphuric acid from calcium sulphate.

In 1799 Claude Louis Berthollet (1748-1822), as a result of his investigations of the formation of trona in the soda lakes of Egypt, was led to the conclusion that chemical affinity is not a constant and unvarying force, but that it may be greatly influenced by the mass of the reacting substances. A reaction which, under certain conditions, takes place in one direction may, by a variation of the masses of the reacting substances, be caused to take place in the reverse direction. In later years the effect of " mass " found its quantitative expression in Guldberg and Waage's law of mass action.

[1] Now *Jardin des Plantes*

About the middle of last century the view was put forward that the heat of chemical action could be taken as a measure of chemical affinity; and in 1854 and 1864, respectively, the two pioneer workers in thermochemistry, Hans Peter Jürgen Julius Thomsen (1826-1908), of the University of Copenhagen, and the French chemist, Marcelin Pierre Eugène Berthelot (1827-1907), stated the principle that of all possible chemical reactions occurring spontaneously, *i.e.*, without the aid of external energy, those take place which are accompanied by the greatest evolution of heat. This theorem Berthelot called the *principle of maximum work*, work being here identified with the heat of chemical reaction, which was regarded as being equal to the decrease of the total energy of a system. According to this theorem, only those reactions could take place spontaneously which are accompanied by evolution of heat. Although, as will be made clear presently, this principle holds good under certain conditions, *e.g.*, at and in the neighbourhood of the absolute zero, it has no general validity. This is shown by the fact that not a few reactions are known which take place spontaneously with *absorption* of heat. The general validity of the principle of maximum work is disproved also by the occurrence of reversible reactions and the existence of chemical equilibria; for it is clear that if one of the reactions takes place with evolution of heat, the reverse reaction must take place with absorption of heat. It may also be pointed out that the assumption on which the principle of maximum work is based, namely, that the heat of reaction is equal to the decrease of total energy of a system, holds only when the reaction takes place without the performance of external work.

It was thought by some, also, that a measure of chemical affinity is to be found in the *velocity* with which a reaction takes place; but this view clearly becomes untenable when one considers the fact that many substances, *e.g.*, hydrogen and oxygen, between which one recognises that there is great affinity, do not combine when brought together at the ordinary temperature but do so only in the presence of a catalyst.

It was not till 1884 that van't Hoff, in his *Etudes de dynamique chimique*, pointed out that, on the basis of the second law of thermodynamics, a measure of chemical affinity is to be found in the *maximum external work* (the "work of chemical affinity") which can be obtained when a chemical reaction is carried out reversibly and isothermally. A system, we have seen, may be regarded as possessing a certain work content or capacity for doing work (A), but the absolute amount is not determinable. It is only the change in this capacity, when one system passes spontaneously into another system, that can be measured by the maximum amount of work which can be done. This change may be represented by $-\Delta A$, whereby it is indicated that in a spontaneously occurring reaction there is a *decrease* in the capacity for doing work. This quantity, $-\Delta A$, is therefore a measure of the affinity of a reaction, when the volume remains constant, and depends only on the initial and final systems.

When a reaction is carried out, as it very frequently is, at constant (atmospheric) pressure and at constant temperature, the total external work is the sum of the electrical

or other energy available for use, and the work done by expansion against the constant pressure. The latter work is represented by $p \cdot \Delta v$, where Δv is the increase of volume accompanying the process.[1] The work available for use may be called the *available energy* or the *free energy* G.[2] Here, again, one can measure only the differences in the free energies of systems, and one may write :

Maximum work done = difference in free energy $+ p \cdot \Delta v$.

or

$$-\Delta A = \qquad -\Delta G \qquad + p \cdot \Delta v.$$

That is to say,

$$-\Delta G = -\Delta A - p \cdot \Delta v.$$

In any process which takes place spontaneously at constant temperature and constant pressure, $-\Delta G$ represents the maximum *useful* work, or *available work*, which can be obtained, and is equal to the maximum work, $-\Delta A$, of the reversible change at constant temperature and pressure less the external work, $p \cdot \Delta v$, done by expansion under constant pressure. This decrease in the free energy, $-\Delta G$, may be taken as representing the " affinity " of the chemical process. One may say, therefore, that a reaction can take place spontaneously only when it is accompanied by a decrease in the free energy ; and, conversely, when for a given reaction in a given direction the difference of free energy is negative, that reaction is thermodynamically possible although it may not take place to any noticeable extent in the absence of a suitable catalyst.

Gibbs-Helmholtz Equation.—The relation between the change in the intrinsic or total energy of a system, as measured in a calorimeter, and the maximum work or free energy change can be obtained by combining the first and second laws of thermodynamics. Since the first law can be expressed by $\Delta U = q - w$, or $\Delta U = q + \Delta A$, and the second law by the equation, $q = T\left(\frac{\partial(-\Delta A)}{\partial T}\right)$, it follows that

[1] The value of $p \cdot \Delta v$ is constant and is independent of the manner in which the reaction is carried out. The magnitude of the available energy, however, varies, and is a maximum when the reaction is carried out reversibly.

[2] The term " free energy " was introduced by Helmholtz, who, however, applied the term to the maximum work done ($-\Delta A$). The distinction made above is very useful and is due especially to G. N. Lewis. G was called by Willard Gibbs the " thermodynamic potential."

$$\Delta U - \Delta A = T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_v,$$

or

$$\Delta A - \Delta U = T\left(\frac{\partial \cdot \Delta A}{\partial T}\right)_v.$$

Also, since $\Delta H = \Delta U + p \cdot \Delta v$ (p. 258), and $p \cdot \Delta v = \Delta G - \Delta A$, one may write,

$$\Delta G - \Delta H = T\left(\frac{\partial \cdot \Delta G}{\partial T}\right)_p.$$

In the preceding equations, the subscripts v and p indicate that the process occurs at constant volume and at constant pressure respectively.

The above equations are different forms of the often-called *Gibbs-Helmholtz Equation*. The last form is, perhaps, the most useful, since most chemical reactions are carried out at constant atmospheric pressure.

From the Gibbs-Helmholtz equation the important conclusion can be drawn that the change in the intrinsic energy of a system (U or ΔU), or the heat of reaction as measured in a calorimeter, will be equal to the external work done (A or ΔA) only when the temperature coefficient of the work done is equal to nought ($dA/dT = 0$), or when the reaction takes place at the absolute zero ($T = 0$). Under these conditions, therefore, $A = U$, and the Thomsen-Berthelot principle of maximum work is valid ; and only those reactions will take place spontaneously (*i.e.*, with performance of external work) which are accompanied by evolution of heat, A and U both being positive. Further, when $dA/dT = 0$, $dU/dT = 0$. That is, the heat of reaction is independent of the temperature. From this it follows, by Kirchhoff's law (p. 270), that the specific heat of the reactants is the same as the specific heat of the resultants ; and since the molecular heats of solid compounds are, in many cases, equal to the sum of the atomic heats of the constituent elements, the Thomsen-Berthelot principle must also be valid in the case of reactions involving such substances. The Thomsen-Berthelot principle, therefore, enshrines at least a partial truth.

The possibility that a reaction may take place spontaneously with *absorption* of heat (endothermic reaction) also follows from the Gibbs-Helmholtz equation. For, if the temperature coefficient dA/dT is positive and if the quantity $T \cdot \frac{dA}{dT}$ is greater than A (which will be the case

especially at high temperatures), then the expression $A - T \cdot \frac{dA}{dT}$ will be negative, and therefore U will be negative. That is, the reaction takes place with absorption of heat.

Since the temperature coefficient of chemical affinity dA/dT is generally small compared with the maximum work A, it follows that at low or moderate temperatures most reactions are exothermic; and heats of reaction, when positive and large, may be taken as representing, approximately, relative chemical affinities.

The quantity $T\frac{dA}{dT}$ represents what is known as the *bound* or *latent* energy, or energy unavailable for external work, and one sees that an endothermic reaction can take place spontaneously because there is a decrease of free energy (or external work is done), but an absorption of heat takes place because more energy becomes bound or latent than is given out as external work $\left(T\frac{dA}{dT} > A\right)$.

Entropy.—The relation between the intrinsic energy of a system and the maximum work or free energy obtainable when the system undergoes change, can be represented by the equations

$$U = A + TS$$

and

$$H = G + TS,$$

where S is the capacity factor of the isothermally unavailable energy or of the bound energy in a reversible isothermal process. It is called *entropy*. For a process occurring at constant temperature, therefore, one has the relation,

$$\Delta G = \Delta H - T\Delta S.$$

If a reversible process takes place isothermally, at a temperature T, in a non-isolated system, and is accompanied by an absorption of heat, q, no useful work is done and there is merely a transfer of unavailable energy, TS. The change (increase) in the unavailable energy of the system will be $T \cdot \Delta S$ (T being constant), and this will be equal to the heat absorbed, q. The increase of entropy, therefore, is

$$\Delta S = \frac{q}{T},$$

where q is the heat absorbed in a reversible isothermal

process, carried out at the absolute temperature T. ΔS, it may be noted, has the dimensions of energy divided by temperature, and can be expressed in calories per degree. By means of this relationship it is possible to calculate the change in entropy accompanying a reversible process.

Thus, in the vaporisation of 1 gram-molecule of water at 100° C., carried out reversibly under the pressure of its own vapour, the heat absorbed is the molar heat, or latent heat per gram multiplied by the molecular weight. Hence, the increase of entropy in the process is

$$\Delta S = \frac{539{\cdot}6 \times 18}{373} = 26{\cdot}04 \text{ cal. per degree.}$$

In a similar manner one may calculate the entropy increase accompanying the process of fusion.

Since $\Delta S = L_{\text{vap.}}/T$, one may state Trouton's Rule (p. 101) in the form : Normal liquids have the same entropy change of vaporisation.

Entropy Change in Spontaneous Reactions.—It has been pointed out (p. 298) that spontaneous reactions, which can take place without addition of energy from outside, take place with performance of external work or are accompanied by a decrease of the free energy ; and the extent to which a process can take place spontaneously can be expressed in terms of ΔA or ΔG. It can also be expressed in terms of ΔS.

The increase of entropy, ΔS, in a reversible process, that is, in a process which takes place under conditions of equilibrium, has already been considered. In the case of a spontaneously occurring reaction, the process is not reversible, and in the process some of the energy becomes unavailable (TS) ; and if the reaction takes place at constant temperature the increase of entropy, ΔS, is a measure of the irreversibility of the process. *A spontaneously occurring chemical reaction or physical change is accompanied by an increase of the total entropy of the system* ; and from a knowledge of the entropies of substances it is possible to state the direction of spontaneously occurring reactions or physical changes.

Thermodynamic Deduction of the Law of Mass Action.—The law of mass action was enunciated by Guldberg and Waage on the basis of the experimental determination of the velocity of chemical reactions, and an equivalent expression can be deduced on the basis of the kinetic theory with the help of certain assumptions regarding the motion and collision of molecules. A broader and more general

derivation of the condition of equilibrium, independent of the nature of the reacting substances and of the particular course which a reaction may follow, can, however, be obtained by the use of the concepts of maximum work and free energy discussed in the preceding pages. To illustrate this, one may consider a particular case of a gaseous equilibrium, namely,

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$

From whichever side the condition of equilibrium is reached there is a decrease of free energy, and *at equilibrium the free energy change is zero.*

In order to derive the condition of equilibrium in the case of the above balanced reaction, a mechanism must be made use of by means of which the reaction can be carried out reversibly and isothermally. Such a device, known as the "equilibrium box," was imagined by van't Hoff. This box is supposed to be furnished with a number of walls or membranes, each of which is permeable only to one of the constituents of the reaction mixture. With the help of this device one can calculate the maximum work done in converting 1 gram-molecule of carbon monoxide at the partial pressure P_1, and 1 gram-molecule of steam at the partial pressure P_2 into 1 gram-molecule of carbon dioxide at partial pressure P_3, and 1 gram-molecule of hydrogen at partial pressure P_4. These partial pressures are chosen quite arbitrarily. In the equilibrium box the four gases are supposed to be present as an equilibrium mixture, the partial pressures of the different gases being p_1, p_2, p_3, and p_4 respectively.

The carbon monoxide and steam are supposed to be contained in cylinders with frictionless pistons, and the gases are expanded reversibly until their partial pressures are p_1 and p_2, the same as those of the respective gases in the equilibrium box. The work done by the gases in the process is $RT \log_e \frac{P_1}{p_1}$ and $RT \log_e \frac{P_2}{p_2}$ respectively. The cylinders are now brought into contact with the appropriate membranes in the equilibrium box, and 1 gram-molecule of carbon monoxide and 1 gram-molecule of steam are passed into the equilibrium box. Since the partial pressures of the gases in the cylinders and in the equilibrium box are the same, no work is done in the process. The carbon monoxide

and steam immediately react in the box with production of carbon dioxide and hydrogen, but the volume of the equilibrium mixture is supposed to be so large that no appreciable change in the composition is produced. By means of cylinders and pistons, 1 gram-molecule of carbon dioxide and 1 gram-molecule of hydrogen, at the partial pressures p_3 and p_4, are now removed from the equilibrium box through the appropriate membranes; an operation which again involves no work. These two gases are now brought to the pressures P_3 and P_4, the work thereby done by the system being $RT \log_e \frac{p_3}{P_3}$ and $RT \log_e \frac{p_4}{P_4}$. The total work done in the series of operations is :

$$\text{Work} = RT\left(\log_e \frac{P_1}{p_1} + \log_e \frac{P_2}{p_2} + \log_e \frac{p_3}{P_3} + \log_e \frac{p_4}{P_4}\right),$$

or, rearranging the logarithmic quantities,

$$\text{Work} = RT \log_e \frac{p_3 p_4}{p_1 p_2} - RT \log_e \frac{P_3 P_4}{P_1 P_2}.$$

If the partial pressures of the constituents in the equilibrium box had had any other values, say p_1', p_2', p_3', and p_4', the total work would have been :

$$\text{Work} = RT \log_e \frac{p_3' p_4'}{p_1' p_2'} - RT \log_e \frac{P_3 P_4}{P_1 P_2}.$$

The total work in the two cases, however, must be the same, since the operations are carried out reversibly, and the work therefore depends only on the initial and final systems. Consequently,

$$\frac{p_3 p_4}{p_1 p_2} = \frac{p_3' p_4'}{p_1' p_2'} = K_p.$$

This is an expression for the law of mass action applied to gases which obey the gas laws. Instead of partial pressures one may employ concentrations, and so obtain the expression

$$\frac{c_3 c_4}{c_1 c_2} = K_c.$$

This expression, one will readily understand, can be generalised for balanced reactions involving varying numbers of gram-molecules of the constituents; and one may also,

in a manner similar to the above, derive the mass law expression for equilibrium in dilute solutions which obey the gas laws, by making use of the osmotic work involved in the transfer of substance from one concentration to another.

Measurement of Affinity or Decrease of Free Energy.—The decrease of free energy or the affinity of a chemical reaction can be studied from a knowledge of the equilibrium constant of a balanced reaction. Taking the case just discussed as an example, the decrease of free energy when carbon monoxide, steam, carbon dioxide and hydrogen at the partial pressures P_1, P_2, P_3, and P_4, respectively react so as to produce the equilibrium mixture in which the partial pressures of the constituents are p_1, p_2, p_3, and p_4, is

$$-\Delta G = RT \log_e \frac{p_3 p_4}{p_1 p_2} - RT \log_e \frac{P_3 P_4}{P_1 P_2}.$$

$$= RT \log_e K_p - RT \log_e \frac{P_3 P_4}{P_1 P_2}.$$

This expression is known as the *van't Hoff isotherm.*

Since the decrease of free energy of a chemical change will obviously depend on the values of the initial pressures of the reactants and the final pressures of the resultants, the affinity is defined as the decrease of free energy which results when the partial pressures (or concentrations) of the reactants are initially equal to unity, and when the final pressures (or concentrations) of the resultants are also unity. From this it follows that when carbon monoxide and steam, each at the partial pressure of 1 atmosphere, react so as to form carbon dioxide and hydrogen, each of which has also the partial pressure of 1 atmosphere, the decrease of free energy is given by

$$-\Delta G = RT \log_e K_p.$$

Or, if the initial concentrations of the reactants and the final concentrations of the resultants are each unity, then

$$-\Delta G' = RT \log_e K_c.$$

The free energy of a reaction may thus be calculated from determinations of the equilibrium constant at a given temperature.

Calculations of Affinity.—A few examples may be given to illustrate the application of the expressions given above for the calculation of the affinity of a chemical reaction.

It was found by W. Nernst and H. von Wartenberg[1] that the degree of dissociation of water vapour at 1000° K. and under a pressure of 1 atmosphere is 3×10^{-7}. Starting, therefore, with 1 gram-molecule of water vapour in 1 litre, the concentrations of hydrogen and of oxygen at equilibrium are 3×10^{-7} and $\frac{3}{2} \times 10^{-7}$ gram-molecules respectively. The equilibrium constant of the reaction $H_2 + \frac{1}{2}O_2 = H_2O$ is given by the expression

$$K = \frac{1}{(3 \times 10^{-7})(1{\cdot}5 \times 10^{-7})^{\frac{1}{2}}} = 8{\cdot}61 \times 10^9.$$

Owing to the very small degree of dissociation, the concentration of water vapour has been put equal to unity. From this one calculates

$$\begin{aligned} -\Delta G &= RT \log_e K \\ &= 2{\cdot}303 \times 1{\cdot}987 \times 1000 \times \log_{10} 8{\cdot}61 \times 10^9 \\ &= 45{,}510 \text{ cal.} \end{aligned}$$

This represents the decrease of free energy when 1 gram-molecule of steam, at a pressure of 1 atmosphere, is produced at 1000° K. by the combination of hydrogen and oxygen, each at atmospheric pressure.

One may also calculate the affinity of reactions taking place in heterogeneous systems, as is illustrated by the following examples.

In the case of the equilibrium,

$$CaO + CO_2 \rightleftharpoons CaCO_3,$$

the pressure of carbon dioxide has a definite value at a given temperature. If, at constant temperature, the pressure of carbon dioxide is increased, formation of carbonate will take place, whereas diminution of the pressure will bring about the dissociation of the carbonate. Suppose 1 gram-molecule of carbon dioxide at temperature T and under atmospheric pressure to be contained in a cylinder with piston, and let the gas be expanded reversibly and isothermally till the pressure is equal to the dissociation pressure p of calcium carbonate at the given temperature. In this process the system does work equal to $RT \log_e 1/p$. Let the gas be now brought in contact with calcium oxide, and let the gas be compressed reversibly so that it combines with the calcium oxide. The work thereby done on the gas is $pv = RT$. The total work gained in the series of operations is—

$$\text{Total work} = RT \log_e 1/p - RT.$$

If a very large volume of the gas were taken and the reaction carried out at constant volume, the work would have been equal to $RT \log_e 1/p$. Therefore, at atmospheric pressure and at constant volume, one finds

$$-\Delta G = RT \log_e 1/p.$$

[1] *Z. physikal. Chem.*, 1906, **56**, 513.

At 1273° K. the dissociation pressure of calcium carbonate is equal to 271 cm. of mercury, or 271/76 atmosphere. One therefore finds

$$-\Delta G = 2{\cdot}303 \times 1{\cdot}987 \times 1273 \times \log_{10} 76/271$$
$$= -3220 \text{ cal.}$$

That is, since at 1273° K., and under atmospheric pressure, $-\Delta G$ has a negative value, the reaction $CaO + CO_2 = CaCO_3$ does not take place spontaneously, but rather the reverse reaction, or the dissociation of the carbonate.

In determining the affinity of a dissociation process, it may, in some cases, be necessary to proceed indirectly. Thus, in order to determine the affinity of the reaction $Fe + \frac{1}{2}O_2 = FeO$, one may proceed as follows. The affinity of the reaction $FeO + H_2 = Fe + H_2O$ can be calculated from the equilibrium constant $K = p_{H_2O}/p_{H_2}$, which at 1000° K. is equal to 0·57. Consequently, $-\Delta G_1 = RT \log_e K = 2{\cdot}303 \times 1{\cdot}987 \times 1000 \times \log_{10} 0{\cdot}57 = -1118$ cal. The affinity $(-\Delta G_2)$ of the reaction $H_2 + \frac{1}{2}O_2 = H_2O$ is, as we have found, equal to 45,510 cal. Therefore the affinity $(-\Delta G_3)$ of the reaction $Fe + \frac{1}{2}O_2 = FeO$ is obtained by subtracting the affinity of the first reaction from that of the second; or

$$-\Delta G_3 = -\Delta G_2 + \Delta G_1$$
$$= 45{,}510 + 1118 = 46{,}628 \text{ cal.}$$

One may also calculate the affinity of a reaction taking place in the solid state, *e.g.*, transformation of monoclinic into rhombic sulphur. At any temperature other than the transition point, only one of the polymorphic forms is stable, although the other may exist as a metastable form owing to the slowness with which transformation takes place. It is thus possible to determine the solubilities of the two forms C_1 and C_2 in a given solvent. Suppose, now, that 1 gram-molecule of monoclinic sulphur is dissolved to a saturated solution in some solvent, and the solution diluted reversibly to the concentration C. The work done by the system in the dilution process is $RT \log_e C_1/C$. If rhombic sulphur is similarly treated, the work done is $RT \log_e C_2/C$. Since the two forms are identical in solution, one can carry out a process of dissolving monoclinic sulphur and crystallising out rhombic sulphur, the whole operation being a combination of the first process with the reverse of the second, and is equivalent to the conversion of 1 gram-molecule of monoclinic sulphur to 1 gram-molecule of rhombic sulphur. The work of dissolving the one modification counterbalances the work of crystallising out the other, and the net work is

$$RT \log_e C_1/C - RT \log_e C_2/C,$$

or

$$-\Delta G = RT \log_e \frac{C_1}{C_2}.$$

If $C_1 > C_2$, there is a decrease of free energy, which shows that the monoclinic sulphur is the unstable form at the temperature T, and that it has the greater solubility. Since the free energy equation contains no reference to the solvent, it follows that the ratio of the solubilities of the two forms at any temperature must be the same for all solvents. Further, at the transition point, $-\Delta G = 0$, and at this temperature, therefore, the solubilities are equal $(C_1 = C_2)$.

At 25° the ratio of the solubilities in various solvents of the two modifications has been found to be [1]

$$\frac{C_m}{C_{rh}} = 1{\cdot}28.$$

At 25° C., therefore,

$$-\Delta G = 2{\cdot}303 \times 1{\cdot}987 \times 298 \times \log_{10} 1{\cdot}28$$
$$= 146 \text{ cal.}$$

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[1] J. N. Brönsted, *Z. physikal. Chem.*, 1906, **55**, 371.

Affinity and Electromotive Force.—In the case of reactions involving electrolytes, the decrease of free energy or the affinity of a reaction can also be calculated from measurements of the electromotive force of suitable voltaic cells, the electrical energy supplied by such cells being equal to the decrease of free energy accompanying the chemical reaction in the cell (Chap. XV.).

In the case of the Daniell cell, for example, in which zinc dips in a solution of zinc sulphate and copper in a solution of copper sulphate, the two solutions being separated by a porous diaphragm, the reaction which takes place may be represented by the equation $Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu$. That is, when electrical energy is being supplied by the cell, zinc loses electrons and passes into solution as zinc ions and copper ions take up electrons and are discharged at the copper electrode.

Electrical energy can be expressed as the product of the electromotive force or fall of potential in volts, and the amount of electricity in coulombs; and the product so obtained gives the energy in volt-coulombs or joules. Since the amount of electricity associated with 1 gram-equivalent of an ion is the same for all ions, namely, 96,500 coulombs (1 faraday), the energy involved in the discharge of 1 gram-ion of substance will be zFE, where z is the valence of the ion, F is 1 faraday, and E is the e.m.f. of the cell. The free energy change of the reaction $Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu$ will therefore be

$$-\Delta G = 2 \times 96{,}500 \times 1{\cdot}1 = 212{,}390\,j. = 50{,}782 \text{ cal.}$$

The e.m.f. of the cell depends on the concentration of the solutions, the value 1·1 volt being given when the solutions have normal concentration. The concentrations of zinc and copper ion for which the e.m.f. would become zero ($-\Delta G = 0$) can be calculated from the equation $-\Delta G = 2{\cdot}303RT \log_{10} K$, where $K = [Zn^{\cdot\cdot}]/[Cu^{\cdot\cdot}]$. It is found that, at 25° C.,

$$\log_{10} K = \frac{50782}{2{\cdot}303 \times 1{\cdot}987 \times 298},$$

or

$$K = 1{\cdot}6 \times 10^{37}.$$

Since $[Zn^{\cdot\cdot}]$ cannot exceed 1 or 2 units (saturated solution),

the concentration of copper ions must become excessively small if the e.m.f. is to fall to zero.

In a similar manner one can calculate the affinity of complex ion formation and so obtain a measure of the stability of a complex salt. Thus the cell

$$\mathrm{Ag} \;\Big|\; \begin{matrix} 0{\cdot}05\text{N} - \mathrm{K_2Ag(CN)_3} \\ 0{\cdot}95\text{N} - \mathrm{KCN} \end{matrix} \;\Big|\; \begin{matrix} \text{normal solution} \\ \text{of Ag} \end{matrix} \;\Big|\; \mathrm{Ag}$$

was found [1] to have an e.m.f. of 1·327 volt at 18°. If the concentration of silver ions in the right-hand compartment is assumed to be unity (normal solution), and if C is the concentration of silver ions in the left-hand compartment produced by the dissociation $\mathrm{Ag(CN)_3''} \rightleftharpoons \mathrm{Ag^{\cdot}} + 3\mathrm{CN'}$, then, as will be shown in Chap. XV.,

$$\text{e.m.f.} = 1{\cdot}327 = 2{\cdot}303 \,.\, \frac{\boldsymbol{RT}}{\boldsymbol{F}} \log_{10} \frac{1}{C}.$$

From this one finds $C = 8 \times 10^{-24}$.

If it be assumed that the complex salt and the potassium cyanide are completely ionised, the equilibrium constant is calculated to be

$$K = \frac{[\mathrm{Ag^{\cdot}}] \times [\mathrm{CN'}]^3}{[\mathrm{Ag(CN)_3''}]} = \frac{8 \times 10^{-24} \times 0{\cdot}95^3}{0{\cdot}05} = 1{\cdot}37 \times 10^{-22}.$$

Consequently,
$$-\Delta G = 2{\cdot}303 \,.\, \boldsymbol{RT} \log_{10} 1{\cdot}37 \times 10^{-22}$$
$$= -29{,}150 \text{ cal.}$$

The negative value of $-\Delta G$ indicates that it is the reaction

$$\mathrm{Ag^{\cdot}} + 3\mathrm{CN'} \longrightarrow \mathrm{Ag(CN)_3''}$$

which takes place spontaneously with decrease of free energy.

Variation of Equilibrium with Temperature.—It has already been pointed out that the effect of change of temperature on a system in equilibrium can be predicted qualitatively by means of the theorem of Le Chatelier. It can, however, now be shown that a quantitative relation between the equilibrium constant and temperature can be obtained by combining the Gibbs-Helmholtz equation with the van't Hoff isotherm.

Since
$$\Delta G - \Delta H = T\left(\frac{\partial \,.\, \Delta G}{\partial T}\right)_p \quad . \quad . \quad . \quad (1)$$

and
$$-\Delta G = \boldsymbol{RT} \log_e K_p - \boldsymbol{RT} \log_e \frac{P_3 P_4}{P_1 P_2} \quad . \quad . \quad (2)$$

it follows that

$$\frac{d \,.\, \Delta G}{dT} = \frac{-\Delta H}{T} - \boldsymbol{R} \log_e K_p + \boldsymbol{R} \log_e \frac{P_3 P_4}{P_1 P_2} \quad . \quad (3)$$

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[1] G. Bodländer and W. Eberlein, *Z. anorgan. Chem.*, 1904, **39**, 197.

Further, on differentiating equation (2) with respect to temperature, one obtains [1]

$$\frac{d\,.\,\Delta G}{dT} = -\boldsymbol{R}\log_e K_p - \boldsymbol{RT}\frac{d\log_e K_p}{dT} + \boldsymbol{R}\log_e \frac{P_3P_4}{P_1P_2} \quad (4)$$

Combination of equations (3) and (4) leads to the equation

$$\frac{d\log_e K_p}{dT} = \frac{\Delta H}{\boldsymbol{RT}^2} = -\frac{q_p}{\boldsymbol{RT}^2},$$

where q_p is the heat *evolved* when the reaction takes place at constant pressure. When the reaction takes place at constant volume, one has

$$\frac{d\log_e K_c}{dT} = \frac{\Delta U}{\boldsymbol{RT}^2} = -\frac{q_v}{\boldsymbol{RT}^2},$$

where q_v is the heat evolved at constant volume. This equation is known as the *van't Hoff isochore.*[2]

Since, in the expression for the equilibrium constant K, the reactants appear in the denominator, a negative value of $\frac{d\log_e K}{dT}$ indicates that with rise of temperature the equilibrium is shifted from right to left, and that this reaction takes place with absorption of heat (q being negative); a behaviour predicted by the theorem of Le Chatelier.

If it be assumed that the heat of reaction remains constant over a given small range of temperature, the van't Hoff isochore can be integrated, and yields the expression

$$\log_e K_1 - \log_e K_2 = \frac{q_p}{\boldsymbol{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

or $$\log_{10}\frac{K_1}{K_2} = \frac{q_p}{2{\cdot}303 \times 1{\cdot}987}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right) = \frac{q_p}{4{\cdot}577}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right).$$

By means of this equation the value of K_2 at the absolute temperature T_2 can be calculated if K_1 and q are known;

[1] In carrying out this differentiation, one must bear in mind that

$$\frac{d}{dT}(\boldsymbol{RT}\log_e K_p) = \boldsymbol{R}\log_e K_p + \boldsymbol{RT}\frac{d\log_e K_p}{dT};$$

and that

$$\frac{d}{dT}(\boldsymbol{RT}\log_e \mathrm{P_3P_4/P_1P_2}) = \boldsymbol{R}\log_e \mathrm{P_3P_4/P_1P_2} + \boldsymbol{RT}\left(\frac{d\log_e \mathrm{P_3P_4/P_1P_2}}{dT}\right).$$

Since $\mathrm{P_1}$, $\mathrm{P_2}$, $\mathrm{P_3}$, and $\mathrm{P_4}$ are arbitrarily chosen and are independent of the temperature, $\boldsymbol{RT}\left(\frac{d\log_e \mathrm{P_3P_4/P_1P_2}}{dT}\right) = 0$.

[2] From the Greek, meaning equal volume.

and, further, if the values of K_1 and K_2 at the absolute temperatures T_1 and T_2 are known, one may calculate the value of q, the heat of reaction.

To illustrate the application of the van't Hoff isochore, one may consider the industrially important reaction

$$CO_2 + H_2 = CO + H_2O - 10{,}500 \text{ cal.}$$

which takes place in water-gas ovens. It has been found that at the temperature 1273° K.

$$K_p = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} = 1{\cdot}62.$$

The value of the equilibrium constant at 973° K. will then be given by the expression

$$\log_{10} \frac{K_{973}}{K_{1273}} = -\frac{10500}{4{\cdot}577}\left(\frac{1273 - 973}{1273 \times 973}\right).$$

Therefore, $$\log_{10} K_{973} = \log_{10} K_{1273} - 0{\cdot}5557$$

and $$K_{973} = 0{\cdot}451.$$

At lower temperatures, therefore, the value of $\frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}}$ is less than at higher temperatures, showing that, at lower temperatures, the reaction

$$CO + H_2O \longrightarrow CO_2 + H_2$$

is favoured, a reaction which is accompanied by evolution of heat. When, therefore, it is desired to favour the reaction,

$$CO + H_2O \longrightarrow CO_2 + H_2,$$

for the production of industrial hydrogen from water-gas, the reaction is caused to take place in the presence of a catalyst at a low temperature [450°-500°]. For the production of water-gas, however, a high temperature, say 1100°-1200° C., is employed so as to diminish the oxidation of carbon monoxide by the excess of steam.

Since a solid in contact with a saturated solution also constitutes a system in equilibrium, it is possible to calculate the heat of solution from the values of the solubility S_1 and S_2 at the absolute temperatures T_1 and T_2. Thus, applying the van't Hoff isochore, one has

$$\frac{d \log_e S}{dT} = \frac{-L}{RT^2},$$

or $$\log_{10} \frac{S_1}{S_2} = \frac{L}{4{\cdot}577}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right)$$

where L is the calorimetric heat of solution [evolved] in a saturated solution per gram-molecule. In the case of succinic acid, for example, 100 g. of water dissolve 2·88 g. and 4·22 g. of the acid at 0° and at 8·5° C., respectively. Therefore,

$$L = 4{\cdot}577 \times \frac{T_1 \times T_2}{T_2 - T_1} \times \log_{10} \frac{2{\cdot}88}{4{\cdot}22}$$

$$= 4{\cdot}577 \times \frac{273 \times 281{\cdot}5}{281{\cdot}5 - 273} \times \log_{10} \frac{2{\cdot}88}{4{\cdot}22}$$

$$= -6868 \text{ cal.}$$

The experimentally determined heat of solution is $-55 \times 118 = -6490$ cal. The heat of solution is negative [heat absorbed], and, consequently, one finds that the solubility increases with rise of temperature.

The Nernst Heat Theorem.—In a previous section it was shown that the maximum work or the decrease of free energy of a reaction can be calculated from determinations of the equilibrium constant, or from measurements of the e.m.f. of a voltaic cell; and when one is dealing with non-electrolytic systems one is restricted almost entirely to the former method. The question arises, however, whether it may not be possible to calculate the free energy or the maximum work from purely thermal measurements. Were this possible one would be able to determine from purely thermal data the condition of equilibrium for a particular reaction. This, it is found, can be done with considerable success in the case of systems involving only solids and liquids.

The Gibbs-Helmholtz equation (p. 300) can be written in the form $A - U = T\frac{dA}{dT}$, and on dividing this throughout by T^2 one obtains

$$\frac{1}{T}\cdot\frac{dA}{dT} - \frac{A}{T^2} = -\frac{U}{T^2},$$

or

$$\frac{d}{dT}\left(\frac{A}{T}\right) = -\frac{U}{T^2}.$$

This equation, on being integrated, yields

$$\frac{A}{T} = -\int\frac{U}{T^2}\cdot dT + I \quad . \quad . \quad . \quad (1)$$

where I is the integration constant.

In order that one may be able to calculate the value of A when U is known, it is necessary (1) to express U as a function of T, and (2) to know the value of I.

According to Kirchhoff's law (p. 270) the variation of U with T is given by the expression

$$\frac{dU}{dT} = c_1 - c_2,$$

and, since the specific heats can be expressed as a function of T, this equation can be integrated in the form

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \ldots \quad . \quad . \quad (2)$$

Equation (1), therefore, after both sides have been multiplied by T, can be written

$$A = -T\int(U_o + \alpha T + \beta T^2 \ . \ . \ .)\frac{dT}{T^2} + IT$$

$$= IT + U_o - \alpha T \log_e T - \beta T^2 - \frac{\gamma}{2}T^3 \ . \ . \ . \ . \quad (3)$$

On differentiating this expression, one obtains

$$\frac{dA}{dT} = I - \alpha - \alpha \log_e T - 2\beta T - \frac{3}{2}\gamma T^2 \ . \ . \ . \quad . \quad (4)$$

Further, from equation (2) it follows that

$$\frac{dU}{dT} = \alpha + 2\beta T + 3\gamma T^2 \ . \ . \ . \quad . \quad . \quad (5)$$

From the Gibbs-Helmholtz equation it is clear that when $T = 0$, $A = U$; but to this conclusion Nernst added the theorem that at the absolute temperature not only is $A = U$, but $\frac{dA}{dT} = 0$ and $\frac{dU}{dT} = 0$. In other words, Nernst concluded that *the curves showing the variation of A and of U with the temperature meet tangentially at the absolute zero, so that* $A = U$ *not only at the absolute zero but also for some distance above the absolute zero.* This is known as the *Nernst heat theorem.*[1]

In order that $\frac{dA}{dT}$ (equation 4) may become zero when $T = 0$, it is necessary to put not only $I = 0$ but also $\alpha = 0$, since, otherwise, $-\alpha \log_e T$ would become infinite. One can therefore write

$$\frac{dA}{dT} = -2\beta T - \frac{3}{2}\gamma T^2 \ . \ . \ .$$

and also,
$$\frac{dU}{dT} = 2\beta T + 3\gamma T^2 \ . \ . \ .$$

or
$$c_1 - c_2 = 2\beta T + 3\gamma T^2 \ . \ . \ .$$

Hence,
$$U = U_o + \beta T^2 + \gamma T^3 \ . \ . \ .$$

and
$$A = U_o - \beta T^2 - \frac{\gamma}{2}T^3 \ . \ . \ .$$

It is clear, therefore, from the above equations, that since the coefficients β, γ, etc., can be calculated from the specific

[1] Through the introduction of the Nernst heat theorem one is enabled to integrate the Gibbs-Helmholtz equation.

heats of the reactants and resultants at the given temperature T, A and U can be calculated from purely thermal data. When β, γ, etc., are known, however, one can calculate the value of U_o from the heat of reaction U at the temperature T, and therefrom one can calculate the value of A, the maximum work obtained from the reaction. It follows, also, that the equilibrium constant of a reaction, which can be calculated from A, can also be calculated from purely thermal data.

Confirmation of the validity of the Nernst heat theorem was obtained by F. Koref, working in Nernst's laboratory,[1] in the case of the fusion of benzophenone and of betol, two substances which can be very greatly supercooled. Since $\frac{dU}{dT} = c_1 - c_2 = 2\beta T + 3\gamma T^2$, it follows that as the temperature approaches the absolute zero, the difference between the specific heats of solid and supercooled liquid should tend to zero. The following values for betol are in harmony with this deduction :—

Betol.		Benzophenone.	
T.	$\frac{dU}{dT} = c_1 - c_2$.	T.	$\frac{dU}{dT} = c_1 - c_2$.
320°	0·362 − 0·295 = 0·067	295°	0·3825 − 0·3051 = 0·0774
240°	0·256 − 0·2205 = 0·0355	137°	0·1526 − 0·1514 = 0·0012
130°	0·148 − 0·144 = 0·004	...	...

Applications of the Nernst Heat Theorem.—To illustrate the application of the Nernst heat theorem, one may calculate the transition point of monoclinic and rhombic sulphur. From the difference between the specific heats of rhombic and monoclinic sulphur, one finds that in the expression $U = U_o + \beta T^2$ [higher powers of T being neglected], $\beta = 1{\cdot}15 \times 10^{-5}$; and from determinations of the heat of transformation one finds $U_0 = 1{\cdot}57$, so that $U = 1{\cdot}57 + 1{\cdot}15 \times 10^{-5} T^2$, an expression which is in harmony with the determinations of J. N. Brönsted [2] and G. Tammann,[3] as the following numbers show :—

T.	U_{observed}.	$U_{\text{calculated}}$.	
273°	2·40	2·43	[Brönsted.]
368°	3·19	3·13	[Tammann.]

[1] See Nernst, *J. Physique*, 1910, [4], **9**, 721.
[2] *Z. physikal. Chem.*, 1906, **55**, 371.
[3] *Kristallisieren und Schmelzen*, pp. 274, 275.

For A, therefore, one has the expression

$$A = 1{\cdot}57 - 1{\cdot}15 \times 10^{-5}T^2.$$

The values of A calculated from this expression are in agreement with the values obtained by Brönsted from determinations of the solubility, as is shown by the numbers in the following table :—

T.	$A_{\text{Brönsted.}}$	$A_{\text{Nernst.}}$
273°	0·72	0·71
288·5°	0·64	0·61
291·6°	0·63	0·59
298·3°	0·57	0·55

Moreover, since, at the transition point, $A = 0$, the temperature of the transition point is calculated to be

$$T = \sqrt{\frac{1{\cdot}57}{1{\cdot}15 \times 10^{-5}}} = 369{\cdot}5° \text{ K.} = 96{\cdot}5° \text{ C.}$$

Direct determinations of the transition point give the temperature 95·5° C.

The Nernst heat theorem may also be applied to the calculation of the e.m.f. of a voltaic cell. Thus the heat of the reaction $\frac{1}{2}Pb + AgCl = \frac{1}{2}PbCl_2 + Ag$ is given by the expression $U = 11{,}904 + 0{\cdot}010062\,T^2$. At 25°, therefore, the value of A will be $A = 11{,}904 - 0{\cdot}010062 \times 298^2 = 11{,}011$ cal. When, therefore, one equates the electrical energy with the maximum work, one calculates that, in the case of the cell.

$$Pb \mid PbCl_2(s) \text{ ; saturated solution } \mid AgCl(s) \text{ ; saturated solution } \mid Ag$$

$$FE = 11{,}011 \text{ cal., or } 96{,}500 \times 0{\cdot}2390 \times E = 11{,}011,$$

and therefore

$$E = \frac{11{,}011}{23{,}073} = 0{\cdot}475 \text{ volt.}^1$$

[1] The factor 0·2390 is introduced in order to convert the product of volts and coulombs [$96{,}500 \times E$] into calories.

CHAPTER XIV

LAW OF MASS ACTION APPLIED TO SOLUTIONS OF ELECTROLYTES

Ostwald's Dilution Law.—It has already been pointed out that, according to the theory of electrolytic dissociation, an electrolyte when dissolved in water undergoes spontaneous dissociation into positively and negatively charged ions ; and, in the case of a weak electrolyte, the extent to which ionisation takes place depends on the temperature and on the concentration of the solution. At a given temperature there exists, therefore, a definite equilibrium between the un-ionised molecules of the electrolyte and the ions, which depends only on the concentration and to which, therefore, one can apply the law of mass action.

In a dilute solution of acetic acid, for example, there exists the equilibrium

$$CH_3.COOH \rightleftharpoons CH_3.COO' + H^{\cdot},$$

and if one applies to this equilibrium the law of mass action one obtains, as the equilibrium condition at constant temperature,

$$\frac{[CH_3.COO'] \times [H^{\cdot}]}{[CH_3.COOH]} = K.$$

If in a given volume v of solution there is 1 gram-equivalent of electrolyte, and if α is the degree of dissociation, the *amount* of un-ionised electrolyte at equilibrium will be $(1-\alpha)$, and the amount of each of the ions will be α gram-equivalent. The *concentration* of un-ionised molecules will therefore be $\frac{(1-\alpha)}{v}$, and the concentration of each of the

ions $\frac{\alpha}{v}$. On substituting these values in the equilibrium equation, one obtains the expression

$$\frac{\alpha^2}{(1-\alpha)v} = K,$$

or, since $\alpha = \Lambda_v/\Lambda_\infty$ (p. 230), the equilibrium equation can also be written

$$\frac{\Lambda_v{}^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)v} = K.$$

From these expressions it is clear that, at constant temperature, the degree of ionisation and the equivalent conductivity must vary with dilution in such a way that at each concentration the expressions $\frac{\alpha^2}{(1-\alpha)v}$ and $\frac{\Lambda_v{}^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)v}$ remain constant for any given electrolyte. The constant K is called the *dissociation* or *ionisation constant.*

The application of the law of mass action to electrolytic equilibria was first made by Wilhelm Ostwald, and the equilibrium equation $\alpha^2/(1-\alpha)v = K$ is the mathematical expression of what is generally known as *Ostwald's Dilution Law.* The law has been confirmed for a large number of *weak* or slightly ionised acids and alkalis. The numbers given in the following table, in which the values of K for acetic acid are calculated from determinations of the equivalent conductivity of solutions at 25°, illustrate the applicability of the law.[1]

EQUIVALENT CONDUCTIVITY AND DISSOCIATION OF ACETIC ACID AT 25°

v.	Λ.	α	$K \times 10^5$.
13·57	6·086	0·0157	1·845
27·14	8·591	0·0222	1·851
54·28	12·09	0·0312	1·849
108·56	16·98	0·0438	1·849
217·1	23·81	0·0614	1·851
434·2	33·22	0·0857	1·849
868·4	46·13	0·1190	1·850
1737·0	63·60	0·1641	1·854
3474·0	86·71	0·2236	1·855
∞	387·7	...	...

[1] J. Kendall, *J. Chem. Soc.*, 1912, **101**, 1275.

As the mean of the best determinations, the dissociation constant of acetic acid is found to be $1{\cdot}81 \times 10^{-5}$. In the case of acids and alkalis, the dissociation constant is generally called the *affinity constant.*

In calculating the above value of the affinity constant of acetic acid, α has been taken as equal to Λ_v/Λ_∞. If account is taken of the influence of concentration on the mobility of the ions (p. 231), and the concept of activity introduced,[1] the affinity constant is found to be $1{\cdot}75 \times 10^{-5}$. The constant calculated on this basis is known as the thermodynamic or true dissociation constant.

The Strength of Acids and Alkalis.—Acid properties, as we have seen, are the properties of hydrogen ion, so that the greater the concentration of hydrogen ion the more pronounced will be the acid properties. Since, for any given total concentration of acid, the concentration of hydrogen ion will depend on the degree of ionisation α, it can be seen that the efficiency of a substance as an acid, or the *strength* of an acid, will depend on the extent to which it undergoes ionisation at a given dilution. Since the affinity constant gives a relationship between the degree of ionisation and concentration, it is clear that we have in it a measure of the strength of the acid or of its tendency to ionise. The value of the affinity constant is a characteristic of the acid. Alkali properties, similarly, depend on the hydroxide ion, and the affinity constant gives a measure of the strength of the alkali.[2]

When one is dealing with a weak or slightly ionised electrolyte, that is, with one for which the value of α at a given dilution is small, one may neglect α in comparison with unity in the expression $\alpha^2/(1-\alpha) = K \cdot v$. One obtains, therefore, the expression $\alpha^2 = K \cdot v$, or $\alpha = \sqrt{K \cdot v} = \sqrt{K/c}$, from which the value of α at any given dilution v in litres, or at a concentration c in gram-equivalents per litre, can be calculated.[3] From the expression, $\alpha = \sqrt{K/c}$, it follows that

[1] See D. A. MacInnes and T. Shedlovsky, *J. Amer. Chem. Soc.*, 1931, **53,** 2419; 1932, **54,** 1429; H. S. Harned and R. W. Ehlers, *ibid.*, 1932, **54,** 1350. See also, J. F. J. Dippy, *Chem. Rev.*, 1939, **25,** 151.

[2] This has special reference to aqueous solutions. In accordance with the wider definition of an acid given on p. 488, the strength of an acid depends on the looseness with which a proton is bound to the acid anion.

[3] Where α is not negligible compared with unity, the value of α can be calculated from the mass law equation by means of the expression [the solution of the quadratic equation for α],

$$\alpha = \sqrt{K \cdot v + \frac{(K \cdot v)^2}{4}} - \frac{K \cdot v}{2} = \sqrt{\frac{K}{c} + \frac{K^2}{4c^2}} - \frac{K}{2c}.$$

in an equivalent normal solution ($c = 1$), the degree of ionisation of a weak electrolyte will be equal to the square root of the dissociation constant. Moreover, for any two weak acids or alkalis in solutions of the same concentration, one has

$$\alpha_1 = \sqrt{K_1 v} \text{ and } \alpha_2 = \sqrt{K_2 v}$$

or

$$\frac{\alpha_1}{\alpha_2} = \frac{\sqrt{K_1}}{\sqrt{K_2}}.$$

That is to say, for two weak or slightly ionised electrolytes *the degrees of ionisation at any given dilution, which is the same for both, are proportional to the square root of the ionisation constants.*

From a knowledge of the affinity constant of a weak acid (or weak alkali) one can also calculate the concentration of $[H^{\cdot}]$ (or of OH'). Thus, since $[H^{\cdot}] = [A']$, $[H^{\cdot}]^2 = K \cdot [HA]$, where $[HA]$ is the concentration of the un-ionised molecules. If, however, the acid is weak, one may, without great error, put $[HA] =$ total concentration of acid, and one obtains the expression $[H^{\cdot}]^2 = K \cdot [\text{acid}]$, or $[H^{\cdot}] = \sqrt{K \cdot [\text{acid}]}$.

The relation between the concentration of hydrogen ion, the degree of ionisation of an acid, and the affinity constant may also be expressed in another manner which will be found useful. In the case of a weak acid, one may write the mass law equation in the form

$$\frac{[A']}{[HA]} = \frac{K}{[H^{\cdot}]},$$

and, since $[HA] = [\text{total acid}] - [A']$, one obtains

$$\frac{[A']}{[\text{acid}] - [A']} = \frac{K}{[H^{\cdot}]} \text{ or } \frac{[A']}{[\text{acid}]} = \frac{K}{K + [H^{\cdot}]} = \alpha.$$

This expression may be transformed into

$$\frac{1}{[H^{\cdot}]} = \frac{1}{K} \cdot \frac{\alpha}{1 - \alpha},$$

from which one obtains

$$\log_{10} \frac{1}{[H^{\cdot}]} = \log_{10} \frac{1}{K} + \log_{10} \frac{\alpha}{1 - \alpha}.$$

This expression is useful for the purpose of plotting graphically the relation between the hydrogen-ion concentration and the degree of ionisation.

That the strength of acids and of alkalis may vary greatly is shown by the numbers in the tables below, in which are given the values of the affinity constants at 25° for a number of weak monobasic acids and weak monoacid bases.[1]

It may be noted that the strength of acids and of alkalis can be determined not only by measurements of the conductivity but also by measurements of the velocity of hydrolysis of esters, of the hydrolysis of salts, etc., and of electromotive force.

AFFINITY CONSTANTS OF WEAK MONOBASIC ACIDS (25°)

	K.		K.
Salicylic acid . .	$1{\cdot}00 \times 10^{-3}$	Benzoic acid . .	$6{\cdot}2 \times 10^{-5}$
Nitrous acid . .	$4{\cdot}6 \times 10^{-4}$	Acetic acid . .	$1{\cdot}813 \times 10^{-5}$
Formic acid . . .	$2{\cdot}1 \times 10^{-4}$	Hydrocyanic acid (18°)	$1{\cdot}32 \times 10^{-9}$
Lactic acid . . .	$1{\cdot}36 \times 10^{-4}$	Phenol . . .	$1{\cdot}06 \times 10^{-10}$

AFFINITY CONSTANTS OF WEAK ALKALIS (25°)

	K.		K.
Dimethylamine . .	$5{\cdot}0 \times 10^{-4}$	Ammonia . . .	$1{\cdot}81 \times 10^{-5}$
Methylamine . .	$4{\cdot}0 \times 10^{-4}$	Aniline . . .	$3{\cdot}5 \times 10^{-10}$
Trimethylamine . .	$6{\cdot}5 \times 10^{-5}$	Carbamide [urea] .	$1{\cdot}5 \times 10^{-14}$

Ionisation of Polybasic Acids.—When a polybasic acid is dissolved in water, the different acid hydrogen atoms do not undergo ionisation with equal readiness. Thus, when a dibasic acid, which may be represented generally by the formula H_2A, is dissolved in water, ionisation takes place in stages or steps as represented by the equilibrium equations

$$1.\ H_2A \rightleftarrows H^{\cdot} + HA'.$$

$$2.\ HA' \rightleftarrows H^{\cdot} + A''.$$

When dealing with a weak dibasic acid, one may apply to each of these equilibria the law of mass action and so obtain the expressions

$$(1)\ \frac{[H^{\cdot}] \times [HA']}{[H_2A]} = K_1, \text{ and } (2)\ \frac{[H^{\cdot}] \times [A'']}{[HA']} = K_2.$$

[1] For the variation of the affinity constant with temperature see Harned, *J. Amer. Chem. Soc.*, 1934, **56**, 1050.

Each stage of the ionisation process, therefore, has its own dissociation or affinity constant, the ion HA′ acting as a weak acid ; and the values of these affinity constants give a measure of the extent to which each stage of ionisation takes place at any given dilution. The smaller the K_2 value relatively to K_1, the smaller will be the extent to which the second stage of ionisation occurs at any given dilution, or the greater must be the dilution of the solution before the second stage of ionisation becomes appreciable. Thus, a dibasic (or polybasic) acid may behave, so far as ionisation is concerned, as a monobasic acid, even when the dilution is considerable.

The following numbers, giving the values of the molecular conductivity μ (which, since the acid behaves as a monobasic acid, is the same as the equivalent conductivity) of succinic acid, $COOH.CH_2.CH_2.COOH$, at 25°, will serve to illustrate this point: v is the dilution in litres.

$v =$	16	64	256	1024	2048	∞
$\mu =$	11·40	22·47	43·50	81·64	109·5	356
$100\alpha =$	3·20	6·32	12·24	22·95	30·82	...
$K \times 10^5 =$	6·62	6·67	6·68	6·68	6·71	

Since the affinity constant K is calculated according to the mass law equation for a monobasic acid, it follows that, up to a dilution of at least 2048 litres, succinic acid ionises with production of only one hydrogen ion per molecule of the acid.

Similarly, a tribasic acid, such as phosphoric acid, H_3PO_4, ionises in three stages :

1. $H_3PO_4 \rightleftarrows H^{\cdot} + H_2PO_4'$.
2. $H_2PO_4' \rightleftarrows H^{\cdot} + HPO_4''$.
3. $HPO_4'' \rightleftarrows H^{\cdot} + PO_4'''$.

It is to be noted that the ions H_2PO_4' and HPO_4'' are to be regarded as weak acids.

In the following table are given the values of the ionisation constants of a number of polybasic acids at 25° :—

DIBASIC ACIDS

	K_1.	K_2.
Oxalic acid, $H_2C_2O_4$ . .	$3{\cdot}8 \times 10^{-2}$	$4{\cdot}9 \times 10^{-5}$
Malcic acid, $H_2 . C_4H_2O_4$.	$1{\cdot}17 \times 10^{-2}$	$2{\cdot}6 \times 10^{-7}$
Tartaric acid, $H_2 . C_4H_4O_6$.	$1{\cdot}3 \times 10^{-3}$	$9{\cdot}7 \times 10^{-5}$
Succinic acid, $H_2 . C_4H_4O_4$.	$6{\cdot}65 \times 10^{-5}$	$2{\cdot}7 \times 10^{-6}$
Carbonic acid, H_2CO_3 . .	$3{\cdot}3 \times 10^{-7}$	$6{\cdot}0 \times 10^{-11}$
Hydrogen sulphide, H_2S . .	$9{\cdot}1 \times 10^{-8}$	$1{\cdot}0 \times 10^{-15}$

The case of carbonic acid is different from that of the other acids considered here, inasmuch as the concentration of the free acid, H_2CO_3,

is not known, but only that of the anhydride, CO_2. If we assume the equilibrium

$$H_2CO_3 \rightleftarrows CO_2 + H_2O,$$

and apply the law of mass action, we obtain

$$\frac{[CO_2] \times [H_2O]}{[H_2CO_3]} = K_1.$$

In this equation the concentration of the water may be regarded as constant, and we may therefore incorporate it in the constant on the right-hand side and so obtain

$$\frac{[CO_2]}{[H_2CO_3]} = K_2.$$

Since the concentration of H_2CO_3 is always small compared with that of the free CO_2, K_2 is always large. Since the molecule H_2CO_3 ionises, as has been stated, according to the equation $H_2CO_3 \rightleftarrows H^{\cdot} + HCO_3'$, we obtain

$$\frac{[H^{\cdot}] \times [HCO_3']}{[H_2CO_3]} = K_3.$$

This represents the " real " or " true " dissociation constant of the acid H_2CO_3 which is probably fairly large. The concentration of H_2CO_3 is, however, not known, but only the concentration of the anhydride CO_2 which is practically equal to the total concentration of dissolved carbonic acid, the concentration of H_2CO_3 being very small compared with that of CO_2. Since, as we have seen

$$\frac{[CO_2]}{[H_2CO_3]} = K_2 \text{ or } [H_2CO_3] = \frac{[CO_2]}{K_2},$$

we can write

$$\frac{[H^{\cdot}] \times [HCO_3']}{[H_2CO_3]} = K_3, \text{ or } \frac{[H^{\cdot}] \times [HCO_3']}{[CO_2]} = \frac{K_3}{K_2} = K_4.$$

K_4 may be called the *apparent dissociation constant*, and it is this constant which can be experimentally determined.

TRIBASIC ACIDS

	K_1.	K_2.	K_3.
Phosphoric acid, H_3PO_4 .	9×10^{-3}	$1{\cdot}4 \times 10^{-7}$	$2{\cdot}7 \times 10^{-12}$
Boric acid, H_3BO_3 . .	7×10^{-10}	...	...

Influence of Constitution on the Strength of Acids.[1]—In the case of organic acids, it is found, the affinity constant or the strength of the acid depends on the composition and constitution. In the case of the fatty acids the affinity constant decreases as one ascends the series ; that is, substitution of a hydrogen atom by CH_3 decreases the strength of the acid. Similarly, decrease of the affinity constant is brought about by substitution by $-NH_2$.

On the other hand, substitution of hydrogen by halogens and by the groups $-C_6H_5$, $-OH$, $-CN$, etc., increases the affinity constant. Moreover, substitution by the atoms or groups, $-CH_3$, $-Cl$, $-OH$, $-NO_2$, etc., in the nucleus

[1] See Dippy, *Chem. Rev.*, 1939, **25**, 151.

of the aromatic acids, increases the strength of the acid, the effect being greatest when substitution takes place in the ortho-position. The following table is given in illustration :—

INFLUENCE OF SUBSTITUTION ON THE AFFINITY CONSTANT OF ACIDS AT 25°

	K.		K.
Acetic acid . . .	$1{\cdot}81 \times 10^{-5}$	Benzoic acid . .	$6{\cdot}2 \times 10^{-5}$
Phenylacetic acid . .	$5{\cdot}45 \times 10^{-5}$	*o*-hydroxybenzoic acid .	$1{\cdot}0 \times 10^{-3}$
Hydroxyacetic acid .	$1{\cdot}49 \times 10^{-4}$	*m*- „ „ .	$8{\cdot}54 \times 10^{-5}$
Monochloracetic acid .	$1{\cdot}52 \times 10^{-3}$	*p*- „ „ .	$2{\cdot}80 \times 10^{-5}$
Cyanacetic acid . .	$3{\cdot}65 \times 10^{-3}$	*o*-nitrobenzoic acid .	$6{\cdot}4 \times 10^{-3}$

Strong Electrolytes.—The success with which the electrolytic dissociation theory of Arrhenius explains the behaviour of weak or slightly ionised electrolytes in solution and the fact that, as will appear later, many phenomena, such as the hydrolysis of salts, the behaviour of indicators, the influence of one electrolyte on another, etc., can be treated quantitatively by applying the law of mass action to such systems, established the value of the theory in co-ordinating, in a rather remarkable manner, a wide range of quantitative relationships. It remained, however, until comparatively recent years, an increasingly felt weakness of the theory that it fails to give an equally satisfactory account of the behaviour of strong electrolytes, such as the ordinary salts and the mineral acids and alkalis.

That the Ostwald dilution law is not applicable to strong electrolytes is shown by the numbers in the following table, which refer to solutions of potassium chloride at 18° ($\Lambda_\infty = 130{\cdot}1$).

v.	Λ.	$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$.	$\frac{\alpha^2}{(1-\alpha)v}$.
10	112·0	0·862	0·541
50	120·0	0·923	0·222
100	122·4	0·942	0·154
500	126·3	0·972	0·0681
1000	127·3	0·980	0·0485
5000	128·8	0·991	0·0223

In 1907, Kohlrausch showed, as has already been pointed out (p. 229), that, in the case of dilute solutions of strong electrolytes, the variation of equivalent conductivity with concentration is expressed by the equation $\Lambda_c = \Lambda_0 - k\sqrt{c}$, where Λ_c is the equivalent conductivity of a solution containing c gram-equivalents per litre, and Λ_0 the equivalent conductivity at infinite dilution. This expression, also obtained empirically, shows that the equivalent

conductivity varies linearly with the square root of the concentration, and is obviously not in harmony with the law of mass action. It remained without a basis in theory until the year 1923.

According to the classical theory of Arrhenius, the equivalent conductivity of a solution depends on the concentration of the ions and on their mobility. Since the latter was thought to be independent of the concentration, a view disproved by A. A. Noyes in 1902, the degree of ionisation, which governs the concentration of the ions, was assumed to be given by the expression $\alpha = \Lambda v/\Lambda_\infty = \Lambda_c/\Lambda_o$. The ions, moreover, were regarded as having a random distribution and electrical attraction between the ions was neglected.

As has already been pointed out (p. 166), modern views regarding atomic structure, the nature of valency and the existence of ions even in the crystalline state, have led to the theory of complete ionisation of salts in solution. In such solutions, however, the electrolyte may not behave as if it were completely ionised, that is, as if the ions were entirely free, owing to the existence of *interionic forces*, and the deviations from the ideal state of complete independence of the ions will increase with the concentration of the solution. In such solutions, as S. R. Milner first showed,[1] there can be no random distribution of the ions owing to the coulomb forces (electrical attractions and repulsions) between the ions. Although Milner was able to deduce a relation between the depression of the freezing-point of a solution of a strong electrolyte and the dilution, he failed to obtain a satisfactory expression for the electrical conductivity. Stimulated by the publication of an erroneous theory of conductivity put forward by the Indian chemist, Jnanendra C. Ghosh, in 1918, P. Debye, now Professor of Physics, Cornell University, Ithaca, N.Y., took up the investigation of the problem and, along with his assistant E. Hückel succeeded in calculating the effect of interionic forces on the mobility of ions, and in obtaining an expression for the equivalent conductivity of a solution.[2]

According to the theory of Debye and Hückel, as in the theory of Milner, there can be no random distribution of ions, for, owing to interionic forces, an ion will build up an " atmosphere " of ions of opposite sign. Moreover, when an ion moves under the influence of an applied electromotive force the ionic atmosphere will be unsymmetrical, for the ion has to build up a new ionic atmosphere in front, while the atmosphere behind the moving ion will be dispersed. The dispersal of the ionic atmosphere, however, requires a certain amount of time (" time of relaxation "), and there will therefore always be, in the rear of a moving ion, an excess of ions of opposite sign whereby the mobility of the ion will be diminished. Moreover, regarding the electrification in the ionic atmosphere as continuous, the motion of, say, a positively charged reference ion will be retarded by the movement in the opposite direction of negative ions, the effect being that of a viscous electrical drag (electrophoretic effect). The total reduction of the mobility of an ion was found to be *proportional to the square root of the concentration,*

[1] *Phil. Mag.*, 1912, **23**, 551; 1913, **25**, 742.

[2] *Physikal. Z.*, 1923, **24**, 305; 1924, **25**, 145; *Trans. Faraday Soc.*, 1927, **23**, 234.

and by taking into account the factors influencing the mobility of an ion, Debye and Hückel deduced an expression for the variation of the equivalent conductivity with the concentration. This expression, however, did not show entirely satisfactory agreement with the experimental values. The Norwegian physicist, Lars Onsager, then pointed out, in 1926, that in calculating the effect of the unsymmetrical distribution of ions around a moving ion, account must be taken of the Brownian movement of the ion.[1] Introducing the necessary correction into the Debye-Hückel equation, Onsager obtained the expression for a z-valent binary electrolyte :

$$\Lambda_c = \Lambda_o - \left[\frac{0{\cdot}986 \times 10^6}{(D{\cdot}T)^{\frac{3}{2}}} \cdot (2 - \sqrt{2}) \cdot z^2 \cdot \Lambda_o + \frac{58{\cdot}0}{(D{\cdot}T)^{\frac{1}{2}}\eta} \cdot z \right] \cdot \sqrt{2zc}.$$

In this expression c is the concentration in gram-equivalents per litre, D is the dielectric constant, and η is the coefficient of viscosity of the solvent at the absolute temperature T. The equation is of the form $\Lambda_c = \Lambda_o - k\sqrt{c}$, of the same form, that is, as the equation obtained empirically by Kohlrausch. By means of the Debye-Hückel-Onsager equation, therefore, the change of the equivalent conductivity with dilution can be calculated in the case of a dilute solution of a strong electrolyte which undergoes complete ionisation. For solutions of a uni-univalent electrolyte in the undermentioned solvents at 25° C. the equation takes the following forms [2] :—

Water : $\Lambda_c = \Lambda_o - (0{\cdot}228\Lambda_o + 59{\cdot}8)\sqrt{c}$.

Methyl alcohol : $\Lambda_c = \Lambda_o - (0{\cdot}957\Lambda_o + 158{\cdot}1)\sqrt{c}$.

Ethyl alcohol : $\Lambda_c = \Lambda_o - (1{\cdot}256\Lambda_o + 87{\cdot}8)\sqrt{c}$.

The values of the equivalent conductivity calculated by means of the above equation agree well with the experimental values in the case of *dilute* solutions of strong electrolytes in water and in methyl alcohol; and the equation may be regarded as representing the behaviour of an electrolyte which undergoes complete ionisation. Deviations from the values calculated by this equation may be regarded as due to some form of ionic association, such as the formation of ionic doublets which simulate un-ionised molecules. The

[1] *Physikal. Z.*, 1926, **27**, 388 ; 1927, **28**, 277.

[2] H. Hartley, *Reports of British Association*, **1931**, 31.

extent to which this will occur will depend on the interionic forces, and these, in turn, will depend on the dielectric constant of the solvent. It will depend, also, on the extent to which the ions undergo solvation, *i.e.*, on the chemical nature of the ions and of the solvent. In a complete theory of the behaviour of a strong electrolyte, therefore, chemical as well as purely physical properties, must be taken into account.

It may be pointed out that in the case of non-electrovalent strong electrolytes, *e.g.*, hydrogen chloride, reversible electrolytic dissociation takes place, as in the case of weak electrolytes, but the properties of solutions of such electrolytes are modified by the action of interionic forces.

Activity Coefficient.—It was pointed out (p. 324) that, in the case of strong electrolytes, the Arrhenius coefficient $\alpha = \Lambda_v/\Lambda_\infty$ cannot be regarded as representing the degree of dissociation of the electrolyte, and consequently the effective concentration of an ion will not be represented by $\alpha \,.\, c$ where c is the concentration of the electrolyte. In the case of strong electrolytes, therefore, the concept of the degree of dissociation should be replaced by the concept of *activity*, due to G. N. Lewis (p. 286). If, in the case of a binary electrolyte, the activities of the cation and anion are represented by a_+ and a_-, and the activity of the undissociated solute by a_2, the equation for equilibrium is

$$\frac{a_+ a_-}{a_2} = K.$$

At infinite dilution the activity of each ion is put equal to its molality (or number of gram-molecules in 1000 g. of water), and this is known if complete dissociation is assumed. In the absence of information regarding the concentration of the undissociated electrolyte, it is convenient to choose the standard state so that K is unity, and therefore $a_+ a_- = a_2$. At infinite dilution, $a_+ = a_- = \sqrt{a_2}$, but since this equality of the ion activities cannot be assumed at other concentrations, Lewis introduced the concept of *mean ion activity*, or $a_\pm = \sqrt{a_+ a_-} = \sqrt{a_2}$. On dividing the mean ion activity by the molality, one obtains the expression $\frac{a_\pm}{m}$, which Lewis called the *activity coefficient* and represented by γ. One has, therefore, $a_\pm \rightleftharpoons \gamma \,.\, c$, where c is the concentration in gram-molecules in 1000 g. of water. In order to find the effective

concentration of an ion, then, it is better to use the expression $\gamma . c$ instead of the expression $\alpha . c$ in the case of a strong electrolyte. A comparison of the values of γ and of α is given in the following table, the solutions containing 0·01 gram-molecule of salt in 1000 g. of water :—

	KCl.	NaCl.	KNO_3.	K_2SO_4.
γ . .	0·922	0·922	0·916	0·687
α . .	0·941	0·936	0·935	0·832

It is seen that the values of α are in all cases greater than the values of γ; and the differences between the two sets of values become greater in more concentrated solutions. Although, at the above dilution, the values of γ and α are not greatly different in the case of salts formed from two univalent ions, the values are markedly different in the case of salts of multivalent ions (*e.g.*, K_2SO_4).

In the following table are given the values of the activity coefficients of a few electrolytes at different dilutions :—

Concentration in Gram-molecules per 1000 g. of Water.	Activity Coefficients.				
	HCl.	NaCl.	KCl.	KOH.	H_2SO_4.
0·01	0·924	0·922	0·922	0·92	0·617
0·02	0·894	0·892	0·892	0·89	0·519
0·05	0·860	0·842	0·840	0·84	0·397
0·1	0·814	0·798	0·794	0·80	0·313
0·2	0·783	0·752	0·749	0·75	0·244

Determination of the Activity Coefficient.—The activity coefficient may be determined in various ways, *e.g.*, from freezing-point and vapour pressure determinations and from measurements of the electromotive force of cells (Chap. XV.). In the case of strong uni-univalent electrolytes (*e.g.*, sodium chloride), in concentrations not exceeding 0·01 gram-molecule in 1000 g. of water. Lewis has deduced the expression $\gamma = 1 - 3\left(1 - \frac{\theta}{2\lambda m}\right)$, where m is the concentration in gram-molecules per 1000 g. of water, θ is the depression of the freezing-point, and λ is the molecular lowering of the freezing-point (per 1000 g. of solvent) at infinite dilution : λ for water is 1·858°.

In presence of other strong electrolytes, the activity coefficient of a strong electrolyte depends on the ionic strength of the solution ; and in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.

Ionisation of Water.—It has already (p. 238) been pointed out that water is ionised to a slight extent into hydrogen ion and hydroxide ion, so that there exists the equilibrium $H_2O \rightleftharpoons H^{\cdot} + OH'$. To this equilibrium one may also apply the law of mass action and so obtain the expression [1]

$$\frac{[H^{\cdot}] \times [OH']}{[H_2O]} = K.$$

Since the concentration of the ions is very small, the concentration of the un-ionised water molecules may be regarded as constant [$= 1000/18 = 55{\cdot}5$ gram-molecules per litre]. One obtains, therefore, the relation $[H^{\cdot}] \times [OH'] = \text{constant} = K_w$. That is to say, *in water or any aqueous solution the product of the concentrations of hydrogen ion and hydroxide ion is constant.*

The concentration of hydrogen ion in water at 18°, as determined from conductivity measurements (p. 239), is $0{\cdot}8 \times 10^{-7}$ gram-equivalent per litre: and since the concentration of hydroxide ion must be the same, the product of concentrations is equal to about $0{\cdot}64 \times 10^{-14}$. This is the *ionic product* K_w of water.

The value of the ionic product of water can be determined also from the velocity of hydrolysis of methyl acetate, from the degree of hydrolysis of a salt of a weak acid, and from measurements of electromotive force (Chap. XV.). Its value at different temperatures is given in the following table [2]:—

IONIC PRODUCT OF WATER

Temperature.	$K_w \times 10^{14}$.	Temperature.	$K_w \times 10^{14}$.
10°	0·295	35°	2·14
15°	0·46	37°	2·45
18°	0·59	40°	3·02
20°	0·69	60°	9·33
25°	1·02	80°	23·4
30°	1·48	100°	51·3

The variation of K_w with temperature is given by the expression [3]

$$\log K_w = 14{\cdot}000 - 0{\cdot}0331(t° - 25) + 0{\cdot}00017(t° - 25)^2.$$

[1] It may be noted that hydrogen ion exists in solution as $H_3O^{\cdot}$ ions.

[2] See also H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194.

[3] W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1936, **32**, 1397; Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194.

Heat of Ionisation of Water.—From the values of the ionisation constant of water at different temperatures one may calculate the heat of ionisation of water. Thus, applying the van't Hoff isochore (p. 311), one obtains

$$\log_{10}\frac{K_1}{K_2}=\frac{q}{4{\cdot}577}\cdot\left(\frac{T_2-T_1}{T_1\times T_2}\right)$$

and since K_w is proportional to K, the ionisation constant,[1] one may substitute Kw for K. From the values of Kw at 20° and at 25°, the heat of ionisation is calculated to be

$$q=\frac{4{\cdot}577\times 293\times 298\times\log_{10}\frac{0{\cdot}69}{1{\cdot}02}}{5}=-13{,}570\text{ cal.}$$

The heat of combination of hydrogen and hydroxide ions to form water is therefore +13,570 cal. This agrees very well with the value derived from the heat of neutralisation of a strong acid by a strong base (p. 269).[2]

Equilibrium between Electrolytes with a Common Ion.—When the solutions of two electrolytes which have an ion in common are mixed, the dissociation of each electrolyte will in general be diminished. This follows, in fact, as a necessary consequence from the law of mass action. Only when the concentration of the common ion is the same can the solutions be mixed without the one electrolyte influencing the ionisation of the other.

This conclusion can be deduced in the case of, say, two weak acids, to which the Ostwald dilution law can be applied. Thus, for two such acids one has

$$[\mathrm{H}^{\cdot}]_1\times[\mathrm{A}']_1=K_1[\mathrm{HA}]_1$$

and

$$[\mathrm{H}^{\cdot}]_2\times[\mathrm{A}']_2=K_2[\mathrm{HA}]_2.$$

If the volume v of the first acid solution be mixed with volume v' of the second, and if it be assumed that no change of ionisation occurs, then the concentrations of the different ions and molecules will be

$$\frac{[\mathrm{H}^{\cdot}]_1v+[\mathrm{H}^{\cdot}]_2v'}{v+v'};\ \frac{[\mathrm{A}']_1v}{v+v'};\ \frac{[\mathrm{A}']_2v'}{v+v'};\ \frac{[\mathrm{HA}]_1v}{v+v'};\ \frac{[\mathrm{HA}]_2v'}{v+v'}.$$

There must, therefore, exist the equilibrium,

$$\frac{[\mathrm{H}^{\cdot}]_1v+[\mathrm{H}^{\cdot}]_2v'}{v+v'}\times\frac{[\mathrm{A}']_1v}{v+v'}=K_1\frac{[\mathrm{HA}]_1v}{v+v'},$$

or

$$\frac{[\mathrm{H}^{\cdot}]_1v+[\mathrm{H}^{\cdot}]_2v'}{v+v'}\times[\mathrm{A}']_1=K_1[\mathrm{HA}]_1.$$

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[1] The ionisation constant is equal to $K_w/55{\cdot}5$.

[2] W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1936, **32**, 1937; Harned and Hamer, *J. Amer. Chem. Soc.*, 1935, **55**, 2194.

In the solution of the first acid, however, there exists the equilibrium $[H^\cdot]_1 \times [A']_1 = K_1[HA]_1$, and if no change in the degree of ionisation takes place, it follows that

$$\frac{[H^\cdot]_1 v + [H^\cdot]_2 v'}{v + v'} = [H^\cdot]_1 \text{ and therefore } [H^\cdot]_1 = [H^\cdot]_2.$$

From this it is seen that if the ionisation of the one acid is not to be altered by addition of a solution of another acid, the concentration of the hydrogen ion in the two solutions must be the same. Such solutions are called *isohydric solutions.*

At what concentrations, it may now be asked, will two acids be isohydric ?

Let it be assumed that in the mixed solution c_1 is the concentration of the acid HA_1, and that c_2 is the concentration of the acid HA_2; and let α_1 and α_2 be the degree of ionisation of the two acids. Then, applying the law of mass action, one has

For the first acid :

$$K_1 = \frac{[H^\cdot] \times [A']_1}{[HA]_1} = [H^\cdot]\frac{\alpha_1 c_1}{(1-\alpha_1)c_1} = [H^\cdot]\frac{\alpha_1}{1-\alpha_1},$$

or $$\frac{1}{\alpha_1} = 1 + \frac{[H^\cdot]}{K_1}.$$

For the second acid :

$$K_2 = \frac{[H^\cdot] \times [A']_2}{[HA]_2} = [H^\cdot]\frac{\alpha_2 c_2}{(1-\alpha_2)c_2} = [H^\cdot]\frac{\alpha_2}{1-\alpha_2},$$

or $$\frac{1}{\alpha_2} = 1 + \frac{[H^\cdot]}{K_2}.$$

If, further, x_1 and x_2 are the concentrations of the pure acids which are isohydric, then x_1 and x_2 must be such that the degree of ionisation is also α_1 and α_2. Consequently,

$$K_1 = \frac{\alpha_1^2 x_1}{1-\alpha_1}, \text{ or } x_1 = K_1 \cdot \frac{1-\alpha_1}{\alpha_1^2},$$

and

$$K_2 = \frac{\alpha_2^2 x_2}{1-\alpha_2}, \text{ or } x_2 = K_2 \cdot \frac{1-\alpha_2}{\alpha_2^2}.$$

But it has already been found that $K_1 = [H^\cdot] \cdot \frac{\alpha_1}{1-\alpha_1}$ and $K_2 = [H^\cdot]\frac{\alpha_2}{1-\alpha_2}$, and therefore

$$x_1 = [H^\cdot]\frac{\alpha_1}{1-\alpha_1} \times \frac{1-\alpha_1}{\alpha_1^2} = [H^\cdot] \cdot \frac{1}{\alpha_1}.$$

Similarly,

$$x_2 = [H^\cdot] \cdot \frac{1}{\alpha_2}.$$

Therefore,

$$x_1 = [H^\cdot] \times \left(1 + \frac{[H^\cdot]}{K_1}\right) = [H^\cdot] + \frac{[H^\cdot]^2}{K_1},$$

and

$$x_2 = [H^\cdot] + \frac{[H^\cdot]^2}{K_2}.$$

When, however, K_1 and K_2 are small, then

$$x_1 = \frac{[H^\cdot]^2}{K_1} \text{ and } x_2 = \frac{[H^\cdot]^2}{K_2},$$

and therefore

$$\frac{x_1}{x_2} = \frac{K_2}{K_1}.$$

One sees, therefore, that solutions of weak acids will be isohydric when the concentrations are inversely proportional to the dissociation constants.

When non-isohydric solutions of acids of different strength are mixed the ionisation of the weaker acid is altered more than that of the stronger acid.

The influence of one electrolyte on the ionisation of another electrolyte with a common ion can be well illustrated by the following two simple experiments. (1) When equal volumes of dilute solution (say N/300) of potassium thiocyanate and ferric chloride are mixed a distinct blood-red coloration is given, owing to the formation of *un-ionised* ferric thiocyanate If one now dissolves in the solution a little solid potassium thiocyanate, the concentration of the thiocyanate ions will be increased, and the colour of the solution will become deeper, owing to a decrease of the ionisation of the ferric thiocyanate and the consequent increase of the concentration of un-ionised ferric thiocyanate. (2) The weak acid, *p*-nitrophenol, is colourless in the un-ionised state but yellow when ionised. When this substance is dissolved in water a pale yellow solution is obtained, owing to the presence of the yellow anion. If, however, a few drops of hydrochloric acid are added to the solution the colour disappears, showing that the ionisation of the *p*-nitrophenol has been diminished practically to zero by the increase in the concentration of hydrogen ions.

The ionisation of a weak acid is diminished not only by the addition of a strong acid but also by the addition of a soluble salt of the acid. Thus the ionisation of acetic acid will be diminished by the addition of sodium acetate. Salts are, with very few exceptions, largely ionised in solution, and consequently, when sodium acetate is added to a solution of acetic acid the acetate ion concentration is increased ; and it follows that the reaction $H^\cdot + Ac' \longrightarrow HAc$ must take place in order that the mass law equilibrium may be maintained. *By the addition of one of its salts, therefore, the ionisation of a weak acid is diminished and the concentration*

of hydrogen ion is reduced. This fact is of very great practical importance.

The effect of adding to the solution of a weak acid small amounts of a salt of that acid can be calculated approximately from the law of mass action. The dissociation equilibrium of the weak acid is given by the expression

$$\frac{[H^{\cdot}] \times [A']}{[HA]} = K.$$

Let the total concentration of the acid be c_1, and let the concentration of the added salt be c_2. Since the acid is a weak acid the concentration of the anion in the pure acid solution will be very small, and, as the ionisation is diminished by the salt, the concentration of the anion *derived from the acid* will, in the mixed solution, become negligibly small. The concentration of the anion in the equilibrium mixture will therefore be practically equal to the concentration of the anion from the salt ; that is, it will be equal to c_2 if it be assumed that the activity coefficient of the salt is unity. (In dilute solutions this assumption does not involve more than a relatively small error.) Moreover, since the ionisation of the weak acid in presence of the salt is very small, the concentration of the un-ionised acid may be put equal to the total concentration of acid, that is, equal to c_1. One obtains, therefore, the important relationship

$$\frac{[H^{\cdot}] \times [A']}{[HA]} = K, \text{ or } [H^{\cdot}] = \frac{K \,.\, [\text{acid}]}{[\text{salt}]}.$$

From this it is seen that the concentration of hydrogen ion in the solution is regulated by the strength of the acid and by the ratio $\frac{[\text{acid}]}{[\text{salt}]}$.

How great may be the diminution of the ionisation of a weak acid (and of the hydrogen ion concentration) by the addition of a salt of the acid is well illustrated by the effect of addition of sodium acetate to a solution of acetic acid. In an N/8-solution of acetic acid the degree of ionisation is 0·0119. The concentration of hydrogen ion in this solution is therefore $0{\cdot}0119/8 = 0{\cdot}0015$ gram-equivalent per litre. If to this solution one adds sodium acetate in amount equivalent to the acid ($c_1 = c_2$) the concentration of hydrogen ion becomes numerically equal to the affinity constant of the acid ; that

is, equal to 0·000018 gram-equivalent per litre, or equal to about $\frac{1}{800}$ of its original concentration.

In the following table are given the calculated values of the expression

$$[H^{\cdot}]=\frac{K\,.\,[\text{acid}]}{[\text{salt}]}$$

for solutions containing different proportions of acetic acid and sodium acetate :—

$\frac{\text{Acetic Acid}}{\text{Sodium Acetate}}$	$[H^{\cdot}]$ in Gram-equivalents per Litre.	$\frac{\text{Acetic Acid}}{\text{Sodium Acetate}}$	$[H^{\cdot}]$ in Gram-equivalents per Litre.
16 : 1	$2{\cdot}88\times10^{-4}$	1 : 2	$0{\cdot}90\times10^{-5}$
8 : 1	$1{\cdot}44\times10^{-4}$	1 : 4	$0{\cdot}45\times10^{-5}$
4 : 1	$0{\cdot}72\times10^{-4}$	1 : 8	$0{\cdot}22\times10^{-5}$
2 : 1	$0{\cdot}36\times10^{-4}$	1 : 16	$0{\cdot}11\times10^{-5}$
1 : 1	$1{\cdot}81\times10^{-5}$	...	...

From the above table it will be seen that by varying the relative concentrations of acetic acid and sodium acetate the hydrogen ion concentration can be varied over a wide range.

In deriving the above expression for the concentration of hydrogen ions it was assumed that the activity coefficient of sodium acetate is equal to unity. This, however, is not strictly true, and the hydrogen ion concentration will therefore vary somewhat with dilution, owing to change in the activity coefficient of the sodium acetate. The values of hydrogen ion concentration given in the table can therefore be regarded as only approximately correct.

Just as the ionisation of a weak acid is diminished by the addition of a salt of the acid, so the ionisation of a weak alkali will be diminished by the addition of a salt of the base, *e.g.*, addition of ammonium chloride to a solution of ammonium hydroxide ; and the relations which obtain here find mathematical expression in equations analogous to those derived for weak acids and their salts.. Thus, we have

$$[OH']=\frac{K\,.\,[\text{alkali}]}{[\text{salt}]},$$

where K is the affinity constant of the alkali. The application of this equation is subject to the same limitations and restrictions as in the case of a weak acid.

Solubility Product of Electrolytes.—When a solid electrolyte is shaken with water, solution of the solid will take place until, at a given temperature, the concentration of the solute attains a certain value, after which no more solid dissolves. The solution is then said to be *saturated*. Between the solid electrolyte and the un-ionised molecules in the saturated solution equilibrium exists. If the concentration of the solute molecules is reduced below the saturation concentration, more solid will dissolve ; if, on the other hand, the concentration of the solute molecules is increased, say, by evaporation of the solvent, some of the solute will crystallise out, and the saturation concentration will be again established.

In the saturated solution of an electrolyte, however, the molecules of the solute will also be in equilibrium with the ions into which they dissociate, so that, for a binary electrolyte, we have the equilibrium condition

$$[\text{Cation}] \times [\text{anion}] = K \,.\, [\text{un-ionised salt}].$$

In a *saturated* solution the concentration of the un-ionised salt molecules is constant, at constant temperature, so that *the product of concentrations of the cation and anion must also be constant.* This constant product is known as the *solubility product.*[1] Whenever, in the case of a given electrolyte, the product of concentrations of its ions in a solution exceeds the solubility product, separation of the solute from solution will occur if supersaturation is supposed excluded ; but if the product of concentrations is less than the solubility product, a further quantity of the solute can pass into solution.

The use of precipitation reactions in analytical chemistry for the purpose of classifying the different cations into groups depends on differences of solubility product. When, for example, one passes hydrogen sulphide into a solution of copper sulphate, copper sulphide is precipitated because the product of concentrations of sulphide ion, formed by the ionisation of hydrogen sulphide [$H_2S \rightleftharpoons 2H^{\cdot} + S''$] and of copper ion exceeds the solubility product of copper sulphide (1×10^{-42}). Even when the concentration of the sulphide ion is reduced by addition of hydrogen ion [acid], the solubility product of copper sulphide is so small that precipitation still takes place. That is to say, copper sulphide is

[1] When the electrolyte is not a binary one the ionic concentrations must be raised to the appropriate power. Thus, silver sulphate ionises into 2 $Ag^{\cdot}$ and SO_4''. The solubility product will therefore be $[Ag^{\cdot}]^2 \times [SO_4'']$.

precipitated by hydrogen sulphide even from acid solution. Other metals of the second group of the analytical table behave similarly. If, however, hydrogen sulphide is passed into an acidified solution of a zinc salt, no sulphide is precipitated, because in the acid solution the concentration of sulphide ion is so low that even in a saturated solution of, say, zinc sulphate, the product of concentrations $[Zn^{\cdot\cdot}] \times [S^{''}]$ is less than the solubility product of zinc sulphide (say, 1×10^{-20}). If hydrogen sulphide is passed into a *neutral* solution of zinc sulphate, precipitation of zinc sulphide takes place, but only incompletely, because the hydrogen ions formed as a result of the reaction

$$Zn^{\cdot\cdot} + H_2S = ZnS + 2H^{\cdot}$$

reduce the ionisation of the hydrogen sulphide, and the product of concentrations $[Zn^{\cdot\cdot}] \times [S^{''}]$ no longer exceeds the solubility product. The concentration of hydrogen ion can be reduced and precipitation thereby rendered complete by addition of sodium acetate, the acetate ion combining with the hydrogen ion to form un-ionised acetic acid.

Since cadmium sulphide is more soluble than the other sulphides of the second group, complete precipitation can be secured only if the concentration of hydrogen ion (acid concentration) is not too high and concentration of sulphide ion, therefore, not too low.

In the case of the precipitation of hydroxides, also, it is found that, whereas ferric hydroxide, for example, is precipitated by ammonium hydroxide even in presence of ammonium chloride (which reduces the concentration of hydroxide ion), magnesium hydroxide is not precipitated in presence of ammonium chloride, owing to the reduction of the product of ion concentrations to below the solubility product. In absence of ammonium chloride, however, the solubility product is exceeded and precipitation takes place.

The application of the law of mass action enables one also to explain why a weak or moderately weak acid may produce a precipitate from the solution of a salt of a weak but not of a strong acid. Thus, oxalic acid will precipitate calcium oxalate completely from a solution of calcium acetate but not from a solution of calcium nitrate or chloride. In the former case, one has the reaction

$$Ca\overline{Ac}_2 + H_2C_2O_4 = CaC_2O_4 + 2H\overline{Ac},$$

the concentrations of oxalate ions being sufficient to give a product

$$[Ca^{\cdot\cdot}] \times [C_2O_4''],$$

which is greater than the solubility product. Moreover, the acetic acid which is formed is so slightly ionised that it does not appreciably alter the ionisation of the stronger oxalic acid. If, however, one adds oxalic acid to a solution of calcium nitrate, nitric acid is formed, and the increase of concentration of hydrogen ion thereby produced reduces the ionisation of the oxalic acid to such an extent that the concentration of oxalate ions soon falls below that necessary to give the solubility product of calcium oxalate. The precipitation, therefore, is incomplete.

As the converse of what has been said above, one has the rule that sparingly soluble salts of weak acids are soluble in strong acids, but not the sparingly soluble salts of strong acids.

Similarly, in a solution of potassium chromate, one has the equilibrium

$$CrO_4'' + 2H^{\cdot} \rightleftarrows Cr_2O_7'' + H_2O ;$$

and if the concentration of hydrogen ions is not too great, the concentration of chromate ions will be sufficient to give a precipitate when the solution is added to the solution of a barium salt. When, however, the concentration of hydrogen ion is increased by the addition of, say, hydrochloric acid, the concentration of chromate ions is so greatly diminished that no precipitate is given. It is for this reason that in group 4 of the analytical tables, barium carbonate is dissolved in acetic, not in hydrochloric, acid before carrying out the test with potassium chromate.

In the preceding paragraphs the application of the concept of solubility product in analytical chemistry has been discussed in a qualitative manner: a more quantitative treatment may now be undertaken.

Since the solubility of an electrolyte depends on its solubility product it is clear that the solubility will be lowered by addition to the solution of another electrolyte with a common ion. Thus, in a saturated solution of silver acetate, $CH_3.COOAg$, we have

$$[Ag^{\cdot}] \times [CH_3.COO'] = \text{constant},$$

and if the concentration of, say, the acetate ion is increased by addition of sodium acetate, the concentration of silver ion must be correspondingly diminished. That is to say, silver acetate will separate out in the solid state, or the solubility of the silver acetate will be lowered. Addition of silver nitrate ($Ag^{\cdot}$) will similarly lower the solubility of silver acetate.[1] The following numbers make this clear :—

SOLUBILITY OF SILVER ACETATE AT 25°

Concentration of Sodium Acetate (Gram-molecule per Litre).	Solubility of Silver Acetate (Gram-molecule per Litre).	Concentration of Silver Nitrate (Gram-molecule per Litre).	Solubility of Silver Acetate (Gram-molecule per Litre).
...	0·0660	...	0·0660
0·0654	0·0433	0·0327	0·0535
0·262	0·0243	0·0654	0·0444
0·652	0·0167	0·1307	0·0334

The influence of one electrolyte on the solubility of another electrolyte with a common ion is well demonstrated by passing hydrogen chloride into a saturated solution of sodium chloride. Solid sodium chloride crystallises out. Similarly, barium nitrate is precipitated from its saturated solution on addition of concentrated nitric acid. Here the solutions are so concentrated that the effect cannot simply be explained by the principle of the solubility product.

Quantitative account of the influence of an electrolyte on the solubility of another electrolyte with a common ion can be taken in certain cases. Thus, in the case of a sparingly soluble binary salt, *e.g.*, silver chloride, the saturated solution is so dilute that the concentration of the ions may be assumed to be equal to the concentration of the salt (complete ionisation). If S_0 represents the solubility of the salt or the concentration of the cation and of the anion in a pure saturated solution, then $S_0^2 = K_s$ = solubility product. If a saturated solution of the salt be now prepared, not in pure water but in a solution of an electrolyte containing a common ion, the concentration of which is x, the new ionic equilibrium will be given by the expression $S(S+x) = K_s = S_0^2$, where S is the solubility in a solution of an electrolyte with a common ion. This expression can be made more exact, according to the classical theory of electrolytes, by correcting the concentrations for the degree of ionisation of the salts.

[1] A. A. Noyes, *Z. physikal. Chem.*, 1890, **6**, 241.

In this way one obtains,[1] $aS(aS+a_1x)=(a_0S_0)^2$, and the value of S is given by the expression

$$S=-\frac{xa_1}{2a}+\sqrt{S_0{}^2\left(\frac{a_0}{a}\right)^2+\frac{x^2}{4}\left(\frac{a_1}{a}\right)^2}.$$

This expression, however, based on the older theory of electrolytic solutions, holds only approximately or not at all in the case of moderately soluble salts, and when more than slight additions of a foreign salt are made, because strong electrolytes do not behave in accordance with the law of mass action, and the effect of interionic attraction cannot be neglected.

It has already been pointed out that the law of mass action can be applied to strong electrolytes if, in place of ordinary concentrations, one uses activities, the activity being equal to the concentration multiplied by the activity coefficient. Moreover, in the case of strong electrolytes, modern theory shows that the activity coefficient depends on the charge on the ions and on the ionic strength of the solution, the logarithm of the activity coefficient being proportional to the product of the charges on the ions and to the square root of the ionic strength. That is, $\log \gamma = K \,.\, z_1z_2 \,.\, \sqrt{\mu}$. In the case of a saturated solution of an electrolyte in pure water and in a solution of a foreign salt, the mean activity of the undissociated solute, a_2, and therefore also the mean ionic activity, $a_\pm$, will be the same in the two solutions, since the solute molecules are in equilibrium with the solid electrolyte. If the mean ionic molality in pure water and in the solution of a foreign salt is represented by m_0 and m, respectively, it follows that, since $\gamma = a_\pm/m$, $\gamma_0 m_0 = \gamma \,.\, m$. Consequently, $\log m/m_0 = \log \gamma_0/\gamma =$ constant $\times (\sqrt{\mu_0} - \sqrt{\mu})$, where μ_0 and μ are the ionic strengths in pure water and in the solution containing a foreign electrolyte. From this it is seen that if μ is increased by addition of a foreign electrolyte, m will increase relatively to m_0. That is, the solubility of the salt will increase. Moreover, since γ depends on the valency of the ions, the enhancing effect of an electrolyte on the solubility of a salt is all the greater the higher the valency of the ions.

On the other hand, when the foreign salt contains an ion

[1] See Creighton and Ward, *J. Amer. Chem. Soc.*, 1915, **37**, 2333; Kendall and Andrews, *ibid.*, 1921, **43**, 1545.

in common with the solute the solubility tends to be diminished in accordance with the law of mass action ; and in general this effect is greater than the enhancing effect due to increase of ionic strength. Thus the solubility of thallium chloride is reduced by addition of potassium chloride and of thallous nitrate, but is increased by potassium nitrate and still more by potassium sulphate.[1] This behaviour is, however, not always found, and the enhancing effect of ionic strength may more than balance the common ion effect. Thus the solubility of barium nitrate is increased by the presence of barium hydroxide, and the solubility of barium hydroxide is increased by addition of barium nitrate.

In considering the effect of a salt on the solubility of another salt with a common ion, it was assumed that no chemical action takes place. When, however, chemical action occurs, addition of an electrolyte may also increase the solubility of a salt with a common ion. Thus, when excess of potassium cyanide is added to a solution of silver nitrate, the precipitate of sparingly soluble silver cyanide redissolves owing to the formation of the complex ion $Ag(CN)_3''$. One has, then, the equilibria

$$\underset{\text{Solid.}}{AgCN} \rightleftarrows \underset{\text{In solution.}}{AgCN + 2CN'} \rightleftarrows Ag(CN)_3''.$$

By the addition of cyanide ions the concentration of silver cyanide molecules in solution is reduced by combination to form complex ions. The first equilibrium, therefore, is disturbed, and more silver cyanide must pass into solution.

Mixtures of Electrolytes with no Ion in Common.—In the case of two strong electrolytes, *e.g.*, NaCl and KBr, no change in the ionisation of either will be brought about on mixing their solutions, provided the solutions are sufficiently dilute, because both these salts and the salts which could be formed from them by double decomposition are highly ionised, and in moderately dilute solution the ionisation may be regarded as complete. Very different, however, is the result when there are produced in the mixed solution the ions of a weak acid or weak alkali or, generally, of a slightly ionised electrolyte. In this case very marked and important changes in the degree of ionisation may occur. Thus, when

[1] Bray and Winninghoff, *J. Amer. Chem. Soc.*, 1911, **33**, 1663 ; Randall and Chang, *ibid.*, 1928, **50**, 1535.

a solution of sodium acetate is added to a solution of hydrochloric acid, there are brought together the ions $Na^{\cdot}$, Ac', $H^{\cdot}$ and Cl'. The ions $H^{\cdot}$ and Ac' are, however, the ions of a weak acid, and since, for this acid, the ratio $\frac{[H^{\cdot}] \times [Ac']}{[HAc]}$ is small ($1{\cdot}8 \times 10^{-5}$), it follows that the greater part of the hydrogen ions and the acetate ions will combine to form un-ionised acetic acid; and the concentration of hydrogen ions in the solution will be greatly diminished. The ions $Na^{\cdot}$ and Cl', being the ions of a strong electrolyte, do not combine but remain free in solution. One sees, therefore, that when the salt of a weak acid, *e.g.*, sodium acetate or sodium borate, is added to an acid solution, the concentration of hydrogen ions can be greatly diminished; and the diminution will be all the greater the weaker the acid from which the added salt is formed.

An approximate calculation of the effect of adding a solution of sodium acetate to a solution of, say, hydrochloric acid can readily be made. If one mixes together equal volumes of N/8 solutions of sodium acetate and hydrochloric acid the resulting mixture would be N/16 with respect to hydrogen ions and also with respect to acetate ions, if no reaction took place between the ions and if complete ionisation of the sodium acetate and hydrochloric acid is assumed. In an N/16 solution of acetic acid, however, the degree of ionisation is 0·0167, and the concentration of hydrogen ions in such a solution is therefore only $\frac{0{\cdot}0167}{16} = 0{\cdot}00104$ gram-equivalent per litre. In the mixed solution, therefore, the concentration of hydrogen ion, instead of being N/16 = 0·0625 gram-equivalent per litre, will only be 0·00104 normal. If excess of sodium acetate is added, the hydrogen ion concentration will, as we have seen, be much less.

The diminution of the hydrogen ion concentration is clearly illustrated by the following experiment. A solution of ferrous ammonium sulphate is slightly acidified with hydrochloric acid, and then saturated with hydrogen sulphide. No precipitate of ferrous sulphide is obtained. If, now, solid sodium acetate is added to the solution, the concentration of hydrogen ions is reduced and a precipitate is formed.

In like manner the concentration of hydroxide ions can be diminished by the addition of the salt of a weak alkali, *e.g.*, by ammonium chloride.

Hydrolysis of Salts.—The fact that water is ionised into $H^{\cdot}$ and OH' is of great importance, because it gives rise to the possibility of interaction between these ions and the ions of a dissolved salt. Thus, for example, it is found that when sodium carbonate, sodium borate, or potassium cyanide is dissolved in water the solution does not have a neutral but an alkaline reaction; that is, the concentration of OH' is

greater than in pure water, or greater than, say, 1×10^{-7} gram-equivalent per litre.

This behaviour will be readily understood from a consideration of the case of potassium cyanide. When this salt is dissolved in water it undergoes ionisation into $K^{\cdot}$ and CN'. In the solution, however, there are also present, although in small amount, $H^{\cdot}$ and OH', due to the ionisation of the water; and since hydrocyanic acid, HCN, is a very weak acid, combination takes place between the CN' and the $H^{\cdot}$ to form un-ionised HCN, and this process goes on until the very small product of concentrations of $H^{\cdot}$ and CN', corresponding to the equilibrium

$$\frac{[H^{\cdot}] \times [CN']}{[HCN]} = 1{\cdot}32 \times 10^{-9},$$

is established. The process which takes place here and which consists in the production of free acid and free alkali by the interaction of the ions of water with the ions of the salt, is known as *hydrolysis* or *hydrolytic dissociation*. In the case under consideration the process can be represented by the equation

$$K^{\cdot} + CN' + H^{\cdot}OH' = HCN + K^{\cdot} + OH'.$$

We see, therefore, that hydrogen ions are removed from the solution to form un-ionised hydrocyanic acid, and the solution acquires an alkaline reaction owing to the presence of free hydroxide ions. (Potassium hydroxide is a strong alkali, and therefore the ions $K^{\cdot}$ and OH' can exist free in presence of each other.)

The behaviour shown by potassium cyanide is shown also by other salts formed from a strong base and a weak acid. *In all such cases the aqueous solution of the salt will exhibit an alkaline reaction.* Similarly, the aqueous solutions of all salts formed from a weak base and strong acid (*e.g.*, urea hydrochloride) will show an *acid* reaction, owing to the combination of the hydroxide ions of the water with the cation of the salt, and the consequent production of free hydrogen ions in the solution.[1]

The extent to which hydrolysis takes place depends on the strength of the weak acid, or weak base, from which the salt is formed. The general solution of the problem is somewhat complicated, and we shall consider here the case

[1] Hydrolysis may be greatly increased when the acid or base is sparingly soluble. This is found in the case of ferric chloride.

where hydrolysis takes place to only a moderate extent, say, about 1 per cent., as in the case of potassium cyanide.

The hydrolytic equilibrium is given by the equation

$$\text{salt} + \text{water} \rightleftharpoons \text{base} + \text{acid},$$

and since the concentration of the water can be regarded as constant, one obtains the expression

$$\frac{[\text{base}] \times [\text{acid}]}{[\text{unhydrolysed salt}]} = K_h = \text{hydrolysis constant.}$$

If x be the degree of hydrolysis or the fractional amount of salt hydrolysed, and if c be the total concentration of salt, then, when hydrolytic equilibrium has been established, the concentration of the free base and free acid will be $x \,.\, c$, and the concentration of the unhydrolysed salt will be $(1-x)c$. Inserting these values in the above equation, therefore, one obtains $\frac{x^2c}{(1-x)} = K_h$. Since the base formed by hydrolysis is, by assumption, a strong base, it may, with a small error, be regarded as being completely ionised,[1] and the degree of hydrolysis x will therefore be given by the ratio $x = \frac{[\text{OH}']}{[\text{total salt}]} = \frac{[\text{OH}']}{c}$. If, then, the concentration of OH′ be determined by its catalytic influence (p. 488), or by any of the methods to be discussed later, the degree of hydrolysis and the hydrolysis constant can be calculated.

A relationship can also be derived between the hydrolysis constant, the ionic product of water, and the affinity constant of the weak acid. For the ionic product of water we have $K_w = [\text{H}^\cdot] \times [\text{OH}']$, and therefore $[\text{H}^\cdot] = \frac{K}{[\text{OH}']} = \frac{K_w}{x \,.\, c}$. Further, for the weak acid we have $K_a = \frac{[\text{H}^\cdot] \times [\text{A}']}{[\text{HA}]}$. The concentration of the hydrogen ion is given by the preceding equation; the concentration of the anion may be put equal to the concentration of the unhydrolysed salt, because the amount of anion furnished by the acid will be practically negligible, *i.e.*, $[\text{A}'] = (1-x)c$; and the concentration of the un-ionised HA may, on account of the small degree of ionisation, be

[1] Or the concentrations may be multiplied by the activity coefficients given on page 393. If the activity coefficients of the salt and base are equal they will cancel out.

taken as equal to the free acid, *i.e.*, $[HA]=x\,.\,c$. Inserting these different values, therefore, we obtain

$$K_a=\frac{[H^{\cdot}]\times[A']}{[HA]}=\frac{\frac{K_w}{x\,.\,c}\times(1-x)c}{x\,.\,c}=K_w\,.\,\frac{1-x}{x^2c}.$$

Hence,
$$\frac{x^2\,.\,c}{(1-x)}=K_h=\frac{K_w}{K_a}.$$

If, therefore, K_w and K_a are known, one can calculate the degree of hydrolysis x by means of the equation

$$x=\frac{-1}{2c}\,.\,\frac{K_w}{K_a}+\sqrt{\frac{1}{4c^2}\,.\,\left(\frac{K_w}{K_a}\right)^2+\frac{1}{c}\,.\,\frac{K_w}{K_a}}.$$

When the degree of hydrolysis x is small, so that $(1-x)$ may be taken as equal to unity, that is, when K_a is large compared with K_w, the expression for the degree of hydrolysis x simplifies to

$$x=\sqrt{\frac{1}{c}\,.\,\frac{K_w}{K_a}}.$$

From this it is seen that the degree of hydrolysis is proportional to the square root of the dilution, and since $x=\frac{[OH']}{c}$, one obtains the expression

$$[OH']=\sqrt{c\,.\,\frac{K_w}{K_a}},$$

where c represents the total concentration of salt.

From the equations which have just been obtained it is clear that the degree of hydrolysis is inversely proportional to $\sqrt{K_a}$, so that the smaller the value of K_a, or the weaker the acid, the greater will be the degree of hydrolysis.

Further, since the value of K_w increases fairly rapidly with rise of temperature, whereas the value of K_a remains nearly constant, it follows that the degree of hydrolysis will increase rapidly with rise of temperature. This fact can be clearly demonstrated by heating a dilute, nearly colourless solution of ferric chloride, when the liquid will acquire a deep reddish-brown colour owing to the production of ferric hydroxide by hydrolysis.

The relation which has been established between the

degree of hydrolysis, K_w and K_a, makes it possible to calculate the value of any one of these factors (*e.g.*, K_w) if the values of the other two are known. Thus, it was found by J. Shields (1893) that the degree of hydrolysis (x) of sodium acetate in N/10-solution at 25° is 0·00008. Since K_a for acetic acid is $1{\cdot}81 \times 10^{-5}$, the calculated value of K_w is

$$K_w = K_a \cdot \frac{x^2}{(1-x)v} = 1{\cdot}81 \times 10^{-5} \times \frac{(0{\cdot}00008)^2}{(1-0{\cdot}00008) \times 10}$$
$$= 1{\cdot}81 \times 10^{-5} \times 6{\cdot}4 \times 10^{-10} = 1{\cdot}16 \times 10^{-14}.$$

For the hydrolysis of a salt of a weak base and a strong acid, formulæ analogous to those given above will be obtained, but K_b, the affinity constant of the base, will take the place of K_a, the affinity constant of the acid, and one will have $K_h = \frac{K_w}{K_b}$, and $[H^{\cdot}] = \sqrt{c \cdot \frac{K_w}{K_b}}$. As an example of this type of hydrolysis, the hydrochloride of urea may be taken.

When one is dealing with the hydrolysis of a salt of a weak acid and a weak base it can be assumed that the ionisation of the acid and of the base, formed as the result of hydrolysis $BA + H_2O \rightleftharpoons HA + BOH$, is very small. If x is the fraction of the salt hydrolysed, then $(1-x)c$ is the concentration of the unhydrolysed salt, which we shall assume to be completely ionised. Therefore,

$$[A'] = (1-x)c = [B^{\cdot}]$$

and

$$[HA] = x \cdot c = [BOH].$$

One has also the following equilibrium equations :—

$$K_w = [H^{\cdot}] \times [OH'],$$

$$K_a = \frac{[H^{\cdot}] \times [A']}{[HA]} = [H^{\cdot}] \cdot \frac{(1-x)c}{x \cdot c},$$

and

$$K_b = \frac{[B^{\cdot}] \times [OH']}{[BOH]} = [OH'] \cdot \frac{(1-x)c}{x \cdot c},$$

from which it follows that $K_a \cdot K_b = K_w \cdot \frac{(1-x)^2}{x^2}$,

and consequently,

$$\frac{x^2}{(1-x)^2} = \frac{[\text{acid}] \times [\text{base}]}{[\text{unhydrolysed salt}]^2} = \frac{K_w}{K_a \cdot K_b}.$$

From this expression it is clear that x, the degree of hydrolysis,

is independent of the dilution, as is shown by the numbers in the following table (Arrhenius, 1898).[1]

DEGREE OF HYDROLYSIS OF ANILINE ACETATE AT 25°

Dilution in Litres (v).	x.	Dilution in Litres (v).	x.
12·5	0·546	200	0·556
25·0	0·558	400	0·554
50·0	0·564	800	0·569
100·0	0·551	...	...

From the equilibrium equations given above, it is seen that $K_a=[H^{\cdot}]\,.\,\frac{(1-x)}{x}$, and therefore $[H^{\cdot}]=K_a\,.\,\frac{x}{1-x}=\sqrt{\frac{K_wK_a}{K_b}}$ = constant. Similarly, [OH′] = constant. *In solutions of a salt of a weak acid and a weak base the concentrations of hydrogen and of hydroxide ion are constant at all dilutions.*[2] Moreover, if $K_a=K_b$, *i.e.*, if the affinity constant of the acid is the same as the affinity constant of the base, the concentration of hydrogen ion will be equal to the concentration of the hydroxide ion. No matter, therefore, how great may be the degree of hydrolysis, the solution will exhibit no acid or alkaline reaction. This is found in the case of solutions of ammonium acetate.

Determination of the Degree of Hydrolysis.—It has already been pointed out that a definite relation exists between the degree of hydrolysis of a salt, the ionic product of water, and the affinity constant of the weak base or weak acid from which the salt is formed. Consequently, if one knows the values of K_w, K_a, and K_b, the degree of hydrolysis can be calculated.

Besides this indirect method there are also several more direct experimental methods, by means of which the degree of hydrolysis of a salt can be obtained.

1. *Distribution between Two Non-miscible Solvents.*—This method will be discussed in Chap. XX.

2. *Electrical Conductivity.*—The conductance of an aqueous solution of the salt of a weak base (*e.g.*, aniline

[1] This is not strictly true, as it has been assumed that the activity coefficient of the salt is unity.

[2] At high dilutions slight deviations from constancy may be found when the ionisation constants of acid and base are different. (See Griffith, *Trans. Faraday Soc.*, **1922, 17,** 525.)

hydrochloride), or of a weak acid, is due partly to the ions of the unhydrolysed salt and partly to the ions (more especially the hydrogen ion or hydroxide ion), of the acid or base formed by hydrolysis, as indicated in the case, for example, of aniline hydrochloride, by the two equilibria

$$\begin{array}{ccc} C_6H_5 . NH_3Cl & \underset{\text{(1)}}{\rightleftharpoons} & C_6H_5 . NH_3^{\cdot} + Cl' \\ \downarrow\uparrow \text{(2)} & & \\ C_6H_5 . NH_2 + H^{\cdot} + Cl' & & \end{array}$$

If a quantity of the weak base (or acid) which, in the presence of its salt, can be regarded as completely un-ionised, is added to the solution, the hydrolysis of the salt will be diminished (reaction 2) but the ionisation (reaction 1) will be unaffected. From measurements of the conductivity of pure solutions of the salt (in which, therefore, hydrolysis occurs) and of solutions containing excess of the weak base (or weak acid), the degree of hydrolysis can be calculated.[1]

If one considers here only the simplest case, that of, say, a strong monobasic acid with a weak monoacid base, the hydrolytic equilibrium in dilute solution is given by the expression

$$K_h = \frac{x^2}{(1-x)v}$$

where v is the volume in litres containing 1 gram-molecule of salt and x is the degree of hydrolysis. The amount of unhydrolysed salt is represented by $(1-x)$ and the amount of the free acid by x. For the equivalent conductivity Λv of the solution of hydrolysed salt, therefore, one has

$$\Lambda_v = (1-x)\Lambda'_v + x \,.\, \Lambda''_v$$

where Λ'_v and Λ''_v are the equivalent conductivities at the dilution v litres of the unhydrolysed salt and of the strong acid respectively. The former, as has been stated, can be calculated from determinations of the conductance of the salt solution in presence of excess of the weak base. The degree of hydrolysis of the salt at the given dilution is then given by the expression

$$x = \frac{\Lambda_v - \Lambda'_v}{\Lambda''_v - \Lambda'_v}.$$

In the case of a solution of 1 gram-molecule of aniline hydrochloride in 1024 litres, it was found that, at 25°, $\Lambda_v = 144{\cdot}0$ and $\Lambda'_v = 103{\cdot}3$; Λ''_v for hydrochloric acid is 383. One finds, therefore,

$$x = \frac{144{\cdot}0 - 103{\cdot}3}{383 - 103{\cdot}3} = \frac{40{\cdot}7}{279{\cdot}7} = 0{\cdot}14.$$

Under the above conditions aniline hydrochloride is hydrolysed to the extent of 14 per cent. Comparison with the value given in the table on page 349 shows that the hydrolysis increases greatly with dilution.

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[1] G. Bredig, *Z. physikal. Chem.*, 1894, **13**, 321; A. A. Noyes, Y. Kato, and R. B. Sosman, *J. Amer. Chem. Soc.*, 1910, **32**, 159.

3. *Determination of Concentration of Hydrogen Ion or Hydroxide Ion.*—Since, as has been pointed out, the degree of hydrolysis x is given by the expression $x=\frac{[OH']}{c}$, or by $x=\frac{[H^{\cdot}]}{c}$, one may calculate the value of x if the concentration of hydroxide ion or of hydrogen ion is known. The concentration of these ions can be determined by measurements of electromotive force (Chap. XV), by means of indicators (p. 355), or by measurements of the velocity of inversion of cane sugar, hydrolysis of an ester, decomposition of ethyl diazoacetate, etc.[1]

Thus the degree of hydrolysis of urea hydrochloride was determined by J. Walker and J. K. Wood [2] from determinations of the velocity of inversion of cane sugar and of the hydrolysis of methyl acetate.

Since the degree of hydrolysis is given by the ratio of the concentration of free acid present in the solution of the partially hydrolysed salt to that which would be present if the salt were completely hydrolysed, and since the latter is measured by the velocity coefficient (k_1) in the pure acid solution, and the former by the velocity coefficient (k_2) obtained after the addition of an equivalent amount of urea, it follows that $x=\frac{k_2}{k_1}$.

Since the velocity coefficient is not strictly proportional to the concentration of free *acid* present, and may also be affected by the neutral salt, an approximate determination of the degree of hydrolysis is first made. In the case of N/2 solution at 25°, x was found to be approximately 0·65 A solution of hydrochloric acid and sodium chloride was then prepared so that it was N/2 with respect to total chloride, but contained only 65 per cent. of this as free acid. The velocity coefficient obtained with this solution was then compared with that obtained with the solution of urea hydrochloride. In an actual experiment k_1 was found to be 0·001021 and k_2 to be 0·001081. The degree of hydrolysis x, therefore, is $\frac{0{\cdot}65\times 1081}{1021}=0{\cdot}688$.

From the value of x, the hydrolysis constant K_h is calculated to be

$$K_h=\frac{x^2}{(1-x)v}=\frac{0{\cdot}688^2}{(1-0{\cdot}688)\times 2}=0{\cdot}759.$$

Further, on calculating the affinity constant of urea at 25° from the relation $K_b=K_w/K_h$, one obtains

$$K_b=\frac{1{\cdot}02\times 10^{-14}}{0{\cdot}759}=1{\cdot}35\times 10^{-14}.$$

Measurements of the velocity of decomposition of ethyl diazoacetate, which is catalytically accelerated by hydrogen ion,[3] have been employed by E. Spitalsky[4] for the determination of the hydrolysis of potassium dichromate:

$$Cr_2O_7'' + H_2O \rightleftharpoons 2CrO_4'' + 2H^{\cdot}.$$

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[1] See H. Jörgensen, *Die Bestimmungen der Wasserstoffionenkonzentration und deren Bedeutung für Technik und Landwirtschaft.*

[2] *J. Chem. Soc.*, 1903, **83**, 484.

[3] G. Bredig and W. Fraenkel, *Z. Elektrochem.*, 1905, **11**, 525.

[4] *Z. anorgan. Chem.*, 1907, **54**, 265.

4. *Depression of the Freezing-point.*—The degree of hydrolysis may also be calculated from determinations of the depression of the freezing-point.[1]

5. *Measurements of Electromotive Force.*—This method will be discussed in Chap. XV.

The following table indicates the extent to which several well-known salts undergo hydrolysis in aqueous solution at 25°. The concentration of the solutions is in all cases N/10.

HYDROLYSIS OF SALTS

	Degree of Hydrolysis.
Sodium acetate	0·008 per cent.
Sodium borate (borax)	0·5 ,,
Potassium cyanide	1·12 ,,
Aniline hydrochloride	1·6 ,,
Sodium carbonate	3·17 ,,
Aniline acetate (N/39·3)	51·3 ,,

Amphoteric Electrolytes.—The term amphoteric electrolyte has been applied to substances which can act both as acids and as bases; that is to substances which, according to the older view, can give rise both to hydrogen ion and to hydroxide ion. According to modern views regarding acids and bases (p. 488), an amphoteric electrolyte is a substance which can act both as a proton donor and as a proton acceptor.

Although the term may be applied to water and to certain metal hydroxides, *e.g.*, aluminium hydroxide, the most important amphoteric electrolytes are the amino-acids, the molecules of which possess two different centres of acidity and basicity. Thus, in the case of aqueous solutions of amino-acetic acid $NH_2.CH_2.COOH$, one may have the reactions

$$NH_2.CH_2.COOH \rightleftarrows NH_2.CH_2.COO' + H^{\cdot}$$

and

$$NH_2.CH_2.COOH + H^{\cdot} \rightleftarrows NH_3^{\cdot}CH_2.COOH.$$

Amino-acetic acid, therefore, may yield both a cation and an anion. Besides these forms, one can also expect the formation of the "salt" form, $NH_3^{\cdot}.CH_2.COO'$, a so-called "hermaphrodite ion" or dipolar ion[2] which, although it carries electric charges, is a non-conductor.[3] This may be regarded

[1] See J. B. Goebel, *Z. physikal. Chem.*, 1914, **89**, 49.
[2] Ingold, *Chem. Rev.*, 1934, **15**, 225.
[3] N. Bjerrum, *Z. physikal. Chem.*, 1922, **104**, 147.

as formed by the combination of $NH_2.CH_2.COO'$ with the proton yielded by the amino-acetic acid.

It will be clear that since an amphoteric electrolyte can act both as an acid and as a base, it will have an acid ionisation constant K_a, as well as a basic ionisation constant K_b. In the case of amino-acetic acid, for example, according to the theory of amphoteric electrolytes put forward by J. Walker,[1] $K_a = [H^{\cdot}][X']/[X]$, where X′ is the ion, $NH_2.CH_2.COO'$ or $NH_3OH.CH_2.COO'$, and X is $NH_2.CH_2.COOH$; and $K_b = [X^{\cdot}][OH']/[X]$ or $K_b/K_w = [X^{\cdot}]/[X][H^{\cdot}]$ where $X^{\cdot}$ is the cation $\dot{N}H_3.CH_2.COOH$. The constants K_a and K_b have been calculated from determinations of the degree of hydrolysis of the compounds of the amphoteric electrolyte with strong acids and with strong bases, and from measurements of the conductivity of salts of the amphoteric electrolytes.[2]

According to the theory put forward by Bjerrum,[3] however, K_a refers not to the equilibrium $NH_2.CH_2.COOH \rightleftarrows NH_2.CH_2.COO' + H^{\cdot}$, but to the dissociation of the $\dot{N}H_3$ group, that is, to the equilibrium

$$NH_3.CH_2.COOH \rightleftarrows NH_2.CH_2.COOH + H^{\cdot};$$

and K_b has reference to the basic ion $NH_2.CH_2.COO'$. While Walker, therefore, was of opinion that the ion $NH_2.CH_2.COO'$ unites with $H^{\cdot}$ to form $NH_2.CH_2.COOH$, Bjerrum's view is that it forms $\dot{N}H_3.CH_2.COO'$; and while Walker assumed that $\dot{N}H_3.CH_2.COOH$ dissociates to give $NH_2.CH_2.COOH$, Bjerrum assumes that dissociation takes place with production of $\dot{N}H_3.CH_2.COO'$. Support for Bjerrum's view is obtained from a consideration of the following facts. If, in the case of amino-acetic acid K_a, with the value $3{\cdot}4 \times 10^{-10}$, referred to the yielding up of $H^{\cdot}$ by the carboxyl group, the value ought to be comparable with that for acetic acid $1{\cdot}8 \times 10^{-5}$, whereas, on Bjerrum's view, it ought to be comparable with the constant for the equilibrium $\dot{N}H_3.CH_3 \rightleftarrows CH_3.NH_2 + H^{\cdot}$ which is equal to 2×10^{-11}. That the value in the case of glycine is somewhat greater may be attributed to the influence of the $-COO'$ group. Again, if one accepts

[1] *Proc. Roy. Soc.*, 1904, A, **73**, 155; **74**, 271.

[2] See K. Winkelblech, *Z. physikal. Chem.*, 1901, **36**, 546; H. Lundén, *ibid.*, 1906, **54**, 532; J. Walker, *J. Chem. Soc.*, 1903, **83**, 182; J. K. Wood, *ibid.*, 1906, **89**, 1839.

[3] *Z. physikal. Chem.*, 1923, **104**, 152.

Walker's interpretation of K_b, the value, in the case of glycine, namely, $2{\cdot}4 \times 10^{-12}$, should be comparable with the value for methylamine, namely, 5×10^{-4}, whereas, according to Bjerrum's view, it should be comparable with the value for the basic function of the acetate ion $K_b = 5{\cdot}5 \times 10^{-10}$. The smaller value in the case of glycine may reasonably be attributed to the presence of the positively charged $NH_3^{\cdot}$ group. It will be seen that the above comparison favours the views of Bjerrum.

It may be pointed out that if $K_a = K_b$, the activity of hydrogen ion will be equal to the activity of hydroxide ion, and the solution will have a neutral reaction.

Hydrogen Ion Exponent.—In the preceding pages the concentrations of hydrogen ion have been expressed in terms of normality or of gram-equivalents per litre. Following, however, a usage introduced by the Danish biochemist, S. P. L. Sörensen, hydrogen ion concentrations are now very frequently expressed in terms of what is called the *hydrogen ion exponent*, a number obtained by giving a positive value to the negative power of 10 in the expression, 1×10^{-n} normal. This hydrogen ion exponent was originally represented by the symbol $p_{H^{\cdot}}$; but, for typographical reasons, the symbol is most suitably written pH.[1]

This method of expressing the concentration of hydrogen ion in a solution has the advantage that all degrees of acidity or alkalinity, from that of a solution containing 1 gram-equivalent of hydrogen ion per litre to that of a solution containing 1 gram-equivalent of hydroxide ion per litre, can be expressed by a series of positive numbers from 0 to 14 instead of by the more cumbersome expressions of the form 1×10^{-n} normal. Thus the concentration of 1 gram-equivalent of hydrogen ion per litre, which, when expressed in terms of normality, can be written $[H^{\cdot}] = 1 \times 10^{-0}$, can be more simply represented as $p\text{H} = 0$.[2] Similarly, for pure water in which the concentration of hydrogen ion is 1×10^{-7} normal, the pH value is 7, the negative index of 10 being expressed as a positive number. The expression $p\text{H} = 7$, therefore, represents water-neutrality, and all solutions which contain a higher concentration of hydrogen ions than water

[1] The letter "p" is used here because it stands for an exponent or "power" (French, *puissance*; German, *Potenz*).

[2] It should be noted that the symbol $[H^{\cdot}]$ here represents the effective concentration of hydrogen ion, or the activity of hydrogen ion.

(acid solutions) will have pH values *less* than 7. A change of 1 pH unit corresponds to a tenfold change in hydrogen ion concentration.

Similarly, for a solution containing 1 gram-equivalent of hydroxide ion per litre, we have $[OH'] = 1 \times 10^{-0}$ normal. In water or in any aqueous solution, however, the product of concentrations of hydrogen ion and hydroxide ion is constant, and is expressed by the equation $[H^{\cdot}] \times [OH'] = 1 \times 10^{-14}$ at 25°. Consequently, if $[OH'] = 1 \times 10^{-0}$, the concentration of hydrogen ion in the solution of alkali must be $[H^{\cdot}] = \frac{1 \times 10^{-14}}{1 \times 10^{-0}} = 1 \times 10^{-14}$; and the pH of this solution will therefore be 14. The concentration of hydrogen ion in solutions more alkaline than water, and having a hydroxide ion concentration up to 1 gram-equivalent per litre, will therefore be represented by pH values between 7 and 14.

In order to make clear the meaning of the pH value and its relation to the hydrogen ion concentration expressed in terms of normality, a few cases may be considered more fully. In pure water the concentration of hydrogen ion is approximately 0·0000001 gram-equivalents per litre, or 1×10^{-7} normal. Taking the exponent of 10 in this expression as a positive number, we obtain $p\text{H} = 7$. Instead of writing $[H^{\cdot}] = 1 \times 10^{-7}$ (normal being understood), one can also write $\log_{10}[H^{\cdot}] = -7$, or $-\log_{10}[H^{\cdot}] = 7$. We see, therefore, that the pH value is equal to the logarithm of the hydrogen ion concentration with negative sign, or $p\text{H} = \log_{10}\frac{1}{[H^{\cdot}]}$.

In order to convert concentration values into pH values, one proceeds as follows. To find the pH value of a solution in which $[H^{\cdot}] = 2 \times 10^{-6}$ normal: the logarithm of 2 is 0·301 and the logarithm of 2×10^{-6} is therefore

$$\bar{6}\cdot301 = 0\cdot301 - 6 = -5\cdot699.$$

(It is necessary to remember that the decimal part of a logarithm is always positive.) We see, therefore, that

$$\log_{10}(2 \times 10^{-6}) = -5\cdot699 \text{ or } -\log(2 \times 10^{-6}) = 5\cdot699 = p\text{H}.$$

On the other hand, in order to find the concentration in gram-equivalents per litre corresponding to a given pH value, we can proceed as in the following case. The pH value of a solution is 6·495, what is the concentration of hydrogen ion? According to what was said above, $6\cdot495 = -\log[H^{\cdot}]$, and therefore $\log[H^{\cdot}] = -6\cdot495$. Writing this logarithm with a negative characteristic and a positive mantissa (decimal part), one obtains $\log[H^{\cdot}] = -6\cdot495 = \bar{7}\cdot505$. On looking up the tables one finds that the number corresponding to the logarithm 0·505 is 3·20, so that the number corresponding to the logarithm $\bar{7}\cdot505$ is $3\cdot20 \times 10^{-7}$. The hydrogen ion concentration is therefore $3\cdot20 \times 10^{-7}$ normal.

In working with *p*H values it is important to bear in mind that high *p*H values correspond to low hydrogen ion concentrations.

For convenience of reference, a list of *p*H and the corresponding hydrogen ion concentrations value is given in the following table :—

HYDROGEN ION CONCENTRATIONS AND *p*H VALUES

*p*H (n = a Whole Number).	Gram-equivalents per Litre	*p*H (n = a Whole Number).	Gram-equivalents per Litre.
$n{\cdot}00$	$1{\cdot}00 \times 10^{-n}$	$n{\cdot}50$	$3{\cdot}16 \times 10^{-(n+1)}$
$n{\cdot}05$	$8{\cdot}91 \times 10^{-(n+1)}$	$n{\cdot}55$	$2{\cdot}82$,,
$n{\cdot}10$	$7{\cdot}94$,,	$n{\cdot}60$	$2{\cdot}51$,,
$n{\cdot}15$	$7{\cdot}08$,,	$n{\cdot}65$	$2{\cdot}24$,,
$n{\cdot}20$	$6{\cdot}31$,,	$n{\cdot}70$	$2{\cdot}00$,,
$n{\cdot}25$	$5{\cdot}63$,,	$n{\cdot}75$	$1{\cdot}78$,,
$n{\cdot}30$	$5{\cdot}02$,,	$n{\cdot}80$	$1{\cdot}59$,,
$n{\cdot}35$	$4{\cdot}47$,,	$n{\cdot}85$	$1{\cdot}41$,,
$n{\cdot}40$	$3{\cdot}98$,,	$n{\cdot}90$	$1{\cdot}26$,,
$n{\cdot}45$	$3{\cdot}55$	$n{\cdot}95$	$1{\cdot}12$,,

Titration of Acid by Alkali. Change of *p*H during Neutralisation.—By means of electrometric measurements (Chap. XV.) it is an easy matter to follow the change in hydrogen ion concentration during the neutralisation of an acid by an alkali. The results which are obtained are instructive.

When a weak acid, such as acetic acid, is neutralised with a strong alkali (NaOH), hydrogen ions combine with hydroxide ions to form water, and a salt of the acid is formed. As neutralisation proceeds, therefore, one obtains a series of solutions containing diminishing amounts of the weak acid and increasing amounts of the salt of the acid. It has, however, been learned that for mixtures of a weak acid and of a salt of the acid, the hydrogen ion concentration is given, approximately, by the expression $[H^{\cdot}] = K \cdot \frac{[\text{acid}]}{[\text{salt}]}$, where K is the affinity constant of the acid.

This may be written $\frac{1}{[H^{\cdot}]} = \frac{[\text{salt}]}{K \cdot [\text{acid}]}$, and if one takes the logarithms of both sides, one obtains $\log\frac{1}{[H^{\cdot}]} = \log\frac{1}{K} + \log\frac{[\text{salt}]}{[\text{acid}]}$.

Or, $p\mathrm{H} = \log \frac{1}{K} + \log . \frac{[\text{salt}]}{[\text{acid}]}$. This expression, therefore, will give the variation of the pH value of the solution during neutralisation, and it shows that when the acid is half neutralised, *i.e.*, when [salt] = [acid], $p\mathrm{H} = \log \frac{1}{K}$. Conversely, if one determines, electrometrically, the variation of pH with neutralisation, and if one plots the value of pH against the volume of standard alkali added, one can read off from the curve the value of pH corresponding to half neutralisation, and calculate therefrom the value of K, the affinity constant of the acid. The neutralisation curve of acetic acid is shown in Fig. 90. Since the affinity constant of acetic acid is 0·000018 or $1{\cdot}8 \times 10^{-5}$, the pH value of the solution at half neutralisation is 4·74.

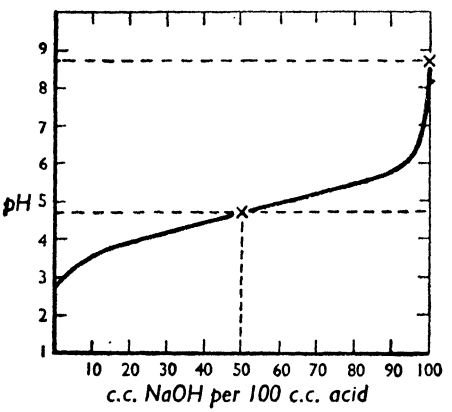


FIG. 90.

Since sodium acetate undergoes hydrolysis, the pH value of the solution of the salt will not be 7, the value for water neutrality, but will be greater. Experiment shows it to be 8·87 in 0·1 normal solution at the ordinary temperature.

The affinity constant of a weak acid can also be calculated, more accurately, by making use of the relation: $K = [\mathrm{H}^{\cdot}] \times [\text{salt}]/[\text{acid}]$. After each addition of alkali to the acid, the concentration of hydrogen ion is determined electrometrically. Since the concentration of salt in the solution will be proportional to the volume, x, of alkali added, and the concentration of acid to the quantity $(x_e - x)$, where x_e is the volume of alkali required for complete neutralisation, it follows that $K = [\mathrm{H}^{\cdot}] \times x/(x_e - x)$. A series of K-values is thus obtained, and the mean taken.

In the case of a polybasic acid, such as phosphoric acid, the neutralisation curve (Fig. 91) will consist of a series of sections corresponding to the different stages of dissociation.

Points K_1 and K_2 are the pH values (2·03 and 7·1) corresponding to the dissociation constants of the reactions, $H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4'$ and $H_2PO_4' \rightleftharpoons H^{\cdot} + HPO_4''$ respectively.

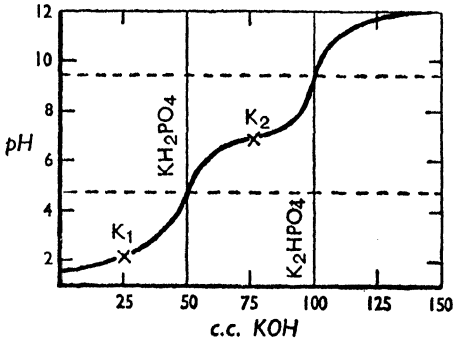


FIG. 91

The third dissociation constant lies at $p\mathrm{H} = 12{\cdot}4$. It is clear that a solution of K_3PO_4 will have a strongly alkaline reaction ($p\mathrm{H} = 13{\cdot}6$).

Hydrogen Ion Concentrations and Indicators.—The electrometric method of determining the concentration of hydrogen ion in solution is fundamentally the most important, because it is by this method that the results obtained by other methods are ultimately controlled. A simpler method, however, has been worked out whereby, with the help of various *indicators*, the actual concentration (activity) of hydrogen ion in a solution can be quickly and easily ascertained.[1]

An indicator may be defined as a weak acid (or weak alkali) of which the anion (or cation) has a different colour from the un-ionised molecule.[2] Thus, phenolphthalein, a weak acid (or, it may be, a *pseudo-acid*), is colourless in the un-ionised state (in acid solution) but red in the ionised state

[1] Measurements of e.m.f. give effective concentrations or activities, and indicators which are standardised by means of e.m.f. measurements also indicate activities.

[2] It may be that this definition is not strictly accurate, and that the un-ionised acid (or alkali) may undergo a tautomeric change, so that in an acid (or alkaline) solution, in which the ionisation of the indicator is entirely repressed, one obtains the colour, not of the un-ionised acid, but of a tautomeric form. Such a change, however, will not involve any essential alteration in the discussion given here; the only point to be remarked being that what is called here the dissociation constant of the indicator involves not merely the equilibrium between the un-ionised acid and its ions, but also the equilibrium between the un-ionised acid and its tautomeric form. It may therefore be called its apparent dissociation constant.

(in alkaline solution). Similarly, *p*-nitrophenol is colourless in acid solution but yellow in alkaline. In some other cases, however, the indicator is coloured both in the un-ionised and in the ionised state, so that passage from the acid to the alkaline state is accompanied by a change of colour. Thus, methyl orange is red in acid solution (un-ionised form) but yellow in alkaline solution (colour of anion).

Dissociation Curve.—The behaviour and application of indicators will be most easily understood if one plots the dissociation curve of the indicator, regarded as a weak acid; that is, if one plots the hydrogen ion concentration (or, preferably, the *p*H value) against the degree of ionisation of the indicator acid. The dissociation curve of *p*-nitrophenol is shown in Fig. 92. This curve has been calculated by means of the equation (p. 351),

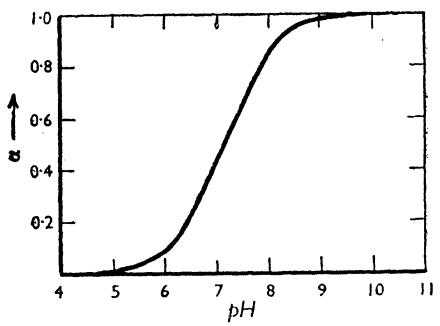


FIG. 92.

$$p\mathrm{H} = \log \frac{1}{[\mathrm{H}^{\cdot}]} = \log \frac{1}{K} + \log \frac{\alpha}{1-\alpha},$$

where K is the dissociation constant of the indicator acid. For *p*-nitrophenol $K = 6{\cdot}5 \times 10^{-8}$, and $\log 1/K = 7{\cdot}19$.

It is clear from this equation that the dissociation curves must all have the same form but occupy different positions on the *p*H axis, according to the value of K, the dissociation constant of the indicator acid. Moreover, it will be seen from the equation given above that when $\alpha = 0{\cdot}5$,

$$\log_{10} \frac{1}{[\mathrm{H}^{\cdot}]} = p\mathrm{H} = \log_{10} \frac{1}{K}.$$

In other words, half the indicator is ionised when the hydrogen ion concentration of the solution is equal to the dissociation constant of the indicator.

When one considers the curve (Fig. 92) for *p*-nitrophenol, which has a K value $= 6{\cdot}5 \times 10^{-8}$ (or $\log 1/K = 7{\cdot}19$) and which is colourless in presence of excess of acid but yellow in presence

of excess of alkali, it is seen that so long as [H·] is greater than about 1×10^{-5} (pH = 5), the indicator will be practically completely un-ionised and therefore colourless. If, however, one reduces the concentration of hydrogen ion, the indicator will undergo ionisation to some extent and the colour of the ionised indicator will begin to make its appearance. If it be assumed that the depth of colour, as compared with the completely ionised indicator, is proportional to the degree of ionisation α, then the dissociation curve of the indicator may be regarded as giving a relationship between [H·] and the depth of colour of the solution as compared with an acid or alkaline solution containing the same concentration of indicator. In the case of two-colour indicators, variation of [H·] will lead to a variation in shade, intermediate between the colours of the un-ionised and the ionised indicator.

From what has just been said and from a consideration of Fig. 92, it will be clear that the application of indicators to the determination of the concentration of hydrogen ion depends on the fact that the different indicator acids (or alkalis) are of different strengths, or have different dissociation constants, and, consequently, exhibit the characteristic colours of the un-ionised and of the ionised indicator at different concentrations of hydrogen ion. By the addition of an indicator to a solution, therefore, it is possible to tell whether the hydrogen ion concentration is greater or less than a certain value. Thus, if no colour is shown when p-nitrophenol is added to an aqueous solution, one can say that the pH value of the solution is equal to or is less than, say, 5·5 ([H·] equal to or greater than $3{\cdot}16 \times 10^{-6}$ gram-equivalent per litre). On the other hand, if a yellow colour is obtained equal in depth to that given when the same amount of p-nitrophenol is added to a strongly alkaline solution, one can say that the pH value of the solution is equal to or greater than, say, 7 ([H·] equal to or less than 1×10^{-7} gram-equivalents per litre).[1]

In order to be able to determine the hydrogen ion concentration of a solution by means of indicators, it is necessary to have a series of indicators the K values of which are distributed over the whole range of pH values to

[1] Owing to the eye being unable to detect the complete range of colour changes, it is found that the useful range of colour change of an indicator may be taken, roughly, as lying between the pH values at which the indicator is ionised to the extent of 5 per cent. and 60 per cent.

Indicator.	Concentration of Hydrogen Ions (Gram-equivalents per Litre).													Concentration of Indicator Solution (per Cent.).	Drops of Indicator to 10 c.c. of Test Liquid.
	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}		
Crystal violet .	Green	Green-blue	Blue	Violet										0·05	3-8
Tropæolin OO .		Red	Flesh	Yellow										0·01	3-5
Benzyl anilino-azo-benzene . .			Red	Orange										0·02 (in 50% alcohol)	5-10
Methyl orange .			Red	Orange-red	Orange	Yellow								0·01	3-5
Methyl red . .				Violet-red	Red	Orange	Yellow							0·02 (in 60% alcohol)	4
Para-nitrophenol .						None	Greenish	Yellow						0·04 (in 6% alcohol)	3-20
Rosolic acid . .							Yellow	Pink	Red					0·05 (in 50% alcohol)	3-5
Orange I. (α-naphthol orange)								Yellow	Orange-red	Red				0·01	4-10
Phenolphthalein .									None	Pink	Red			0·05 (in 50% alcohol)	3-20
Thymolphthalein .											None	Blue		0·04 (in 50% alcohol)	3-20
Tropæolin O (Resorcinol yellow)												Green-yellow	Orange	0·01	5·10
B.D.H. Universal .				Pale red	Red	Orange-red	Orange	Greenish yellow	Green	Greenish blue	Violet	Reddish violet			3

be investigated, and which give definite colour changes for particular concentrations of hydrogen ion.

A mixture of indicators may also be used, and, from the colour produced when such a mixed indicator is added to a solution, information is obtained regarding the approximate concentration of hydrogen ion in the solution.

The chart on page 358 gives for a series of indicators the colours which they show when added to solutions of different hydrogen ion concentration. The thick lines indicate the concentrations at which the colour change is sharpest.[1]

By means of electrometric measurements (Chap. XV.) it is an easy matter to determine the concentration of hydrogen ion at which the different indicators show their colour change and so obtain a knowledge of the range of *p*H values, or the *p*H zone, for which the indicators are suitable. In the table on p. 360 is given the useful range of *p*H values of a number of the more important indicators.

Indicators in Acid-alkali Titrations.—In carrying out an acid-alkali titration the aim is to ascertain, with the help of an indicator, the point of acid-alkali equivalence, a point which will not necessarily coincide with that of water-neutrality (*p*H = 7).

If one plots the *p*H value against percentage neutralisation, in the case of different acids and alkalis, one obtains a series of curves such are as shown in Figs. 93-96. In Fig. 93 is shown a typical curve for the neutralisation of a strong acid by a strong alkali (N/10 HCl and N/10 NaOH). This curve shows that in the neighbourhood of the equivalence point small departures from equivalence are accompanied by large variations in the *p*H value. The curve shows a nearly perpendicular portion. It follows, therefore, that the equivalence end-point can be determined with sharpness. This also is the case when one is titrating a weak acid (acetic acid) with a strong alkali (NaOH), or a strong acid (HCl) with a weak alkali (NH_4OH), as indicated by the curves in Figs. 94 and 95. When, however, one titrates a weak acid with a weak alkali (acetic acid with ammonium hydroxide) no sharp end-point will be obtained, owing to hydrolysis. The curve, in this case (Fig. 96), does not show at any point a very great variation of *p*H with variation in the amount of acid or of alkali. A weak acid, therefore, cannot be satisfactorily titrated with a weak alkali.

[1] See also A. D. Mitchell, *New Indicators and other Reagents employed in Volumetric Analysis* (Inst. of Chemistry).

Indicator.	Colour.		*p*H Range.
	Acid.	Alkali.	
Crystal violet	Green	Violet	0·0 to 2·0
Thymol blue	Red	Yellow	1·2 „ 2·8
Tropæolin 00	Red	Yellow	1·3 „ 3·2
Bromphenol blue	Yellow	Blue	3·0 „ 4·6
Methyl orange	Red	Yellow	3·1 „ 4·4
Methyl red	Red	Yellow	4·2 „ 6·3
p-Nitrophenol	Colourless	Yellow	5·0 „ 7·0
Litmus	Red	Blue	5·0 „ 7·0
Bromcresol purple	Yellow	Purple	5·2 „ 6·8
Bromthymol blue	Yellow	Blue	6·0 „ 7·6
Neutral red	Red	Orange	6·8 „ 8·0
Rosolic acid	Yellow	Red	6·9 „ 8·0
Cresol red	Yellow	Red	7·2 „ 8·8
α-Naphtholphthalein	Red	Blue	7·3 „ 8·7
Thymol blue	Yellow	Blue	8·0 „ 9·6
Phenolphthalein	Colourless	Red	8·3 „ 10·5
Thymolphthalein	Colourless	Blue	9·3 „ 10·5
Tropæolin 0	Yellow	Orange	11·0 „ 13·0

An examination of Figs. 93, 94, and 95 will show that, even when a sharp end-point can be obtained, the equivalence point can be sharply determined only if a suitable indicator

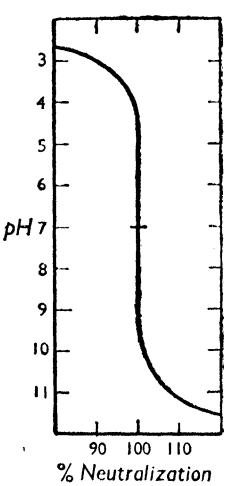


FIG. 93.

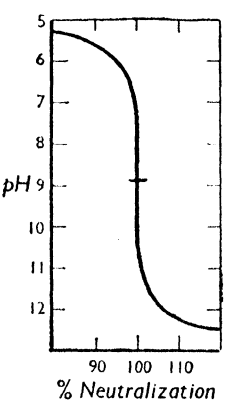


FIG. 94.

is employed. When a strong acid is titrated with a strong alkali, the almost perpendicular portion of the curve (Fig. 93) extends from about $p\mathrm{H} = 4$ to $p\mathrm{H} = 10$, and the equivalence

point corresponds to pH = 7. Any indicator, therefore, the pH range of which lies between 4 and 10, may be satisfactorily employed, *e.g.*, methyl orange, methyl red, litmus or phenolphthalein. When, however, a weak acid (acetic acid) is titrated with a strong alkali (Fig. 94) an indicator must be used which has a pH range lying between, say, 7 and 11, *e.g.*, rosolic acid, cresol red or phenolphthalein. If methyl orange or methyl red or litmus were used, an end-point would be indicated when the solution was still distinctly acid. In the case of acetic acid and sodium hydroxide (N/10), the equivalence point corresponds to pH = 8·87. In the titration of a strong acid with a weak alkali (ammonium

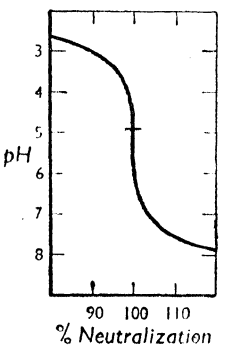


FIG. 95.

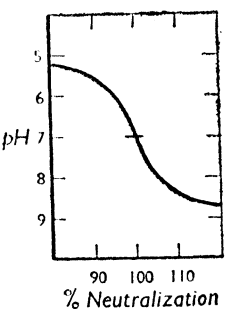


FIG. 96.

hydroxide), on the other hand, the steep portion of the neutralisation curve (Fig. 95) lies between about pH = 3·5 and pH = 6·5. In this case, therefore, one must use as indicator methyl orange or, better, methyl red. With hydrochloric acid and ammonium hydroxide (N/10) the equivalence point corresponds to pH = 5·13.

From what has been said above regarding indicators, the fact that in the titration of polybasic acids, *e.g.*, phosphoric acid, with alkali, different end-points are obtained according to the indicator employed will be readily understood. When phosphoric acid is titrated with sodium hydroxide in presence of methyl orange the colour change takes place when one equivalent of alkali has been added, *i.e.*, when there has been formed in the solution the salt NaH_2PO_4. At this point the pH value of the solution is 4·4 (*cf.* Fig. 91), and methyl orange, therefore, undergoes change in colour from

red to orange or yellow. If, however, the titration is carried out with phenolphthalein as indicator, the end-point is not reached, *i.e.*, the indicator does not change colour until two equivalents of alkali have been added, and the salt Na_2HPO_4 has been formed. The *p*H of the solution at this point is 9·28 and the phenolphthalein, therefore, shows a pink colour.

Buffer Solutions.—In order that the indicator method may be successfully applied to the determination of hydrogen ion concentrations, it is necessary to have at one's command standard solutions, the *p*H value of which is definitely known and which are readily reproducible. For this purpose so-called " buffer " solutions or regulators are employed, *i.e.*, solutions the *p*H value of which undergoes relatively very little change on addition of acid or alkali.

We have already seen that when one adds sodium acetate to acetic acid the ionisation of the latter, and consequently the $[H^{\cdot}]$, is reduced. If to such a mixture a small quantity of hydrochloric acid is added, there will be no equivalent increase of $[H^{\cdot}]$ in the solution, because the added hydrogen ion will, for the most part, combine with the acetate ion present to form acetic acid, which will be practically unionised. The increase of hydrogen ion concentration, therefore, will be comparatively slight. Similarly, if sodium hydroxide is added to the solution, combination with the reserve of acetic acid takes place and, again, the hydrogen ion concentration remains practically unchanged. A mixed solution of acetic acid and sodium acetate, therefore, acts as a " buffer " (A. Fernbach and L. Hubert) against change of hydrogen ion concentration.

Buffer or regulator solutions, therefore, are such as contain only a small actual concentration of hydrogen ion (or hydroxide ion) but a large reserve of potential ions (*e.g.*, acetate ion and hydrogen ion). They possess what is called a " reserve acidity " and " reserve alkalinity." When, therefore, acid or alkali is added, combination with the potential ions takes place, and the concentration of hydrogen ion in the solution undergoes comparatively little change. These buffer mixtures, therefore, are of much value for the purpose of preparing standard solutions of definite hydrogen ion concentration which are insensitive to additions of small quantities of acid and alkali. By varying the proportions of the constituents, also, solutions of different hydrogen ion

concentration can easily be prepared. The exact concentration of hydrogen ion is determined electrometrically. A number of such buffer solutions have been suggested and used,[1] of which the following solutions are examples :—

Acetic Acid and Sodium Acetate.			Primary Potassium and Secondary Sodium Phosphate.		
*p*H.	Acetic Acid (Gram-molecule per Litre).	Sodium Acetate (Gram-molecule per Litre).	*p*H.	$\frac{M}{15}$. KH_2PO_4.	$\frac{M}{15}$.Na_2HPO_4.
3·6	0·185	0·015	5·288	9·75 ml.	0·25 ml.
4·0	0·164	0·036	5·906	9·0 „	1·0 „
4·4	0·126	0·074	6·468	7·0 „	3·0 „
4·8	0·080	0·020	6·813	5·0 „	5·0 „
5·2	0·042	0·158	7·168	3·0 „	7·0 „
5·6	0·019	0·181	7·731	1·0 „	9·0 „

It has already been pointed out that the variation of *p*H during the neutralisation of a weak acid by a strong alkali is given by the expression $pH = \log\frac{1}{K} + \log \cdot \frac{[salt]}{[acid]}$, and the graphic representation of this change is shown in Fig. 90 (p. 354). From this figure it is seen that although the *p*H value changes rapidly at the beginning of the neutralisation and also at the end, the change in *p*H for a given small addition of alkali is comparatively slight in solutions in which the acid has been neutralised to an extent of 20-80 per cent. Throughout this range the slope of the neutralisation curve is comparatively small. The change of *p*H is least, or the buffering action is a maximum, when the acid has been half neutralised or when [salt]=[acid].

The effect of adding acid to a simple buffer solution, consisting of a weak acid and its salt, can be readily calculated in an approximate manner. In the case of a solution which is 0·1N with respect to acetic acid and to sodium acetate, we have

$$pH = \log \cdot \frac{1}{0{\cdot}000018} + \log \frac{0{\cdot}1}{0{\cdot}1} = 4{\cdot}74.$$

If to this mixture hydrochloric acid is added in such amount that, if added to water, it would yield a 0·01N solution (*p*H=2, if the acid is regarded as completely ionised), hydrogen ions will combine with acetate ions to form acetic acid (un-ionised). The concentration of acetate ions (salt) will therefore be reduced from 0·1N to 0·09N, and the acid concentration will be increased from 0·1N to 0·11N, and the *p*H of the solution will be given by the expression

$$pH = \log\frac{1}{0{\cdot}000018} + \log\frac{0{\cdot}09}{0{\cdot}11} = 4{\cdot}74 - 0{\cdot}087 = 4{\cdot}653.$$

The change in *p*H is therefore comparatively slight.

In the case of mixtures of primary and secondary sodium or potassium phosphate, it has to be borne in mind that the ion H_2PO_4' acts as an acid and undergoes ionisation into $H^+ + HPO_4''$. A solution, therefore, in which NaH_2PO_4 and Na_2HPO_4 are present in equal concentration, corresponds to a solution in

[1] See W. M. Clark, *The Determination of Hydrogen Ions*; H. T. S. Britton, *Hydrogen Ions*; Kolthoff and N. H. Furman, *Indicators*.

which the acid H_2PO_4' is half neutralised. Since the affinity constant of the acid H_2PO_4' is $1{\cdot}4 \times 10^{-7}$, the *p*H of the solution containing equivalent amounts of primary and secondary phosphate will be

$$p\text{H} = \log \frac{1}{1{\cdot}4 \times 10^{-7}} = 6{\cdot}9.$$

By selecting acids of different strengths, buffer solutions can be prepared covering different ranges of *p*H values.

The effect of such solutions in regulating the hydrogen ion concentration of a solution is clearly shown by the following experiment. A mixture of acetic acid and sodium acetate is made up, as given in the table (p. 363), so as to have $p\text{H} = 3{\cdot}6$. To 10 ml. of this solution, contained in a test-tube, add 1 – 2 drops of methyl orange indicator. To 10 ml. of a 1 per cent. solution of sodium chloride contained in a similar test-tube, add the same volume of methyl orange solution as before, and drop in 0·01N-HCl until the colour shade is the same as in the former case. Both solutions will then have the same *p*H value. To each solution add 0·5 ml. of a 1 per cent. solution of gelatin, a substance which has the property of combining with acid. In the case of the buffered solution no change in colour is observed, but in the case of the unbuffered solution of hydrochloric acid the hydrogen ion concentration is reduced and the colour of the indicator changes to yellow.

CHAPTER XV

CHEMICAL ENERGY AND ELECTRICAL ENERGY. ELECTROMOTIVE FORCE

IT is to Alessandro Volta (1745-1827), Professor of Natural Philosophy in the University of Pavia, that science owes the construction of the first *voltaic cell*, an apparatus by means of which a continuous current of electricity can be obtained through the transformation of chemical energy into electrical energy. In considering the electrical energy supplied by such a cell, one has to bear in mind that electrical energy, like other forms of energy, is a product of two factors—the *intensity factor*, represented by the fall of potential or electromotive force (e.m.f.), and the *capacity factor*, represented by the quantity of electricity. If the fall of potential, or e.m.f., is expressed in *volts* and the quantity of electricity in *coulombs* the energy will be expressed in volt-coulombs. One has, then, the relations

1 volt-coulomb = 1 joule = 1×10^7 ergs = 0·2390 cal.
1 cal. = 4·185 volt-coulombs. $R = 8{\cdot}315$ volt-coulombs.

Electrical Energy and Chemical Energy.—It might, perhaps, be thought that the electrical energy given out by a voltaic cell could be put equal to the chemical energy of the reaction taking place in the cell as measured by the heat of reaction ; and this view was first suggested by William Thomson (Lord Kelvin) in 1851 and by Hermann von Helmholtz. Although approximately true in some cases the Thomson-Helmholtz rule has no general validity.

In the case of a Daniell cell, for example, in which zinc dips in a solution of 1 gram-molecule of zinc sulphate in 100 gram-molecules of water, and copper in a solution of 1 gram-molecule of copper sulphate in 100 gram-molecules of water, the e.m.f. is found to be 1·096 volt at 0°. Since zinc ion is bivalent, the amount of electricity associated with the passage of 1 gram-atom of zinc into the ionic state will be $2 \times 96{,}500$ coulombs, and the electrical energy will therefore be $1{\cdot}096 \times 2 \times 96{,}500 = 211{,}600$ joules. The heat of the reaction,

$$Zn + CuSO_4, 100H_2O = Cu + ZnSO_4, 100H_2O,$$

is found to be 209,910 joules. The electrical energy, therefore, is approximately equal to the heat of reaction.

In the case, however, of the Clark cell,

$$Zn \mid \begin{matrix}\text{saturated solution} \\ \text{of } ZnSO_4,\ 7H_2O\end{matrix} \vdots \text{paste of } Hg_2SO_4 \mid Hg$$

the reaction which takes place when the cell is giving out electrical energy is $Zn + Hg_2SO_4 = ZnSO_4 + 2Hg$; and the heat of this reaction is 338,320 joules. Since the e.m.f. of the cell is 1·434 volt at 15°, the electrical energy, per gram-atom of zinc, will be $1{\cdot}434 \times 2 \times 96{,}500 = 276{,}700$ joules. The electrical energy obtained, therefore, is only 82 per cent. of the heat of reaction.

Again, In the case of the cell,[1]

$$Hg \mid \begin{matrix}0{\cdot}01\text{N-KCl} \\ \text{saturated with } Hg_2Cl_2\end{matrix} \parallel \text{N-}KNO_3 \parallel \begin{matrix}0{\cdot}01\text{N-KOH} \\ \text{saturated with } Hg_2O\end{matrix} \mid Hg$$

in which the reaction $Hg_2Cl_2 + 2KOH = 2KCl + Hg_2O + H_2O$ takes place, the e.m.f., at 18·5°, is 0·1636 volt (S. Bugarsky, 1897). The electrical energy, therefore, per gram-molecule of mercurous oxide formed, will be

$$0{\cdot}1636 \times 2 \times 96{,}500\,j., \text{ or } 0{\cdot}1636 \times 2 \times 23{,}070 = 7545 \text{ cal.}^2$$

The heat of reaction, however, is −3280 cal. Although the heat of reaction is negative, a positive amount of electrical energy is obtained, or, an endothermic reaction which takes place spontaneously can do a certain amount of external work.

The above examples show that the electrical energy given out by a voltaic cell cannot be put equal to the chemical energy as measured by the heat of reaction. *The electrical energy given out by a cell is a measure of the change not of the total energy but of the free energy.*

Reversible and Irreversible Cells.—Before one can find the relation between the electrical energy of a cell and the heat of reaction, it is necessary to distinguish between reversible and irreversible cells. When the Daniell cell gives out electrical energy, zinc passes into solution as zinc ion and copper ion is discharged and deposited as metallic copper on the copper electrode. If the same amount of electricity as was taken from the cell be now sent through the cell in a direction opposite to that of the current given by the cell, copper will pass into solution as copper ion, and zinc ion will be discharged and deposited as metallic zinc on the zinc electrode; and the amounts of copper dissolved and of zinc deposited will be exactly equal to the amount of copper which had been previously deposited and of zinc which had

[1] The double vertical lines ‖ indicate the elimination of the liquid junction potential.

[2] F has the value of 23,070 cal. per volt.

passed into solution. The cell, therefore, will be in exactly the same state as it was initially. The Daniell cell is completely reversible.

When, however, the cell, Zn | H_2SO_4, aq. | Cu, is giving out electrical energy, zinc passes into solution and hydrogen is evolved at the copper electrode. If a current be now sent through the cell in the opposite direction, copper will pass into solution, and hydrogen will be liberated at the zinc electrode. This cell, therefore, is irreversible and cannot be brought back to its initial state by passing an electric current through the cell.

To obtain a definite relation between electrical energy and chemical energy, one must use a reversible cell. When a reversible cell is allowed to work reversibly by giving out only a very small current, and so being at each moment in a state of equilibrium, the work done by such a cell will be the maximum work which the cell can produce. This maximum work, per gram ion, will be represented by $E.zF$, where E is the e.m.f. of the cell, z is the valency of the ion transported, and F is 1 faraday or 96,500 coulombs.

The Gibbs-Helmholtz Equation.—The relation between chemical energy and electrical energy was deduced by Willard Gibbs (1878) and by von Helmholtz (1882). It has already been shown (p. 301) that the increment of free energy, ΔG, of a reversible reaction is given by the expression

$$\Delta G - \Delta H = T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p$$

Since, in the case of a reversible voltaic cell, $\Delta G = -E.zF$, or, since the diminution of free energy, $-\Delta G$, is equal to the electrical energy, $E.zF$, one obtains the relations

$$-E.zF - \Delta H = -zFT\frac{dE}{dT}$$

and

$$-\Delta H = zF\left(E - T\frac{dE}{dT}\right)$$

where dE/dT is the temperature coefficient of electromotive force. From this expression it is clear that the electrical energy will be equal to the chemical energy only when the latent heat $T\frac{dE}{dT}$ is zero ; that is, when $dE/dT = 0$.

The following examples may be quoted in confirmation of the above equation [1]:—

(1) Cell: Zn | Saturated solution of $ZnSO_4$, $7H_2O$ || Saturated solution of $CuSO_4$, $5H_2O$ | Cu.

Reaction $Zn + CuSO_4 = Cu + ZnSO_4$.

$E_{15°} = 1{\cdot}0934$; $dE/dT = -0{\cdot}000429$; $-\Delta H_{calc.} = 56{,}089$ cal.; $-\Delta H_{obs.} = 55{,}189$ cal.

(2) Cell: Cd | Saturated solution of $CdCl_2$, $2{\cdot}5H_2O$ || AgCl | Ag.

Reaction $Cd + 2AgCl + 2{\cdot}5H_2O = CdCl_2,\ 2{\cdot}5H_2O + 2Ag$.

$E_{25°} = 0{\cdot}67531$; $dE/dT = -0{\cdot}00065$; $-\Delta H_{calc.} = 40{,}030$ cal.; $-\Delta H_{obs.} = 39{,}530$ cal.

(3) Cell: Hg | 0·01N-KCl saturated with Hg_2Cl_2 || N-KNO_3 || 0·01N-KOH saturated with Hg_2O | Hg.

Reaction $Hg_2Cl_2 + 2KOH = 2KCl + Hg_2O + H_2O$.

$E_{25°} = 0{\cdot}1636$; $dE/dT = +0{\cdot}000837$; $-\Delta H_{calc.} = -3709$ cal.; $-\Delta H_{obs.} = -3280$ cal.

If, therefore, a reaction is allowed to take place in a voltaic cell so that chemical energy is transformed into electrical energy, *the heat of the reaction can be calculated from determinations of the e.m.f. of the cell and of the temperature coefficient of the electromotive force.* It may, however, be pointed out that in order to obtain approximately correct values of the heat of reaction, the temperature coefficient of e.m.f. must be determined with a high degree of accuracy.

It should be noted that in determining the e.m.f. of the cell, liquid junction potentials must be eliminated.

When the change of e.m.f. with temperature is expressed in the form

$$E_t = E_{25}[1 + \alpha(t - 25)],$$

the diminution of free energy and heat of reaction can be calculated by means of the expressions [2]

$$(-\Delta G)_T = (-\Delta G)_{298}[1 + \alpha(T - 298)] \quad \text{and} \quad (-\Delta H)_{298} = (-\Delta G)_{298}(1 - 298\alpha).$$

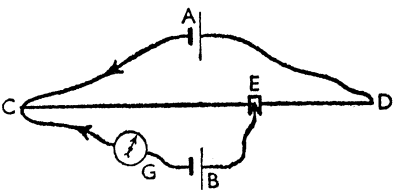
Measurement of Electromotive Force.—The method usually employed for the measurement of the e.m.f. of a cell is that known as the Poggendorff compensation method, an outline only of which can be given here.

If a source of electricity A (Fig. 97), of constant e.m.f., is connected with the two ends of a wire CD, of uniform resistance, the fall of potential along the wire will be uniform. The difference of potential between C and any point E

[1] S. Bugarsky, *Z. anorgan. Chem.*, 1897, **14**, 145; A. Klein, *Z. physikal. Chem.*, 1901, **36**, 361; E. Cohen, F. D. Chattaway, and W. Tombrock, *ibid.*, 1907, **60**, 706; H. S. Taylor and G. St J. Perrott, *J. Amer. Chem. Soc.*, 1921, **43**, 486.

[2] See J. H. Ellis, *J. Amer. Chem. Soc.*, 1916, **38**, 737.

of the wire will be proportional to the distance CE, and will be equal to the fraction CE/CD of the total fall of potential along the wire. If another cell B, the e.m.f. of which is less than that of A, is inserted along with a suitable indicating instrument, such as an electrometer or galvanometer, in a side circuit, CGBE, so that it is opposed to A, and if the sliding contact E is moved along the wire until no current passes through the instrument G, then the e.m.f. of B is equal to that of A multiplied by CE/CD.



7FIG. 9.

If the e.m.f. of the cell A, the working cell, were quite constant and sufficiently accurately known, the measurement of an unknown e.m.f. could be made in the manner described. As a rule, however, neither of the above conditions is fulfilled. It is therefore necessary to have a standard cell, the e.m.f. of which is accurately known. The point of balance E on the bridge wire is then determined when the standard cell occupies the place of B; and then the point E′ (say) when the cell of unknown e.m.f. is in place of B. The unknown e.m.f. is then obtained from the relation

$$\frac{CE}{CE'} = \frac{\text{e.m.f. of standard cell}}{\text{unknown e.m.f.}}.$$

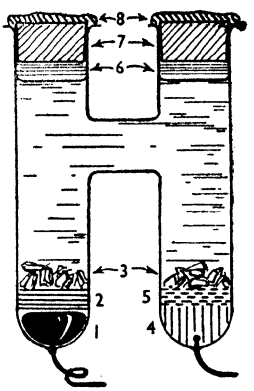


FIG. 98.

1. Mercury.
2. Paste of cadmium sulphate and mercurous sulphate.
3. Saturated solution and large crystals of cadmium sulphate.
4. Cadmium amalgam.
5. Small crystals of cadmium sulphate.
6. Paraffin.
7. Cork.
8. Sealing-wax.

The experimental arrangement just described has been called the *Latimer-Clark potentiometer*.[1] As working cell, one generally employs a lead accumulator, and as standard, the cadmium standard cell, the construction of which is shown in Fig. 98. The cadmium amalgam contains 12·5 per cent. of cadmium, and the electrolyte is a saturated solution of hydrated cadmium sulphate ($CdSO_4,\frac{8}{3}H_2O$). The e.m.f. of this cell is 1·0185 volt at 15° and 1·0181 volt at 25°. Mercury forms the positive, the amalgam the negative pole.

Seat of Electromotive Force of a Cell.—If the poles of a voltaic cell represented by the scheme

Metal I.	Solution containing ions of metal I.	Solution containing ions of metal II.	Metal II.

[1] For other methods of measurement see Findlay, *Practical Physical Chemistry* (Longmans).

are connected by a resistance wire, sudden differences of potential are possible (1) at the junction of the wire with the poles ; (2) at the junction between metal I. and the solution ; (3) at the junction between metal II. and the solution ; (4) at the junction between the two solutions. Under ordinary conditions, when the temperature is constant, the potential differences under (1) vanish. Not so, however, the potential difference which arises at the junction between the two solutions and which is known as the *liquid junction potential* or *diffusion potential.* Although this potential, which is due to differences in the rate of diffusion of the cations and anions, can in some cases be calculated from the mobilities of the ions (p. 242), it is better, where possible, to reduce the liquid junction potential to a negligible value. Two chief ways of doing this are, first, to have present in the two solutions a relatively large (and equal) concentration of an indifferent electrolyte (*e.g.*, potassium nitrate) ; and second, to insert between the two solutions a " salt bridge " consisting of a saturated solution of potassium chloride or of ammonium or potassium nitrate. When this is done, practically the only differences of potential which occur are those at the junctions of the metals with the solutions, and the e.m.f. of the cell will then depend only on these.

Electrode Potentials.—When zinc is placed in contact with a solution of zinc sulphate the metal becomes negatively charged relatively to the solution. To account for this, Nernst (1888) introduced the idea of *electrolytic solution pressure.* Just as a liquid passes into vapour until the pressure of the vapour formed has a definite value, so zinc when placed in a solution of one of its salts will pass into solution as zinc ions. The zinc will therefore become negatively charged relatively to the solution. Owing to the large charge which they carry, the ions do not move away from the metal but are held by electrostatic attraction and form an " electrical double layer " ; and equilibrium will be attained when only a very minute, unweighable amount of zinc has passed into the ionic state. The tendency of the metal to form ions will be balanced by the tendency of the ions to give up their charge, and this will be all the greater the greater the concentration of the ions. The " electrode potential " or the potential difference established between a metal and a solution, therefore, will depend on the

concentration of the ions of the metal in the solution. In the case of zinc the electrolytic solution pressure is so great that the metal forms ions in all solutions of its salts, and therefore always becomes negatively charged relatively to the solution. The metal copper, on the other hand, has such a small electrolytic solution pressure, or the ions have such a tendency to give up their charge, that the metal becomes positively charged when placed even in the most dilute solutions of a copper salt.[1] The sign and value of the potential which is established between a metal and a solution will depend, therefore, on the metal and on the concentration of its ions in the solution. When the metal is positive with respect to the solution, it is said to have a positive (+) potential; when it is negative to the solution, it is said to have a negative (−) potential.[2]

The electrodes just referred to are reversible with respect to a cation (electrodes of the first class); but one may also have electrodes which are reversible with respect to an anion (electrodes of the second class). Thus, when silver, in contact with solid silver chloride, is immersed in a solution of potassium chloride, that is, when one has the electrode Ag | AgCl(*s*), KCl |, the potential will depend on the concentration of the chloride ion, and the electrode will be reversible with respect to this ion. If a current is passed from the metal to the solution, silver ions will combine with chloride ions to form silver chloride; and if a current is sent from the solution to the electrode, silver ions will be discharged at the electrode and chloride ions set free. The calomel electrode referred to below is also reversible with respect to the anion.

Measurement of Electrode Potentials.—In order to measure the potential between an electrode and a solution it is necessary to have another electrode and solution, the potential difference between which is known. These two electrodes can then be combined to form a voltaic cell, the e.m.f. of which can be determined, and since the e.m.f. is the arithmetical sum or difference of the two electrode

[1] Only in solutions in which the concentration of copper ion has been reduced to a very minute value through the formation of complex ions, *e.g.*, through the addition of excess of potassium cyanide, does the copper send ions into the solution and so become negatively charged.

[2] There is, unfortunately, no universal agreement with regard to this convention, and some writers, especially in America, use the opposite algebraic signs to those given above.

potentials depending on the sign of these potentials, the value of the unknown electrode potential can be calculated. As auxiliary electrode, one may employ what is generally known as the *normal calomel electrode*, which consists of mercury in contact with a normal solution of potassium chloride saturated with mercurous chloride. More frequently now, an electrode with a *saturated solution* of potassium chloride is used. A simple form of the calomel electrode is shown in Fig. 99. A platinum wire, sealed into a glass tube, makes contact with the mercury.

Since the absolute value of an electrode potential is not known with any degree of certainty, it is customary to determine only the *relative* potential, or potential referred to some standard electrode, the potential of which is taken as zero. As standard electrode there is now generally taken the *normal hydrogen electrode* in which the hydrogen is under atmospheric pressure and the acid solution contains hydrogen ion at unit activity.[1] The potential of this electrode is taken as zero at all temperatures. On this basis the potential of the normal calomel electrode at 25° is +0·2812 volt, and that of the electrode with a saturated solution of potassium chloride, +0·2422 volt. The potential of the deci-normal electrode is +0·3335 volt.

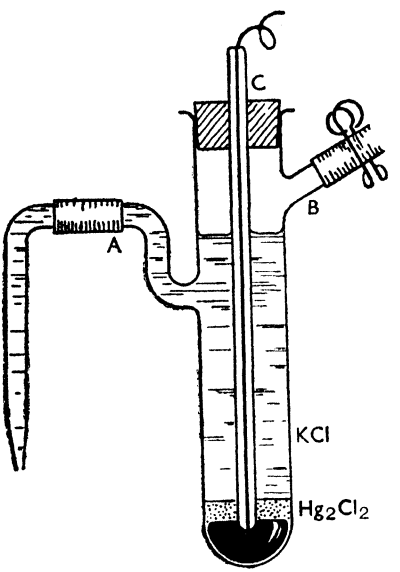


FIG. 99.

In order, for example, to determine the relative potential between, say, zinc and a deci-normal solution of zinc sulphate, a "half-cell," of the form shown in Fig. 99, in which a zinc electrode is in contact with a deci-normal solution

[1] Formerly the acid solution was defined as normal with respect to hydrogen ion, calculated by means of the conductivity ratio, Λ_v/Λ_∞ : that is, the concentration of hydrogen ion was given by $\alpha \,.\, c = 1$, where c is the total concentration of acid.

of zinc sulphate, is combined into a voltaic cell with a normal calomel electrode, as represented diagrammatically by the scheme

$$\text{Zn} \mid 0{\cdot}1\text{N-ZnSO}_4 \parallel \text{N-KCl, Hg}_2\text{Cl}_2 \mid \text{Hg}$$

$$\xrightarrow{0{\cdot}791} \qquad \xrightarrow{0{\cdot}281}$$

$$\xrightarrow{1{\cdot}072}$$

This is simply done by allowing the side tubes of the half-cells to dip in a solution of potassium chloride or of ammonium nitrate. The e.m.f. of this cell is found to be about 1·072 volt, the direction of flow of positive electricity being indicated by the arrow.[1] Since the calomel electrode has a potential of +0·281 volt, and since the flow of positive electricity is from the solution to the metal, as indicated in the diagram, it follows that the potential difference between zinc and the solution of zinc sulphate must be −0·791 volt, and this must assist the potential at the mercury electrode, because the combination of the two potentials amounts to 1·072 volt. That is to say, the flow of positive electricity must be from the zinc to the solution, as has already been pointed out.[2]

In the following table is given a list of electrode potentials at 25°, referred to the potential of the hydrogen electrode with hydrogen ion at unit activity as zero. The ions in the different solutions have unit activity.

ELECTRODE POTENTIALS AT 25°

		E_0.		E_0.
K	$K^{\cdot}$	−2·9241	Pb | $Pb^{\cdot}$	−0·122
Na	$Na^{\cdot}$	−2·7146	$Pt(H_2)$ | $H^{\cdot}$ |	0·00
Zn	$Zn^{\cdot\cdot}$	−0·7618	Cu | $Cu^{\cdot\cdot}$	+0·3441
Fe	$Fe^{\cdot\cdot}$	−0·441	Ag | $Ag^{\cdot}$	+0·7978
Cd	$Cd^{\cdot\cdot}$	−0·4013	Hg | $Hg_2^{\cdot\cdot}$	+0·7986
Ni	$Ni^{\cdot\cdot}$	−0·231	Pt | OH' | O_2 |	+0·3976
Sn	$Sn^{\cdot\cdot}$	−0·136	$Pt(H_2)$ | OH' |	−0·8280

From the values of the standard electrode potentials it is easy to calculate the e.m.f. of a cell made by combining any two of these electrodes with

[1] It is customary to represent a voltaic combination in such a way that positive electricity flows *inside* the cell from left to right, or negative electricity from right to left. In the outer circuit, *negative* electricity flows from the left-hand to the right-hand electrode. The e.m.f. of the cells is then said to be positive, and the accompanying reaction takes place with decrease of free energy; or $E \cdot zF = -\Delta G$.

[2] It will be clear that when the two electrode potentials have different algebraic signs, as in the above case, the e.m.f. of the cell will be equal to the arithmetical sum of the potentials. When the electrode potentials have the same algebraic sign, both positive or both negative, the e.m.f. of the cell will be equal to the arithmetical difference of the potentials. By using arrows to indicate the direction of flow of positive electricity, errors can be readily avoided.

elimination of a liquid junction potential. Thus, the e.m.f. of the cell

$$\underset{\longrightarrow}{\mathrm{Zn}} \mid \mathrm{Zn}^{\cdot\cdot} \parallel \mathrm{Cu}^{\cdot\cdot} \mid \underset{\longrightarrow}{\mathrm{Cu}}$$
$$0{\cdot}7618 \qquad 0{\cdot}3441$$

in which zinc and copper ion have unit activity, will be $0{\cdot}7618 + 0{\cdot}3441 = 1{\cdot}1059$ volt.

The above arrangement of the metals forms what is known as the *potential* or *electrochemical series* of the metals. The greater the negative value of the potential the greater is the tendency of the metal to pass into the ionic state. It follows, therefore, that a metal with a more negative potential will displace from solutions of its salts any other metal which comes after it in the above list. Thus, zinc or iron will displace copper from solutions of copper salts ; and copper will displace silver or mercury. Metals which precede hydrogen in the list will bring about an evolution of the gas when placed in a normal solution of hydrogen ion ; but an anomalous behaviour is sometimes met with owing to the existence of an overvoltage (p. 393), or to the formation of protective oxide films on the metal.

Platinum in contact with chlorine, bromine, or iodine, and with a solution containing chloride, bromide, or iodide ion respectively, also acquires a definite potential, the normal chlorine, bromine, and iodine electrode potentials being $+1{\cdot}359$, $+1{\cdot}066$, and $+0{\cdot}536$ volt respectvely. Chlorine, therefore, has a greater tendency to form ions than bromine or iodine, and, consequently, chlorine will displace these elements from solutions of bromides or iodides. (Since these elements give negatively charged ions, the formation of the ions in solution renders the solution negative to the electrode, or the electrode positive to the solution.)

Influence of Concentration on Electrode Potentials.—It has already been mentioned that the electrode potential depends on the concentration of the ions furnished by the electrode. The relation between potential and ionic concentration can be calculated as follows :—

If a metal, the electrolytic solution pressure of which is p, is partially immersed in a solution containing the ions of the metal, a certain potential E will be established when the osmotic pressure of the metal ions in the solution is P. If a current of electricity is passed reversibly through the electrode until 1 gram-ion of the metal has passed into solution, the work expended will be $E \,.\, zF$ where z is the valency of the ion and F is 96,500 coulombs. (The volume of solution is supposed to be so large that no change in the osmotic pressure is caused by the solution of 1 gram-ion of metal.) If the above process be now carried out when the osmotic pressure of the metal ion in the solution is $P - dP$, then the work done will be $(E - dE) \,.\, zF$, and the difference of the two amounts of work will be $zF \,.\, dE$. This must be equal to the osmotic work done in transferring 1 gram-ion from the osmotic pressure P to the osmotic pressure $P - dP$, that is to say, equal to $V \,.\, dP$, where V is the volume of solvent

in which 1 gram-ion is dissolved. Therefore, $zF \cdot dE = V \cdot dP$; and if it be assumed that the gas laws hold for the solution $V = RT/P$. Consequently, $zF \cdot dE = RT \cdot dP/P$, and $E \cdot zF = RT \log_e P + \text{constant}$. The value of the integration constant is obtained from the fact that $E = 0$ when $P = p$. The constant, therefore, is equal to $-RT \log_e p$. It follows, therefore, that $E = \frac{RT}{zF} \cdot \log_e \frac{P}{p}$.

For any other solution in which the osmotic pressure of the metal ion is P', one would have $E' = \frac{RT}{zF} \cdot \log_e \frac{P'}{p}$. Consequently, $E = E' + \frac{RT}{zF} \cdot \log_e \frac{P}{P'}$. Taking the osmotic pressure as proportional to the concentration and using decadic logarithms, one obtains

$$E = E' + \frac{2{\cdot}303RT}{zF} \log_{10} \frac{C_+}{C'_+}$$

and if the potential E' is put equal to E_0 when $C'_+ = 1$

$$E = E_0 + \frac{2{\cdot}303RT}{zF} \log_{10} C_+$$

Since it is with the effective concentration of the ion that one is concerned, that is, with the activity of the ion, it is better to represent the relation between electrode potential and ionic activity thus

$$E = E_0 + \frac{2{\cdot}303RT}{zF} \log_{10} a_+$$

where E_0 is the electrode potential when the activity of the cation is unity.

On the assumption that the cation and anion have the same activity, one has $a_+ = \gamma \cdot c$, where γ is the activity coefficient of the electrolyte.

In the case of an electrode reversible with respect to an anion, one has

$$E = E_0 - \frac{2{\cdot}303RT}{zF} \log_{10} a_-.$$

Since the factor $\frac{2{\cdot}303RT}{F} = \frac{2{\cdot}303 \times 8{\cdot}32 \times 298}{96500} = 0{\cdot}0591$ at 25°, it follows from the above equations that, in the case of an electrode which yields univalent ions, a tenfold increase or decrease of ionic activity will alter the electrode potential at 25° by 0·0591 volt. Increase of concentration of a cation reduces the electrode potential in the case of negative potentials, but increases the potential in the case of positive potentials.

The factor $\frac{2{\cdot}303RT}{F}$ has the value 0·0571 volt at 15° C., and 0·0577 volt at 18°.

From the above discussion it will readily be understood that from determinations of the variation of electrode potential with concentration it is possible to ascertain the valency z of an ion. In this way it has been found that the mercurous ion has the symbol $Hg_2^{\cdot\cdot}$ (A. Ogg, 1899).[1]

[1] See G. A. Linhart, *J. Amer. Chem. Soc.*, 1916, **38**, 2356.

Concentration Cells.—Since the potential of an electrode varies with the ionic concentration, or rather ionic activity, a voltaic cell in which the electrodes are of the same metal but are in contact with solutions of different ionic activity should have a definite e.m.f. ; and this e.m.f. will, *as a first approximation*, be equal to the difference of the two electrode potentials. Such a cell is called a *concentration cell* (with transport or migration).

In the case of the concentration cell,

$$\text{Metal} \;\Big|\; \begin{matrix}\text{solution containing}\\ \text{metal ions } (a_1)\end{matrix} \;\Big|\; \begin{matrix}\text{solution containing}\\ \text{metal ions } (a_2)\end{matrix} \;\Big|\; \text{metal},$$

the electrode potentials will be

$$E_1 = E_0 + 2{\cdot}303\frac{RT}{zF}\log_{10} a_1$$

and

$$E_2 = E_0 + 2{\cdot}303\frac{RT}{zF}\log_{10} a_2,$$

and therefore the e.m.f. of the cell will be given, approximately, by the expression

$$E = E_1 - E_2 = 2{\cdot}303\frac{RT}{zF}\log_{10}\frac{a_1}{a_2}.$$

This expression, however, is true only when there is no liquid junction potential ; that is, when the cation and the anion have the same rate of diffusion or the same mobility. In general this is not the case, and a difference of potential will be set up at the junction of the two solutions which will be all the greater the greater the difference in the rates of diffusion. The ion of greater mobility will diffuse more rapidly into the dilute solution, and an electrical double layer will thus be produced at the junction of the two solutions, and the more dilute solution will thus take the charge of the more rapidly diffusing ion. The total e.m.f. of the cell will therefore be $E = E_1 - E_2 + E_3$, where E_3 is the liquid junction potential. For a uni-univalent electrolyte this potential between the more concentrated and the less concentrated solution is calculated to be [1]

$$E_3 = \frac{u_c - u_a}{u_c + u_a} \cdot 2{\cdot}303\frac{RT}{F}\log_{10}\frac{a_2}{a_1},$$

where $a_1 > a_2$. u_c and u_a are the mobilities of the cation and anion respectively. The more concentrated solution will

[1] Nernst, *Z. physikal. Chem.*, 1888, **2**, 613.

therefore become negatively charged when $u_c > u_a$. The e.m.f. of a concentration cell with a uni-univalent electrolyte will therefore be[1]

$$E = 2{\cdot}303\frac{RT}{F}\log_{10}\frac{a_1}{a_2} - \frac{u_c - u_a}{u_c + u_a} \cdot 2{\cdot}303\frac{RT}{F}\log_{10}\frac{a_1}{a_2}$$

$$= \frac{2u_a}{u_c + u_a} \cdot 2{\cdot}303\frac{RT}{F}\log_{10}\frac{a_1}{a_2}.$$

As a more general expression for the e.m.f. of a concentration cell, one obtains

$$E = \frac{u_a}{u_c + u_a} \cdot \frac{\nu}{z_-} \cdot 2{\cdot}303\frac{RT}{z_+F}\log_{10}\frac{a_1}{a_2},$$

where ν is the number of ions formed by 1 molecule of the electrolyte, z_- the valency of the anion, z_+ the valency of the cation for which the electrode is reversible, and a_1 and a_2 are the activities of the cation in the two solutions. In the case of most salts u_c and u_a do not vary greatly, and so the liquid junction potential is small, being equal to 0·004 volt between deci-normal and centi-normal solutions of silver nitrate at 15°. With similar solutions of hydrochloric acid, however, the liquid junction potential amounts to 0·037 volt.

Since the calculation of the liquid junction potential is somewhat uncertain, it is advisable to eliminate it by inserting between the two electrode solutions a "salt-bridge" of potassium chloride or ammonium nitrate. The efficiency of these salts is due to the fact that the cation and anion have nearly the same mobility.

The expression given above for the e.m.f. of a concentration cell may be tested by applying it to the cell Ag | 0·01N-$AgNO_3$ | 0·1N-$AgNO_3$ | Ag. Assuming that the activity of the ions is given by $\gamma_1 c_1$ and $\gamma_2 c_2$, the e.m.f. at 18° is calculated to be

$$E = 0{\cdot}528 \times 2 \times 0{\cdot}0577 \log_{10}\frac{0{\cdot}072}{0{\cdot}0090}$$

$$= 0{\cdot}055.$$

This latter value agrees exactly with that determined experimentally.

Cells with Amalgam Electrodes.—When an amalgam is used as an electrode in contact with a solution containing the ions of the metal dissolved in the mercury, the potential of the electrode depends not only on the concentration (activity) of the metal ions in the solution but also on the concentration

---

[1] When the electrodes are reversible with respect to the anion

$$E = \frac{2u_c}{u_c + u_a} \cdot 2{\cdot}303\frac{RT}{F}\log_{10}\frac{a_1}{a_2}.$$

of the metal in the amalgam. Two amalgam electrodes, therefore, of different concentration, immersed in a common solution, will form a cell the energy of which will correspond to the work done in transferring the dissolved metal from an amalgam in which its concentration (activity) is c_1 to an amalgam in which its concentration is c_2. Assuming, as is true in most cases, that the metal dissolves in the monatomic state in mercury, it is found that the e.m.f. of a cell with amalgam electrodes of different concentration is given by the expression $\text{e.m.f.} = 2{\cdot}303 \frac{RT}{F} \log_{10} \frac{c_1}{c_2}$.

Gas Electrodes and Gas Cells.—Hitherto one has been dealing only with metal electrodes which are in equilibrium with ions of the metal in solution. It has, however, been found that a platinum electrode, immersed in a solution saturated with an ion-forming gas, *e.g.*, hydrogen, oxygen,

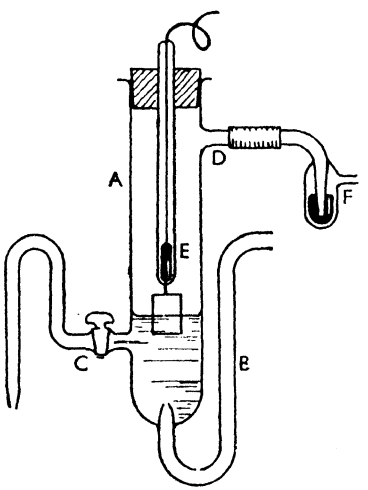


FIG. 100.

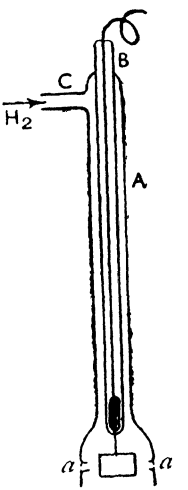


FIG. 101.

chlorine, etc., and containing the ions of the gas—hydrogen ion, oxygen or hydroxide ion,[1] chloride ion, etc.—constitutes a reversible electrode and acquires a definite potential dependent on the pressure of the gas and on the concentration of its ions in solution. By means of cells constructed with such electrodes one can determine the free energy of gas reactions and the concentration (activity) of the ions in the solution. Of the different gas electrodes the most important is the hydrogen electrode.

[1] The oxygen ions, O'', are derived from a dissociation of the hydroxide ions, according to the equation $4OH' \rightleftarrows 2O'' + 2H_2O$.

Various forms may be given to the gas electrode, depending to some extent on the conditions under which it is to be used. In the case of the hydrogen electrode, the forms shown in Figs. 100 and 101 are very convenient. In the case of the electrode vessel shown in Fig. 100, a platinum plate, coated with platinum black, sealed into a glass tube E, forms the electrode. Electrical connection with the outside circuit is made with the help of a small quantity of mercury in E. The platinum electrode dips into a solution containing hydrogen ion, and is partly surrounded by hydrogen gas which is passed in by the tube B and escapes through D and the mercury seal trap F. While the gas is being passed the tap on the tube C must be closed.

In the case of the Hildebrand electrode (Fig. 101), the platinum plate is sealed into the tube B and connection with the outer circuit can be made with the help of mercury. The lower end of the tube A is immersed in the acid solution, and hydrogen is passed in through the side tube C. The hydrogen escapes through the holes *a*, *a*, so arranged that the platinum electrode is partly immersed in the liquid and partly surrounded by the gas.

The potential of the hydrogen electrode will, like the potential of an amalgam electrode, depend on the concentration of the hydrogen in the electrode, and this, in turn, will depend on the pressure of the gas. For a given pressure, say atmospheric, the electrode potential will depend on the effective concentration of the hydrogen ion in the solution in the same way as the potential of a reversible metal electrode. That is,

$$E = E_0 + 2{\cdot}303\,\frac{RT}{F}\log_{10}[\mathrm{H}^{\cdot}],$$

where E_0 is the potential of the normal hydrogen electrode. Or one may also write

$$E = E_0 + 2{\cdot}303\,\frac{RT}{F}\log_{10}a_{\mathrm{H}}.$$

where E_0 is the potential of the hydrogen electrode when the activity of hydrogen ion is equal to unity, and a_{H}. is the activity of hydrogen ion in the given solution.

In the case of the hydrogen ion concentration cell,

$$\mathrm{Pt(H_2)} \mid [\mathrm{H}^{\cdot}]=a_1 \mid [\mathrm{H}^{\cdot}]=a_2 \mid \mathrm{Pt(H_2)},$$

the e.m.f. of which is given by the expression $E = \frac{2u_a}{u_c+u_a} \cdot 2{\cdot}303\frac{RT}{F}\log_{10}\frac{a_1}{a_2}$, correction for the liquid junction potential is relatively large, since u_a/u_c+u_a is equal to about 0·17. When, therefore, the ratio of ionic activities is 10 : 1, the e.m.f. of the cell at 15° will be $0{\cdot}17 \times 2 \times 0{\cdot}0571 = 0{\cdot}0194$ volt.

The Antimony Electrode.—Just as the hydrogen electrode is regarded as being in equilibrium with hydrogen ions in solution, so an oxygen electrode might be regarded as being in equilibrium with negatively charged oxygen ions ($O^{''}$)

formed in the reversible process, $2OH' \rightleftharpoons O'' + H_2O$. The potential of an oxygen electrode would therefore depend on the concentration of hydroxide ions in solution ; and since, in aqueous solutions, the product of concentrations of hydrogen ion and hydroxide ion is constant, at a constant temperature, the potential of the oxygen electrode will depend on the concentration (or activity) of hydrogen ions in the solution.

The oxygen gas electrode, it appears, is not strictly reversible, but a metal electrode in contact with its oxide may be regarded as a reversible oxygen electrode with the gas at a pressure equal to the dissociation pressure of the oxide. One of the most satisfactory of such electrodes is the antimony electrode with the metal in contact with its oxide, Sb_2O_3. This behaves as a reversible electrode, the potential of which is given by the expression [1]

$$E = E_0 - \frac{2{\cdot}303RT}{F}\log_{10}a_{H^+} = E_0 + \frac{2{\cdot}303RT}{F}p\mathrm{H}.$$

This linear relationship between E and pH holds over the range, $p\mathrm{H} = 2$ to $p\mathrm{H} = 7$, and the value E_0 must be determined for each electrode with the help of buffer solutions. With alkaline solutions in which $p\mathrm{H} > 8$ the linear relationship no longer holds, and the electrode must be standardised in solutions of known pH.

With the help of the e.m.f. $-p$H curve for a given antimony electrode, the pH of a solution can readily be obtained by determining the e.m.f. of the cell,

Antimony electrode.	Solution of unknown pH.	Calomel electrode.

Unlike the hydrogen electrode, the antimony electrode can be used in presence of oxidising agents or of colloids.

Oxidation and Reduction.—When one considers the reaction.

$$6FeSO_4 + 3Cl_2 = 2FeCl_3 + 2Fe_2(SO_4)_3$$

from the point of view of the ionic theory, one can represent the reaction thus

$$6Fe^{\cdot\cdot} + 3Cl_2 = 6Fe^{\cdot\cdot\cdot} + 6Cl'.$$

From this equation one sees that when a ferrous salt is oxidised to a ferric salt each gram-atom of ferrous ion gains

[1] Parks and Beard, *J. Amer. Chem. Soc.*, 1932, **54**, 856 ; Perley, *Ind. Eng. Chem.* (*Anal.*), 1939, **11**, 316, 319.

one unit (1 faraday) of positive electricity or *loses* one unit of negative electricity, *the negative charge so lost being taken up by the oxidising agent* (chlorine). Oxidation, therefore, involves the loss of electrons (negative electricity) and reduction the gain of electrons, or the loss of a positive charge. The oxidation of a ferrous to a ferric salt can therefore be represented most simply by the equation

$$Fe^{\cdot\cdot} - \ominus = Fe^{\cdot\cdot\cdot}.$$

When an anion is oxidised or reduced, oxidation, similarly, is accompanied by a decrease, and reduction by an increase of the negative charge. Thus the oxidation of ferrocyanide to ferricyanide ion is represented by the equation

$$Fe(CN)_6'''' - \ominus = Fe(CN)_6'''.$$

From this point of view all reactions which take place in a voltaic cell are oxidation-reduction reactions. Thus, in the reaction in the Daniell cell,

$$Zn + Cu^{\cdot\cdot} \longrightarrow Zn^{\cdot\cdot} + Cu,$$

the zinc loses electrons (oxidation) and the copper ions gain electrons (reduction).

Oxidation-Reduction Potentials.—When an unattackable electrode, such as platinum, is immersed in a solution containing both ferrous and ferric ions, or some other substance in the reduced and oxidised state, a certain electrode potential is established, the value of which will depend on the affinity of the ions for electricity, or on their tendency to pass from a higher to a lower state of oxidation. If the system has oxidising properties it will take up electrons from the electrode and so leave the electrode positively charged relatively to the solution; but if the system has reducing properties it will give up electrons to the electrode, which will then become negatively charged relatively to the solution. The sign and magnitude of the electrode potential thus give a measure of the oxidising or reducing power of a system, and the potential is called the oxidation-reduction (O/R) potential of the system.[1]

When a platinum electrode is placed in a solution containing ferrous and ferric ions the electrode potential will depend on the ratio of ionic activities, $a_{Fe^{\cdot\cdot\cdot}}/a_{Fe^{\cdot\cdot}}$, and is given by the expression

$$E = E_0 + 2{\cdot}303\frac{RT}{F}\log_{10}\frac{a_{Fe^{\cdot\cdot\cdot}}}{a_{Fe^{\cdot\cdot}}},$$

[1] Gerke, *Chem. Rev.*, 1925, **1**, 377; Clark, *ibid.*, 1925, **2**, 127; Conant, *ibid.*, 1926, **3**, 1; Michaelis, *Oxidation-Reduction Potentials.*

E_0 being the potential which is established when the ratio $a_{Fe^{...}}/a_{Fe^{..}} = 1$. At 25°, $E_0 = +0{\cdot}772$ volt.[1] Similarly, the value of E_0 for the electrode Pt $\left| \begin{matrix} Sn^{....} \\ Sn^{..} \end{matrix} \right.$ in acid solution is $-0{\cdot}154$ volt.[2]

The above expression may be generalised. If one calls the substance in the reduced state the *reductant*, and the substance in the oxidised state the *oxidant*, the process of oxidation can be represented by the equation

$$\underset{\text{Red}}{\text{Reductant}} - n\ominus \rightleftharpoons \underset{\text{Ox}}{\text{Oxidant}}.$$

The electrode potential which is established when an unattackable electrode is immersed in a solution containing both reductant and oxidant is given by the expression

$$E_h = E_0 + 2{\cdot}303\frac{RT}{nF}\log_{10}\frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

where E_h represents the electrode potential expressed in terms of the normal hydrogen electrode as zero, n is the number of negative charges lost by the reductant on being converted into the oxidant. An electrode which has a positive E_h value will have oxidising properties as compared with hydrogen; and an electrode which has a negative E_h value will have reducing properties.

Oxidation-Reduction Potential Curves.—By means of the equation for the oxidation-reduction potential of a system one can calculate the potential of systems containing different proportions of the oxidised and reduced forms. On plotting the values of E_h against the percentage amount of the oxidised form,[3] curves such as are shown in Fig. 102 are obtained. From these curves it is seen that on adding an oxidising agent to an O/R system the change of electrode potential is relatively large at the beginning and end of the oxidation process, and comparatively small in the case of systems containing from 20 to 80 per cent. of the oxidised form. Oxidation-reduction systems, the potential of which varies only slightly with change in the ratio $C_{\text{Ox}}/C_{\text{Red}}$, are said to be "poised." Such systems are analogous to buffer solutions.

[1] See Schumb and Sweetser, *J. Amer. Chem. Soc.*, 1935, **57**, 871

[2] See Huey and Tartar, *ibid.*, 1934, **56**, 2585.

[3] Concentrations are here substituted for activities.

The slope of the intermediate portion of the O/R potential curves depends on the number of negative charges, n, lost by the reductant on being converted into the oxidant.

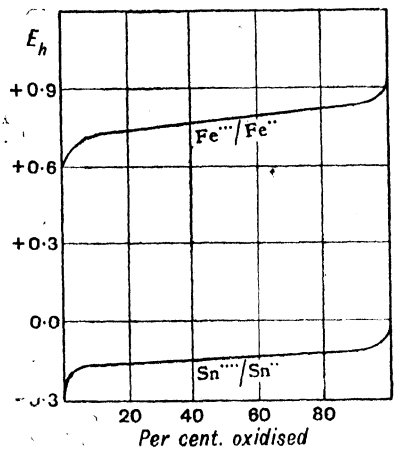


FIG. 102.

The Quinhydrone Electrode.—A large number of systems composed of organic, un-ionised compounds are found to give reversible oxidation-reduction potentials which are dependent, in accordance with the above expression, on the ratio of concentrations (activities) of the oxidised and reduced compounds. Since, moreover, in many such cases the transfer of electrons in the oxidation-reduction process is effected by means of hydrogen ions, the electrode potential depends also on the hydrogen ion concentration (activity) of the system.

An example of an O/R potential in an organic system is found in the reduction of quinone to hydroquinone, represented by the equilibrium

$$\underset{\text{Quinone (Q).}}{C_6H_4O_2} + 2H^{\cdot} + 2\ominus \rightleftharpoons \underset{\text{Hydroquinone } (QH_2).}{C_6H_6O_2}.$$

When a platinum electrode is immersed in an acid solution containing both quinone and hydroquinone, an oxidation-reduction potential is established which is represented at 18° by the equation,[1]

[1] In dilute solutions the activity coefficients may be taken equal to unity and the molal concentrations equal to the activities.

$$E = E_0 + \frac{0{\cdot}0577}{2} \log_{10} \frac{[Q][H^{\cdot}]^2}{[QH_2]}$$

$$= E_0 + \frac{0{\cdot}0577}{2} \log_{10} \frac{[Q]}{[QH_2]} + 0{\cdot}0577 \log_{10} [H^{\cdot}].$$

Therefore, when $[Q] = [QH_2]$, $E = E_0 + 0{\cdot}0577 \log_{10} [H^{\cdot}]$. This condition is satisfied when quinhydrone, a compound of one molecule of quinone with one molecule of hydroquinone, is dissolved in the solution. In such a case it is clear that the electrode potential changes with change in the concentration of hydrogen ion in the same way as does the potential of the hydrogen electrode. The value of E_0 has been found to be $+0{\cdot}7175 - 0{\cdot}00074t$ volt, referred to the normal hydrogen electrode, t being the temperature centigrade. At 18°, therefore, $E_0 = +0{\cdot}7042$ volt. The potential of the quinhydrone electrode exhibits a *salt effect* due to an alteration of the activity ratio of quinone and hydroquinone.

Oxidation-Reduction Indicators.—Of the organic compounds which have been found to form reversible O/R systems, many show different colours in the oxidised and reduced states. Thus, methylene blue in the oxidised state has a blue colour, whereas in the reduced state (leuco-compound) it is colourless. Since, however, the potential of an electrode immersed in a solution containing both oxidised and reduced forms depends on the relative concentrations of the two forms, it follows that the colour of the solution will also be related to the electrode potential. Thus, if one adds an oxidising agent (*e.g.*, solution of potassium ferricyanide) to a solution of leuco-methylene blue of definite pH value, and if one determines the value of the electrode potential in the solution after each addition of ferricyanide, then on plotting the electrode potentials against the percentage amount of compound oxidised, a curve, such as is shown in Fig. 103, is obtained. The position of the curve on the E axis depends on the indicator and on the hydrogen ion concentration of the solution, but the electrode potential is definite for a given value of pH. From Fig. 103 it is seen that

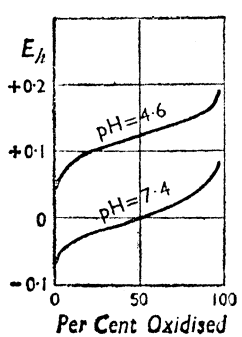


FIG. 103.

when pH = 7·4, methylene blue will exist in the leuco form if the electrode potential of the solution has a negative (reducing) value of −0·1 volt, or more. On the other hand, if the electrode potential of the solution has a positive (oxidising) value of +0·1 or more, the methylene blue will exist in the oxidised (blue) form. In solutions having electrode potentials between −0·1 and +0·1, methylene blue will exist partly in the leuco and partly in the blue form, when the pH value of the solution is 7·4.

With other coloured organic compounds, capable of forming reversible O/R systems, similar curves giving the relation between E_h and the ratio [Ox]/[Red] are obtained, and as the O/R potentials of these systems are different, use can be made of these substances for the purpose of indicating the O/R potential of the system—attention being also paid to the pH of the solution. The electrode potential at 30°, corresponding to the half stage of oxidation, *i.e.*, [Ox]=[Red], is given for a number of substances in the following table :—

Indicator.	pH.					
	6·0.	6·4.	6·8.	7·0.	7·4.	7·8.
Indigo disulphonate	−0·069	−0·092	−0·114	−0·125	−0·143	−0·160
Indigo trisulphonate	−0·028	−0·051	−0·072	−0·081	−0·099	−0·114
Indigo tetrasulphonate	+0·006	−0·017	−0·037	−0·046	−0·062	−0·077
Methylene blue	+0·047	+0·031	+0·017	+0·011	−0·002	−0·014
Toluylene blue	+0·162	+0·141	+0·123	+0·115	+0·101	+0·088
2 : 6-Dichlorophenol-indo-*o*-cresol	+0·261	+0·228	+0·196	+0·181	+0·152	+0·125

By means of the above and other substances it is possible to determine, approximately at least, the O/R potential of a solution.

The Glass Electrode.—The concentration of hydrogen ions in a solution may be determined by means of the glass electrode. This electrode is especially useful in the case of oxidising and reducing solutions, colloidal sols, and biological fluids. Its use depends on the fact that when a glass surface is in contact with a solution there is established between the glass and the solution a potential difference which depends on

the concentration of hydrogen ions in the solution.[1] Thus, in the arrangement

$$\text{Hg} \mid \text{Hg}_2\text{Cl}_2, \text{N-KCl} \parallel \underset{(a_1)}{\text{H}^\cdot} \mid \underset{\text{membrane}}{\text{Glass}} \mid \underset{(a_2)}{\text{H}^\cdot} \parallel \text{N-KCl}, \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$$

the e.m.f. depends on the concentrations (activities) of the hydrogen ions in the two solutions on either side of the membrane, and is given by the expression

$$E = K + \frac{2{\cdot}303RT}{F} \log_{10} \frac{a_2}{a_1},$$

where K is an "asymmetry potential" dependent on the nature of the glass, etc., and a_1 and a_2 are the hydrogen ion activities.

The action of the glass electrode is doubtless due to the glass acting as a membrane permeable to hydrogen ions but impermeable to other ions. The value of the "asymmetry potential" can be determined with the help of solutions of known pH. The glass electrode is unsuitable for use in alkaline solutions with a pH greater than 10.

Applications of Electromotive Force Measurements.—It has already been pointed out that from measurements of the e.m.f. of the appropriate voltaic cells the affinity or diminution of the free energy of a reaction and also the heat of a reaction can be calculated. Further applications of such measurements may now be indicated.

1. *Solubility of Sparingly Soluble Salts.*[2]—In order to determine the solubility of, say, silver chloride, the silver ion concentration cell

$$\text{Ag} \mid \text{AgCl}, 0{\cdot}01\text{N-KCl} \parallel \underset{\text{NH}_4\text{NO}_3}{\text{Saturated solution of}} \parallel 0{\cdot}01\text{N-AgNO}_3 \mid \text{Ag}$$

may be fitted up. One electrode is in contact with a solution of silver nitrate in which the concentration of silver ion is supposed known, and the other electrode is in contact with a solution of potassium chloride of known concentration saturated with silver chloride. The potassium chloride serves to increase the conductivity of the solution, and to give a known concentration of chloride ion. The e.m.f. of this cell at 15° is given by the expression $\text{e.m.f.} = 0{\cdot}0571 \log_{10} \frac{0{\cdot}0093}{x}$, where 0·0093 represents the concentration of silver ion in the 0·01N solution of silver nitrate ($\alpha = 0{\cdot}93$),[3] and x is the concentration of silver ion in the potassium chloride-silver chloride solution. If it is assumed that the potassium chloride is completely ionised, the concentration of chloride ion in this solution will be 1×10^{-2} gram-ion per litre; and if one applies the law of solubility product, one obtains $[\text{Ag}^\cdot] \times [\text{Cl}'] = \text{solubility product} = K_s$.

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[1] Haber and Klemensiewicz, *Z. physikal. Chem.*, 1909, **67**, 385.

[2] H. M. Goodwin, *Z. physikal. Chem.*, 1894, **13**, 577; R. Abegg and A. J. Cox, *ibid.*, 1903, **46**, 1.

[3] More strictly, one would employ the activity coefficient $\gamma = 0{\cdot}90$.

The value of K_s is then found by multiplying the concentration of $Ag^{\cdot}$ as given by the value of the e.m.f. of the above cell by 1×10^{-2} (or, more correctly, by this number multiplied by the degree of ionisation (0·94), or by the activity coefficient (0·92) of potassium chloride in centinormal solution). Since, in pure aqueous solution, the concentration of silver ion is equal to the concentration of chloride ion, it follows that the concentration of either is equal to $\sqrt{K_s}$. Further, if it be assumed that the silver chloride is completely ionised (activity coefficient equal unity), then $\sqrt{K_s}$ also gives the concentration of silver chloride in the solution, *i.e.*, the solubility.

2. *Stability of Complex Ions.*

3. *Concentration of Hydrogen Ion.*—The concentration (activity) of hydrogen ion in a solution can be obtained from the e.m.f. of a cell formed by combining a hydrogen electrode immersed in the given solution with a normal hydrogen electrode (p. 378). The e.m.f. of the cell is equal to $2{\cdot}303\frac{RT}{F}\log_{10}a_{H^{\cdot}}$. The concentration (activity) of hydrogen ion can therefore be calculated. In place of the normal hydrogen electrode one may use a calomel electrode, preferably with saturated solution of potassium chloride, in order to eliminate the liquid junction potential. One then has

$$\text{E.m.f.} = E_{\text{calomel}} - E_{\text{hydrogen}}$$

$$= E_{\text{calomel}} - 2{\cdot}303\frac{RT}{F}\log_{10}a_{H^{\cdot}}.$$

Therefore,

$$E_{\text{calomel}} - \text{e.m.f.} = 2{\cdot}303\frac{RT}{F}\log_{10}a_{H^{\cdot}}.$$

It should be noted that E_{calomel} is the potential of the calomel electrode referred to that of the normal hydrogen electrode as zero.

Instead of the hydrogen electrode, which is not suitable for use in presence of reducible substances or of ions of metals which have positive (+) electrode potentials (*e.g.*, copper, silver), one may use the quinhydrone electrode (p. 383). To the solution under investigation one adds 1 – 2 grams of quinhydrone per 100 ml. of solution and stirs well. A *bright* platinum electrode is immersed in the solution and combined into a cell with a calomel electrode, with elimination of the liquid junction potential. The concentration (activity) of hydrogen ion in the solution can then be calculated from the equations

$$\text{E.m.f.} = E_{\text{quinhydrone}} - E_{\text{calomel}}$$

$$= 0{\cdot}704 + 2{\cdot}303\frac{RT}{F}\log_{10}a_{H^{\cdot}} - E_{\text{calomel}}$$

or

$$2{\cdot}303\frac{RT}{F}\log_{10}a_{H^{\cdot}} = \text{e.m.f.} - 0{\cdot}704 + E_{\text{calomel}}.$$

From this one can calculate the value of $a_{H^{\cdot}}$.

The quinhydrone electrode cannot be used with solutions which have a *p*H value greater than 8; that is, with solutions the hydrogen ion concentration (activity) of which is less than 1×10^{-8} normal.

An antimony electrode (p. 379) or a glass electrode (p. 385) may also be used for the determination of the hydrogen ion concentration.

By means of the hydrogen electrode one is also able to study the influence of neutral salts on the activity of hydrogen ion (*salt effect*). Thus the potential of a hydrogen electrode immersed in a solution of, say, 0·01N hydrochloric acid is determined, and also the potential after increasing amounts of potassium chloride have been added to the acid. If E_o is the electrode potential in pure acid solution, and E_s the potential when a definite amount of salt has been added to the acid, then $E_o - E_s = 2{\cdot}303\frac{RT}{F}\log_{10}\frac{a}{a_o}$ where a is the activity of hydrogen ion in presence of salt and a_o the activity in the pure acid solution.

Assuming that the activities of hydrogen ion and chloride ion are equal, a_o can be put equal to γc, where γ is the activity coefficient and c the concentration of the acid.

4. *Hydrolysis of Salts.*[1]—The degree of hydrolysis of a salt x is given by the expressions (p. 343) $x=\frac{[OH']}{c}$ and $x=\frac{[H^{\cdot}]}{c}$, where c is the concentration of the salt. If, therefore, one determines the concentration of hydrogen ion in the solution of the salt in the manner already described, the value of x can be calculated.

5. *Determination of Equilibrium Constants and of Free Energy.*—It has been pointed out (p. 306) that by applying the van't Hoff isotherm,

$$-\Delta G = RT \log_e K - RT \log_e x,$$

where x is the initial mass law ratio of concentrations of resultants and reactants, one can calculate the value of K, the equilibrium constant, if the value of x is known. Since, in the case of electrolytic reactions, the diminution of free energy can be determined from measurements of the e.m.f. of an appropriate voltaic cell, such measurements also enable one to calculate the value of the equilibrium constant. Thus, in the case of the reaction,

$$TlCl + KSCN \text{ aq.} = TlSCN + KCl \text{ aq.},$$

which reaches an equilibrium state when $[Cl']/[SCN'] = K$, the value of K can be calculated from the e.m.f. of the cell,

$$\text{Tl-amalgam} \mid TlCl, KCl \text{ (sol.)} \parallel KSCN \text{ (sol.)}, TlSCN \mid \text{Tl-amalgam},$$

in which $[Cl']/[SCN'] = x$. When $x < K$, the positive current will flow in the cell from right to left, thereby causing an increase in the concentration of chloride ion and a decrease in the concentration of thiocyanate ion. At 20° the e.m.f. of the above cell, when $x = 0{\cdot}84$, was found to be 0·0105 volt.[2] One calculates, therefore,

$$\log_{10} K = \frac{0{\cdot}0105}{0{\cdot}0581} + \log_{10} 0{\cdot}84$$
$$= 0{\cdot}1807 - 0{\cdot}0757 = 0{\cdot}1050.$$

Hence, $K = 1{\cdot}27$. The value found by chemical analysis is 1·24.

When the initial concentrations of reactants and resultants are equal to unity, then $x = 1$, and one has e.m.f. $= 2{\cdot}303\frac{RT}{F}\log_e K$. The e.m.f. of the voltaic cell can then be calculated from the normal electrode potentials (p. 373). Thus, in order to find the value of the ionic product of water at 25°, one has[3]

$$\text{Electrode potential: } Pt(H_2) \mid H^{\cdot} \mid . \quad E_0 = 0{\cdot}00.$$
$$\text{Reaction: } \tfrac{1}{2}H_2 = H^{\cdot} + \ominus.$$

$$\text{Electrode potential: } Pt(H_2) \mid OH' \mid . \quad E_0 = -0{\cdot}8280.$$
$$\text{Reaction: } \tfrac{1}{2}H_2 + OH' = H_2O + \ominus.$$

By subtracting the latter equation from the former, one obtains $H_2O = H^{\cdot} + OH'$ and the diminution of free energy of this reaction is equal to E . $F = -0{\cdot}8280F$

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[1] H. G. Denham, *J. Chem. Soc.*, 1908, **93**, 41.

[2] Carl Knüpffer, *Z. physikal. Chem.*, 1898, **26**, 255. See also A. Findlay, *ibid.*, 1900, **34**, 409.

[3] For determinations of the dissociation constant of water, see Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194; E. J. Roberts, *ibid.*, 1930, **52**, 3877; Harned and Donelson, *ibid.*, 1937, **59**, 1280, 2032, 2304.

volt-coulombs, the reaction taking place spontaneously from right to left. Therefore,

$$-0{\cdot}8280 = 2{\cdot}303\frac{RT}{F}\log_{10} K_w = 0{\cdot}05915 \log_{10} K_w.$$

Therefore, $K_w = 1{\cdot}005 \times 10^{-14}$.

The *decrease of free energy* of a reaction can be calculated by means of the equation: $-\Delta G = 2{\cdot}303RT \log_{10} K$, where K is the equilibrium constant. Thus, for the reaction, $TlCl + SCN' = TlSCN + Cl'$, the equilibrium constant at 25° is equal to 1·27. The decrease of free energy will therefore be

$$-\Delta G = 2{\cdot}303 \times 1{\cdot}987 \times 298 \log_{10} 1{\cdot}27 = 141{\cdot}6 \text{ cal.}$$

6. *Potentiometric Analysis.*—Since the potential of an electrode, dipping in the solution of an electrolyte, depends on the concentration (activity) of

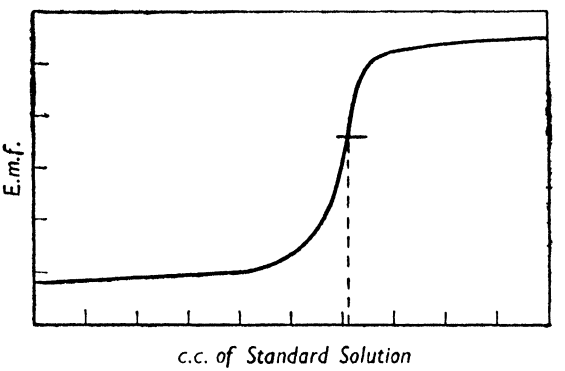


FIG. 104.

certain ions, one may use determinations of the potential as an "indicator" in volumetric analysis. Thus, in the case of the voltaic combination,

$$\text{Ag} \;\Big|\; \begin{matrix}\text{solution of}\\ AgNO_3\end{matrix} \;\Big\|\; KNO_3 \;\Big\|\; \begin{matrix}\text{calomel or other}\\ \text{standard electrode,}\end{matrix}$$

the cell will have a certain e.m.f. depending on the concentration of silver ion in the solution of silver nitrate. On adding a standard solution of sodium chloride to the silver nitrate, the e.m.f. of the cell will alter, slowly at first, because the change of electrode potential depends on the *fractional* amount of silver ion removed. As the amount of chloride added approaches equivalence to the amount of silver in the solution, the fraction of the silver ion concentration removed by each drop of chloride solution rapidly increases, and there is a correspondingly rapid change in the e.m.f. Later, as excess of chloride is added, the e.m.f. again shows a slow change. On plotting the e.m.f. against volume of standard chloride added, a curve of the form shown in Fig. 104 is obtained. The end point of the titration is given by the point of inflexion on the curve.[1]

Titration of acid solutions by alkali can similarly be carried out by using a hydrogen electrode immersed in the acid solution; and a solution of a ferrous salt can be titrated with dichromate, using a platinum electrode (oxidation-

[1] The point of inflexion can be most easily found by plotting the values of $\Delta E/\Delta v$ against the volume of titrating solution. At the point of inflexion the value of $\Delta E/\Delta v$ is a maximum.

reduction potential). For the potentiometric titration of oxidation-reduction reactions, the platinum and tungsten electrodes are very convenient.[1] Many other analyses may be carried out potentiometrically.[2]

7. **Determination of Affinity Constants of Acids.**—As has already been pointed out (p. 354), the affinity constant of a weak acid, based on the ordinary mass law equations, can be determined from the curve giving the change of pH on neutralisation of the acid by an alkali, the pH being determined by one of the methods already described. These methods may involve the uncertainty of a liquid junction potential or of the value of the potential of a calomel electrode on the normal hydrogen scale; but a method which avoids these uncertainties and which enables the *thermodynamic dissociation constant* of a weak acid to be determined has been developed.[3]

The e.m.f. (E) of the cell, without liquid junction,

$$\text{Ag} \mid \text{AgCl, NaCl}(m_3), \text{NaA}(m_2), \text{HA}(m_1) \mid H_2(1 \text{ atm.}),$$

where m_1, m_2, m_3 are the concentrations (molalities) of the weak acid, HA, of its sodium salt and of sodium chloride respectively, is given by the expression

$$E = E_0 - (RT/F) \log_e a_{H'} a_{Cl'}.$$

E_0 is the e.m.f. of a cell, Ag | AgCl, HCl | H_2, in which the mean activity of the hydrochloric acid is unity. E_0 is therefore known. Since the thermodynamic dissociation constant (K) of the acid is equal to $a_{H'} a_{A'}/a_{HA}$, the above equation can be written in the form

$$E = E_0 - RT/F\left(\frac{a_{Cl'} a_{HA}}{a_{A'}} \times \frac{a_{H'} a_{A'}}{a_{HA}}\right).$$

Since the mean activity, a, is equal to γm (p. 286) where γ is the activity coefficient and m is the molality, one may also write:

$$E = E_0 - \frac{RT}{F} \log_e \frac{m_{Cl'} m_{HA}}{m_{A'}} - \frac{RT}{F} \log_e \frac{\gamma_{Cl'} \gamma_{HA}}{\gamma_{A'}} - \frac{RT}{F} \log_e K.$$

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[1] Gay, *Ind. Eng. Chem.* (*Anal.*), 1939, **11**, 383.

[2] See I. M. Kolthoff and N. H. Furman, *Potentiometric Titrations*; H. T. S. Britton, *Hydrogen Ions*.

[3] H. S. Harned and R. W. Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350; J. F. J. Dippy, *Chem. Rev.*, 1939, **25**, 151.

Hence,

$$E - E_0 + \frac{RT}{F} \log_e \frac{m_{Cl'} m_{HA}}{m_{A'}} = -\frac{RT}{F} \log_e \frac{\gamma_{Cl'} \gamma_{HA}}{\gamma_{A'}} - \frac{RT}{F} \log_e K$$

$$= -\frac{RT}{F} \log_e K'.$$

At infinite dilution the activity coefficients all become equal to unity and K' equal to K. Since E_0 is known and E can be measured, the left-hand side of the equation can be evaluated, it being noted that $m_{Cl'} = m_3$, $m_{HA} = m_1 - [H^+]$, and $m_{A'} = m_2 + [H^+]$. The value of $[H^+]$ is calculated, with sufficient accuracy, from an approximate value of the dissociation constant. The values of $-RT/F \,.\, \log_e K'$ so obtained are plotted against the ionic strength of the mixture in the cell and extrapolated to zero concentration, the intercept giving the value of $-RT/F \,.\, \log_e K$. From this, K can be obtained.

8. *Determination of Transport Numbers.*—The e.m.f. (E_t) of the concentration cell with transport

$$\text{Ag} \mid \text{AgCl, LiCl } (a_1) \mid \text{LiCl } (a_2), \text{AgCl} \mid \text{Ag},$$

in which the electrodes are reversible with respect to chloride ion, is given by the expression $E_t = \frac{2 \,.\, u_c}{u_c + u_a} \,.\, \frac{RT}{F} \log_e \frac{a_1}{a_2}$. If, however, a cell is constructed in which lithium amalgam is inserted between the two solutions of lithium chloride, one obtains what is known as a *concentration cell without transport*, because lithium chloride is not transferred from one solution to the other when current is taken from the cell. Such a cell, which may be represented by the scheme,

$$\text{Ag} \mid \text{AgCl, LiCl } (a_1) \mid \text{Li(Hg)}_x \mid \text{LiCl } (a_2), \text{AgCl} \mid \text{Ag},$$

may be regarded as consisting of two cells, namely,

$$\text{Ag} \mid \text{AgCl, LiCl } (a_1) \mid \text{Li(Hg)}_x$$

and $$\text{Li(Hg}_x) \mid \text{LiCl } (a_2), \text{AgCl} \mid \text{Ag},$$

and the e.m.f. (E) of the cell will be equal to the sum of the electromotive forces of the two simple cells; that is, $E = \frac{2RT}{F} \log_e \frac{a_1}{a_2}$. If, therefore, one determines the e.m.f. of

the concentration cell with transport and the e.m.f. of the concentration cell without transport, the transport number of the cation can be calculated from the relation [1] $n_c = \frac{u_c}{u_c + u_a} = \frac{E_t}{E}$. This is illustrated by the numbers in the following table :—

TRANSPORT NUMBER OF LITHIUM ION IN LITHIUM CHLORIDE AT 25°

Concentration Ratio.	E.	E_t.	Transport Number.	
			$n_c = E_t/E$.	Hittorf (18°).
1·0 : 0·1	116·5	35·43	0·304	0·304
0·3 : 0·03	111·2	35·21	0·317	0·320
0·01 : 0·001	114·0	39·05	0·343	...

9. *Determination of Activity Coefficients.*—In the case of an electrode reversible for both cation and anion, the e.m.f. of a concentration cell without transport would be given by the expression

$$E = \frac{2 \cdot 303RT}{zF} \cdot \log_{10} \frac{a'_+ \times a'_-}{a''_+ \times a''_-}.$$

Since $\sqrt{a_+ \times a_-} = \gamma \cdot c$ (p. 390), one may write

$$E = \frac{2 \cdot 303RT}{zF} \cdot \log_{10} \frac{\gamma_2^2 c_2^2}{\gamma_1^2 c_1^2} = \frac{2 \times 2 \cdot 303RT}{zF} \cdot \log_{10} \frac{\gamma_2 c_2}{\gamma_1 c_1},$$

which, for a uni-univalent electrolyte at 25°, becomes $E = 0 \cdot 1183 \log_{10} \gamma_2 c_2 / \gamma_1 c_1$. As the concentration c_1 approaches zero, γ_1 approaches unity, and the e.m.f. then becomes $E = 0 \cdot 1183 \log_{10} \gamma_2 c_2 / c_1$. This value can be obtained by an extrapolation method. It thus becomes possible to determine the activity coefficient of an electrolyte at different concentrations. By this means it has been found that the activity coefficient decreases with increasing concentration, passes through a minimum, and then increases. This is illustrated by the numbers in the table on p. 393.

[1] See, for example, D. A. MacInnes and J. A. Beattie, *J. Amer. Chem. Soc.*, 1920, **42**, 1117, 1128; A. C. Harris and H. N. Parton, *Trans. Faraday Soc.*, 1940, **36**, 1139.

The activity coefficient of one electrolyte in presence of other electrolytes can similarly be determined.

ACTIVITY COEFFICIENTS AT 25°

Concentration.	0·01.	0·05.	0·1.	0·5.	1.	3.	4.
LiCl . . .	0·901	0·819	0·779	0·725	0·757	1·174	1·554
HCl . . .	0·904	0·829	0·796	0·757	0·810	1·320	1·762

Polarisation.—When one electrolyses a solution of an electrolyte between platinum plates, metal or gas is deposited on or liberated at the electrodes, which thus acquire a certain potential depending on the nature of the metal or gas liberated. The electrodes are said to be *polarised,* and they constitute, along with the electrolyte, a voltaic cell which has a certain e.m.f. known as a *polarisation electromotive force.* This acts against the e.m.f. of the electrolysing current, as is shown by interrupting the electrolysing current and connecting the two electrodes by means of a conductor. A current is given opposite in direction to the electrolysing current.

When hydrogen is liberated at the cathode or oxygen at the anode, polarisation can be prevented by the presence of an oxidising substance at the cathode and a reducing substance at the anode. Such substances are known as *depolarisers.* Thus, manganese dioxide acts as a depolariser in the Leclanché cell.

Polarisation, however, may be produced not only by the deposition of the products of electrolysis on the electrodes, but also by changes of concentration in the neighbourhood of the electrodes. Thus, when a solution of, say, copper sulphate is electrolysed between copper electrodes, copper is dissolved at the anode and is deposited at the cathode, and no chemical work is done. Consequently, the e.m.f. necessary to electrolyse the solution will simply be that which is necessary to overcome the resistance of the solution, and this will, in accordance with Ohm's law, be equal to IR, where I is the strength of current and R is the resistance of the solution. This relation, however, is true only at the beginning of the electrolysis. When, for example, 1 faraday of electricity has been passed through the solution, 0·62 gram-equivalent of copper sulphate will have been formed at

the anode, 0·62 being the transport number of the sulphate ion in the solution of copper sulphate. At the cathode the effect of deposition and migration will be that 0·62 gram-equivalent of copper sulphate will have been removed from the solution in the neighbourhood of that electrode. The concentration of copper sulphate at the two electrodes will therefore no longer be the same, and one will have a copper sulphate concentration cell, the e.m.f. of which will oppose that of the electrolysing current. This is known as *concentration polarisation*. Such polarisation may be diminished by vigorous stirring.

Decomposition Potential of Electrolytes.—When a voltage of, say, 0·5 volt is applied to two platinum electrodes immersed in dilute sulphuric acid it is found that a current passes through the solution. Owing, however, to the discharge in minute amount of hydrogen and hydroxide ion (oxygen) at the two electrodes, a polarisation e.m.f., equal and opposite to the applied voltage, is established, and the current falls practically to zero. Diffusion, however, of the liberated hydrogen and oxygen takes place away from the electrodes, and a small current, the so-called *residual current*, continues to pass. As the applied voltage is gradually increased, there is a slow increase in the residual current until, when the applied voltage reaches a certain value, the current begins rapidly to increase with increase in the applied e.m.f. The voltage at which this rapid increase in the electrolysing current commences is called the *decomposition potential* of the particular solution. If one plots the current strength against the applied e.m.f., a curve, such as is shown in Fig. 105, is obtained. The decomposition potential, it is clear, will be equal to the difference of the potentials at the anode and cathode plus the (generally negligible) fall of potential IR between the electrodes. Since the electrode potentials depend on the ionic concentrations, so also will the decomposition potential. In the case of a zinc chloride solution in which the concentration (activity) of zinc ion and chloride ion is unity the decomposition potential will be equal to $+1{\cdot}3594-(-0{\cdot}7618)=2{\cdot}1212$ volts, $+1{\cdot}3594$ and

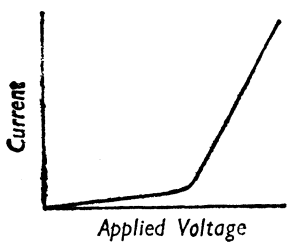


FIG. 105.

$-0{\cdot}7618$ volts being the potentials of the normal chloride and zinc electrodes respectively.

Since the different metals when immersed in solutions of their salts acquire different potentials (p. 373), it follows that the decomposition potential of the salts of different metals with the same anion will be different, as is shown in the following table, which gives the values of the decomposition potential of a number of salts in normal solution.

DECOMPOSITION POTENTIALS

	Volts.		Volts.
Zinc sulphate	2·55	Cobalt sulphate	1·92
Nickel sulphate	2·09	Copper sulphate	1·49
Nickel chloride	1·85	Silver nitrate	0·70
Lead nitrate	1·52	Sulphuric acid	1·67
Cadmium sulphate	2·03	Hydrochloric acid	1·31

Use is made of the above behaviour in the electrolytic separation of metals, *e.g.*, copper and zinc or copper and nickel. From the above table it will be seen that so long as the voltage of the electrolysing current is kept below 2 volts no zinc or nickel will be deposited. Moreover, the normal electrode potential of copper, referred to that of hydrogen, is $+0{\cdot}344$ volt, and that of the nickel electrode $-0{\cdot}231$ volt. As the solution becomes less concentrated the tendency of copper ion to give up its electric charge diminishes by approximately 0·029 volt for a tenfold decrease in concentration; but since the difference between the electrode potentials of copper and nickel amounts to about $0{\cdot}57 = 0{\cdot}029 \times 20$, it follows that the concentration of copper ion would have to be reduced to 1×10^{-20} normal before the potential of the copper electrode falls to that of the nickel electrode. A complete separation of copper from nickel can therefore be effected electrolytically.

From a study of decomposition potentials it is deduced that when a solution of, say, sodium sulphate is electrolysed, there is a discharge at the anode, not of sulphate ions followed by the reaction $SO_4 + H_2O = H_2SO_4 + O$ but of hydroxide ions followed by the reaction $2OH = H_2O + O$.

Overvoltage.—It might be thought that it would be impossible to deposit electrolytically from solution any metal which has an electrode potential more negative than hydrogen. This, however, is not the case, since zinc, for example, can be deposited electrolytically from feebly acid solution. The explanation of this is to be found in the occurrence of an

overvoltage when gases are evolved as the result of electrolysis. In the case of the cell

$$Pt(H_2) \mid \text{N-acid} \mid (O_2)Pt,$$

in which hydrogen and oxygen under atmospheric pressure are in contact with platinised platinum electrodes, the e.m.f. is found to be about 1·12 volt. One would expect, therefore, that when a normal acid solution is electrolysed, decomposition with evolution of hydrogen and oxygen would take place when the applied voltage exceeds 1·12 volts, if the electrodes act as reversible electrodes. This is found to be nearly the case when platinised platinum electrodes and small currents are employed. When, however, smooth platinum electrodes are used, the decomposition potential is higher, about 1·7 volt; and with other metal electrodes the decomposition potential varies with the nature of the metal. The difference between the reversible gas electrode potential and the potential at which gas commences to be evolved in electrolysis is known as the *overvoltage*. This overvoltage is met with not only in the case of hydrogen but also in the case of oxygen and of other gases. In the electrolysis of normal solutions of sulphuric acid the following cathodic overvoltages have been found :—

Electrode.	Overvoltage.	Electrode.	Overvoltage.
Platinum (platinised)	0·005	Tin	0·53
Platinum (polished)	0·09	Lead	0·64
Silver	0·15	Zinc	0·70
Nickel	0·21	Mercury	0·78
Copper	0·23		

The values of the overvoltage, however, vary considerably with the conditions of experiment, and are also influenced by the presence of foreign substances in the solution.

The production of a cathodic overvoltage corresponds to an increased concentration of hydrogen at the electrode, and increases the reducing properties of the electrode. This fact plays an important part in the electrolytic reduction of organic compounds.

Lead Accumulator.—The familiar lead accumulator is a voltaic cell, the e.m.f. of which depends on polarisation. When an electric current is passed between two lead plates immersed in sulphuric acid of specific gravity 1·20, hydrogen

is evolved at the cathode, and lead dioxide, PbO_2, is formed at the anode. The cell Pb | H_2SO_4 | PbO_2 is formed, the e.m.f. of which is about 2·0 volts. The e.m.f. depends on the concentration of the acid. When this cell is being discharged there takes place the chemical reaction,

$$PbO_2 + 2H_2SO_4 + Pb = 2PbSO_4 + 2H_2O + 87{,}000 \text{ cal.}$$

That is to say, lead sulphate is formed at both electrodes. If, now, an electric current be passed through the discharged cell in a direction opposite to that of the current given by the cell, the lead sulphate at the cathode is reduced to lead with production of sulphuric acid ; and the lead sulphate at the anode is converted to lead dioxide.[1] The original cell, therefore, is reconstituted. During discharge, it will be observed, sulphuric acid is used up, and during charge it is formed. The density of the acid solution, therefore, decreases during discharge and increases during charge.

[1] At the anode the discharged sulphate ions may be regarded as reacting with the lead sulphate to give $Pb(SO_4)_2$, which then undergoes hydrolysis with production of lead dioxide and sulphuric acid.

CHAPTER XVI

HETEROGENEOUS EQUILIBRIA AND THE LAW OF MASS ACTION. DISTRIBUTION LAW

In the case of homogeneous systems, it has been learned, the law of mass action enables one to formulate the conditions of equilibrium in terms of the molar concentrations of the reacting substances. It will now be shown that even in the case of *heterogeneous systems*, or systems which are made up of different physically distinct parts, the law of mass action may also be applied when the assumption can be made that the heterogeneous equilibrium depends on an equilibrium in a homogeneous system.

Two Solid Compounds in Equilibrium with a Gas.—In the case of the equilibrium, $CaCO_3 \rightleftharpoons CaO + CO_2$, it may legitmately be assumed that calcium carbonate and calcium oxide possess a certain, even if very small, vapour pressure, and that the heterogeneous equilibrium is dependent on, or is associated with, the equilibrium between the substances in the gaseous state. To this homogeneous equilibrium one can then apply the law of mass action and obtain the expression

$$\frac{p_1 \times p_2}{p_3} = K_p,$$

where p_1, p_2, and p_3 are the partial pressures of carbon dioxide, calcium oxide, and calcium carbonate respectively, the partial pressures being proportional to the concentrations. So long, however, as solid calcium oxide and calcium carbonate are present, the pressures p_2 and p_3 must be constant. At a given temperature, therefore, the pressure of carbon dioxide will be constant. This conclusion has been borne out by experiment, the *dissociation pressures*

at different temperatures being given in the following table [1] :—

Temperature. °C.	Pressure in Millimetres. of Mercury.
600	2·35
700	25·3
800	168
900	773
1000	2710

At 898° the dissociation pressure is equal to 1 atmosphere.

The experimental values of the dissociation pressure show that dissociation of the carbonate increases with rise of temperature. According to the theorem of Le Chatelier (p. 277), therefore, one can predict that dissociation will be accompanied by *absorption of heat*; and the amount of heat absorbed, per gram-molecule of carbon dioxide formed, can be calculated by applying the van't Hoff isochore (p. 311). Assuming that the heat of dissociation is constant over a particular range, one obtains the expression

$$\log_{10}\frac{p_1}{p_2}=\frac{q}{2{\cdot}303\,.\,\boldsymbol{R}}\cdot\left(\frac{T_2-T_1}{T_1T_2}\right)$$

where p_1 and p_2 are the equilibrium pressures of carbon dioxide at the absolute temperatures T_1 and T_2, q is the heat of dissociation, and $\boldsymbol{R}$ is the gas constant in heat units, 1·987 cal. Since at 750° c. and at 800° c. the dissociation pressures were found to be 68 mm. and 168 mm. respectively, one has

$$\log_{10}\frac{68}{168}=\frac{q}{2{\cdot}303\times1{\cdot}987}\times\left(\frac{1073-1023}{1023\times1073}\right)$$

$$-0{\cdot}3928=\frac{q}{4{\cdot}577}\times\frac{50}{1023\times1073},$$

$$q=-\frac{0{\cdot}3928\times4{\cdot}577\times1023\times1073}{50}$$

$$=-39{,}460\text{ cal.}$$

The value determined experimentally by Julius Thomsen at ordinary temperatures is −42,900 cal.

A behaviour similar to that which has just been discussed

[1] J. Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 938.

is found also in the case of other systems in which a solid compound gives rise on dissociation to a solid and a gas, *e.g.*, salt hydrates, compounds of ammonia with silver chloride, etc.

As the change of the dissociation pressure with temperature follows the same general law as the change of vapour pressure of a liquid with temperature (p. 91), the heat of dissociation can be calculated from the slope of the curve obtained by plotting $\log p$ against $1/T$ where p is the dissociation pressure.

Dissociation of a Solid Compound into two Gaseous Compounds.—When crystalline ammonium hydrosulphide is sublimed, the molecules undergo practically complete dissociation in the vapour state into ammonia and hydrogen sulphide, and, at a given temperature, an equilibrium is established, represented by the expression $NH_4SH \rightleftharpoons NH_3 + H_2S$. Applying the law of mass action to this equilibrium, one obtains the expression

$$p_1 \times p_2 = K_p \cdot p_3,$$

where p_1, p_2, and p_3 are the partial pressures of ammonia, hydrogen sulphide, and ammonium hydrosulphide respectively. Since, however, p_3 must be constant, in presence of solid hydrosulphide, it follows that $p_1 \times p_2 = K'_p$. That is, at any given temperature the product of the partial pressures of ammonia and of hydrogen sulphide must be constant. If the dissociation pressure of the pure hydrosulphide is represented by P, then the partial pressure of each of the dissociation products will be $\frac{1}{2}P$, and, consequently, the product of the partial pressures will be $\frac{P^2}{4} = K'_p$. At 15·2° the dissociation pressure amounts to 263 mm., and at 27·6° to 572 mm.[1] The partial pressure of each of the dissociation products at the above temperatures would therefore be 131·5 mm. and 286 mm. respectively.

If to the above system in equilibrium one adds excess of one of the dissociation products, the partial pressure of that substance will be increased and, consequently, the partial pressure of the other dissociation product will be correspondingly diminished. In other words, the dissociation of the solid will be diminished, and a certain amount of

[1] J. Walker and J. S. Lumsden, *J. Chem. Soc.*, 1897, **71**, 428.

solid will be deposited. Moreover, while the *product* of the partial pressures of the dissociation products will remain constant, their *sum*, or the total pressure, will be all the greater the greater the difference between the partial pressures. This is confirmed by the following experimental numbers, obtained by Isambert in 1881 at the temperature 17·3°

NH_3, p_1.	H_2S, p_2.	$p_1 \times p_2$.	$p_1 + p_2$.
150 mm.	150 mm.	22,500 mm.	300 mm.
103 ,,	214 ,,	22,000 ,,	317 ,,
53·5 ,,	419 ,,	22,420 ,,	472·5 ,,
416 ,,	55·9 ,,	23,250 ,,	471·9 ,,

The deviation of the product of partial pressures from constancy is to be attributed to experimental error.

If the solid is vaporised in an atmosphere of one of the products of dissociation, dissociation is reduced. If the initial pressure of the product of dissociation is x mm., then, at equilibrium, $p'(x+p') = K'_p$, where $p' = \frac{1}{2}P'$, P' being the new dissociation pressure of the solid. Knowing x and K'_p, the dissociation pressure of the pure solid, p' and P', can be calculated.

The law of mass action may also be applied to the equilibria produced by the dissociation of pairs of substances which give rise to a common product of dissociation, *e.g.*, mixtures of ammonium hydrosulphide and dimethylammonium hydrosulphide,[1] These two compounds, on dissociation, give rise to the equilibria

$$NH_4HS \rightleftharpoons NH_3 + H_2S$$
$$NH_2(CH_3)_2HS \rightleftharpoons (CH_3)_2NH + H_2S,$$

the common product of dissociation being hydrogen sulphide.

If P_1 and P_2 are the dissociation pressures of the pure hydrosulphides at the given temperature, and if p_1 and p_2 are the partial pressures of ammonia and of dimethylamine in the gas mixture, then the partial pressure of the hydrogen sulphide will be (p_1+p_2). On applying the law of mass action one obtains the two equations

$$p_1(p_1+p_2) = \frac{P_1^2}{4} \text{ and } p_2(p_1+p_2) = \frac{P_2^2}{4}.$$

[1] J. Walker and J. S. Lumsden, *loc. sit.*

If P_1 and P_2 are known, one can calculate the partial pressures p_1 and p_2 and the total pressure $[p_1+p_2+(p_1+p_2)]=2(p_1+p_2)$.

In the case of the dissociation of ammonium carbamate there is produced the equilibrium

$$NH_2 . CO . ONH_4 \rightleftharpoons 2NH_3+CO_2,$$

and for the isothermal dissociation, therefore, one has the expression $p_1^2 \times p_2 = K_p . p_3$, where p_1, p_2, and p_3 are the partial pressures of ammonia, carbon dioxide, and ammonium carbamate respectively. Therefore, since p_3 is constant in presence of solid carbamate, $p_1^2 \times p_2 =$ constant. If P is the dissociation pressure at the given temperature of the pure carbamate, $p_1 = \frac{2}{3}P$ and $p_2 = \frac{1}{3}P$, and therefore $p_1^2 \times p_2 = \frac{4P^3}{27}$.

It is clear from this expression that addition of excess of ammonia will diminish the dissociation to a greater extent than will addition of excess of carbon dioxide.[1]

One other example of the application of the law of mass action to heterogeneous equilibria may be given. In the case of the classical reversible reaction,

$$Fe_3O_4+4H_2 \rightleftharpoons 3Fe+4H_2O,$$

the law of mass action gives, as the condition for equilibrium at a given temperature,

$$\frac{p_1^3 \times p_2^4}{p_3 \times p_4^4} = \text{constant},$$

where p_1 and p_3 are the partial pressures of Fe and of Fe_3O_4, and p_2 and p_4 are the partial pressures of water vapour and of hydrogen. Hence, it follows that at equilibrium, $\frac{p_2^4}{p_4^4}$, or the ratio of the partial pressures of water vapour and of hydrogen, is constant. The experimental values obtained

Water Vapour, p_2.	Hydrogen, p_4.	$\frac{p_2}{p_4}$.
8·8	13·5	0·65
25·1	37·4	0·67
35·4	54·1	0·65
49·3	71·8	0·68

[1] Isambert, *Compt. rend.*, 1881, **93**, 731; 1883, **97**, 1212; T. R. Briggs and V. Migrdichian, *J. Phys. Chem.*, 1924, **28**, 1121.

at 900° C. by G. Preuner [1] confirm this prediction (see table on p. 402).

The Distribution Law.—In 1872 it was found by Berthelot and E. Jungfleisch [2] that when iodine in varying amounts is added to a mixture of carbon disulphide and water, or when solutions of iodine in carbon disulphide are shaken with water, the iodine distributes itself between the two solvents in such a way that, at a given temperature, the ratio of concentrations is constant. That is,

$$\frac{\text{Concentration of iodine in carbon disulphide}}{\text{Concentration of iodine in water}} = \frac{c_1}{c_2} = K.$$

The constant K is known as the *partition coefficient*. The results obtained by Berthelot and Jungfleisch at 18° are shown in the following table :—

Grams of Iodine in 10 ml. CS_2 (c_1).	Grams of Iodine in 10 ml. H_2O (c_2).	$K = \frac{c_1}{c_2}$.
1·74	0·0041	420
1·29	0·0032	400
0·66	0·0016	410
0·41	0·0010	410
0·076	0·00017	440

A similar behaviour is found in the case of the distribution of succinic acid at 15° between water and ether, as the numbers in the following table show :—

Grams of Acid in 10 ml. of Water.	Grams of Acid in 10 ml. of Ether.	$\frac{c_1}{c_2}$.
0·024	0·0046	5·2
0·070	0·013	5·2
0·121	0·022	5·4

It was pointed out, however, by Nernst in 1891 that the ratio c_1/c_2 is constant *only when the solute has the same molecular weight in each of the solvents*, and the distribution law may therefore be formulated thus : *When a solute distributes itself between two non-miscible solvents*,[3] *there exists* FOR

[1] *Z. physikal. Chem.*, 1904, **47**, 385.

[2] *Ann. chim. phys.*, 1872, [4], **26**, 396, 408.

[3] The law does not apply when the two solvents are appreciably soluble in each other, or when their mutual solubility is altered by the solute.

EACH MOLECULAR SPECIES, *at a given temperature, a constant ratio of distribution between the two solvents, and this ratio is independent of any other molecular species which may be present.*

The law just stated holds strictly only for ideally dilute solutions. If it were valid at all concentrations, then, on shaking two non-miscible solvents with excess of a solute, two saturated solutions would be obtained, and the partition coefficient would be equal to the ratio of the solubilities of the solute in the two solvents. This may be regarded as being approximately the case when the solute is only slightly soluble.

When the solute does not have the same molecular weight in the two solvents, the ratio of concentrations c_1/c_2 will no longer be constant.

If, in the second solvent, associated molecules A_n are formed, there will exist the equilibrium $A_n \rightleftharpoons nA$ between the associated and unassociated molecules. If α is the fraction of the associated molecules which is dissociated into the simple molecules, the concentrations of the associated and unassociated molecules at equilibrium will be $(1-\alpha)c$ and $n \,.\, \alpha c$; and, therefore, according to the law of mass action, $(\alpha c)^n/(1-\alpha)c = \text{constant}$. When α is small, that is, when the degree of association is large, α may be neglected compared with unity, and therefore $\alpha c = K \,.\, \sqrt[n]{c}$. In other words, the concentration of the simple molecules is proportional to $\sqrt[n]{c}$. The partition coefficient then becomes $c_1/\sqrt[n]{c_2} = K$.

This relation is confirmed in the case of the distribution of benzoic acid between water and benzene, the acid existing mainly as associated molecules, $(C_6H_5COOH)_2$, in benzene solution. The experimental numbers are given in the following table :—

Grams of Benzoic Acid in 10 ml. of Water.	Grams of Benzoic Acid in 10 ml. of Benzene.	$\frac{c_1}{c_2}$.	$\frac{c_1}{\sqrt{c_2}}$.
0·0150	0·242	0·062	0·0305
0·0195	0·412	0·048	0·0304
0·0289	0·970	0·030	0·0293

Whereas the ratio c_1/c_2 shows great variation, the ratio $c_1/\sqrt{c_2}$ is nearly constant. When the solutions are made very dilute, the ratio $c_1/\sqrt{c_2}$ no longer remains constant, owing

to the increase in the ionisation of benzoic acid in aqueous solution and to the increasing dissociation of the associated molecules in the benzene solution.[1] From the change in the value of the partition coefficient in dilute solutions the extent of the dissociation of the associated molecules can be calculated.

Thus, let c_1 = the concentration of the solute in the aqueous layer, c_2 = the concentration in the benzene layer, and α = the degree of ionisation of the acid in water. Then $c_1(1-\alpha)$ will be equal to the concentration of the normal unionised molecules in the aqueous layer.

If d is the affinity constant of the acid, $d = \alpha^2/(1-\alpha)v$, where v is the volume in litres containing 1 gram-molecule of acid. Hence,

$$\alpha = \frac{d \cdot v}{2}\left(\sqrt{1+\frac{4}{d \cdot v}} - 1\right).$$

(For benzoic acid, $d = 6 \times 10^{-5}$.)

Further, according to the distribution law, the ratio of concentrations of the single molecules in the two solutions is constant. Therefore, if m = concentration of the *single* molecules in benzene, $\frac{c_1(1-\alpha)}{m} = k$ or $m = \frac{c_1(1-\alpha)}{k}$. On applying the law of mass action to the dissociation of the double into single molecules, one obtains the relation $\frac{m^2}{c_2 - m} = K$, since $(c_2 - m)$ is the concentration of the double molecules. On inserting the value of m from the preceding equation, one finds

$$K = \frac{[c_1(1-\alpha)]^2}{k^2 \cdot c_2 - c_1(1-\alpha)k}.$$

Since K is constant independently of the concentration, it follows that for any other concentrations c_1' and c_2' in the aqueous and benzene solutions,

$$\frac{[c_1'(1-\alpha')]^2}{k^2 \cdot c_2' - c_1'(1-\alpha')k} = K = \frac{[c_1(1-\alpha)]^2}{k^2 \cdot c_2 - c_1(1-\alpha)k}.$$

With the help of these two equations the value of k can be calculated. From the value of k one can obtain the value of m and hence also the value of K, the dissociation constant of the complex molecules. The correctness of the above equations is supported by the experimental numbers given in the following table :—

DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE AT 10°

c_1.	c_2.	Molecular Volume.	α.	$c_1(1-\alpha)$.	m.	$c_2 - m$.	$K = \frac{m^2}{c_2 - m}$.
0·0429	0·1449	568	0·169	0·0357	0·0510	0·0939	0·0277
0·0562	0·2380	434	0·149	0·0474	0·0677	0·1703	0·0269
0·0823	0·4726	296	0·125	0·0720	0·1029	0·3697	0·0286
0·1124	0·8843	217	0·104	0·1007	0·1439	0·7404	0·0279
0·1780	2·1777	137	0·0866	0·1626	0·2323	1·9454	0·0277
0·2430	4·0544	100·4	0·0747	0·2249	0·3213	3·7331	0·0276
0·2817	5·4851	86·6	0·0695	0·2621	0·3743	5·1108	0·0274
						Mean .	0·0277

[1] W. S. Hendrixson, *Z. anorgan. Chem.*, 1897, **13**, 73.

Applications of the Distribution Law.—From what has been said above it is clear that from a study of the ratio of distribution of a substance between two non-miscible solvents, the *relative* molecular weight of the substance in the two solvents can be determined. Further, from the change, if any, in the value of the partition coefficient with dilution, information can be obtained regarding changes in the molecular weight due to association or dissociation. Determinations of the distribution of a substance between two non-miscible solvents may also be employed for the investigation of various homogeneous equilibria, of which the following cases may be taken as examples :—

1. *Hydrolysis of Salts.*—Since in the aqueous solution of a salt of a weak base and a strong acid, or of a weak acid and a strong base, there is an equilibrium between the salt, the free base, and the free acid, this equilibrium can be calculated from determinations of the partition of the weak base or weak acid between water and another solvent, such as benzene or chloroform.

Thus, if an aqueous solution of, say, aniline hydrochloride, which is partially hydrolysed into aniline and hydrochloric acid, is shaken with benzene, the free aniline will distribute itself between the water and the benzene in the ratio of the partition coefficient. Hence, from the concentration of aniline in the benzene solution, the concentration of the free aniline, and from this the degree of hydrolysis, in the aqueous solution, can be calculated in the following manner :—

The hydrolysis of a salt is represented by the equation

$$\text{Salt} + \text{water} \rightleftharpoons \text{base} + \text{acid},$$

and for all mixtures of acid and base, or of salt and water, the equilibrium is given by the law of mass action as $m_1 \times m_2 = k \,.\, m_3 \times m_4$, where m_1, m_2, m_3, m_4 are the concentrations of base, acid, salt, and water respectively. Since the concentration of the water can be regarded as constant, m_4 is constant, and $k \,.\, m_4$ may be put equal to K.

Let c_1 = initial amount of hydrochloric acid.
c_2 = initial amount of aniline (or weak base).
c = concentration in gram-equivalents per litre of the weak base in the aqueous layer.
F = coefficient of partition of the base between water and the other solvent, say, benzene.
q = volume of benzene employed per 1000 ml. of water.

When the equilibrium is established, $c = m_1$, and if there are c g. in 1000 ml. of the aqueous solution, there must be cqF g. in the benzene solution. Hence the total quantity of free base is $c(1 + q\text{F})$. The initial amount of base was c_2, hence there must be $c_2 - c(1 + q\text{F})$ g. of the base in the form of the salt (existing in the aqueous layer only). The concentration of the salt is therefore $m_3 = c_2 - c(1 + q\text{F})$. There must, of course, be an equivalent amount of acid in combination, and as the initial amount was c_1, the amount of combined acid must be $c_1 - c_2 + c(1 + q\text{F})$ g. As the salt exists only in the aqueous layer (1000 ml. in volume), the concentration of the acid is $m_2 = c_1 - c_2 + c(1 + q\text{F})$.

Substituting these values for m_1, m_2, and m_3 in the above equation, one obtains

$$c[c_1 - c_2 + c(1 + q\mathrm{F})] = K \,.\, [c_2 - c(1 + q\mathrm{F})],$$

or

$$K = \frac{c[c_1 - c_2 + c(1 + q\mathrm{F})]}{c_2 - c(1 + q\mathrm{F})}.$$

If the acid and base are taken in equivalent proportions, *i.e.*, if one dissolves the salt in water, then $m_1 = m_2$, and $m_3 = c_2 - m_1$. Hence $m_1^2 = K \,.\, (c_2 - m_1)$.

Having obtained the value of K and knowing the value of c_2, one can calculate the value of m_1. The degree of hydrolysis, however, is the ratio of free base actually present to what would be present if no salt formation took place, *i.e.*, if the whole of the base taken remained free. The degree of hydrolysis is therefore given by m_1/c_2, or the percentage hydrolysis by $100m_1/c_2$.

The following determinations of the degree of hydrolysis of aniline hydrochloride may be given in illustration.[1] The volume of benzene per 1000 ml. of water (q) may be taken as 59 ml.

HYDROLYSIS OF ANILINE HYDROCHLORIDE AT 25°

Base.	F.	Initial Concentration of Acid and Base.	Weight of Hydrochloride from 50 ml. of Benzene Solution.	c.	Percentage Hydrolysis.
Aniline	10·1	0·09969	0·0806	0·00123	1·56
		0·03138	0·0406	0·000621	2·51

2. *Constitution of Complex Halide Ions.*—The reaction between bromine and bromides and between iodine and iodides can also be studied by means of distribution determinations.[2] If a solution of bromine in carbon disulphide is shaken with water the bromine will distribute itself between the two solvents, and the concentration in the aqueous layer will be, say, D gram-molecules per litre. On shaking the carbon disulphide solution with an aqueous solution of potassium bromide containing A gram-molecules per litre, the concentration of bromine in the aqueous layer is found to be B gram-molecules per litre. The quantity (B − D) gram-molecules must therefore have combined with the bromide ion, the potassium bromide being regarded as completely ionised. If it be assumed that the ion Br_3' is formed, there will be an equilibrium in the aqueous solution represented by the expression $Br_3' \rightleftharpoons Br_2 + Br'$. If, then,

$$[Br_3'] = c = (\mathrm{B} - \mathrm{D}),$$
$$[Br_2] = c_2 = \mathrm{D},$$
$$[Br'] = c_1 = \mathrm{A} - (\mathrm{B} - \mathrm{D}),$$

then, according to the law of mass action,

$$\frac{[Br_2] \times [Br']}{[Br_3']} = \frac{\mathrm{D}[\mathrm{A} - (\mathrm{B} - \mathrm{D})]}{(\mathrm{B} - \mathrm{D})} = K.$$

[1] R. C. Farmer, *J. Chem. Soc.*, 1901, **79**, 863; R. C. Farmer and Warth, *ibid.*, 1904, **85**, 1713.

[2] M. Roloff, *Z. physikal. Chem.*, 1894, **13**, 341; A. A. Jakowkin, *ibid.*, 1896, **20**, 19; H. M. Dawson, *J. Chem. Soc.*, 1901, **79**, 238.

The constancy of K, calculated from the experimental determinations carried out by Roloff at 32·6°, as indicated in the following table, confirms the accuracy of the above assumption.

D.	B.	A.	K.
0·0261	0·1111	0·250	0·0507
0·0259	0·0686	0·125	0·0499
0·0257	0·0472	0·0625	0·0490

The reaction between ammonia and copper sulphate in aqueous solution may also be studied by means of distribution experiments.[1]

[1] H. M. Dawson, *J. Chem. Soc.*, 1906, **89**, 1666.

CHAPTER XVII

HETEROGENEOUS EQUILIBRIA. THE PHASE RULE

The Phase Rule.—Although, as was pointed out in the preceding chapter, the law of mass action can be applied in the case of certain heterogeneous systems with the help of certain assumptions regarding the molecular state of the substances taking part in the equilibria, the mass law cannot be applied to very many heterogeneous equilibria when neither the number of different molecular aggregates nor the degree of their complexity is known. In 1874, however, Josiah Willard Gibbs enunciated the general theorem, usually known as the PHASE RULE, by which he defined the conditions of equilibrium in a heterogeneous system as a relation between the number of what are called the *phases* and the *components* of the system.[1] The phases of a system are *the different homogeneous but physically distinct portions which are marked off in space and separated from the other portions of the system by boundary surfaces.* Thus, ice, water, and water vapour are three phases of the same chemical substance, water. Although a phase must be physically homogeneous, it need not be chemically simple. Thus, a gaseous mixture or a solution may form a phase. In the case, for example, of the system, sodium chloride—saturated solution—vapour, there are three phases, a solid, a liquid, and a gaseous, the liquid phase being a homogeneous mixture.

The *components* of a system are not to be confused with the *constituents*. As employed in the statement of the phase rule, components are defined as *the* SMALLEST NUMBER *of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.*

[1] For a fuller account of the Phase Rule than can be given here, see **Findlay**: ***The Phase Rule and its Applications*** **(Dover Publications).**

Thus in the case of the system $CaCO_3 \rightleftharpoons CaO + CO_2$ there are three constituents in equilibrium, but the number of components is only two ; and any two of the constituents may be selected as components. Thus, making, as is usual, the simplest choice, that of CaO and CO_2, one can express the composition of all the phases present by the following equations :—

$$CaCO_3 = CaO + CO_2,$$
$$CaO = CaO + 0CO_2,$$
$$CO_2 = 0CaO + CO_2.$$

It should always be borne in mind that it is the *number*, not the *nature*, of the components that is of importance. In any given system the *number* of the components is definite, but may alter with alteration of the conditions of experiment. At ordinary temperatures, water forms a one-component system ; but if the temperature is raised to such a degree that dissociation of the water vapour takes place, the system becomes one of two components, namely, hydrogen and oxygen. The number of components being fixed, the actual selection of the components is made on grounds of simplicity, suitability, or generality of application.

The phase rule can be stated in the equational form

$$F = C + 2 - P,$$

or

$$F = n + 2 - r,$$

where C and n are the number of components, P and r are the number of coexisting phases, and F is what is known as the *degree of freedom*, or *variance*, of the system. By " degree of freedom " one means *the number of variable factors, temperature, pressure and composition of the phases,*[1] *which must be arbitrarily fixed in order that the condition of the system may be perfectly defined.*

Thus if one is dealing with one component existing in a single phase, we have

$$F = 1 + 2 - 1 = 2.$$

The system has two degrees of freedom and is said to be *bivariant.* For example, when a given mass of water exists solely as vapour, the state of the system is undefined unless two of the variables—pressure, temperature,

[1] Equilibrium may be influenced by electrical, surface, gravitational or other forces, but these are excluded from consideration here.

concentration (or volume)—are fixed. At any given temperature the vapour can exist under different pressures and occupy different volumes; but if two variables are fixed, *e.g.*, pressure and temperature, then the volume is definite. The condition of the system is perfectly defined.

On the other hand, if the system consists of the two phases, water and vapour, there is only one degree of freedom, or the system is *univariant*. If the temperature is arbitrarily fixed, the pressure under which water and vapour can coexist in equilibrium is also determined. At any given temperature, water has a certain definite vapour pressure. If the conditions are altered—if, for example, the volume of the vapour is diminished—a change in the relative amount of the phases, a so-called *phase reaction*, consisting in this case in a condensation of vapour to liquid, will take place and the pressure will remain constant. Continued diminution of the volume will, of course, lead to the ultimate disappearance of the vapour. Conversely, if the volume is increased, liquid will pass into vapour until the equilibrium pressure for the given temperature is re-established.

Finally, if there are three phases—ice, water, and vapour—coexisting in equilibrium, then the system has no degrees of freedom. It is *invariant*. Three phases of a one-component system can coexist in equilibrium only at one particular temperature and under one particular pressure; and any variation of these factors will lead, by means of phase reactions, to the ultimate disappearance of one or more of the phases, and therefore to the destruction of the system.

The nature of the phase reactions which will take place when the external conditions of a system in equilibrium are altered can be predicted by means of the *theorem of Le Chatelier* (p. 277). Thus, if heat be added to a system in equilibrium, phase reactions will take place which are accompanied by *absorption of heat*; and if heat is withdrawn from a system in equilibrium, reactions will take place which are accompanied by *evolution of heat*. Further, if the pressure on a system in equilibrium is increased, phase reactions will take place which are accompanied by a diminution of volume.

It is important to remember that the phase rule applies only to systems which are in true equilibrium, the chief criterion of which is that the same condition of equilibrium is reached from whichever side it is approached. Thus,

water in contact with hydrogen and oxygen at the ordinary temperature does not form a true equilibrium. On changing the pressure and temperature continuously within certain limits there is no continuous change in the relative amounts of the two gases; but on heating to a sufficiently high temperature there is a sudden change, and the system does not regain its original condition on being cooled to the initial temperature.

The phase rule is a generalisation of the very highest importance, for it not only gives the conditions under which heterogeneous equilibria can exist, but, resting as it does on a purely thermodynamic basis, it is independent of all hypotheses and theories regarding the constitution of matter and the nature of chemical change. The classification, also, of systems by means of the phase rule, according to their variance, enables one to understand why systems which are, apparently, quite different in nature, behave in a similar manner; and it has led to the recognition of otherwise unobserved resemblances between different systems.

Deduction of the Phase Rule.—If a substance exists in two different states, or in two different phases of a system, equilibrium can occur only when the intensity factor of chemical energy, or the *chemical potential*, is the same. This potential depends not only on the composition of the phase but also on the temperature and the pressure (or volume). If, therefore, a system of C components exists in P phases, it is necessary to know the masses of $(C-1)$ components in each of the phases in order to fix the composition of unit mass of each phase. As regards the composition, therefore, each phase possesses $(C-1)$ variables. Since there are P phases, it follows that, as regards composition, the whole system possesses $P(C-1)$ variables. Besides these there are, however, two other variables, viz., temperature and pressure, so that altogether a system of C components in P phases possesses $P(C-1)+2$ variables.

In order to define the state of a system completely it will be necessary to have as many equations as there are variables. If there are fewer equations than there are variables, then, according to the deficiency in the number of the equations, one or more of the variables will have an undefined value; and values must be assigned to these variables before the system is entirely defined. The number of these undefined values gives the variability or the degree of freedom of the system.

The equations by which the system is to be defined are obtained from the relationship between the potential of a compound and the composition of the phase, the temperature and the pressure. Further, as already stated, equilibrium occurs when the potential of each component is the same in the different phases in which it is present. If, therefore, one chooses as standard one of the phases in which all the components occur, then in any other phase in equilibrium with it the potential of each component must be the same as in the standard phase. For each phase in equilibrium with the standard phase, therefore, there will be a definite equation of state for each component in the phase; so that if there are P phases, there will be for each component $(P-1)$ equations, and for C components, therefore, there will be $C(P-1)$ equations.

There are, however, as we have seen, $P(C-1)+2$ variables, and as there

are only C(P − 1) equations, there must be P(C − 1) + 2 − C(P − 1) = C + 2 − P variables undefined. That is to say, the degree of freedom (F) of a system consisting of C components in P phases is F = C + 2 − P.

Systems of one Component

From the equational statement of the phase rule it is clear that when there is only one component existing in one phase the maximum variance is 2. All systems of one component can therefore be perfectly defined by giving values to, at most, two variable factors ; and the equilibrium conditions can be most conveniently represented graphically by a system of rectangular co-ordinates, the axes of which are pressure and temperature (*pt*-diagram). In such a diagram, invariant systems will be represented by points, univariant systems by lines, and bivariant systems by areas. *In a one-component system more than three phases cannot coexist in true equilibrium.*

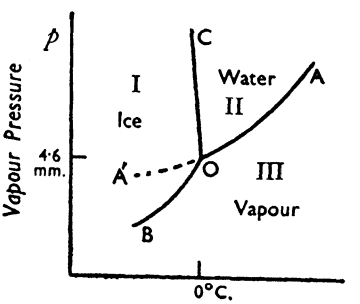


Fig. 106.

In Fig. 106 is given, by way of illustration, a diagrammatic representation of the equilibrium conditions in the case of the substance water in the neighbourhood of 0° C. Since one component, capable of existing in the three phases, solid, liquid, and vapour, can form three univariant systems, we have, in Fig. 106, three curves representing the conditions under which ice and vapour (curve BO), water and vapour (curve OA), and ice and water (curve OC) respectively can coexist in equilibrium. These curves are known as the sublimation curve, vaporisation curve, and curve of fusion respectively. The *direction* of these curves can, as has been pointed out (p. 277), be predicted by the theorem of Le Chatelier ; and the rate of variation of the equilibrium with temperature or pressure can be calculated by means of the Clausius-Clapeyron equation (p. 294). Owing to the fact that the melting of ice is accompanied by a diminution of volume, the melting-point of ice is lowered by increase of pressure (p. 295), and the curve OC, therefore, slopes towards the pressure axis. In those cases where melting is

accompanied by an increase of volume, the melting-point will be raised by increase of pressure, and the curve will slope away from the pressure axis.

When the three phases, ice, water, and vapour, coexist in equilibrium, they form an invariant system. This system, therefore, can exist only at a definite value of the temperature and pressure, represented by the point O (Fig. 106), which is known as a *triple point*, or point at which three phases are in equilibrium in a one-component system This point is, as one sees, the point of intersection of curves of three univariant systems.

At one time it was thought that the curve for solid and vapour passed continuously into the curve for liquid and vapour, but it follows quite clearly from the Clapeyron equation,

$$T\frac{dp}{dT}=\frac{q}{(v_2-v_1)},$$

that this cannot be so. For the transformation solid—→vapour the value of q is greater than for the transformation liquid—→vapour; and since (v_2-v_1) is nearly the same in the two cases, it follows that $\frac{dp}{dT}$ must be greater in the former case than in the latter. That is, the curve for solid and vapour must, in the neighbourhood of the triple point, ascend more rapidly than the curve for liquid and vapour, and the two curves, therefore, must intersect.

Owing to the fact that the triple point for solid-liquid-vapour (S—L—V) represents the temperature at which these three phases are in equilibrium *under the pressure of their vapour* (4·6 mm.), the triple point is not coincident with the normal melting-point of the solid, or the melting-point *under atmospheric pressure* (760 mm.). Since the melting-point of ice is lowered by nearly 0·0Q8° by an increase of pressure of 1 atmosphere, the triple point must lie at about 0·008°, the melting-point of ice under atmospheric pressure being 0°.

Owing to the small volume change on fusion and the relatively large value of the latent heat of fusion of ice, the effect of pressure on the equilibrium temperature is very small. In the case of other substances the effect is greater and, as a general rule, increase of pressure by 1 atmosphere changes the melting-point of a substance by about 0·03°.

The comparatively slight effect produced by pressure on the temperature of equilibrium is characteristic of all systems which are composed only of solid and liquid phases. Such systems are called *condensed systems*.

In Fig. 106 the three curves form the boundaries of three fields or areas which give the conditions of temperature and pressure under which the single phases, solid, liquid, and

vapour, are capable of stable existence. These different areas, as marked in Fig. 106, are regions of stability of the phase common to the two curves by which the area is enclosed. Since the curve for liquid and vapour ends abruptly at the critical temperature, the fields for liquid and vapour will flow into each other above this temperature.

Metastable States Equilibrium.—Although a crystalline solid cannot be heated above its melting-point without fusion occurring, a liquid can, with due care, be cooled below the melting-point of the solid without crystallisation taking place. The liquid is said to be *supercooled*. So long as the presence of the solid phase is carefully avoided, the supercooled liquid can be kept indefinitely without solidifying; and the system, supercooled liquid and vapour, behaves in every way like a stable system. So soon, however, as a small particle of the solid phase is brought in contact with the supercooled liquid, crystallisation takes place. A system which in itself is stable, and which becomes unstable only in contact with a particular phase, is said to be *metastable*. Supercooled water, therefore, is in a metastable condition.

As has already been pointed out, the sublimation curve for ice ascends more rapidly than the vaporisation curve for water in the neighbourhood of the triple point. It follows, therefore, that if the vaporisation curve OA be continued downwards to temperatures below the triple point the continuation of the curve OA′ must lie above the sublimation curve. In other words, the vapour pressure of a supercooled liquid (*metastable system*) must be higher than the vapour pressure of the solid (stable system) at the same temperature. This conclusion is confirmed experimentally, as the numbers in the table below show.

VAPOUR PRESSURE OF ICE AND OF SUPERCOOLED WATER

Temperature.	Pressure in Millimetres of Mercury.		
	Water.	Ice.	Difference.
0°	4·579	4·579	0·000
—2°	3·952	3·879	0·073
—4°	3·404	3·277	0·127
—8°	2·509	2·322	0·187
—10°	2·144	1·947	0·197

The behaviour may be generalised. *In a one-component system the vapour pressure of a metastable phase is, at a given temperature, greater than that of the stable phase.*

Polymorphism.—It has already been mentioned that a substance may frequently exist in more than one crystalline form, possessing different physical properties. According to the definition of phases (p. 409), each of these polymorphic forms constitutes a separate phase of the particular substance, and, consequently, the number of possible systems which may, in such a case, be formed may be considerably increased.

Since in a one-component system there can never be more than three phases in true equilibrium, two different crystalline forms of a substance can coexist in stable equilibrium only with vapour or with liquid, not with both vapour and liquid. Two new triple points, therefore, become possible, namely, S_1—S_2—V and S_1—S_2—L, where S_1 and S_2 denote the two different crystalline forms.

Transition Point.—Just as the triple point S—L—V is the point of intersection of two univariant curves S—V and L—V, so the triple point S_1—S_2—V is the point of intersection of the two curves S_1—V and S_2—V. Below the triple point only one of the solid phases (S_1) can exist in stable equilibrium with vapour; above the triple point only the other solid phase (S_2) will be stable. The triple point S_1—S_2—V is therefore a point at which the relative stability of the two solid phases undergoes change. If more than two crystalline forms are capable of stable existence, other triple points, *e.g.*, S_2—S_3—V, will be possible.

The triple point S_1—S_2—V is also the point of intersection of a third curve, that for the system S_1—S_2. Since this is a univariant system, the temperature at which the two solid phases can coexist will depend on the pressure. When the pressure is the atmospheric pressure, the temperature at which the two solid phases can coexist, and at which the relative stability undergoes change, is known as the *transition point.*

In the following table is given a short list of polymorphic substances and the temperatures of the transition point :—

Substance.	Transition Point.
Ammonium Nitrate—	
α-rhombic ⟶ β-rhombic	32·3°
β-rhombic ⟶ rhombohedral	84·2°
Rhombohedral ⟶ cubic	125·2°
Mercuric iodide	126°
Sulphur	95·5°
Tin	13°

The influence of pressure on the temperature at which two solid phases can coexist in equilibrium, or the influence of pressure on the transition point, can be calculated by means of the Clapeyron equation $\frac{dT}{dp} = \frac{T(v_2 - v_1)}{q}$. Since the passage of the form stable at lower temperatures into the form stable at higher temperatures is accompanied by absorption of heat, q is positive. If, further, $(v_2 - v_1)$ is positive, then $\frac{dT}{dp}$ will be positive, and the transition temperature will be *raised* by increase of pressure. If, however $(v_2 - v_1)$ is negative, the transition temperature will be *lowered* by increase of pressure. Thus the transformation of α-rhombic into β-rhombic ammonium nitrate is accompanied by an increase of volume, while the transformation of β-rhombic into rhombohedral ammonium nitrate is accompanied by a decrease of volume. In the former case the transition point is raised, and in the latter case it is lowered, by increase of pressure, as is shown by the following numbers :—

α-rhombic⟶β-rhombic.		β-rhombic⟶rhombohedral.	
Pressure in Kilograms per Square Centimetre.	Temperature.	Pressure in Atmospheres.	Temperature.
1	32·0°	1	85·85°
200	38·5°	100	84·38°
600	52·9°	200	83·03°
800	60·8°	250	82·29°

Enantiotropy and Monotropy.—In the examples of polymorphism just considered, each crystalline form is stable throughout a definite range of temperature and is capable of undergoing *reversible* transformation into another crystalline

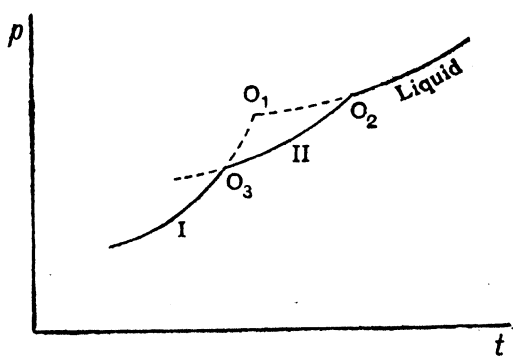


FIG. 107.

form at a definite temperature, the transition point, which lies below the melting-point of the substance. These different pairs of crystalline forms are said to be *enantiotropic*, and the phenomenon is spoken of as enantiotropy.

In the case of an enantiotropic substance, the equilibrium *pt*-diagram will be of the type shown in Fig. 107. Curves I and II are sublimation curves for the two crystalline forms and O_3 is the transition point. O_2 is the melting-point of the crystalline form stable at temperatures above the transition point. The dotted lines represent metastable equilibria, O_1 being the (metastable) melting-point of the crystalline form stable at temperatures below the transition point O_3.

Another behaviour, however, can also be observed. In the case of a number of polymorphic substances, it is found that only one of the solid forms is stable at all temperatures up to the melting-point, the other form being metastable. In this case no transition point is realisable under atmospheric pressure, and transformation of the crystalline forms can take place *only in one direction*. Such behaviour is spoken of as *monotropy*, and the crystalline forms are said to be *monotropic*. The two crystalline forms of benzophenone which melt at 26° (metastable) and 48° (stable) respectively are monotropic. The conditions which obtain here will be understood from the diagram (Fig. 108). The full-drawn curves are the sublimation curve of the stable form and the vaporisation curve of the liquid. O_2 is the triple point S—L—V. The dotted lines represent metastable systems, O_1 being the melting-point of the metastable solid and O_3 the hypothetical transition point.

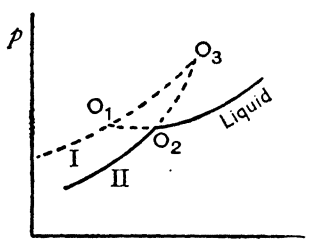


FIG. 108.

Law of Successive Reactions.—In preparative chemistry it is very frequently observed that when a substance is formed in a reaction it appears first not in its most stable form but in a metastable form, which then, more or less rapidly, passes into the stable condition. This behaviour, which was called by Wilhelm Ostwald the *law of successive reactions*, is observed with especial ease and frequency in organic chemistry, where it is often found that when a substance is thrown out from solution it is first deposited as a liquid or as a metastable crystalline solid, which passes later into the form stable at the particular temperature.

This *prior formation of the less stable form* can be readily

demonstrated, for example, by means of *p*-bromoacetanilide or by 2 : 4-dibromoacetanilide. These compounds separate out from solution as a voluminous mass of needle-shaped crystals. When left in contact with the mother liquor, however, these crystals change in time into the more stable compact crystalline form.[1]

The Equilibrium Diagram of the Substance Water.—As a result of the investigations carried out, more especially by Gustav Tammann, Professor of Physical Chemistry in the University of Göttingen, and by Percy Williams Bridgman, at Harvard University,[2] it has been established that water

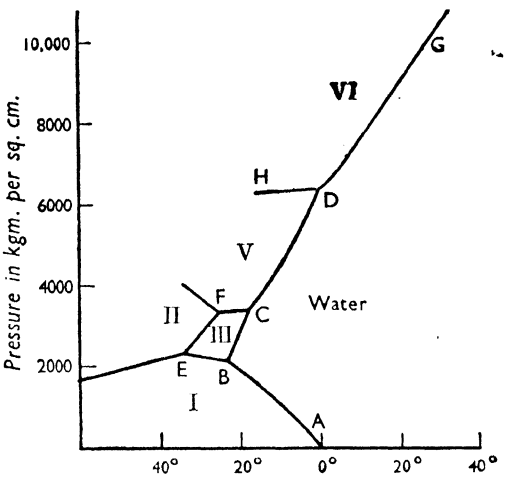


FIG. 109.

can crystallise not only in the form of ordinary ice but also in no fewer than four other enantiotropic crystalline forms, the different forms being designated as ice I (ordinary ice), ice II, ice III, ice V, ice VI.[3] It follows, therefore, that quite a number of stable systems can exist besides that already discussed between ordinary ice, water, and vapour; and a number of other triple points will be found at which three phases coexist in equilibrium. The behaviour found

[1] Chattaway and Lambert, *J. Chem. Soc.*, 1915, **107**, 1766.

[2] Tammann, *Annalen d. Physik*, 1900, [4], **2**, 1, 424; *Z. physikal. Chem.*, 1910, **72**, 609; Bridgman, *Z. anorgan. Chem.*, 1912, **77**, 377; *Proc. Amer. Acad.*, 1912, **47**, 441.

[3] The existence and stability relations of another form, ice IV, have not been definitely settled.

in the case of the substance water is represented graphically in Fig. 109, the values of pressure and temperature corresponding with the different triple points being shown in the following table :—

Point.	System.	Temperature.	Pressure Kilograms per Square Centimetre.
B	Ice I—ice III—liquid	−22·0°	2115
E	Ice I—ice II—ice III	−34·7°	2170
C	Ice III—ice V—liquid	−17·0°	3530
F	Ice II—ice III—ice V	−24·3°	3510
D	Ice V—ice VI—liquid	+ 0·16°	6380

Sulphur.—Sulphur exists in two well-known enantiotropic crystalline forms, rhombic and monoclinic.[1] Rhombic

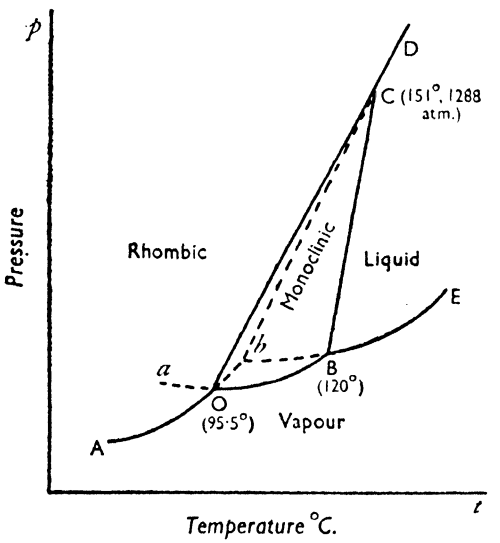


FIG. 110.

sulphur is the stable form up to the transition point 95·5°, and above this temperature monoclinic sulphur is stable. In Fig. 110 is given the equilibrium diagram for the different systems of sulphur as determined by Tammann, which, although not quite accurate, represents qualitatively the relations which exist.

[1] Other crystalline forms are also known, but they will not be considered here.

Point O is the triple point for rhombic sulphur—monoclinic sulphur—vapour, and is therefore the point of intersection of the three univariant curves, S_{rh}—V, S_{mon}—V, and S_{rh}—S_{mon}. At the triple point reversible transformation of rhombic and monoclinic sulphur can take place, these two forms of sulphur being *enantiotropic*. Both forms, however, may be obtained in the metastable state, and transformation to the stable form may take place with great slowness. The curves AO, OB, and BE represent the vapour-pressure curves of rhombic sulphur, monoclinic sulphur, and liquid sulphur respectively.[1] B, therefore, represents the triple point for monoclinic sulphur—liquid—vapour (119·3°).

Curve OC is the transition curve and represents the change of the transition point with pressure. Since the passage of rhombic into monoclinic sulphur is accompanied by an increase of volume ($\Delta v = 0{\cdot}01395$ ml. per gram), it follows that the transition point is raised by increase of pressure (p. 295). From the value of Δv and the heat of transformation, 3·12 cal. per gram, the value of $\frac{dT}{dp}$ can be calculated. Thus, for an increase of pressure of 1 atmosphere (1033·3 g. per sq. cm.), we have, since 1 cal. = 42,670 g.-cm.,

$$dT = \frac{368{\cdot}5 \times 0{\cdot}014 \times 1033}{3{\cdot}12 \times 42670} = 0{\cdot}04.$$

The transition point is raised 0·04° by an increase of pressure of 1 atmosphere.

Since sulphur melts with increase of volume, the melting-point is raised by increase of pressure. The fusion curve BC, therefore, slopes to the right. Since the transition curve also slopes to the right and to a greater extent than the fusion curve, these two curves must cut at a certain pressure and temperature. The point of intersection lies at 151° and a pressure of 1320 kg. per sq. cm., or about 1288 atmospheres. This, then, forms another triple point at which rhombic and monoclinic sulphur are in equilibrium with liquid sulphur. It is represented in the diagram by the point C. *Beyond this point, monoclinic sulphur ceases to exist in a stable condition.* At temperatures and pressures above point C, rhombic sulphur will be the stable modification.

Metastable Systems.—On account of the slowness with which transformation of one crystalline form into another takes place, it has been found possible to heat rhombic sulphur up to its melting-point, 112·8°, and one thus obtains a metastable triple point for S_{rh}—L—V (point *b*). The

[1] Ruff and Graf, *Z. anorgan. Chem.*, 1908, **58**, 209; West and Menzies, *J. Phys. Chem.*, 1929, **33**, 1880.

metastable fusion curve has also been realised. This curve must pass through the triple point C, and beyond this point *it becomes a stable fusion curve.*

As can be seen from Fig. 110, the triangular area OBC represents the conditions for the stable existence of monoclinic sulphur. The existence of this form of sulphur, therefore, is limited on all sides.

Tin.—The metal tin is also capable of existing in two crystalline forms, known as *white tin* and *grey tin.* The former is stable above and the latter is stable below the transition point, which lies at 13°. Owing to the fact that grey tin is less dense than white tin, the surface of the latter, on undergoing transformation into the former, becomes covered with a number of warty masses. On account of the appearance which is thus produced, the transformation of tin was called by Ernst Cohen, Professor of Physical Chemistry in the University of Utrecht, the " tin plague."

Liquid Crystals or Anisotropic Liquids. — A large number of substances, with long molecules, *e.g.*, cholesteryl acetate ($CH_3.COOC_{27}H_{45}$) and *p*-azoxyanisole ($CH_3O.C_6H_4.NON.C_6H_4.OCH_3$), have been discovered which possess the peculiar property of melting sharply, at a definite temperature, to milky liquids which, on being further heated, suddenly become clear, also at a definite temperature. The turbid liquids so obtained were found to be *anisotropic*, and were therefore called *liquid crystals* or *crystalline liquids.* Since, however, it has been found that the molecules in these turbid liquids are not arranged in a crystal lattice but parallelwise, it is better to use the term *anisotropic liquids.* The term *mesomorphic state* has also been suggested.

Various types of the mesomorphic state are believed to exist, of which the two most important are the *nematic* (or fibrous) and the *smectic* (or soapy). In the nematic type the molecules are arranged so that their axes are parallel, but without any other regularity of arrangement. In the smectic type, however, the molecules are regarded as being arranged in layers as well as with their axes parallel.[1]

Since the changes from crystalline solid to anisotropic liquid and from anisotropic liquid to isotropic liquid are reversible, the equilibrium conditions can be represented by a diagram similar to that employed in the case of enantiotropic substances, *e.g.*, sulphur. Thus, in Fig. 111 O is the triple point for solid, anisotropic liquid, and vapour, and

[1] See *Trans. Faraday Soc.*, 1933, **29**, 881.

B is the triple point for anisotropic liquid, isotropic liquid, and vapour. B corresponds, therefore, to the melting-point of a crystalline solid. Curves OE and BD are the transition and fusion curves respectively. In the case of *p*-azoxyanisole, O lies at the temperature 118·3°, and B at the temperature 135·9°. Increase of pressure by 1 atmosphere raises the transition point by 0·032° and the melting-point by 0·0485°. Curves OE and BD, therefore, both slope to the right, the latter to a greater extent than the former.

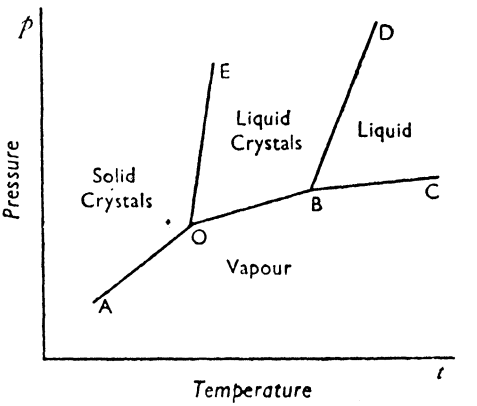


FIG 111.

Experimental Determination of the Transition Point.—In the discussion of polymorphic forms, equality of vapour pressure was taken as the condition for the stable coexistence of two crystalline forms of a substance. One is not, however, dependent on measurements of vapour pressure for the determination of transition points. When one crystalline form passes into another there is an abrupt change in the various physical properties, *e.g.*, density, and any method by which this abrupt change can be detected may be employed for the determination of the transition point.

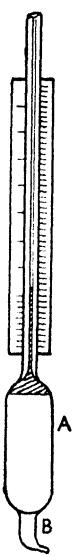


FIG. 112.

1. *Dilatometric Method.*—The change of density or specific volume can be determined by means of the dilatometer (Fig. 112). This consists of a bulb with capillary tube, and forms a sort of large thermometer. A quantity of the substance to be examined is introduced into the bulb through the tube B, which is then sealed off at the blowpipe. The rest of the bulb and a short portion of the capillary are filled with some liquid which is without chemical action on the substance. The dilatometer is placed upright in a large bath, the temperature of which can be slowly raised or lowered. As the temperature is slowly raised the rise in the level of the liquid will be practically uniform, but on passing through the transition point there will be a more or less sudden change in the rate of rise of liquid, owing to the change of volume of the solid.

2. *Solubility Method.*—The transition point is the point of intersection of the solubility curves of the two crystalline forms.

3. *Thermometric Method.*—This method depends on the fact that change from one system to another on passing through the transition point is accompanied by a heat effect—absorption or evolution of heat. On allowing the temperature of the system to fall slowly the rate of cooling will be fairly uniform until the transition point is reached. Owing to the fact that heat is evolved when the crystalline form stable at higher

temperatures passes into the form stable at lower temperatures, there will be a more or less well-marked "arrest" on the cooling curve at the transition point. This method is specially suitable in the case of metals.

4. *Colorimetric Method.*—In some cases, *e.g.*, mercuric iodide, the different crystalline forms have different colours. A small quantity of the substance may be placed in a thin-walled melting-point tube attached to the bulb of a thermometer and placed in a heating bath. On slowly raising the temperature through the transition point a change of colour will be observed.

5. *Electrometric Method.*—This method is applicable to metals, *e.g.*, tin, and to polymorphic forms of salts of metals. If a voltaic cell is constructed with white tin and grey tin as electrodes, and a solution of ammonium stannic chloride as electrolyte, grey tin will be the positive pole at temperatures below the transition point and white tin will be the positive pole at temperatures above the transition point. At the transition point the two electrodes will have the same potential, and no current will flow through a wire joining the two electrodes.

Systems of Two Components

When one applies the phase rule $F = C + 2 - P$ to systems of two components it is seen that the existence of *four* phases in equilibrium is necessary in order to give an invariant system. Two components in three phases constitute a univariant, two components in two phases a bivariant system. Whereas, in the case of one-component systems, the variance cannot exceed 2, in the case of two-component systems there may be a variance of 3. Two components existing in only one phase constitute a tervariant system. In addition to the pressure and temperature, therefore, a third variable factor must be chosen, and as such there is taken the *concentration of the components* in a phase or in phases of variable composition. In systems of two components, not only the pressure and temperature but also the composition of the phases may alter.

Since a two-component system may undergo three independent variations, a system of three co-ordinates in space would be required for the graphic representation of all the possible conditions of equilibrium. In most cases, however, it will be found sufficient to consider the changes brought about in a system by variation of only two of the variable factors, the third factor being regarded as constant. Thus, one may represent the relationship between pressure and temperature, the concentration remaining constant (*pt*-diagram); or one can consider the variation of concentration or composition with temperature, while the pressure remains constant (*tc*-diagram); or, lastly, pressure

and composition may be taken as the variables (*pc*-diagram). Use will be made of such diagrams in what follows.

The System Solid—Gas.—When calcium carbonate is heated, dissociation takes place into calcium oxide and carbon dioxide and gives rise to the equilibrium $CaCO_3 \rightleftharpoons CaO + CO_2$. Since the system is one of two components, CaO and CO_2, and since there are three phases present, namely, two solid phases ($CaCO_3$ and CaO) and one gaseous phase, the system must be univariant. If, therefore, the temperature is fixed, the pressure of the gas will also be defined ; that is, to each temperature there will correspond a certain maximum pressure of carbon dioxide (*dissociation pressure*), and the system will therefore behave like the one-component system, liquid—vapour. If the temperature is maintained constant, increase of volume of the system or reduction of the pressure will cause the dissociation of a further amount of the carbonate until the pressure again reaches the equilibrium value. Diminution of volume, similarly, will bring about the combination of calcium oxide and carbon dioxide.

The experimentally determined values for the equilibrium pressure of the system $CaCO_3 \rightleftharpoons CaO + CO_2$ were given on page 399.

Salts with Water of Crystallisation.—In the dehydration of crystalline salts containing water of crystallisation, one meets with a behaviour similar to that just described. When the salt $CuSO_4, 5H_2O$, for example, is heated, it passes into the salt $CuSO_4, 3H_2O$, and one obtains the equilibrium $CuSO_4, 5H_2O \rightleftharpoons CuSO_4, 3H_2O + 2H_2O_{vap.}$ Since there are three phases present (two solid and one gaseous), the system is univariant, and at a given temperature the vapour pressure of the system will be definite. The variation of pressure with temperature, therefore, will follow the same law as the vapour pressure of a pure liquid, as is indicated by curve A in Fig. 113. The values of the pressure are shown in the following table :—

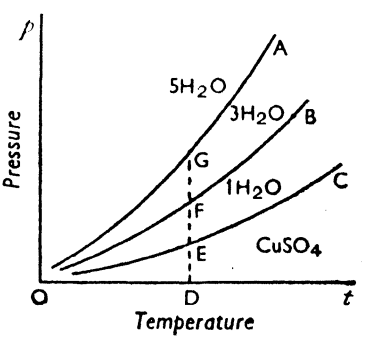


FIG. 113

DISSOCIATION PRESSURES OF COPPER SULPHATE HYDRATES

Temp.	$CuSO_4, 5H_2O \rightleftharpoons CuSO_4, 3H_2O + 2H_2O$.	$CuSO_4, 3H_2O \rightleftharpoons CuSO_4, H_2O + 2H_2O$.	$CuSO_4, H_2O \rightleftharpoons CuSO_4 + H_2O$.
25°	7·8 mm.	5·6 mm.	0·8 mm.
30°	11·6 ,,	...	...
35°	16·5 ,,	11·8 mm.	...
40°	23·2 ,,	...	...
45°	32·8 ,,	22·1 mm.	...
50°	45·4 ,,	30·9 ,,	4·5 mm.
80°	260·1 ,,	183·1 ,,	...

Similarly, the other two possible univariant systems,

$$CuSO_4, 3H_2O \rightleftharpoons CuSO_4, H_2O + 2H_2O,$$
$$CuSO_4, H_2O \rightleftharpoons CuSO_4 + H_2O,$$

will also possess a definite vapour pressure at a given temperature, as is indicated by the curves B and C in Fig. 113 and by the numbers in the above table.

To the dissociation pressure of a salt hydrate one may apply the equation (p. 100), $\frac{d \log_e p}{dT} = \frac{q}{RT^2}$, where q is the heat of dissociation (heat absorbed) per gram-molecule of water vapour. Since, for the vaporisation of pure water we have the expression, $\frac{d \log_e p_w}{dT} = \frac{L}{RT^2}$, where L is the latent heat of vaporisation per gram-molecule, it follows that

$$\frac{d \log_e \frac{p}{p_w}}{dT} = \frac{(q - L)}{RT^2}$$

$(q - L)$ represents the heat of combination of the salt with 1 gram-molecule of liquid water (heat of hydration).

The heat of dissociation of a compound may be calculated or be obtained by a graphic method, as in the case of heat of vaporisation (p. 99).

The phase rule also throws light on the behaviour of an anhydrous salt during hydration. If, at the temperature represented by D (Fig. 113), one adds water vapour to anhydrous copper sulphate contained in an exhausted vessel the pressure will rise without formation of hydrate taking place, because at pressures below the curve C only the anhydrous salt can exist. When the pressure of the vapour is increased to E, however, the hydrate $CuSO_4, H_2O$ will begin to be formed, and as there will now be three phases

present, namely, $CuSO_4$; $CuSO_4$, H_2O ; and water vapour, the system is *univariant* ; and since the temperature is kept constant, the pressure must also be constant. Continued addition of vapour will result merely in the phase reaction $CuSO_4 + H_2O \longrightarrow CuSO_4$, H_2O taking place. When the anhydrous salt has entirely disappeared, *i.e.*, has passed into the monohydrate, the system again becomes *bivariant* and the pressure increases, as shown by the line EF, as more and more water vapour is added. At F the hydrate $CuSO_4$, $3H_2O$ is formed, and the system again becomes univariant, the three phases present being $CuSO_4$, H_2O ; $CuSO_4$, $3H_2O$; and vapour. Since the temperature is constant, the pressure

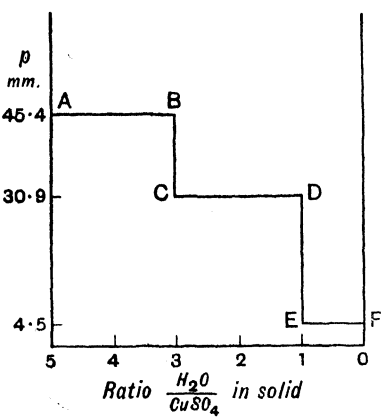


FIG. 114.

will remain constant until the monohydrate has all been converted into the trihydrate. The pressure will then rise with addition of water vapour until point G is reached, when the pentahydrate will be formed and the pressure will once more become constant.

Conversely, on dehydrating $CuSO_4$, $5H_2O$ at constant temperature (say, 50°), it would be found that the pressure would remain constant at the value of the dissociation pressure (45·4 mm.) of the system $CuSO_4$, $5H_2O$—$CuSO_4$, $3H_2O$—vapour, until all the pentahydrate had disappeared and only the trihydrate remained as solid phase (line AB, Fig. 114). Further removal of water would then cause the pressure to fall *abruptly* to the pressure (30·9 mm.) of the system $CuSO_4$, $3H_2O$—$CuSO_4$, H_2O—

vapour, at which value it would remain constant (line CD) until the trihydrate had passed into the monohydrate (at D), when a further sudden diminution of the pressure would occur. The line of constant pressure EF gives the value of the vapour pressure (4·5 mm.) of the system $CuSO_4$, H_2O—$CuSO_4$—H_2O at 50°.

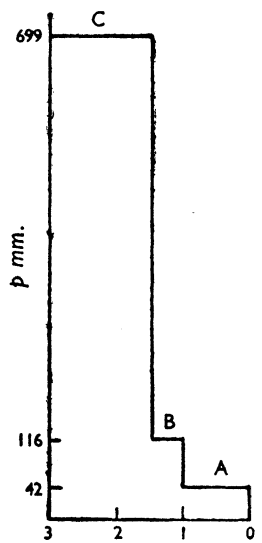


FIG. 115.

It will be clear from the previous discussion that if the partial pressure of the water vapour in the air is less than the dissociation pressure of a salt hydrate at the same temperature, the salt hydrate will give up all or part of its water of hydration. The hydrate will *effloresce*.

A behaviour similar to that shown by calcium carbonate and by the hydrates of copper sulphate will also be shown by other compounds which can dissociate into a solid and a gaseous phase. Thus, Fig. 115 gives the isothermal pressure-composition diagram for the two components NH_3 and AgCl at 16·3°. Here the lines A, B, and C represent the equilibrium pressures of the systems

$$AgCl,\ NH_3 \rightleftharpoons AgCl + NH_3,$$
$$2AgCl,\ 3NH_3 \rightleftharpoons 2(AgCl,\ NH_3) + NH_3,$$
$$2(AgCl,\ 3NH_3) \rightleftharpoons 2AgCl,\ 3NH_3 + 3NH_3$$

respectively.[1]

Constancy of Vapour Pressure and the Formation of Compounds.—The study of the isothermal *pc*-diagram of two component systems which form only solid and gaseous phases is of very great importance, because a means is thereby given of deciding whether the gas phase enters into combination with the solid phase or only undergoes adsorption or solution. Thus, when compounds are formed which dissociate with formation of a solid and a gaseous phase, there is a *step-wise* change in the equilibrium pressure when the gas phase is added to or withdrawn from the system at constant temperature. By this method the existence of oxycarbonates of lead and magnesium has been established,[2] and Wilder

[1] See also A. B. Hart and J. R. Partington, *J. Chem. Soc.*, **1943**, 104.

[2] M. Centnerszwer, G. Falk, and A. Awerbuch, *Z. physikal. Chem.*, 1925, **115**, 29.

D. Bancroft,[1] of Cornell University, employed the method in studying reactions between proteins and hydrogen chloride.

When no compound formation takes place between a solid and gaseous phase, but only adsorption or solution, a *continuous* curve will be obtained, because there will never be more than two phases present—a solid solution and a gas. At constant temperature, therefore, the system will be univariant, or the pressure will vary with the composition. Only in the case where two partially miscible solid solutions are formed, which may possibly occur with palladium and hydrogen, will a stepped curve be obtained in the case of solution formation.

Solutions

In all the cases which have been considered so far, the different phases consisted of a single substance of definite composition, or were definite chemical individuals. Systems, however, will now be studied in which one or more homogeneous phases of *variable composition* are present in equilibrium. To such phases of variable composition there is given the name *solution*, a solution being defined as a homogeneous mixture, the composition of which can undergo continuous variation within the limits of its existence.

The term solution is not restricted to any particular physical state of the substances, so that one may have solutions of gases in gases, in solids or in liquids ; of liquids in liquids or in solids ; of solids in liquids or of solids in solids. The definition of a solution, moreover, draws no distinction between solvent and solute, these being names applied to the two components when one or other of them is present in relatively large amount.

Liquid-Gas Systems. Solutions of Gases in Liquids.—When a gaseous component is passed into a liquid component, absorption or solution takes place to a greater or less extent, and a point is at length reached when the liquid absorbs no more of the gas ; a condition of equilibrium is attained, and the liquid is said to be saturated with the gas. Since there are two components and only two phases in equilibrium, the system is bivariant, and two of the variable factors,

[1] *J. Phys. Chem.*, 1930, **34**, 449, 753.

pressure, temperature, and composition of the solution, must be chosen in order that the condition of the system may be defined. Thus, if the temperature and the pressure are given definite values, the composition of the solution, or the concentration of the gas in the solution must have a definite value.

As the phase rule indicates, the solubility of a gas in a liquid will vary with the pressure, and the general effect of pressure on the solubility can be predicted by means of the theorem of Le Chatelier. Since the absorption of a gas is in all cases accompanied by a diminution of the total volume, this process must be favoured by increase of pressure. This prediction is stated in a quantitative manner in the law enunciated in 1805 by the English chemist, William Henry (1775-1836), and known as *Henry's Law*. This law states that *the amount of a gas dissolved by a given amount of a liquid at a given temperature is proportional to the pressure.* Since the volume of a gas is inversely proportional to the pressure, Henry's law may also be stated in the form : *The volume of a gas absorbed or dissolved by a given volume of a liquid is independent of the pressure.* The experimental numbers given in the following table [1] illustrate this law :—

SOLUBILITY OF CARBON DIOXIDE IN WATER AT 25°

Pressure in Millimetres of Mercury.	Volume of Gas, Measured under the Experimental Conditions, Dissolved by 1 Volume of Water.	Volume of Gas, Measured at N.T.P., Dissolved by 1 Volume of Water.
271	0·825	0·270
495	0·825	0·492
755	0·826	0·751
927	0·826	0·922
1211	0·825	1·205
1350	0·824	1·343

The extent to which a gas is dissolved or absorbed by a liquid at a given temperature is best expressed in terms of the solubility coefficient (S) or the volume of gas, measured under the conditions of the experiment, dissolved by one volume of the liquid. Sometimes, however, the absorption is expressed in terms of the *absorption coefficient* (α) introduced by Bunsen. This is defined as the volume of gas, reduced to N.T.P., dissolved under the pressure of 1 atmosphere by 1

[1] A. Findlay and B. Shen, *J. Chem. Soc.*, 1912, **101**, 1459.

volume of liquid. For the relation between the solubility and absorption coefficients, one has the expressions $S=\frac{a \cdot T}{273}$ and $a=\frac{S \cdot 273}{T}$, where T is the absolute temperature at which absorption takes place. For gases which obey Henry's law, the value both of the solubility coefficient and of the absorption coefficient is independent of the pressure.

Although Henry's law holds fairly accurately in the case of slightly soluble gases, marked deviations are found in the case of very soluble gases, *e.g.*, ammonia, hydrogen chloride. These deviations are no doubt to be attributed to chemical reaction between the components.

Under constant pressure the solubility of a gas will vary with the temperature, and it has been found that the solubility *diminishes* with rise of temperature. This is illustrated by the values of the absorption coefficients given in the following table :—

Temperature.	Carbon Monoxide.	Carbon Dioxide.	Oxygen.	Nitrogen.
0°	0·0354	1·713	0·0489	0·0239
10°	0·0282	1·194	0·0380	0·0196
20°	0·0232	0·878	0·0310	0·0164
30°	0·0200	0·665	0·0261	0·0138
40°	0·0178	0·530	0·0231	0·0118

Solubility of a Mixture of Gases.—Systems which consist of a liquid component and more than one gaseous component are, of course, no longer two-component systems. It will, nevertheless, be convenient to treat such systems here.

When one is dealing with a gas mixture the pressure under which each constituent of the mixture is dissolved is its partial pressure p and not the total pressure of the gas P. If the percentage amount, by volume, of a given gas in a mixture is x the partial pressure is given by $p=\frac{x \cdot P}{100}$; and the amount (volume at N.T.P.) of each gaseous component dissolved is given by the expression $V=\frac{a \cdot v \cdot p}{760}$, where a is the absorption coefficient, v is the volume of the liquid, and p is the partial pressure of the component. When a gas is

shaken with a volatile liquid, one understands by the total pressure, not the external barometric pressure but the external pressure less the vapour pressure of the liquid.

EXAMPLE.—A gas mixture, consisting of 79·0 per cent, of nitrogen, 20·96 per cent. of oxygen, and 0·04 per cent. of carbon dioxide by volume, is shaken with 100 ml. of water at 20°, the external pressure being 760 mm. of mercury. Calculate the amount (volume at N.T.P.) of each gas absorbed. The vapour-pressure of water at 20° = 17·5 mm.

The pressure $P = 760 - 17{\cdot}5 = 742{\cdot}5$ mm. The partial pressure of nitrogen is $\frac{79}{100} \times 742{\cdot}5 = 586{\cdot}6$ mm.; that of oxygen, $\frac{20{\cdot}96}{100} \times 742{\cdot}5 = 155{\cdot}6$ mm.; and that of carbon dioxide, $\frac{0{\cdot}04}{100} \times 742{\cdot}5 = 0{\cdot}297$ mm. The absorption coefficients of the three gases being 0·0164, 0·0310, and 0·878 respectively, the amounts of the three gases absorbed (volumes at N.T.P.) will be

$$\text{Nitrogen}: \frac{0{\cdot}0164 \times 100 \times 586{\cdot}6}{760} = 1{\cdot}266 \text{ ml.} = 65{\cdot}43 \text{ per cent.}$$

$$\text{Oxygen}: \frac{0{\cdot}0310 \times 100 \times 155{\cdot}6}{760} = 0{\cdot}635 \text{ ,, } = 32{\cdot}81 \text{ ,,}$$

$$\text{Carbon dioxide}: \frac{0{\cdot}878 \times 100 \times 0{\cdot}297}{760} = 0{\cdot}034 \text{ ,, } = 1{\cdot}76 \text{ ,,}$$

$$\text{Total . . } \quad 1{\cdot}935 \text{ ml.}$$

The gas mixture expelled on boiling the solution will be found to have a composition in harmony with that calculated.

Owing to the fact that the solubility of a gas is proportional to its partial pressure, a dissolved gas, *e.g.*, ammonia, can be removed, say, from aqueous solution, by bubbling an indifferent gas, *e.g.*, nitrogen, through the solution. Since the partial pressure of ammonia in the bubble of nitrogen is zero, ammonia will diffuse into the bubble and be carried away. A similar explanation can be given of the expulsion of a dissolved gas by boiling the solution. In this case the bubbles of vapour take the place of the bubbles of indifferent gas.

Systems formed of Two Liquid Phases.—When two liquids, *e.g.*, phenol and water, which are only partially miscible at the ordinary temperature, are shaken together, two saturated solutions will be obtained which coexist in equilibrium, namely, a solution of phenol in water and a solution of water in phenol. These coexisting solutions are known as *conjugate solutions*. Since the pressure is constant (atmospheric pressure), the two liquid phases constitute a univariant system, and the composition of the phases will therefore vary with the temperature. As the temperature

PHENOL AND WATER

C_1 and C_2 are the percentage amounts of phenol by weight in the two layers.

Temperature.	C_1.	C_2.
20°	72·16	8·36
30°	69·90	9·22
35°	67·63	9·91
54·83°	59·22	...
57·30°	...	14·87
62·55°	51·87	...
62·74°	...	19·35
65·24°	44·09	...
65·79°	...	30·21
65·84°	34·23	32·23

is raised, the mutual solubility of the phenol and water increases. Consequently, the concentration of phenol in the aqueous layer and the concentration of the water in the phenol layer increase, and at a certain temperature the two conjugate solutions become identical. At this point the two liquid solutions pass into one homogeneous solution, and the temperature at which this occurs is called the *critical solution temperature* or the *consolute temperature*.

The solubility data for phenol and water are given in the above table, and represented graphically in Fig. 116.

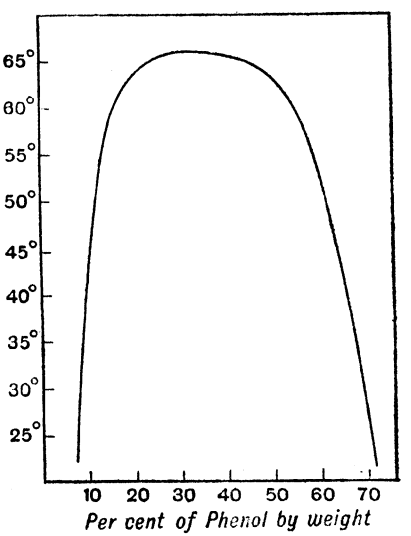


FIG. 116.

The critical solution temperature is found to lie at 65·85° and the critical concentration is 34·0 per cent. of phenol. At all temperatures above the critical solution temperature, phenol and water are miscible with each other in all proportions.

When the temperature and total composition of a phenol-water mixture are represented by a point within

the equilibrium curve, the mixture will separate into two conjugate solutions; but when temperature and composition are represented by a point outside the curve, only one homogeneous solution will be formed.

In the case of phenol and water, the mutual solubility increases with rise of temperature and the critical solution temperature is found in the direction of higher temperatures. In some cases, however, *e.g.*, in the case of triethylamine and water, the mutual solubility increases with lowering of temperature, and the critical solution temperature is therefore found in the direction of lower temperatures (Fig. 117).

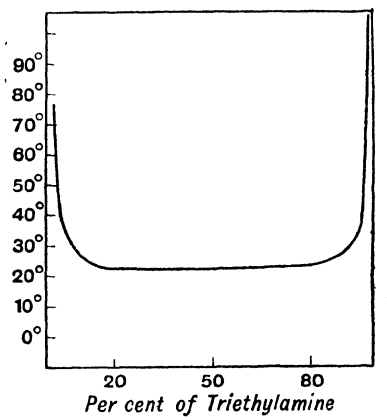


FIG 117.

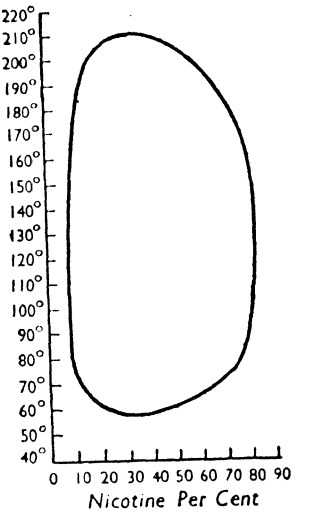


FIG. 118.

Besides those pairs of liquids which show an upper and those which show a lower critical solution temperature, other pairs are known which show both an upper and a lower critical solution temperature, and the equilibrium curve takes the form of a closed curve. Thus, in the case of water and nicotine, the equilibrium curve for which is shown in Fig. 118, there is a lower critical solution temperature at 60°, and an upper critical solution temperature at 210°. Between these two temperatures, mixtures of water and nicotine represented by a point within the closed curve will separate into two liquid layers.

In some cases it is found that pairs of liquids which, under atmospheric pressure, give curves exhibiting only a lower or an upper critical solution temperature, give closed-ring curves when the pressure is increased.

It may be noted that a critical solution temperature cannot be realised for all pairs of partially miscible liquids. Thus, in the case, for example, of water and ether, no critical solution point is realisable at temperatures below the critical point of the solutions, when the system ceases to be heterogeneous.

Influence of Foreign Substances on the Critical Solution Temperature.—For a given pressure the critical solution temperature is a perfectly defined point. It is, however, altered to a very marked extent by the addition of a third substance (impurity) which dissolves either in one or in both of the partially miscible liquids. Although these systems are really three-component systems, the effect of small additions of a substance to a system of two liquid components is of such practical importance that a brief discussion of the regularities observed may be given here.

When the third substance *dissolves in only one of the two liquids* the mutual solubility of the latter is diminished, and the temperature at which the system becomes homogeneous is raised, in the case of systems having an upper critical solution temperature, and lowered in the case of systems having a lower critical solution temperature. The elevation (or the lowering) of the temperature depends not only on the nature and amount of the added substance but also on the composition of the system. In the case of water and phenol the critical solution temperature is raised 12° by the addition of 1·09 per cent. of potassium chloride to the mixture of critical composition.

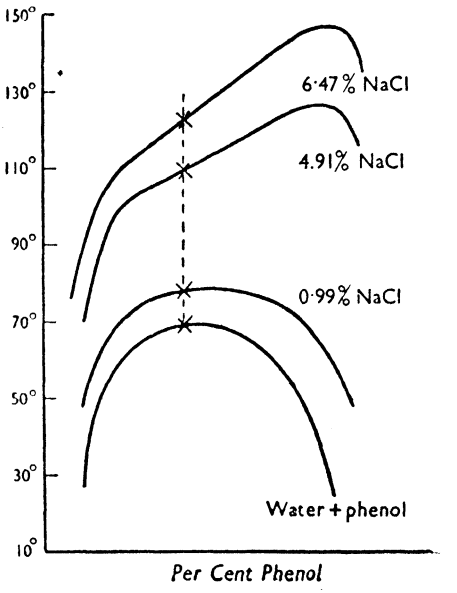


FIG. 119.

Owing to the fact that the influence of the added substance on the temperature at which a liquid-liquid system becomes homogeneous depends on the composition of the system, the equilibrium curve becomes distorted, and the maximum temperature is no longer shown by the system in which the two liquids are present in amounts corresponding with the critical composition (Fig. 119).

When the third substance *dissolves in both liquids* the effect on the critical solution temperature will depend on the relative solubility of the added substance in the two liquids. If the solubility in the two liquids is very different, an upper critical solution temperature may still be raised, and a lower critical solution temperature may be lowered, although to a much less extent than when the added substance is soluble in only one of the liquid components. When, however, the solubility of the added substance in the two liquids is of the same order, the mutual solubility of the two liquids will be increased. Consequently, an upper critical solution temperature will be lowered, and a lower critical solution temperature will be raised. In some cases the effect produced may be very large. Thus the addition of only 0·98 per cent. of sodium oleate to a water-phenol mixture of critical composition lowers the critical solution temperature by no less than 43·7°. This fact is applied to the industrial production of highly concentrated solutions of tar acids (phenols and cresols) used as disinfectants.

The great sensitiveness of the critical solution temperature to impurities has found application not only in analytical chemistry for distinguishing between related substances, such as different oils and fats, but also as a delicate test for the purity of a liquid.

Vapour Pressure of Two Volatile Liquids.—When two volatile liquid components are in equilibrium with vapour, the behaviour observed will depend on whether (1) the two liquids are miscible in all proportions, (2) are only partially miscible, or (3) are immiscible.

(1) When the two components are miscible in all proportions, *e.g.*, alcohol and water, the number of phases cannot exceed two, and such a system, therefore, will be bivariant. If only one variable has a definite value given

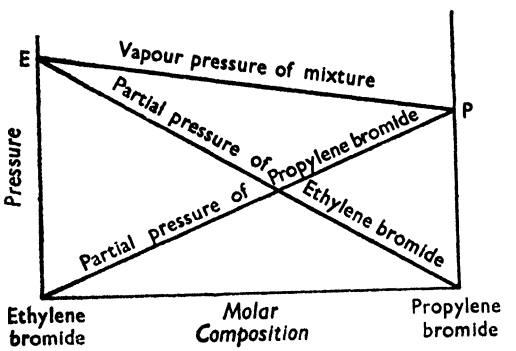


FIG. 120.

to it the system will be univariant. Thus, if the temperature is maintained constant, the (vapour) pressure will vary with the composition of the liquid solution; or if the composition of the solution is fixed the pressure will vary with the temperature.

When one investigates the isothermal pressure-composition curves of mixtures of two completely miscible liquids, three types are found: (*a*) the vapour-pressure curve is a straight line joining the vapour-pressure values of the pure components (Fig. 120); (*b*) the vapour-pressure curve passes through a maximum (Fig. 121); (*c*) the vapour-pressure curve passes through a minimum (Fig. 122).[1]

In the case of two liquids which are chemically closely related—*e.g.*, benzene and toluene, chlorobenzene and bromobenzene, ethylene dibromide and propylene dibromide

[1] J. von Zawidzki, *Z. physikal. Chem.*, 1900, **35**, 129.

—ideal solutions are formed and the partial vapour pressure of each component is proportional to its *molecular concentration* in the mixture. The vapour pressure of the mixture P is therefore given by the formula

$$100P = x \,.\, P_a + (100 - x) \,.\, P_b,$$

where P_a and P_b are the vapour pressures of the two liquids respectively, and x is the molecular percentage of component a.

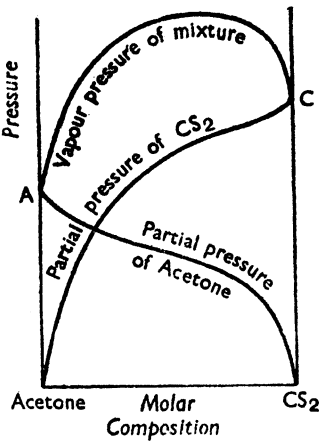


FIG. 121.

In the case of liquids which are not closely related chemically, the solutions which are formed are no longer ideal, and the partial pressure of each component is not proportional to its molecular concentration.[1] In such cases the curve of total vapour pressure may show a maximum, as in the case of acetone and carbon disulphide (Fig. 121), water and propyl alcohol, ethyl alcohol and chloroform; or it may exhibit a minimum, as in the case of acetone and chloroform (Fig. 122), water and hydrogen chloride, water and nitric acid.

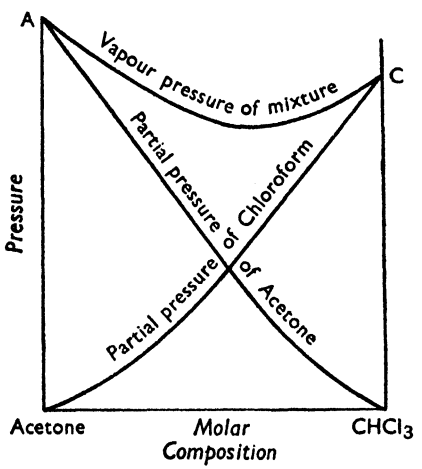


FIG. 122.

Boiling-point Curves.—If the pressure is maintained constant and equal, say, to the atmospheric pressure, the temperature at which the vapour pressure of the system is equal to the atmospheric pressure, *i.e.*, the boiling-point of the solution, will vary with the composition. The curve showing this variation is the boiling-point curve.

[1] See also K. Fredenhagen, *Z. physikal. Chem.*, 1941, B, **48**, 219.

When the curve of total vapour pressure shows neither a maximum nor a minimum, the boiling-point curve will also show neither a maximum nor a minimum ; and the boiling-points of all mixtures will be intermediate between the boiling-points of the pure components, as in the case of mixtures of chlorobenzene and bromobenzene (Fig. 123). The curve will not be rectilineal, but will show a curvature which will be all the greater the more widely the boiling-points of the components are separated. When a solution which gives such a boiling-point curve is distilled, the vapour (distillate) will be richer than the liquid in the component of higher vapour pressure (or lower boiling-point), and the boiling-point will rise as distillation proceeds. By repeated fractional distillation of such a solution, or by distillation through an efficient stillhead, a complete separation of the two components may be effected.[1]

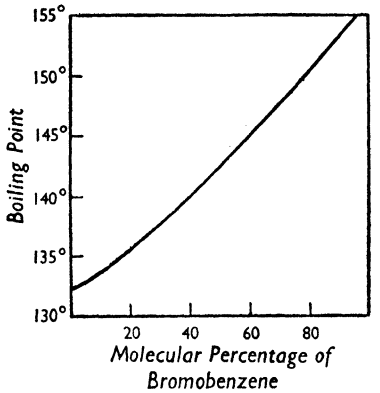


FIG. 123.

This behaviour will be understood more clearly from a consideration of Fig. 124, which represents diagrammatically the composition of the vapour in equilibrium with the liquid mixture. From this it is seen that at any given temperature the liquid mixture is in equilibrium with a vapour which is richer in the component of lower boiling-point. If, therefore, a liquid mixture, a, is distilled, a distillate of composition a' will pass over and the boiling-point of the liquid will rise. When the temperature has risen and the composition of the liquid has altered to a point corresponding to b, the composition of the vapour passing over will alter to correspond

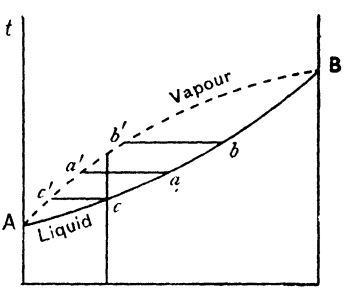


FIG. 124.

[1] See S. Young, *Distillation Principles and Processes* (Macmillan).

to the point b'. If the distillation is interrupted at this point, the distillate will have a composition intermediate between a' and b'. If this distillate is now distilled it will begin to boil at a temperature corresponding, say, to c, and the distillate will have a composition represented by c'. By repeated fractional distillation, therefore, distillates will be obtained which approach more and more closely in composition to the pure component A, of lower boiling-point, and the composition of the residual liquid will approach that of the component B.

By carrying out the distillation with an efficient stillhead, the necessity of collecting the distillate in fractions is avoided. When distillation is in progress, a temperature gradient is established along the stillhead and, on passing upwards, the vapour which condenses is increasingly rich in the more volatile component. Under theoretically perfect conditions the pure component of lower boiling-point drops from the condenser, and the component of higher boiling-point is left in the still.

When the vapour-pressure curve of the liquid solution passes through a maximum the boiling-point curve will pass through a minimum, and when the vapour-pressure curve passes through a minimum the boiling-point curve will show a maximum. In such cases *a separation of the solution into its pure components cannot be effected by distillation, but only a separation into one or other of the components and a mixture of definite composition.* Such a mixture, which boils unchanged at constant temperature under constant pressure, is known as an *azeotropic mixture.*[1]

The behaviour which is observed in such cases will be understood from the boiling-point curve of mixtures of water and propyl alcohol under atmospheric pressure (Fig. 125). In Fig. 125 the lower curve gives the composition of the liquid solution and the upper curve the composition of the vapour phase which is in equilibrium with the liquid.[2] The minimum point corresponds to a mixture containing 71·69 per cent. of propyl alcohol by weight, the boiling-point of which is 87·72°. It is clear from the curves that in the case of solutions containing less than 71·69 per cent. of the alcohol, the vapour is richer in the alcohol than the liquid, whereas in the case of solutions containing more than 71·69 per cent. of the alcohol, the vapour phase is richer in water than the liquid. If one distils a solution of

[1] From α (alpha, a negative particle), ζέω (zeō, to boil), and τρέπω (trepō, to change).

[2] See S. Young and Miss E. C. Fortey, *J. Chem. Soc.*, 1902, **81**, 717

composition a, the vapour which first distils over will have the composition represented by a', and as distillation proceeds, the composition of the solution changes towards c and the composition of the distillate towards c'. If the distillation is stopped when the composition of the liquid is that represented, say, by the point c, the total distillate will have a composition intermediate between a' and c', and will be represented, say, by the point d: that is, the distillate will contain a higher percentage of propyl alcohol than the initial liquid. On distilling a small fraction of this liquid mixture, similarly, a distillate approximating in composition to d' will be obtained; and so, by repeated fractional

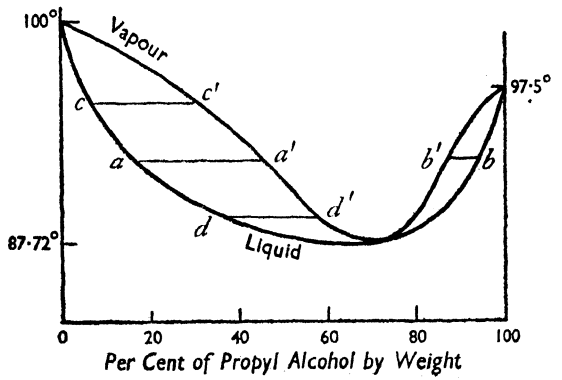


FIG. 125.

distillation, the mixture of minimum boiling-point will ultimately be obtained as *distillate*; the residues from the distillations will have become richer in water, and so one may ultimately effect a nearly complete separation into water and the *mixture of minimum boiling-point.*

Similarly, if one starts with a solution of composition b, the successive fractional distillates will become increasingly rich in water until the composition of the minimum boiling-point mixture is again reached.

The mixture of minimum boiling-point will boil unchanged at constant temperature so long as the pressure remains unchanged. *The composition of the constant boiling-point mixture, however, varies with the pressure.*

Mixtures of acetone and chloroform, water and hydrogen chloride, and water and nitric acid, etc., give boiling-point curves which show a maximum. In the case of water and

nitric acid [1] the *mixture of maximum boiling-point* contains 68·2 per cent. of acid, and boils under atmospheric pressure at 121·7°. When a more dilute solution is distilled, the distillate will be relatively rich in water and the residue will become richer in acid; the temperature of distillation will rise, and a *residue* having the composition of the constant boiling mixture will ultimately be obtained. If a more concentrated acid is distilled, the distillate will be relatively rich in acid, the residue will become more dilute, the boiling-point will rise, and a *residue* having the composition of the constant boiling mixture will be obtained.

As in the case of mixtures of minimum boiling-point, so in the case of mixtures of maximum boiling-point, the composition varies with the pressure.

Separation of the Constituents of an Azeotropic Mixture.—Since two liquids which form an azeotropic mixture cannot be completely separated by distillation at constant pressure, other means must be employed. Since the composition of an azeotropic mixture depends on the pressure under which distillation takes place, a separation of the constituents can be effected, to some extent at least, by distilling the mixture under different pressures. The method, however, would be a very tedious one. In some cases, *e.g.*, the azeotropic mixture of ethyl alcohol and water (95·57 per cent. of alcohol and 4·43 per cent. of water), one of the constituents (water) can be removed chemically (by means of quicklime). Another method which may be employed in the case of ethyl alcohol and water, and in certain other cases, is to add to the binary mixture a third liquid which forms, with the other two, a ternary azeotropic mixture containing all, or practically all of one of the constituents of the binary mixture. Thus, if benzene is added in appropriate amount to the azeotropic mixture of ethyl alcohol and water, a ternary azeotropic mixture (consisting of 18·5 per cent. of alcohol, 7·4 per cent. of water, and 74·1 per cent. of benzene, and boiling at 64·85°) is formed. On distilling the ternary mixture, separation takes place almost completely into the ternary azeotropic mixture (distillate) and absolute ethyl alcohol (residue). The alcohol can be recovered from the azeotropic mixture by adding water, whereby two liquid layers are formed. Of these, the aqueous layer consists almost entirely of alcohol and water, and by distilling this solution the binary azeotropic mixture can be obtained. This is then treated as described.[2]

Vapour Pressure of Partially Miscible Liquids.—When two components form a system of two liquid phases and one vapour phase the system is univariant; and if one of the variables is fixed, the condition of the system is completely defined. Thus, if the temperature is maintained constant, the vapour pressure and composition of the phases will be definite. Addition of one or other component to the system can only bring about a phase reaction and an alteration of the relative amounts of the two liquid phases.

Two types of pressure-composition curves can be obtained. In some cases the vapour pressure of two conjugate solutions may be greater than the vapour pressure of either of the pure components; in other cases it lies between the vapour pressures of the pure components. When a system of two conjugate solutions is distilled, a distillate of constant composition will be obtained so long as the two liquid phases are present. Changes in the relative amounts of

[1] H. J. M. Creighton and J. H. Githens, *J. Franklin Inst.*, 1915, **179**, 161.
[2] Sydney Young, *J. Chem. Soc.*, 1902, **81**, 707.

the two liquid phases, however, may take place with the ultimate disappearance of one of the phases. One is then left with a system of two phases, one liquid and one vapour phase, which will behave in the manner already discussed.

Vapour Pressures of Mixtures of Immiscible Liquids. Distillation with Steam.—When two immiscible liquids coexist with vapour, three phases are present and the system is univariant. The vapour pressure, therefore, will vary with the temperature. If the temperature is maintained constant, the vapour pressure will also have a definite value, and will be equal to the sum of the vapour pressures of the two liquids. When such a system is distilled under constant (atmospheric) pressure, a distillate of constant composition will be obtained so long as the two liquid phases are present. If p_1 and p_2 are the vapour pressures of the two liquids at the temperature of the boiling-point of the mixture, the volumes of vapour which distil over will be proportional to these vapour pressures. Since the mass is given by volume × density, and since the densities of the vapours are proportional to the molecular weights, the *ratios by weight* in which the two liquids will distil over will be $M_1p_1 : M_2p_2$.

The behaviour outlined above is utilised in the process of *distillation with steam*. A mixture of water and nitrobenzene, for example, may be taken as boiling at 99° under ordinary atmospheric pressure (760 mm.). At this temperature the vapour pressures of water and of nitrobenzene are 733 mm. and 27 mm. respectively. Since the molecular weight of water is 18 and that of nitrobenzene 123, the relative weights of these substances in the distillate will be

$$\frac{\text{Weight of water}}{\text{Weight of nitrobenzene}} = \frac{18 \times 733}{123 \times 27} = 3{\cdot}98$$

The percentage amount of nitrobenzene in the distillate will therefore be 20·1 per cent.

Steam distillation is frequently employed in the purification of organic compounds of high molecular weight (*e.g.*, essential oils), the high molecular weight of the compound, relatively to that of water, more than compensating for the low value of the vapour pressure. A relatively larger yield of compound in the distillate is obtained by distilling at a higher temperature by means of steam under a pressure greater than atmospheric.

Equilibrium between Solid and Liquid Phases Only.—Two-component systems in which only solid and liquid

phases coexist are among the most important in the whole range of heterogeneous equilibria. The interest and importance of the investigation of such systems lie in the determination not only of the conditions for the stable existence of the participating substances but also of the conditions under which chemical combination (if any) takes place between the components. From such investigations one may ascertain the nature of any compounds formed and the range of their existence. In the systems to be discussed here it will be assumed that the components are completely miscible in the liquid state.

(a) *The Pure Components only occur as Solid Phases*

Since the two components in the liquid state are miscible in all proportions, there can never be more than one liquid phase, namely, a homogeneous mixture or solution of the two components. Since, also, only the pure components can occur as solid (crystalline) phases, the only systems possible are S_1—L, S_2—L, and S_1—S_2—L where S_1 and S_2 represent the crystalline components and L the liquid solution.[1]

A system which consists of only two phases, S_1—L or S_2—L, will be bivariant. If the pressure is given a definite value, say, atmospheric pressure, then the system will become univariant, or the composition will vary with the temperature; or, if the temperature is fixed, the composition will vary with the pressure. On the other hand, the system S_1—S_2—L is univariant, and if the pressure is fixed, the system will be entirely defined. Under a given pressure the system S_1—S_2—L can exist only at a single definite temperature, and the composition of the liquid phase will also be definite. If, therefore, the equilibria be represented in a temperature-composition diagram, the systems S_1—L and S_2—L will be represented by curves, and the system S_1—S_2—L by a point, as shown in Fig. 126. In this diagram the points A and B represent the melting-points of the pure components. Since the freezing-point of a liquid is lowered by dissolving another substance in it, it follows that if a quantity of the component B is dissolved in molten

[1] Other systems are possible, as will be pointed out, when the solid components can exist in polymorphic forms.

(or liquid) A, the temperature at which solid A will be in equilibrium with the solution will be below the freezing-point of pure A; and the greater the concentration of B in the liquid the lower will be the temperature at which A can exist in equilibrium with it.

The curve AC represents the composition of solutions which are in equilibrium at different temperatures with the solid component A; and the curve BC, similarly, the composition of solutions in equilibrium with solid B. At the point C, where the two curves cut, both solid components can exist in equilibrium with a liquid solution of definite composition, represented by the point C. Point C, therefore, gives the conditions of temperature and composition of the liquid phase under which the system S_1—S_2—L can exist in stable equilibrium under constant pressure.[1] This point, as is clear from the diagram, lies *at a lower temperature than the melting-point of either component.* It is, in consequence, called a *eutectic point* (from the Greek, *eu tectos* = easy melting).

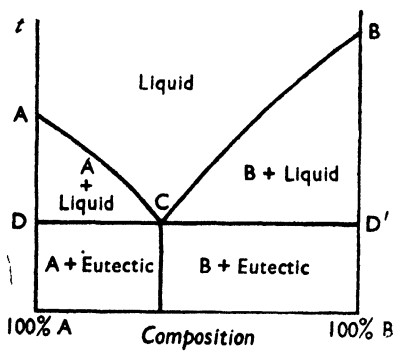


FIG. 126.

At all temperatures lying above the curves AC and BC, the two components can exist only as a homogeneous liquid solution, and at all temperatures below the eutectic horizontal DD', only the solid components or mixtures of the solid components can exist as stable systems. When the temperature and composition are represented by a point in the area ACD, the system will consist of solid A in equilibrium with a liquid solution represented by a point on the curve AC. Similarly, points in the area BCD' give the conditions of temperature and composition for the coexistence of solid B and solution.

If a liquid solution having a composition represented by a point lying to the left of the eutectic point C be cooled down, the solid component A will crystallise out (super-saturation supposed excluded) when the temperature reaches the point on the curve AC corresponding to the initial

[1] The position of point C will, of course, be altered by pressure.

composition of the solution. If the temperature be allowed to fall still farther, more and more of the component A will crystallise out, and the composition of the solution will alter in the direction C. When the composition of the point C is reached, solid B, also, can begin to crystallise out. If one continues to withdraw heat from the system, solid A and solid B will separate out together, and *the temperature will remain constant.* Since the composition of the solution must also remain constant, because point C represents an invariant system when the pressure is constant, it follows that *the components A and B must crystallise out from the eutectic solution in constant proportions.* Although, therefore, the eutectic solution freezes at constant temperature, the solid which separates out is not a compound but a *mixture (or conglomerate) of two solid phases in definite proportions.*

On the other hand, if a liquid mixture having a composition represented by a point lying to the right of the eutectic point be cooled down, the solid component B will separate out, and the composition of the solution will change in the direction of C. When this point is reached, solid A will also crystallise out, and the temperature and composition of the solution will now remain constant while the solid components A and B crystallise out as a eutectic conglomerate.

On cooling down a liquid mixture which has the composition represented by the point C, no solid will crystallise out until the temperature of the eutectic point is reached. At this temperature the eutectic mixture will separate out.

The diagram which has just been studied is generally called the *freezing-point diagram* because it shows the temperatures at which the solid components crystallise out from molten mixtures. When one of the components is a liquid at ordinary temperatures one of the curves is often spoken of as a solubility curve.

The method employed for the determination of the equilibrium curves will depend on the nature of the system to be investigated. Where one of the components is a volatile liquid (*e.g.*, water) at ordinary temperatures, the composition of the solution may be determined by evaporation of the liquid and weighing the solid residue. When both components are solid at ordinary temperatures the course of the equilibrium curves can best be established by determining the freezing-points of homogeneous liquid

mixtures of different initial composition, or the temperatures at which the solid phase begins to crystallise out from the liquid mixture. The mapping of the freezing-point curve is facilitated by a study of the cooling curve.

When a pure substance in the fused state is allowed to cool slowly, and the temperature noted at different times, the graphic representation of the *rate of cooling* will give a continuous curve, *e.g.*, *ab* in Fig. 127, I. When the freezing-point is reached, solid will begin to separate out, and the temperature will remain constant until the liquid has completely solidified. The fall of temperature will then become uniform again (*cd*).

If, however, a solution is allowed to cool slowly, and the cooling curve similarly determined, heat will be evolved when the solid phase is formed, and the rate of cooling will alter. The cooling curve will therefore exhibit a break or abrupt change of direction at the freezing-point of the solution (point *b'*). Since the composition of the solution alters with separation of the solid phase, the temperature will not remain constant but will gradually fall until the eutectic point is reached. A second solid phase is now formed, and the system becomes invariant (the pressure being constant). The temperature will therefore remain constant until complete solidification has occurred (line *c'd'*). Thereafter, the fall of temperature again becomes uniform (*d'e'*). The points *b*, *b'*, and *c'*, at which a "break" occurs in the cooling curve, are called "arrests" or "arrest points" on the cooling curve. The above method of mapping the freezing-point or equilibrium curve is employed especially in the case of mixtures of metals.

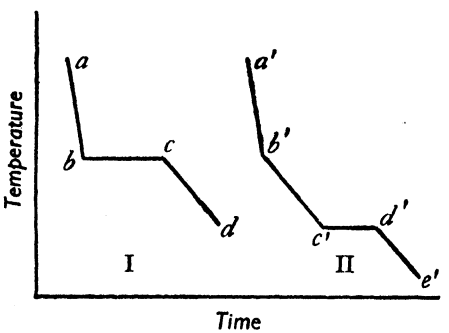


FIG. 127.

Equilibrium diagrams of the type shown in Fig. 126 are given by many pairs of components. Among organic compounds one may mention *o*-nitrophenol (m.p., 44·1°) and *p*-toluidine (m.p., 43·3°): Eutectic point, 15·6°; composition, 52 molecules per cent. of toluidine. Copper (m.p., 1081°) and silver (m.p., 960°), similarly, give a eutectic at 778°, the eutectic solution containing 40 atoms per cent. of copper. A similar diagram is also given by water and silver nitrate (m.p., 208·6°). The eutectic point lies at −7·3°, and at the composition, 47·1 per cent. of silver nitrate. It may be mentioned that in the case of aqueous systems the eutectic point is generally called the *cryohydric* point—a term introduced in 1875 by the English physicist, Frederick Guthrie (1833-86), who thought that the eutectic mixture of ice and salt which separates out in definite proportions was a compound to which he gave the general name of *cryohydrate*.

Polymorphism of Components.—In the case of two-component systems in which the pure components only occur as solid phases, the equilibrium curves AC and BC (Fig. 126) must be continuous so long as the solid phase in equilibrium with the liquid mixture remains unchanged. If, however,

the solid component can exist in enantiotropic, polymorphic forms, the equilibrium curve will show a " break " at the transition point, for at this point two solid (polymorphic) phases will coexist with liquid. This system, therefore, will be invariant, since the pressure is constant. The " break " in the equilibrium curve is, of course, a point of intersection of two equilibrium (solubility) curves, namely, those for each enantiotropic form in equilibrium with solution. *The determination of such points of intersection is a valuable method of determining the transition point of enantiotropic crystalline forms.*

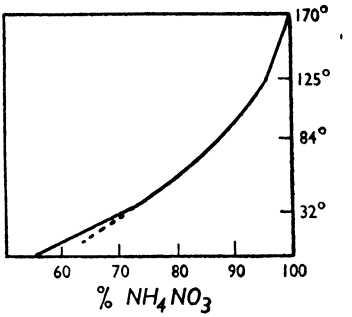


FIG. 128.

Thus, in the case of the system water—silver nitrate, the equilibrium curve for solid silver nitrate in contact with solutions shows a break of 160°, the transition point for rhombic and rhombohedral crystals; and in the system water—ammonium nitrate, breaks are found at 32° and at 125°, the transition points for β-rhombic and α-rhombic and for rhombohedral and regular crystalline forms respectively. The break at 84°, the transition point for α-rhombic and rhombohedral, was too slight to be detected (Fig. 128).

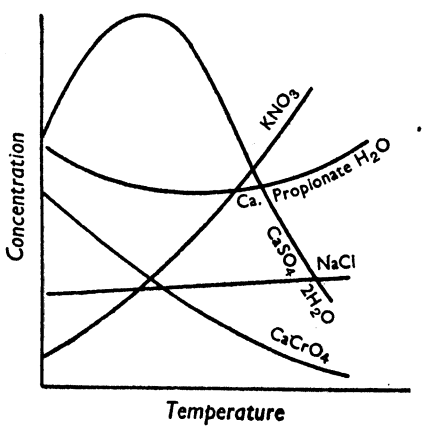


FIG. 129.

In Fig. 126 the equilibrium curves are shown as directed continuously from eutectic point towards the melting-point of the pure component. Expressed in terms of solubility, this means that the solubility of the solid phase increases continuously with rise of temperature. Sometimes, however, the solubility diminishes with rise of temperature, and sometimes the solubility passes through a minimum or a maximum point. The equilibrium curve, therefore, will show corresponding changes in direction.

Frequently, when one of the components is a liquid at ordinary temperatures (*e.g.*, water), the solubility of a substance is expressed in terms of the weight of solid phase (solute) in a definite weight of the other component regarded as solvent. The *solubility curves* so obtained represent portions only of the complete equilibrium diagrams of the particular components, and may have various forms as shown in Fig. 129. The *direction* of the solubility curve depends on whether heat is evolved or absorbed *when the solid phase is dissolved in a large amount of the almost saturated solution.* This is the

so-called *last heat of solution*, and is not to be confused with the integral heat of solution (p. 268). If the last heat of solution is positive (heat evolved), the solubility will diminish with rise of temperature; but if the last heat of solution is negative, the solubility will increase with rise of temperature (theorem of Le Chatelier).

(b) *Compounds are Formed with a Congruent Melting-point*

When two components can form a stable compound which is capable of existing as a solid phase in equilibrium with a liquid phase of the same total composition, and which possesses, therefore, what is called a *congruent melting-point*, a third equilibrium curve (for compound in equilibrium with liquid solution) must be added to the two curves discussed on page 444. Moreover, since the compound has a definite, congruent melting-point, and since this melting-point will be lowered by dissolving in the liquid phase either of the pure components, it follows that *the melting-point of the compound must be a maximum point on the equilibrium curve.* The equilibrium diagram, therefore, takes the general form shown in Fig. 130. In this diagram, A, B, and D are the congruent melting-points of component A, component B, and of the compound A_xB_y respectively. Curve AC gives the composition of liquid solutions of A and B in equilibrium at different temperatures with the component A as solid phase; curve BE gives the composition of solutions in equilibrium with component B as solid phase; and curve CDE gives the composition of solutions in equilibrium with the compound A_xB_y as solid phase. C and E are eutectic points at which eutectic conglomerates of A and A_xB_y and of B and A_xB_y respectively can coexist in contact with solutions of definite composition. The melting-point D of the compound may be higher or lower than that of either component, or it may have an intermediate position. If more

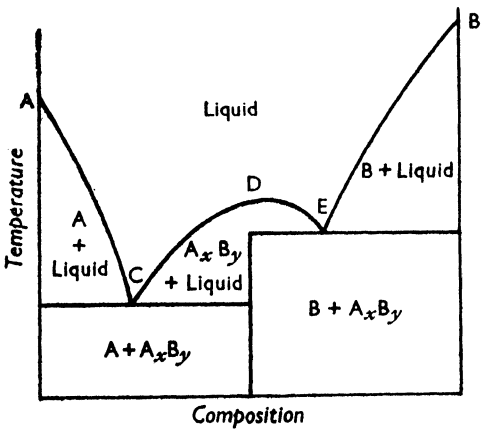


FIG. 130.

than one compound with congruent melting-point can be formed, a series of curves similar to CDE will be obtained—one for each compound. *In each case the maximum point of the curve gives the composition of the compound.* This fact is of much importance, because in many cases, *e.g.*, of alloys, it is not possible to isolate and analyse the compounds.

If the compound were completely undissociated even in the vapour phase, as is the case with the compound of pyridine and methyl iodide, the equilibrium curve for the compound would not be a continuous curve, but the melting-point of the compound D would be the point of intersection of two curves. Ordinarily, however, dissociation does take place in the liquid phase, and one is then dealing with a mixture of molecules the composition of which varies continuously with the temperature. The equilibrium curve, therefore, must also be continuous. The greater the degree of dissociation of the compound the greater will be the flattening of the crown of the equilibrium curve.

Examples of systems which form compounds with congruent melting-points are: phenol (m.p., 40·4°) and α-naphthylamine (m.p., 48·3°), which form a compound containing the components in equimolecular proportions and melting at 28·8° [1]; gold and aluminium, which form several compounds [2]; and water and ferric chloride, which form no fewer than four stable compounds (hydrates), namely,

$Fe_2Cl_6, 12H_2O$; $Fe_2Cl_6 7H_2O$; $Fe_2Cl_6, 5H_2O$; and $Fe_2Cl_6, 4H_2O$.

The equilibrium diagram is shown, in part, in Fig. 131. The dotted lines represent metastable (super-cooled) solutions. The points C, E, G, and J are the melting-points of the hydrates $12H_2O$, $7H_2O$, $5H_2O$, and $4H_2O$ respectively; and the points D, F, H, and K are eutectic points at which the solid phases $12H_2O$ and $7H_2O$, $7H_2O$ and $5H_2O$, $5H_2O$ and $4H_2O$, $4H_2O$ and anhydrous salt respectively coexist with solution.

When a solution, represented by the point x_1 (Fig. 131), is cooled down it will solidify to a mixture of the hydrates $12H_2O$ and $7H_2O$; and the solution x_2, on being cooled down, will deposit the dodecahydrate, and the composition of the solution will alter towards the point D. When this point is reached, the hydrate $7H_2O$ will also separate out. When the mixture, represented by x_3, is cooled down, the liquid will solidify completely as dodecahydrate; and when

[1] J. C. Philip. *J. Chem. Soc.*, 1903, **83**, 821.
[2] Heycock and Neville, *Phil. Trans.*, 1900, **194**, 201.

the mixture x_4 is cooled down, dodecahydrate will be deposited, the composition of the solution will alter in the direction of B, and when this point is reached, complete solidification will take place to a mixture of dodecahydrate and ice.

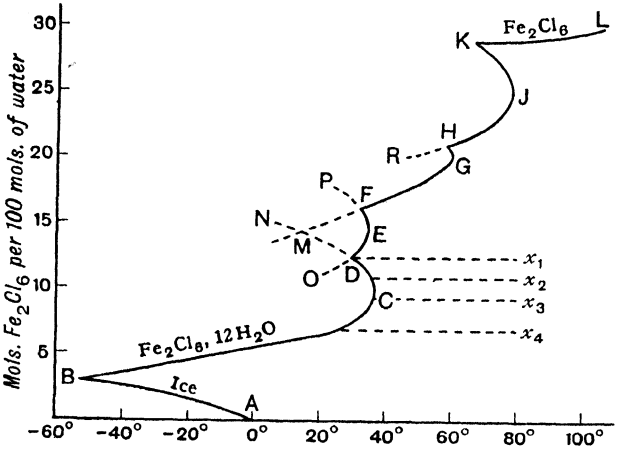


FIG. 131.

Inevaporable Solutions.—If a saturated solution in equilibrium with two hydrates, or with a hydrate and anhydrous salt is heated, the temperature and composition of solution will remain unchanged so long as the two solid phases are present, for such a system is invariant (under constant pressure). In addition, however, the *quantity* of the solution will also remain unchanged, the water which evaporates being supplied by the phase reaction : higher hydrate⟶lower hydrate + water. The same phenomenon is observed at eutectic points at which ice is a solid phase ; so long as the ice is present, evaporation will be accompanied by fusion of the ice, and the quantity of solution will remain constant. Such solutions are called *inevaporable.*

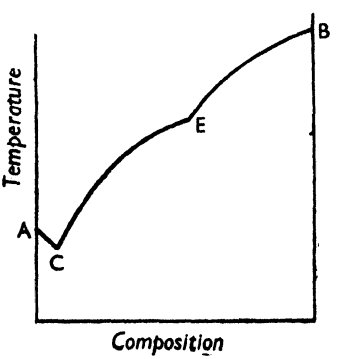


FIG. 132.

(c) *Compounds are formed with Incongruent Melting-point*

When a compound is formed which undergoes decomposition with formation of another solid phase at a temperature below the congruent melting-point of the compound, the equilibrium diagram assumes the general form shown in Fig. 132. In this diagram the compound is represented as undergoing change into pure component B and liquid at the point E, which is called an

incongruent melting-point. This point represents the limit of existence of the compound under the particular constant pressure which is assumed. If a series of compounds can be formed, some of these may have a congruent and some an incongruent melting-point. Each congruent melting-point

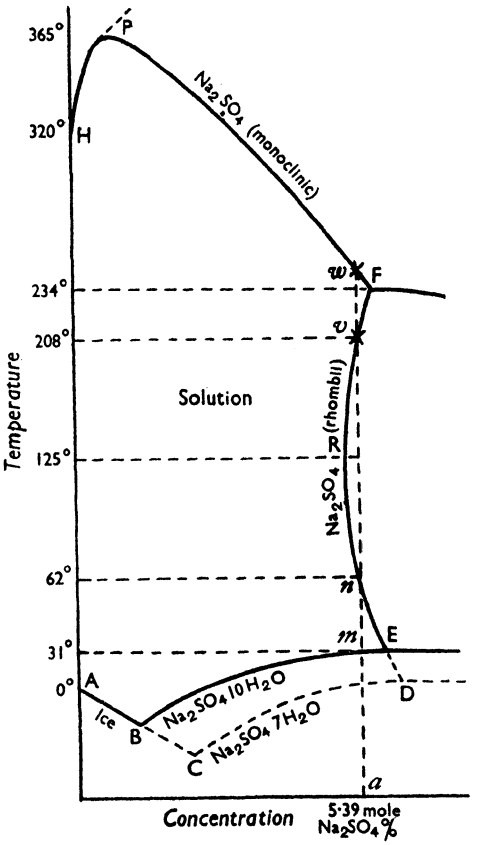


FIG. 133.

will be represented by a temperature maximum, and each incongruent melting-point by a break in the curve.

As an example of the formation of compounds with an incongruent melting-point, one may consider the systems constituted by the two components water and sodium sulphate. This salt can form the two hydrates, Na_2SO_4, $10H_2O$ and Na_2SO_4, $7H_2O$; and the anhydrous salt can

exist in two enantiotropic crystalline forms, rhombic and monoclinic. The equilibrium diagram is shown in Fig. 133. The curve AB is the freezing-point curve, or the curve showing the composition of solutions in equilibrium with ice at different temperatures. B is the cryohydric (eutectic) point. BE is the solubility curve of sodium sulphate decahydrate, the solubility increasing with rise of temperature. At 32·4°, when the solution contains 33·20 per cent. of anhydrous salt, the decahydrate changes into anhydrous salt and water. E represents a transition point or incongruent melting-point. If heat is added to the system the temperature and composition of the solution remain constant and the phase reaction $Na_2SO_4, 10H_2O \longrightarrow Na_2SO_4 + 10H_2O$ takes place. When all the hydrate has disappeared, one obtains a univariant system rhombic sodium sulphate and solution. The solubility curve for rhombic anhydrous sodium sulphate (EF) shows a minimum at about 125°, and ends at F (234°), the pressure at this point being 27·5 atmospheres. At F, transition of rhombic to monoclinic sodium sulphate takes place, and the solubility of the latter decreases with rise of temperature (curve FP). P is the critical point of the solution.

Sodium sulphate heptahydrate is metastable with respect to the decahydrate, and can give rise only to metastable systems. Its solubility at a given temperature is *greater* than that of the decahydrate, as shown by the dotted curve CD. C is a metastable eutectic point and D a metastable transition point.

(d) *Formation of Solid Solutions*

It is observed that, in some cases, there crystallises from a solution not the pure components or compounds of these, but a homogeneous crystalline mixture of the two components, the composition of which varies with the composition of the solution from which it separates. To this homogeneous solid mixture of variable composition van't Hoff gave the name *solid solution.*

When a solid solution separates out in equilibrium with a liquid solution the system will consist of two phases, each of variable composition, and to represent the behaviour of such a system two curves will be required, one giving

the composition of the liquid solution, the other giving the composition of the solid solution. The temperature-composition curve for the liquid phase is called the *liquidus* curve ; that for the solid phase, the *solidus* curve.

When two components are miscible with each other in all proportions in the solid state, there can never be more than one solid phase present, namely, a solid solution of varying composition. If the components are completely miscible in the solid state they will also be completely miscible in the liquid state, and, consequently, there can never be more than three phases in equilibrium—a solid solution, a liquid solution, and vapour. The system, therefore, can never become invariant, and *the temperature-composition curve must be continuous.* If the vapour phase is absent, but if the pressure is maintained constant, the two-phase system solid solution—liquid solution will be univariant.

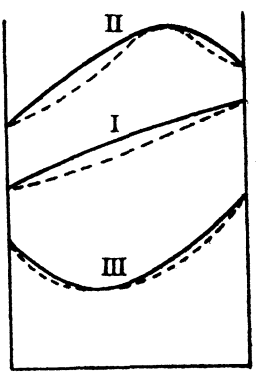


FIG. 134.

Three types of equilibrium curves are found, as indicated in Fig. 134. In some cases the freezing-point of all liquid mixtures lies between the freezing-points of the pure components. The equilibrium curve is then of the type I in Fig. 134. A curve of this type is given by a α-monochlorocinnamic aldehyde and α-monobromocinnamic aldehyde.[1] In other cases the equilibrium curve passes through a maximum or through a minimum. In these diagrams the liquidus curve is shown as a full-drawn curve, the solidus curve being dotted ; and the relative position of these two curves is given by the rule : At any given temperature *the concentration of that component by the addition of which the freezing-point is depressed is greater in the liquid than in the solid phase* ; or, conversely, *the concentration of that component by the addition of which the freezing-point is raised is greater in the solid than in the liquid phase.*

An equilibrium curve which passes through a maximum point is given by the components *d*- and *l*-carvoxime [2] ; and

[1] Küster, *Z. physikal. Chem.*, 1891, **8**, 589.
[2] Adriani, *Z. physikal. Chem.*, 1900, **33**, 469.

a curve passing through a minimum point is given by the components potassium nitrate and sodium nitrate.[1]

Fractional Crystallisation of Solid Solutions.—If a liquid solution represented by x (Fig. 135) is cooled down, solid solution of the composition b will separate out when the temperature has fallen to the point a. If the temperature is allowed to fall to x', and the solid then separated from the liquid, the solid solution so obtained will have the composition represented by the point e. If, now, the solid solution of composition e is completely fused and the fused mass allowed to cool, separation of solid will occur when the temperature has fallen to the point f. The solid solution which is deposited will have the composition g; that is, *it is richer in B than the original solid solution.* By repeating this process the composition of the successive crops of solid solutions which are obtained will approximate more and more to that of the pure component B, while, on the other hand, the composition of the liquid phase produced tends to that of pure A. By a systematic and methodical repetition of the process of fractional crystallisation, a *practically* complete separation of the components can be effected; a perfect separation is theoretically impossible.

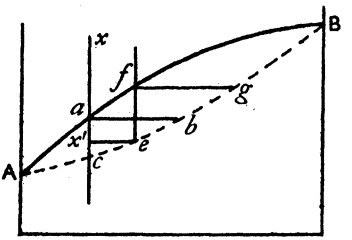


FIG. 135.

In the case of substances the freezing-point of which passes through a maximum, fractional crystallisation will ultimately lead to a solid solution having the composition of the maximum point, while the liquid phase will more and more assume the composition of either pure A or pure B, according as the initial composition was on the A side or the B side of the maximum. In those cases, however, where the curves exhibit a minimum, the solid phase which separates out will ultimately be one of the pure components, while a liquid phase will finally be obtained which has the composition of the minimum point.

When two components are only partially miscible in the solid state, but completely miscible in the liquid state, the coexistence of four phases is possible, namely, two solid solutions—liquid solution and vapour. This system is invariant and can exist only under certain perfectly defined conditions. If the vapour phase is absent and if the pressure

[1] Briscoe and Madgin, *J. Chem. Soc.*, 1923, **123**, 1608.

is fixed, then the three-phase system, two solid solutions and liquid solution, will be invariant and will be able to coexist only at one particular temperature. The composition of the solutions, moreover, will be definite. In the case of all such systems the equilibrium curves can no longer be continuous.

Two types of equilibrium diagram are met with here. In the first type the freezing-point curve exhibits a transition point, and in the second it shows a eutectic point. In Fig. 136, AC gives the composition of liquid solutions with which solid solutions of composition represented by AD are in equilibrium. BC, similarly, gives the composition of liquid

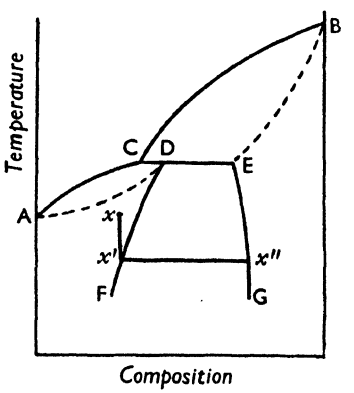


FIG. 136.

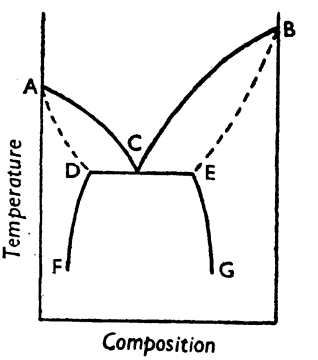


FIG. 137.

solutions in equilibrium with solid solutions BE. At the point C the two liquidus curves intersect, and at this point two solid solutions, represented by D and E, are in equilibrium with the liquid solution C. This type of diagram is given by mixtures of silver nitrate and sodium nitrate.[1]

The second type of diagram is shown in Fig. 137. At the eutectic point the two solid solutions D and E coexist in equilibrium with liquid solution of composition C. On cooling a solution of the composition C the liquid would solidify to a conglomerate of two solid solutions. Many mixtures of metals, *e.g.*, silver and copper, gold and copper, behave in the manner described here.

Changes in Solid Solutions with the Temperature.—Just as the mutual solubility of two liquids alters with the

[1] Hissink, *Z. physikal. Chem.*, 1900, **32**, 542.

temperature, so also may the mutual solubility of two solids. Thus, in Figs. 136 and 137, the curves DF and EG represent the variation of composition of the two solid solutions with temperature. Even when the system is completely solid, therefore, changes may take place with temperature. If, for example, the solid solution x (Fig. 136) is cooled down, separation into two solid solutions x' and x'' will take place when the temperature reaches that of x'. The system will therefore lose its homogeneity. This behaviour is of much importance in connection with metal alloys, and plays an important part in the properties of iron-carbon alloys.

CHAPTER XVIII

THE MECHANISM OF CHEMICAL REACTIONS AND VELOCITY OF CHEMICAL CHANGE

In a previous chapter (XII) homogeneous equilibria have been considered. These equilibria are established as a result of reactions which may occur homogeneously or heterogeneously. It is now necessary to inquire further into the speed and mechanism whereby such equilibria are established. Chemical experience shows that reaction velocity varies over wide limits, for example, hydrogen-oxygen mixtures do not combine at any measurable velocity at room temperature. In the presence of platinum combination occurs at a measurable speed. At temperatures of about 500° C., combination may become so rapid that explosion occurs. Similarly, finely divided phosphorus catches fire in air at room temperature, whereas finely divided sulphur remains unoxidised over very long periods. One of the most striking facts is the enormous influence of temperature in speeding up velocity of reaction. In very few cases is the velocity reduced by increase in temperature. Reactions may occur in the gas, liquid, and solid phases. Considerable progress has been made in the understanding of the mechanism of gaseous reactions: the elucidation of liquid phase reactions is in a less advanced stage in spite of the wealth of experimental material which has accumulated. The study of solid reactions is of peculiar difficulty owing to the relative immobility of atoms in a crystal lattice, therefore relatively little progress has been made with this particular type.

Influence of Concentration on Reaction Velocity.—It was early realised that the concentration of a substance affected its rate of reaction, but Guldberg and Waage in 1867 clearly formulated in the law of mass action (p. 273) the fundamental relationship between velocity and concentration; originally it was stated that velocity is proportional to the product of the concentrations of reacting substances. When dealing

with real reactions the main difficulty is to determine the effective concentration, for this quantity may not necessarily be equal to the concentration of the molecules participating in the reaction. In many reactions the chemical equation describing the overall result of reaction does not give any clue to the way in which concentrations affect velocity.

Measurement of the speed of reactions may most readily be made by measuring some physical property of the system, for example, the change in pressure in a gaseous system, the change in density, refractive index, etc., of a liquid system, provided adequate experiments are made to relate the change in physical property with the chemical changes which have been analytically determined. Where physical methods are inapplicable, chemical analysis of small samples withdrawn from time to time is the most suitable alternative method.

Experimental data have accumulated to show, that if the active mass or effective concentration of a reactant is taken to be given by its concentration, in some cases the velocity may be proportional to the first, second, and even third power of the concentration. Such reactions are spoken of as of the first, second, and third order respectively. It must be emphasised, however, that sometimes fractional orders are observed and that integral orders are by no means the rule.

Reactions of the First Order.—It will be assumed that there is only one reactant, that the rate is strictly proportional to the first power of the concentration of the reactant and that the reaction goes to completion. Suppose the initial concentration is a and that after a time t the concentration has diminished by x, then $a-x$ is the concentration of the substance. By definition, then,

$$\text{Velocity} = \frac{dx}{dt} = k(a-x)$$

k is defined as the velocity coefficient of the reaction. If this equation is rearranged to

$$\frac{dx}{(a-x)} = k \, . \, dt$$

this means that at any instant of time a constant *fraction* of the substance is decomposed. In order to see how the value of $(a-x)$ varies with time, the equation may be integrated.

$$\int_a^{a-x} \frac{dx}{(a-x)} = \int_0 k \,.\, dt$$

since k is by definition constant

$$-\log_e(a-x) = kt + \text{constant.}$$

When $t=0$, $x=0$ and therefore

$$-\log_e a = \text{constant.}$$

Hence,
$$k = \frac{1}{t}\log_e \frac{a}{a-x} = \frac{2{\cdot}303}{t}\log_{10}\frac{a}{a-x} \quad . \quad . \quad \text{(A)}$$

A useful form of the equation which may be used at any stage in the reaction is

$$k = \frac{2{\cdot}303}{t_2 - t_1}\log_{10}\frac{(a-x_1)}{(a-x_2)} \quad . \quad . \quad . \quad \text{(B)}$$

where $(a-x_1)$ and $(a-x_2)$ are the concentrations at times t_1 and t_2 respectively. In order to compute the value of k, the values of x may be measured at a series of times and k computed from equation (A). If, however, it is difficult to determine precisely zero time in preparing the specimen for examination, it is usually more satisfactory to employ equation (B).

It will be observed that the dimensions of k are reciprocal time; the value of k is therefore independent of concentration. The physical meaning of k can be understood in the following way. If $(a-x)$ is put equal to unity, then $\frac{dx}{dt} = k$. That is, k is the rate of change of concentration at unit concentration. The reciprocal of this rate is the average time before a molecule decomposes, and hence k may be taken as the reciprocal of the mean life-time of the molecules undergoing decomposition. Another numerical measure of the rate is the so-called half-life $\tau_{1/2}$. This is the time required for half the material to decompose. The relationship to k can be immediately obtained from the integrated rate equation for then $x = a/2$ and hence

$$k = \frac{2{\cdot}303}{\tau_{1/2}}\log\frac{a}{a/2}$$
$$= 0{\cdot}693\tau_{1/2}^{-1}.$$

EXAMPLES.—Although it is not strictly a chemical reaction the spontaneous break-up of the nucleus of a radio-active atom is given accurately by a first order equation *i.e.*,

$$\log \frac{I_o}{I_t} = \lambda t.$$

where I_o and I_t are the intensity of the emission of particles from the nucleus which is of course strictly proportional to the number present and λ has the same meaning as k. λ is usually called the radio-active constant.

The best example of a first order reaction is the homogeneous decomposition of nitrogen pentoxide vapour which occurs readily in glass vessels at temperatures from 0-100° c. The stoichiometric reaction is

$$2N_2O_5 = 2N_2O_4 + O_2$$

Neither the N_2O_4 nor the O_2 has any effect on the velocity. The following results show the sort of constants obtained in value of k for a reaction which goes smoothly and without side reactions to completion.

Initial pressure of N_2O_5 at 45° c. = 340·2 mm.

t.	(a − x)	k, sec^{-1}	t.	(a − x)	k, sec^{-1}
10 min.	115·4 mm.	$4{\cdot}97 \times 10^{-4}$	50 min.	271·1 min.	$4{\cdot}80 \times 10^{-4}$
20 ,,	173·5 ,,	5·01	60 ,,	289·1 ,,	5·01
30 ,,	217·0 ,,	4·81	70 ,,	302·7 ,,	5·15
40 ,,	248·0 ,,	4·80	80 ,,	312·8 ,,	5·22

The pressure increase is so great in this reaction that a suitable glass Bourdon type of manometer is used as the measuring instrument. Corrections must, of course, be made for the fact that the N_2O_4 is partially dissociated to NO_2. It is interesting to note that even when nitrogen pentoxide is dissolved in inert solvents such as bromine, carbon tetrachloride, ethylene dichloride, etc., the velocity of reaction is precisely the same as it is in the gas phase. In this case it is most convenient to measure the volume of oxygen evolved.

From the fact that the reaction is first order, it may be presumed that the decomposition is concerned with only *one* molecule of N_2O_5. The stoichiometric equation shows, however, that two molecules appear to be concerned in the reaction. It is presumed, therefore, that the first step in the reaction is $N_2O_5 = N_2O_3 + O_2$, followed by the rapid reaction $N_2O_5 + N_2O_3 = 2N_2O_4$. In all such composite reactions the slowest is the rate-controlling step.

Many other first order homogeneous thermal reactions are known, and include the decomposition of many relatively complex organic molecules such as aldehydes, azomethane, nitrous oxide. These reactions are extremely complex, and the first order behaviour does not give a real clue to the mechanism.

Pseudo-unimolecular Reactions.—If a reaction rate is proportional to the first power of the concentration of one of the reactant molecules, and if the concentrations of the other reactants is by some means maintained constant, then the reaction is referred to as pseudo-unimolecular. One of the best examples is the acid hydrolysis of sucrose,

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O\ (\text{acid}) = \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}.$$

This reaction is catalysed by acids in presence of water, the latter concentration remaining constant. The reaction could be followed by determining the concentration of glucose by its reducing capacity for Fehling's solution, but, in fact, it is much more convenient to follow the reaction by measuring the optical rotation of the solution. The optical rotation is precisely proportional to the concentration of the optically active component. Hence, if a_o and a_∞ are the rotations the beginning and end of the experiments, due regard being paid to the sign, then $a = a_o - a_\infty$ and $a - x = a_t - a_\infty$, where a_t is the rotation at time t. Hence, the first order constant is given by the expression

$$k = \frac{2{\cdot}303}{t} \log \frac{a_o - a_\infty}{a_t - a_\infty}.$$

Second Order Reactions.—By definition the rate of such reactions is proportional to the product of the concentrations of the two reactants or to the square of the concentration if only one reactant is present. If a and b are the concentrations respectively of the two reactants, then

$$\frac{dx}{dt} = k(a - x)(b - x).$$

On integration this gives

$$k = \frac{2{\cdot}303}{(a - b)t} \log_{10} \frac{(a - x)b}{(b - x)a}.$$

When the two concentrations are equal,

$$\frac{dx}{dt} = k(a - x)^2,$$

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}.$$

If $x = a/2$, then $\tau_{1/2} = \dfrac{2}{k \cdot a}$.

Thus the half-life is inversely proportional to the initial concentration, whereas with a first order reaction the half-life is independent of concentration. The numerical value of the k thus has the dimensions litres $mols^{-1}$ sec^{-1}. Acetaldehyde decomposes thermally and homogeneously as follows: $CH_3CHO = CH_4 + CO$. The following results show how closely the bimolecular law is obeyed.

INITIAL PRESSURE $a = 363$ mm.

t (sec.)	$a - x$ (mm.).	k, mm.$^{-1}$ sec^{-1}
42	329	$6{\cdot}79 \times 10^{-6}$
105	289	6·71
242	229	6·66
480	169	6·59
840	119	6·72
1440	79	6·82

The bimolecular course of the reaction is not followed except over a restricted range of pressures, and, in fact, at high enough pressures the reaction follows a first order law.

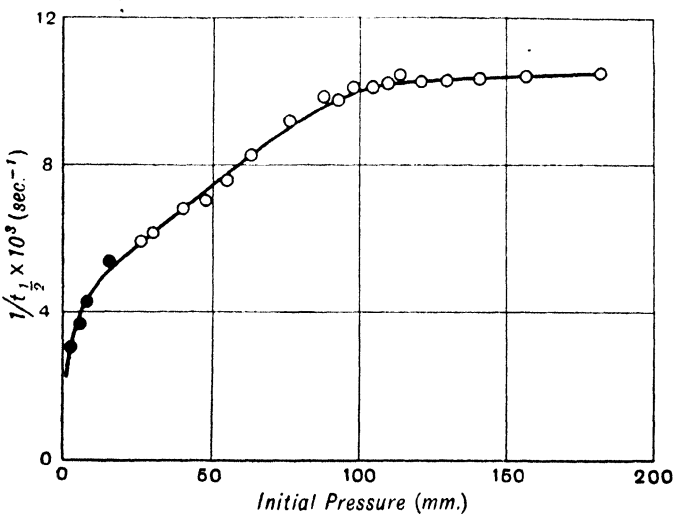


FIG. 138.

(Redrawn from Hinshelwood, *The Kinetics of Chemical Change*, by permission of Oxford University Press.)

A convenient way in which to look for transition of this kind is to plot the reciprocal half-life as a function of concentration. Such a plot is shown in Fig. 138 for the

thermal decomposition of acetone. It will be observed at high pressures the reaction is of the first order, whereas at lower pressures second order characteristics make their appearance, there being a *continuous* transition between the two types.

Third Order Reactions.—If the concentrations of the three reactants are identical, then the velocity expression is

$$\frac{dx}{dt} = k(a-x)^3,$$

which, on integration, yields

$$k = \frac{1}{2t} \cdot \frac{1}{(a-x)^2} - \frac{1}{a^2}.$$

When $x = a/2$, then

$$\tau_{1/2} = \frac{3}{2} - \frac{1}{ka^2}.$$

The dimensions of k will therefore be litres^2 mols^{-2} sec^{-1}. The best examples of third order reactions involve nitric oxide in the following way :—

$$2NO + O_2 = 2NO_2.$$
$$2NO + Cl_2 = 2NOCl.$$
$$2NO + Br_2 = 2NOBr.$$

Reactions of higher order than the third are very rarely encountered and, in fact, are of little account in chemical kinetics and may be disregarded. The reason for this statement will become apparent from what is said below in regard to the mechanism of reactions.

Mechanism of Chemical Change.—Besides the effect of concentration on reaction velocity it is found almost invariably that increase of temperature increases the velocity exponentially. In general, thus

$$\text{Rate} = \text{constant} \cdot e^{-A/RT}.$$

The value of A which has the dimensions of energy since R is in calories per degree. Its magnitude will determine the temperature coefficient. Values of A range from 1,000 to 100,000 calories. The only well-authenticated examples of homogeneous gas reactions in which there is a slight decrease

of rate with increasing temperature are the above-mentioned third order reactions involving nitric oxide.

The thermal decomposition of gaseous hydrogen iodide is a homogeneous reaction, that is, the velocity is independent of the nature of the containing vessel and of its surface-volume ratio and, apart from the effect of concentration, it is not affected by any other factor except temperature. It may be confidently presumed that the reaction wholly takes place in the gas phase and that no type of catalytic agent plays a part. The reaction is strictly of the second order when due account is taken of the reverse reaction, and since the stoichiometric equation also involves two molecules of hydrogen iodide, thus

$$2HI = H_2 + I_2,$$

it must be supposed that the rate is governed by the rate at which hydrogen iodide molecules collide. The surprising fact is that apparently only a small fraction of the collisions results in chemical decomposition, as the following calculations show. The number of collisions which one HI molecule makes with other molecules is accurately given by

$$Z = \sqrt{2} \cdot \pi u \sigma^2 n \text{ per second,}$$

where u is the mean velocity $\left(u = \sqrt{\frac{8}{3\pi}}(\bar{u}^2)^{1/2}$ where $\bar{u}^2$ is the mean squared velocity (p. 59)$\right)$, σ is the molecular diameter in centimetres, and n is the number of molecules per cubic centimetre. The total number of collisions per cubic centimetre is therefore

$$1/2 \cdot \sqrt{2}\, \pi u \sigma^2 n^2,$$

the factor 1/2 being inserted to avoid counting each collision twice. Considering the reaction at 556° K., the following data may be used : $u = 3{\cdot}3 \times 10^4$ cm./sec., $\sigma = 3{\cdot}5 \times 10^{-8}$ cm. If the concentration is taken as 1 gm. molecule/litre, $n = 6{\cdot}1 \times 10^{20}$. Since Avogadro's number is $6{\cdot}1 \times 10^{23}$, then the total number of collisions is $3{\cdot}2 \times 10^{26}$ per c.c. or $3{\cdot}2 \times 10^{29}$ per litre per sec. Expressing this as a fraction of a gram molecule by dividing by N, the result is $1{\cdot}66 \times 10^3$. This really is the maximum possible value of the bimolecular velocity constant. The experimental value is $3{\cdot}5 \times 10^{-7}$.

There must therefore be some other factor that makes collisions so ineffective, and it is necessary to inquire how this factor originates.

When it was found that the rate of reactions was exponentially dependent on temperature, Arrhenius made the suggestion that only specially activated molecules took part in reaction. These active molecules were in equilibrium with normal molecules in the same way that equilibria exist in homogeneous systems. Furthermore, Arrhenius postulated on this basis that

$$\frac{d \log (A)/(A^*)}{dt} = E/RT^2,$$

when E is the energy required to convert a normal molecule into an activated molecule, and (A) and (A^*) are the respective concentrations.

Integration of this equation gives

$$\frac{(A^*)}{(A)} = \text{constant } e^{-E/RT}.$$

In simple enough cases by the application of the principles used in deriving Maxwell's Law for the distribution of velocities it can be shown that the value of the constant is unity, so that the equation is reduced to

$$(A^*) = (A)e^{-E/RT}.$$

If, therefore, we assume that the rate of reaction is really governed by the rate at which activated molecules collide, then the ratio A^*/A will be given by the actual value of the bimolecular constant divided by the maximum possible value calculated from kinetic theory. This ratio is $7{\cdot}9 \times 10^{-18}$ at 556° K. The value of E is 44,000 cal. and $e^{-E/RT} = 5{\cdot}3 \times 10^{-18}$, which is in very good agreement with the ratio of rate to collision number. Thus one of the all-important observations in bimolecular reactions is that provided sufficient energy of activation is present during the collision, reaction immediately ensues. In other words, the rate of collision of activated molecules is numerically equal to the rate of reaction. This is a generalisation of far-reaching importance, since it means that reactivity is determined, not only by the number of collisions, but by energy factors involving exponential terms. It holds to a

first approximation for simple bimolecular reactions. The range of its validity is most easily seen by plotting the energy of activation as a function of the temperature at which the velocity coefficient attains an arbitrarily defined value. The linear relation graph shown on Fig. 139

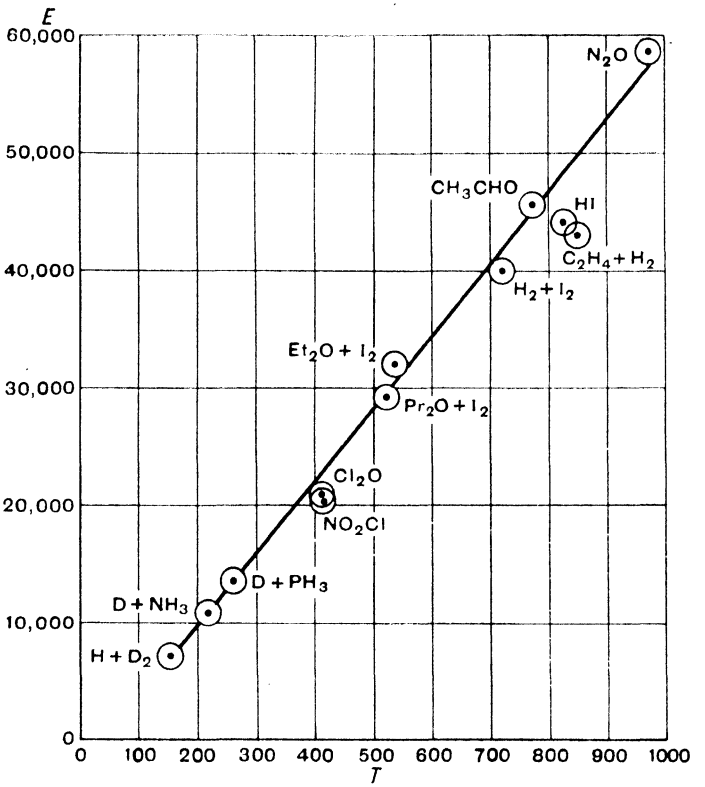


FIG. 139.

(Redrawn from Hinshelwood, *The Kinetics of Chemical Change*, by permission of Oxford University Press.)

shows how well the generalisation holds. With bimolecular reactions involving more complex molecules, the generalisation breaks down. Thus instead of writing $k = Ze^{-E/RT}$, where Z is the collision rate at unit concentration, the expression has to be replaced by $k = PZe^{-E/RT}$, where P is a factor which may be many powers of 10 greater or less than unity. It is sometimes referred to as a steric or temperature independent factor. Where Z is less than unity

it originates because complex molecules have to be oriented appreciably before reaction will occur. The appropriate orientation does not arise at every collision.

The Theory of First Order Reactions.—First order reactions have high temperature coefficients, and, presumably, therefore, activation energy is necessary to effect reaction. The difficulty is to understand how first order characteristics can be exhibited in spite of the fact that activation must necessarily occur by collision between molecules. The explanation first given by Lindemann (now Lord Cherwell) is that there is sometimes a time lag between activation and reaction. Such a time lag exposes the activated molecule to collisions by normal molecules which remove part of the energy of activation. This can most easily be seen by considering the matter quantitatively. Suppose the normal molecules are denoted by A and the activated molecules by A^*, then there are three essential steps in the reaction (a) activation, (b) deactivation, and (c) reaction thus :—

$$\begin{aligned} A + A &= A^* + A \quad k_1, \\ A^* + A &= 2A \quad k_2, \\ A^* &= B \quad k_3, \end{aligned}$$

where B represents the products of reaction. It will be observed there are two ways in which the activated molecules are removed, by deactivation and by spontaneous reaction. These two rates must be equal to the rate of activation. Thus if the concentration of A is constant, the concentration of A^* will be constant, and consequently we may write $d(A^*)/dt = 0$. A stationary concentration or stationary state will be set up. M. Bodenstein was the first to realise the usefulness of the existence of such a stationary state in the analysis of reaction mechanism. We may therefore write

$$\frac{d(A^*)}{dt} = k_1(A)^2 - k_2(A^*)(A) - k_3(A^*) = 0.$$

Solving the equation for A^* gives

$$A^* = \frac{k_2(A)^2}{k_2(A) + k_3}.$$

But the rate of the reaction is

$$\frac{-d(A)}{dt} = k_3(A^*) = \frac{k_2 k_3(A)^2}{k_2(A) + k_3}.$$

If $k_2(A) < k_3$, then

$$-\frac{d(A)}{dt} = \frac{k_2 k_3}{k_2}(A),$$

that is, a first order equation is obtained. This condition, however, is dependent on the assumption that $k_2(A) > k_3$. Physically this means that $k_2(A)(A^*) > k_3(A)$ or that the rate of reaction is smaller than the rate of deactivation. This is equivalent to saying that there is a time lag between activation and reaction. At low enough pressures, however, $k_2(A) < k_3$ and

$$-\frac{d(A)}{dt} = k_2(A)^2$$

and the reaction therefore becomes bimolecular. Thus there will be a continuous transition from a first order to a second order reaction as pressure is decreased. This kind of behaviour has been observed. It is best exhibited by plotting the reciprocal half-life of the reactant as a function of pressure. For first order characteristics, $\tau_{1/2}^{-1}$ is independent of pressure, whereas $\tau_{1/2}^{-1}$ is proportional to pressure for second order characteristics (Fig. 138).

Collision Types.—The above mentioned examples of first, second and third order reactions show the collision types that exist in reaction mechanisms. Furthermore, there may be intermediate orders depending on the time-scale of molecular processes. Most chemical reactions are, however, very much more complex processes, but, by appropriate analysis, the reaction may be broken down to a sequence of collision types of the kinds mentioned above. Each one of these types can be characterised by the method already outlined.

Complex Reactions.—It is outside the scope of this book to discuss complex reactions, but one example may suffice to show the method of attack. The combination of hydrogen and iodine to form hydrogen iodide is a straightforward bimolecular reaction similar in every way to the decomposition of hydrogen iodide. On the other hand, the combination of hydrogen bromide is also homogeneous but follows the following rate equation,

$$+\frac{d(\mathrm{HBr})}{dt} = \text{constant } (\mathrm{H_2})(\mathrm{Br_2})^{1/2},$$

before any appreciable amount of HBr accumulates. The difficulty is to understand why the bromine concentration appears to the power of one-half. Bodenstein made these observations in 1900, and it was not until 1919 that the following valid explanation was advanced simultaneously by Polanyi, Christiansen, and Herzfeld :—

$$Br_2 \rightleftharpoons 2Br,$$
$$Br + H_2 = HBr + H,$$
$$H + Br_2 = HBr + Br.$$

It was suggested that an equilibrium is set up between bromine atoms and molecules, that the bromine *atoms* react with hydrogen molecules in an ordinary bimolecular reaction, the important point being that a hydrogen atom is thus generated. This atom attacks a bromine molecule with the formation of another bromine atom. The bromine atom concentration is therefore not disturbed by the formation of hydrogen bromide. Consequently, if we know the equilibrium constant K for the thermal dissociation of bromine, the concentration of Br is simply given by $(Br) = K^{1/2}(Br_2)^{1/2}$. The rate of formation of HBr will thus be given by twice the rate of interaction of bromine atoms with hydrogen molecules or

$$\frac{d(HBr)}{dt} = 2k(Br)(H_2)$$
$$= 2k(H_2)\ K^{1/2}(Br_2)^{1/2}.$$

Since rates of reaction and concentrations are known, the value of k can be calculated. At 277° c. it has the value $4{\cdot}9 \times 10^{-3}$ litres, mols, and seconds. By measuring the velocity of the reaction at a series of temperatures, the energy of activation works out at 17·7 kg.-cal. If the temperature of the system is high enough, one bromine may cause more than two molecules of hydrogen bromide to be formed. When this occurs the reaction is said to be a chain process, for the cycle of events mentioned above may be repeated several times. The number of such cycles is then called the chain length.

The combination of hydrogen and bromine is typical of a great class of chemical reactions in which the essential step involves atoms instead of activated molecules in the rate-controlling step. The general feature is that of thermal fission of a molecule into atoms (or radicals), which atoms

virtually act as a kind of catalyst in the sense that they are not consumed. After having initiated several chemical cycles, they disappear by combination. Although the chain length is not very large in the $H_2 - Br_2$ reaction, in the combination of H_2 and Cl_2 the value may rise to a million, and in polymerisation of vinyl compounds (p. 521) and the oxidation of hydrocarbon may rise to many thousands.

The question as to whether a reaction will occur by an atom or molecule mechanism is a vital one in elucidating mechanism. There is, however, an overriding energetic factor which may well be illustrated in the $H_2 - I_2$ reaction. The mechanism might have followed that for $H_2 - Br_2$, viz., $I_2 = 2I$, $I + H_2 = HI + H$, $H + I_2 = HI + I$. Although the first step requires a smaller energy of activation than the dissociation of bromine, namely, 35·4 kg.-cal., the second step is likely to be difficult. Although the heat of this reaction cannot be directly determined it can be estimated to be not less than 32 kg.-cal., for the heat of dissociation of hydrogen is 103 kg.-cal. and that of HI 71 kg.-cal. Energetically, therefore, it is a much more economical process for the reaction to proceed through the intermediary of activated molecules.

Chain Reactions.—We have already seen that in analysing the mechanism of the $H_2 - Br_2$ reaction, there is the possibility that one bromine atom might cause the formation of more than two hydrogen bromide molecules. This repetition of cyclic processes is very much more pronounced in other reactions. This is most strikingly demonstrated in the combination of hydrogen and chlorine, in which, under favourable circumstances, as many as a million molecules of HCl may be produced for each chlorine atom introduced into the system by the dissociation of chlorine molecules with radiation. Undoubtedly the mechanism is similar, namely, $Cl + H_2 = HCl + H$ followed by $H + Cl_2 = HCl + Cl$. The chlorine atoms can disappear by combination to Cl_2 molecules, but owing to their exceptional reactivity they may also react even with minute traces of oxygen or other impurities adventitiously present in the system.

Many similar reactions of chlorine with other molecules give rise to similar chain processes with similar general characteristics. Methane, for example, is chlorinated by the following mechanism: $Cl + CH_4 = CH_3Cl + H$, $H + Cl_2 = HCl + Cl$, and so on. All the hydrogen atoms so

generated attack Cl_2 readily, and the cycle of events is ultimately brought to a stop by the disappearance of the chlorine atoms. Likewise, the formation of phosgene proceeds by an exactly similar process: $Cl + CO = COCl$, $COCl + Cl_2 = COCl_2 + Cl$.

Determination of Chain Length.—The number of cycles in a chain process can be determined by measuring, for example, the number of hydrogen chloride molecules formed for each chlorine atom originally introduced into the system. The former is a matter of gas analysis; the latter problem is somewhat more complicated. Chlorine absorbs radiation in the violet, blue, and part of the green of the spectrum, *i.e.*, wave-lengths extending approximately from 3500 A. to 5500 A. When it does so the radiation dissociates the molecule into two atoms. The evidence for this dissociation comes from a variety of sources—first, chemical evidence mentioned above; second, the pressure increase on illumination due to the presence of more particles in the gas mixture; and third, the slight decrease in absorption of light due to the decrease in the concentration of chlorine molecules. There is also evidence that dissociation occurs from the nature of the absorption spectrum which cannot be discussed here. All this evidence points to the fact that one quantum or photon dissociates one molecule, *i.e.*, $Cl_2 + h\nu = 2Cl$, where ν is the frequency of monochromatic radiation and h is Planck's constant. This simple relationship between the number of molecules chemically decomposed and the number of quanta absorbed is usually referred to as *Einstein's Law of Photochemical Equivalence.* Unfortunately this relationship is only occasionally observed, and cannot therefore be given the status of an inviolable law. In performing photochemical experiments with monochromatic radiation, the arrangement is diagrammatically shown in Fig. 140. A source of light, a monochromatic filter, and a lens produce a parallel beam of light which passes through the cylindrical reaction vessel. A second lens focuses an image on the detector, which may either be a thermopile or bolometer, having a surface such that all the radiation is absorbed. Assuming the detector is a linear device, a deflection D_1 is registered. When, say, chlorine gas is allowed into R.V. at a defined pressure, the deflection is reduced to D_2. $D_1 - D_2$ will not be exactly the intensity of the radiation absorbed, since some reflection

occurs at the glass interfaces. If the refractive index is known this correction can be accurately computed provided there is no absorption by the glass. The sensitivity of the detector may be determined by exposing it to radiation from a black body at a known temperature and calculating from the radiation formula the number of ergs per second that fall on the detector. In this way, then, the number of

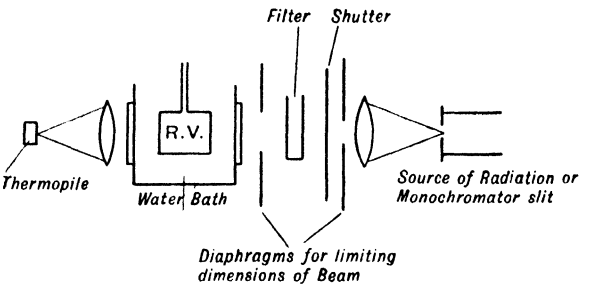


FIG. 140.

(From Farkas and Melville, *Experimental Methods in Gas Reactions*, by permission of Macmillan & Co. Ltd.)

ergs absorbed by the substance in v can be computed in a given time t. The problem now is to convert ergs into quanta. According to the quantum theory of radiation the number of ergs ϵ in a quantum of radiation frequency is given by $\epsilon = h\nu$. Hence the number of quanta (n) absorbed by the system $n = E/h\nu$. ($h = 6{\cdot}55 \times 10^{-27}$ erg. sec.).

The Einstein.—In photochemical reactions it is convenient to deal in mols, and consequently a number of quanta numerically equal to Avogadro's number is referred to appropriately enough as an Einstein. One of the first important matters that have to be settled in dealing with photochemical reactions is to decide whether there is enough energy available in the radiation in order to effect chemical change. For a variety of reasons it is usually found that considerably more energy than the minimum is necessary for chemical transformation. It is of interest to calculate the amount of energy U in an Einstein at different frequencies $U = Nh\nu = Nhc/\lambda$, where c is the velocity of light *in vacuo* and λ is the wave-length in centimetres. Inserting numerical values we have

$$U = 6{\cdot}03 \times 10^{23} \times 6{\cdot}62 \times 10^{-27} \times 2{\cdot}998 \times 10^{10} \times \lambda^{-1}$$
$$= 1{\cdot}197 \times 10^{8}\lambda^{-1} \text{ ergs.}$$

If λ is expressed in Angström units and ergs are converted to calories by dividing by $4{\cdot}18 \times 10^7$, then we have

$$U = 2{\cdot}860 \times 10^8 \lambda^{-1} \text{ cal./gm. mol.}$$

The following table gives some numerical values for various wave-lengths :—

λ (A.)	7500	5900	4900	4500	2000
U (kg.-cal.)	38·1	48·5	58·4	63·5	143·0

These energies are quite comparable with those needed to break chemical bonds, for example, the dissociation energy of iodine is 35 kg.-cal. and that of oxygen 117 kg.-cal. It will also be seen that for radiation in the infra-red, *i.e.*, greater than 8000 A., the magnitude of the quantum would be quite insufficient to produce bond fission.

Quantum Efficiency.—This quantity may be defined as the ratio of the number of molecules chemically transformed to the number of quanta absorbed. It is an exception to find experimentally a ratio of unity ; the values may range from much less than unity up to about one million for the photo reaction between hydrogen and chlorine. The reason for this wide variation is partly physical and partly chemical. It is convenient to illustrate the point by referring again to the $H_2 - Br_2$ reaction, which can be brought about by light absorbed by the bromine. When a light quantum is absorbed by the bromine molecule, the motion of one of the electrons is changed so that the molecule becomes electronically excited. It is possible, then, for the molecule to do two things : (*a*) the reverse of the act of absorption, *i.e.*, to emit the radiation originally absorbed, or fluorescence, (*b*) the molecule is broken into two atoms. This primary act may thus have a quantum efficiency of anything from zero to unity. Once the bromine atom is produced, there is once more a choice of possibilities : (*a*) the atoms may react with a hydrogen molecule thus, $Br + H_2 = HBr + H$; (*b*) the atom combines with another $Br + Br = Br_2$ without, therefore, producing any chemical change whatsoever. The secondary yield may likewise range from zero through unity to quite high values, depending on these relative probabilities. Thus increase of temperature favours (*a*), which has an energy of activation of 17 kg.-cal., whereas (*b*) is not affected. It is therefore not surprising that the essentially composite nature of photochemical

reactions yields quantum efficiencies deviating markedly from unity. In spite of these complications, certain reactions exhibit a simple enough behaviour.

Photodecomposition of Gaseous HI and HBr.—The classical investigations of E. Warburg,[1] made at a time when the quantum theory was just beginning to be applied to chemical problems, laid the foundations of quantitative photochemistry. With hydrogen iodide the following values for the overall quantum yield were obtained :—

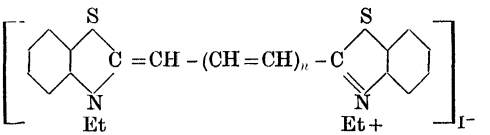
Wavelength *A*.	Quantum Yield.
2070	1·95
2530	2·07
2820	2·2

Considering the elementary stage of photochemical technique in these first experiments, we may say that the quantum yield is 2 and that it does not depend on wavelength and, for that matter, on temperature. The value of 2 is readily explained by the following mechanism. The primary process is fission $HI + h\nu = H + I$. The iodine atom is so unreactive that it simply combines with another. The hydrogen atom, on the other hand, readily attacks another HI molecule, thus : $H + HI \longrightarrow H_2 + I$, and there the process ends.

Photosensitisation.—Although the quantum of radiation that falls on a system may contain sufficient energy to initiate the chemical transformation, the radiation may not be absorbed or, if absorbed, may for various reasons produce no chemical effect. This difficulty can be overcome by the use of photo-sensitizers, whose function is to absorb the light and to transform the energy so acquired into a more chemically useful form. The outstanding example is photosynthesis of carbohydrates by plants, chlorophyll being the sensitiser. Here the essential reaction is the conversion of CO_2 and H_2O into sugars of the general formula $C_6H_{12}O_6$, with eventual conversion into cellulose $(C_6H_{10}O_5)_n$. Even if we restrict the reaction to $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$, this requires 670 kg.-cal. per mol of hexose. The minimum size of quantum would thus correspond to a wave-length of c. 400 A. Carbon dioxide and water begin to absorb at 2000 A. (140 kg.-cal.), and a direct reaction is energetically not feasible. Yet the fact is that chlorophyll sensitises the

[1] *Ber. Berl. Akad.*, **1918**, 300.

reaction to a quantum of energy of about 50 kg.-cal. The reaction must therefore take place in successive stages, each involving a quantum. The overall quantum efficiency is extremely low. The other striking example is the dye photosensitised decomposition of silver halides used in photographic emulsions. The silver bromide and silver iodide embedded in gelatine, which comprises the emulsion, do not absorb except in the blue region of the spectrum. H. W. Vogel, in 1873, discovered that certain dyestuffs, such as eosin and erythrosin, when adsorbed on the surface of the silver halide crystal, produce photographic sensitivity down to wave-lengths of 5500 A. Once the principle was established, intensive research led to the development of a great variety of dyes of the cyanine type



which produce sensitisation even into the infra-red at 10,000 A.

Much simpler examples are found in gas phase reactions. For example, the combination of hydrogen and oxygen can be sensitised by using mercury vapour. Just as sodium vapour absorbs the *D* lines from a sodium flame or electric discharge tube, so mercury vapour strongly absorbs radiation emitted by excited atoms at 2537 A. In absence of added gases both vapours fluoresce, sodium at 5890 and mercury at 2537 A., owing to the excited atoms losing their electronic energy by emission of radiation. At 2537 A. the mercury atoms possess 112 kg.-cal. per gram atom, which is sufficient energy to initiate chemical reactions. Hydrogen, when mixed with mercury at pressures of a few millimetres of mercury or more, destroys all the fluorescence, and similarly the hydrogen becomes active, for it will attack oxygen, nitrous oxide, ethylene, and other gases. The energy acquired by the mercury atom is transferred by collision to the hydrogen molecule and leads to its fission into two atoms. At low enough pressures only a fraction of the excited mercury atoms are so deactivated. The pressure dependence of this process can readily be calculated. Adopting the method used for the hydrogen bromine reaction, we may write an equation showing the way the atoms are formed

and destroyed. If I_{abs} is rate at which mercury vapour absorbs quanta, then if k is a coefficient which measures the effective rate at which hydrogen molecules and excited atoms interact, then

$$I_{abs} = k(Hg')(H_2) + (Hg')/\tau,$$

where $(Hg')/\tau$ is the rate at which excited atoms radiate fluorescence. τ is the mean life of the excited atom and has a value of $1{\cdot}0 \times 10^{-7}$ sec. At a certain measurable hydrogen pressure the intensity of fluorescence can be cut down to half its value in absence of hydrogen ; under these conditions the probability of deactivation by hydrogen and by radiation will be equal.

Hence, $$k(Hg')(H_2)_{1/2} = (Hg')\tau^{-1},$$

or $$k = \{(H_2)_{1/2}\tau\}^{-1}.$$

The value of k can thus be calculated in mols, litres, and seconds. Using then the bimolecular collision rate, the square of the effective collision diameter of the excited mercury hydrogen molecule system can be computed to be 6×10^{-16} cm.[2] This diameter is of the same order as that for molecules (p. 60), and hence the transfer of energy is particularly efficient, occurring at nearly every collision.

The chemical processes occurring after the dissociation of hydrogen are complicated. With oxygen, both hydrogen peroxide and water are produced. Direct interaction with oxygen molecules gives the HO_2 radical which may be hydrogenated to H_2O_2, which may be further reduced to H_2O. Similarly, with ethylene the first step is the formation of the C_2H_5 radical. These radicals may combine to give n-butane or disproportionate to give ethylene and ethane.

Uranium Actinometer.—The UO_2^{++} ion is a good photosensitising ion for many reactions in aqueous solution. The oxalate ion $(COO)_2''$ in particular is readily decomposed, the products being CO, CO_2, and HCOOH. This reaction has been extensively studied, but the precise mechanism is not known. It is, however, so reproducible that it can be used as an actinometer. The quantum yield is only 0·5 but varies only slightly with wave-length from 2200 to 4500 A., the temperature coefficient is 1·03 per 10° C. at 20° C., and dilute solutions of uranyl oxalate at 0·001 to 0·005 M. can be used. Estimation of oxalate is done with permanganate, and consequently, even with weak sources

of radiation, unduly long exposure time is not necessary to decompose a significant fraction of the oxalate.

Photochemistry of Ketones.—The photochemical reactions of polyatomic molecules can become extremely complicated, but some of the main features of ketonic photochemistry are now clear. Absorption occurs in the ultra-violet at wave-lengths around 3000 A., which in saturated ketones is due to the $>C=O$ group. Carbon monoxide is one of the products of reaction, but the quantum yield of the reactions is less than unity. This latter fact simply means that a fraction of the quanta absorbed by the molecule is not effective in giving rise to primary dissociation, the energy being therefore dissipated in chemically ineffective ways within the molecule. If we take acetone we might presume the molecule to break up as follows: $CH_3COCH_3 + h\nu = 2C_2H_6 + CO$, since ethane is produced in amounts approximately equivalent to CO at temperatures of 70° C.

At lower temperatures, and especially in a flow system, appreciable amounts of diacetyl can be detected. Again, working in a flow system the primary products of photolysis are capable of removing mirrors of lead, which is sure proof (see below, p. 478) that free radicals are produced and that the CO is not simply eliminated from the molecules as indicated above. The primary dissociation is therefore into $CH_3CO + CH_3$. The acetyl radical may combine with itself or may be with CH_3 or decompose further into CH_3 and CO. Further, if for example, methyl ethyl ketone is used, the hydrocarbon produced should, on the free radical basis, consist of ethane, propane, and *n*-butane in the ratio 1 : 2 : 1, which is what is found. Although these reactions occur readily enough in the gas phase, acetone does not decompose in the liquid phase. Such an effect might be due to a deactivation of the initially excited molecule, but there is another interesting explanation. When primary dissociation of the molecule occurs, the radicals are hemmed in on all sides; they cannot move rapidly away from the site of production. After a short period they therefore recombine—the overall chemical result being inappreciable. If, however, they are produced in presence of molecules with which they can easily react, apparent decomposition of the ketone ensues. This behaviour is general with ketones and many other polyatomic molecules. The main principle

is that primary dissociation is into radicals and not saturated molecules. These radicals may recombine to give the original molecules—with the result of a diminished quantum yield—or they may undergo a variety of other reactions, thus giving rise to products dependent to a large extent on the pressure and temperature of the system.

The reason for low quantum yields thus becomes evident. It is exceptional to find quantum yields of unity when so many processes militate against high efficiency.

Free Atoms and Radicals.—Enough has already been mentioned about reactions to indicate the important role of free atoms and radicals rather than so-called activated molecules, originally postulated to play the essential part in reactions. It is therefore of importance to consider more direct methods of producing and examining the elementary reactions of free atoms and radicals. In virtue of their high reactivity such bodies only exist for very short periods of time, usually a fraction of a second, consequently, it is impracticable to attempt to measure the occurrence of atomic reactions in a static system—it is, in fact, essential to employ a flow system. This was first done by R. W. Wood, who prepared atomic hydrogen in the following way. The apparatus (Fig. 141) consists of a discharge tube to which hydrogen can be admitted at a pressure of a few millimetres of mercury. The tube is connected to a mercury vapour diffusion pump which produces a linear velocity of flow of gas of the order of 10^3 cm./sec. By means of side tubes, gases and solids may be inserted into the gas stream. At pressures of a few millimetres a discharge will pass through with a potential of a few thousand volts. At low pressures the discharge is red in colour, and the spectrum simplifies so that only the so-called Balmer lines at 4102, 4340, 4861, and 6563 A. appear, indicating, therefore, the presence of hydrogen atoms. These atoms are, however, excited in that they possess considerable electronic energy, which is got rid of when radiation occurs. The spectroscopic evidence therefore points to the dissociation of hydrogen molecules ultimately to excited atoms. If the pumping speed is high enough it should be possible to remove the atoms away from the mixture of electrons, positive ions, excited molecules, and atoms that inevitably exist in a discharge tube. The evidence that some chemically active form of hydrogen exists in the tube leading to the pump is provided by the

following facts. A thin piece of nickel foil is rapidly heated to redness; sodium vapour will luminesce; gases such as hydrogen, carbon monoxide, ethylene, and acetylene are attacked with great ease at room temperature. In fact, with acetylene, there is strong luminescence due to the complete break-up of the molecule into fragments such as C_2 and CH. The concentration of atomic hydrogen can be measured in a variety of ways, and one, the most direct, simply consists

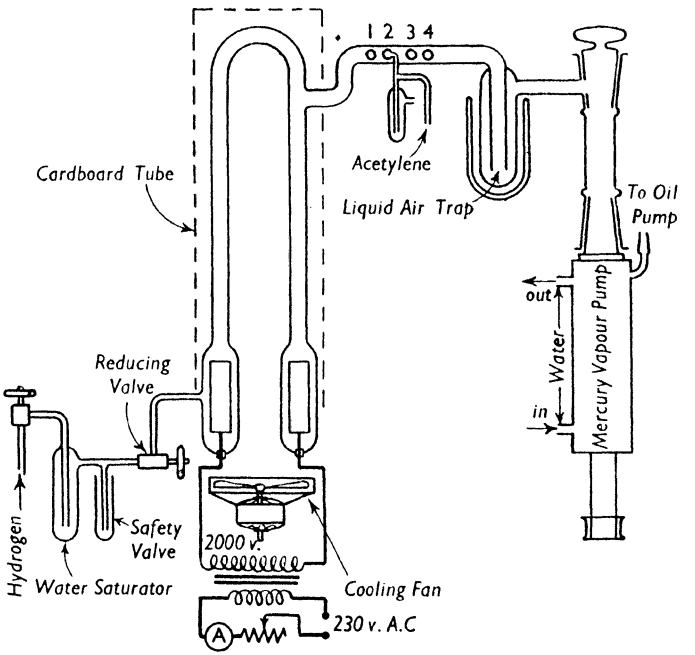


FIG. 141.

in inserting a thermometer of which the bulb is covered with a film of finely divided platinum. All the hydrogen atoms that strike the bulb combine to molecular hydrogen, giving out 103 kg.-cal. per mol of H_2. This heat is sufficient to raise the temperature of bulb several degrees. From the heat capacity of the bulb it is then possible to calculate the concentration of atomic hydrogen. By such methods it can be shown that the concentration of hydrogen decreases rapidly along the tube. This is due to recombination which may occur in the gas or at the walls. By measuring in this way the distance d cm. along the tube for the concentration

to fall to half its value and by measuring the linear rate of flow, e cm./sec., the life-time of the atom is d/e sec. This life-time is not a physical characteristic of the atom because it depends on concentration—the higher the concentration the shorter the life-time. Life-times are, however, within the range $10^{-3} - 10^{-1}$ sec., so that it is not surprising it is impossible to do static experiments with such short-lived entities.

Free Organic Radicals.—The discharge tube method, while suitable for diatomic molecules, is not satisfactory with polyatomic molecules since a multiplicity of atoms, radicals and molecules may be produced in the discharge. It would be quite impossible to identify and examine the behaviour of individual species. F. Paneth discovered a much simpler method of producing alkyl radicals in the gas phase. It was known that metallic alkyls, such as lead tetramethyl, on heating, decompose to give lead and ethane, but if the experiment is carried out in a flow system, the result is rather different. In this system a carrier gas, such as nitrogen, is allowed to bubble through liquid lead tetramethyl. The vapour is decomposed thermally at 700° C. The mixed gases are then swept out of the hot zone with a pump giving a linear flow velocity of *circa* 100 cm./sec. The surprising fact is that a thin lead mirror deposited on the cool part of the tube is removed and the metallic alkyl can be collected in a trap cooled with liquid air in front of the vacuum pump. This observation can only be explained if it is assumed that the $PbMe_4$ molecule breaks up in a succession of stages, thus, $PbMe_3 + Me$, $PbMe_2 + Me$, and so on, the lead atom settling out and the methyl radical being removed by the carrier gas. By altering the position of the detecting mirror it can be shown that the time required to remove a standard mirror is related to the distance d from the zone of decomposition by the relation $\log d = t + \text{const.}$ Since the reciprocal of the time of removal is proportional to the time for the radical to travel the specified distance, such a relation implies that the radicals disappear at a rate proportional to the first power of their concentration. This further means that combination tends to occur on the walls and not in the gas phase. The life-times are again of the order $10^{-3} - 10^{-1}$ sec. While ethyl and propyl radicals can also be made in this way, if attempts are made to prepare higher alkyl radicals, *e.g.*, *n*-butyl,

methyl radicals only are detected. The reason is that these larger radicals are thermally unstable and tend to decompose thus $R . CH_2 . CH_2 - CH_2 \rightarrow R - CH = CH_2 + CH_3$. Similar mirror experiments have been made with many simple organic molecules and it was almost invariably found that radicals are involved in the products of decomposition. This fact would indicate that in the thermal decomposition of molecules there is a greater tendency for the splitting of the molecule into radicals than into simpler molecules. We shall see below that there is good reason to believe that radicals play a large part, not only in gas phase processes. but also in liquid phase reactions.

Chemiluminescence.—This is the phenomenon of the emission of light as a consequence of chemical reaction and thus in a way is the converse of photochemistry. It is customary to exclude luminescence emitted during explosive combination, though the phenomenon has essentially the same origin. Chemiluminescence is observed in both gas and liquid phases ; classical examples of the former are oxidation of phosphorus, sulphur and many of their compounds : of the latter the oxidation of pyrogallol, aminophthalic hydrazide and many others. All these reactions are strongly exothermic, and it would seem that some of the energy can be used in quite a selective fashion to excite the electrons in molecules so that part of the energy is finally removed from the system as radiation. Logically, therefore, if the spectrum of the emitted radiation is analysed, it should be possible to determine the structure of the emitter. It is an unfortunate fact that in the systems mentioned above, this has not been accomplished. Similar chemiluminescence is observed when vapours of sodium and halogen mix at very low pressures. This can readily be demonstrated by heating sodium and iodine in an evacuated tube. The sodium D lines are emitted at the point where the vapours interdiffuse. Hence there is no doubt about the nature of the emitter—it is an excited Na atom. The luminescence is confined to such a narrow zone of the tube that there is little doubt reaction between sodium and iodine occurs very rapidly indeed. F. Haber and M. Polanyi have investigated not only the distribution of the intensity of luminescence but also the distribution of sodium chloride. The first step in the reaction is simply $Na + Cl_2 \rightarrow NaCl + Cl$. This cannot be followed by $Na + Cl \rightarrow$

NaCl (in the gas phase) because so much energy would be liberated that the molecule would be disrupted. At such low pressure there is little probability of a third molecule being present to remove the energy and so stabilise the molecule. The surprising fact in this reaction is that the intensity of the luminescence diminishes if the temperature of the zone of reaction is increased. This is readily explained as follows : In sodium vapour there is present a small fraction of sodium molecules Na_2. The chlorine atoms react with the molecules $Cl + Na_2 \rightarrow NaCl + Na$ in a strongly exothermic reaction the NaCl molecule possessing a very large amount of energy of vibration. The molecule collides with a sodium atom, excites it, finally the energy of excitation is emitted as D light. At higher temperatures the equilibrium concentration of Na_2 molecules decreases and, therefore, with it the intensity of luminescence. If, instead of using Cl_2 we use CH_3Cl, NaCl is still formed, but there is no chemiluminescence for there are no sufficiently energetic molecules capable of exciting sodium atoms.

Inhibition and Retardation of Reactions.—It has been known for a long time that the addition of minute amounts of certain specified substances, *e.g.*, 0·1 per cent. by weight, may completely suppress or seriously cut down the rate of what are believed to be homogeneous reactions. Prominent examples are the stabilisation of solutions of hydrogen peroxide by acetanilide; the retardation of oxidation processes, *e.g.*, of liquid aldehydes, of unsaturated esters, rubber, phosphorus ; the polymerisation of vinyl compounds, such as styrene $C_6H_5CH=CH_2$. The general explanation of this curious behaviour was originally given by H. J. L. Bäckstrøm, who studied particularly the oxidation of benzaldehyde, heptaldehyde, and aqueous sodium sulphite, and found that alcohols in particular were effective in cutting down the rate of oxidation. The magnitude of the effect was such that it was termed negative catalysis—a term now outmoded since the correct explanation has now been given. It was suggested that if a thermal chain reaction were operative and if the retarder were capable of reacting with the chain carriers more easily that the molecule being oxidised, then the breaking of the chain at an early stage would cut out all the subsequent steps. If these chains are long, for example, several thousands, it is then understandable why such small concentrations can

diminish the rate. From the quantum yield in a photochemical reaction it is possible to calculate the chain length, but in a thermal chain reaction no such convenient method is ordinarily available. The following method, however, may be used. In an oxidation reaction such as benzaldehyde—perbenzoic acid C_6H_5COOOH is the primary product of oxidation. Suppose this molecule breaks down thermally to a free radical R which may be the benzoate C_6H_5COO or OH radicals, then the following sequence of reactions may occur.

$$\dot{R}- + O_2 \rightarrow RO_2-$$
$$RO_2 + RH \rightarrow RO_2H + R-$$

RH, RO_2H representing the aldehyde and perbenzoic acid respectively. This cycle of events may go on repeatedly until either the R– or RO_2– radicals interact with each other. It appears that the addition of oxygen to the radical is a very fast reaction, and the second reaction is the rate determining step in the sequence. The RO_2– radicals, therefore, build up to a higher concentration than R–. It is most probable that RO_2– radicals interact and thus destroy each other. Suppose, further, that I represents the rate of decomposition of per-acid into radicals and k_2 represents the velocity coefficient for interaction of two RO_2 radicals. It will be seen that the chain cycle itself does not affect the existence of RO_2 radicals. Hence $I = k_2(RO_2)^2$. But the rate of oxidation, $-d(O_2)/dt$ is simply equal to $k_1(RH)(RO_2)$

or
$$-\frac{d(O_2)}{dt} = k_1(RH)\left(\frac{I}{k_2}\right)^{1/2}.$$

That is, the rate of oxidation is unaffected by the concentration of oxygen—in accord with observation. The chain length is then given by the number of oxygen molecules used up for each radical produced by decomposition of the perbenzoic acid radical. Hence

$$\nu = \frac{-d(O_2)/dt}{I} = \frac{k_1(RH)}{(k_2 I)^{1/2}}.$$

Suppose now an inhibitor such as diphenylamine is added say, to cut down the rate by a factor of ten, then the majority of the RO_2– radicals will react chemically with the amine being thereby destroyed. If k_3 is the bimolecular

coefficient for this process, then, as before, the rate of starting of chains must be equal to their rate of removal or

$$I = k_3(RO_2)\,(X) = \frac{-d(X)}{dt},$$

i.e., the rate of removal of X is equal to the rate of initial production whether retarder is present or not. If the rate of removal can be measured chemically the kinetic chain length may at once be calculated. Bäckstrøm also showed that these reactions can be induced photochemically, the quantum yield reacting values of several hundreds, thus confirming in the most direct manner the general mechanism of oxidation.

Autocatalysis.—In following the course of oxidation reactions it is usually found that the rate of uptake of oxygen increases with the time of experiment to a maximum value and then falls off as the reactants are consumed. Sometimes quite a well marked induction period appears in which practically no oxygen is taken up. This general effect is usually referred to as autocatalysis, the implication of the term being that during the course of reaction something is produced which is capable of inducing the reaction to occur more quickly. The reason for this behaviour is readily comprehended with oxidations for, as the per-acid or hydroperoxide accumulates and, therefore, partially decomposes to free radicals, so the rate of initiation of oxidation is increased. This will tend to increase, but the gradual exhaustion of the substance being oxidised will eventually counteract this increase. There is, however, another possibility. If some adventitious retarder of oxidation is present and this is chemically removed by interaction with RO_2 radical then, provided the rate of initiation remains constant, the rate of oxidation will increase gradually as the retarder is consumed.

Polymerisation Reactions.—We have seen above that oxidations are induced to occur by the thermal decomposition of peroxides into free radicals. It is similarly possible to induce vinyl derivatives such as styrene to form polymers in which the essential reaction is simply

$$n(CH_2{=}CH\,.\,C_6H_5) \rightarrow -(CH_2-CHC_6H_5)_n-$$

One of the most direct ways of proving that this reaction goes by way of radicals is given by the fact that tetraphenyl

succinodinitrile, which breaks into diphenyl-cyano-methyl radicals, also initiates polymerisation, the characteristics of which are precisely similar to those induced by a peroxide such as dibenzoyl peroxide $(C_6H_5COO)_2$. The mechanism of reaction is therefore, analogous to, but simpler than that of oxidation. If the peroxide is written $(RCOO)_2$ the

first step is $(RCOO)_2 \rightarrow 2RCOO$

or $\rightarrow R + RCOO + CO_2$

followed by

$$R + CH_2 = CHC_6H_5 \rightarrow R - CH_2 - CH(C_6H_5)—$$

followed by

$$R—CH_2—CHPh— + CH_2 = CHPh \rightarrow$$
$$R—CH_2—CHPh—CH_2—CHPh—$$

Thus one radical can induce many molecules of monomer to polymerise by a continued radical reaction. The reaction, in this respect, has chain characteristics but with the added advantage that the chain now has a very material existence as a chain of carbon atoms. Using the same principles as those elaborated for oxidations, the so-called kinetic chain length may be found. Here the chain length is finite since these large free radicals ultimately interact. In addition the number of units forming the chain can be computed by measuring the molecular weight of the polymer produced. In absence of complications, the two methods agree very well, as shown in the following figure for the polymerisation of vinyl acetate $CH_2 = CH \cdot O \cdot CO\ CH_3$

Kinetic chain length.	No. of units from osmotic pressure experiments
1460	1400

These two independent methods provide a very powerful proof of the validity of the conceptions used to explain the characteristics of chain reactions, and, incidentally, of the existence of free radicals in the liquid phase. These reactions may also be induced by radiation and even by heating the monomer to a high enough temperature. Here it is believed the initial step is the opening out of the double bond to a diradical which may then grow at both ends.

Ionic Reactions. — Besides molecule-molecule, atom-molecule and radical-molecule interactions in aqueous solution, ions may take part in homogeneous reactions.

Reactions between ions of opposite sign, if they happen to form stable molecules which are not dissociated or are insoluble, proceed at such a high speed that the rate is merely governed by the rate with which the ions can diffuse towards each other. There are, therefore, ion-ion interactions and ion-molecule interactions. In the non-ionic reactions the nature of the medium does not normally have much effect on reaction velocity, but in ionic reactions the properties of the ions are profoundly affected by the presence of other ions which take no part in the reaction at all.

Neutral salt effect.—The effect of neutral salts on ion-ion interactions has been most satisfactorily explained by J. N. Brønsted[1] using the theory of strong electrolytes (Chap. XV, p. 392), introducing the idea of activity of ions. For example, in the reaction

$$CH_2Br \,.\, CO_2' + S_2O_3'' \rightarrow S_2O_3 \,.\, CH_2CO_2'' + Br',$$

the velocity is dependent not only on ionic concentrations but also on the concentration of added neutral electrolyte. According to the Brønsted theory a complex X is formed between the two ions which is in equilibrium with the simple ions. This complex then spontaneously breaks down into the products of reaction—the mechanism in a way being similar to that in a pseudo unimolecular reaction. If the equilibrium is established much more rapidly than the reaction takes place then

$$K = \frac{C_x \cdot f_x}{C_a f_a \times C_b f_b} \quad \text{or} \quad C_x = K_x C_a C_b \,.\, \frac{f_b f_b}{f_x}$$

where f_a, f_b, f_x are the activity coefficients of A, B and X respectively. For the velocity of decomposition of X, we have

$$v = k_x C_x$$

where k_x is the molecular coefficient for decomposition of C_x.

Substituting the values.

$$v = k_x \,.\, K_x \,.\, C_a \,.\, C_b \times \frac{f_a f_b}{f_x}$$

$$= k C_a C_b \,.\, \frac{f_a f_b}{f_x}.$$

[1] *Z. physikal. Chem.*, 1922, **102**, 169; 1925, **115**, 337. See also *Chem. Rev.*, **1928, 5**, 1231; 1932, **10**, 179. *Trans. Faraday Soc.*, 1928, **24**, 630.

The velocity of reaction is proportional not only to the ionic concentrations but also to the activity coefficients, and inversely to the coefficient for the complex. It is the activity coefficients which are strongly affected by the addition of neutral salts. In this treatment f_x cannot of course be measured directly, but it has to be presumed that it will be affected by neutral salts in the same way as f_a and f_b.

In the case of dilute solutions up to 0·1 molal (0·1 mol per 1,000 gm. of solvent) the activity coefficient of an ion of a strong electrolyte depends on its electric charge z and what is called the ionic strength μ of the solution, the ionic strength being given by half the sum of the products of the concentrations of every ion in the solution multiplied by the square of the effective charges. The mathematical relationship according to the theory of strong electrolytes is that

$$\log_{10}(f_a f_b/f_x) = z_a z_b \mu^{1/2},$$

and hence

$$v = k \,.\, C_a C_b \,.\, 10^{z_a z_b \mu^{1/2}}.$$

This expression shows the kind of effects that can be observed though it must be emphasised the absolute value of the constant k cannot be computed. When $z_a z_b$ is positive, *i.e.*, when the reacting ions have the same charge, whether positive or negative, the reaction velocity will increase with increasing ionic strength—so-called positive salt catalysis. When the reacting ions are of opposite sign, the velocity coefficient will decrease with increasing ionic strength—negative salt catalysis. When one of the reactants is uncharged—an ion-molecule interaction—the velocity is unaffected by the ionic strength of the medium. These conclusions are borne out by experiment. If the products of reaction are charged they may alter the ionic strength and, therefore, affect velocity. This effect may naturally be swamped by the addition of a sufficient quantity of neutral electrolyte.

Acid-Base Catalysis.—One of the earliest examples of catalysis is the action of acids and alkalis in accelerating hydrolysis of esters and of disaccharides such as cane sugar. The velocity of such hydrolysis is affected by the concentration of hydrogen and of hydroxyl ions. Further investigation revealed that neutral salts also could influence such reactions, with the result that a much extended theory is needed to

cope with the variety of effects observed. We deal here, however, with the ion-molecule type of reaction.

In order that a satisfactory theory can be developed, especially in non-aqueous solvents, it is necessary to extend the connotation of the terms, acids and bases, to include a much wider range of systems than is customarily dealt with. In 1923 T. M. Lowry and J. N. Brønsted [1] made this extension. According to this theory an acid may be defined as a substance which can give rise to proton ($H^{\cdot}$) or which is a proton donor ; and a base is a substance which can unite with a proton, *i.e.*, a proton acceptor. Thus an acid, like acetic acid, undergoes ionisation to give proton and an anion $HAc \rightarrow H^{\cdot} + Ac'$. Acetic acid and other acids are, therefore, proton donors. On the other hand, the anion of a weak acid can combine with a proton to form the acid and is, therefore, to be regarded as a base or proton acceptor. Thus the acetate ion and the sulphate ion are to be regarded as bases since they unite with protons to form acids,

$$Ac' + H^{\cdot} \rightarrow HAc \text{ and } H^{\cdot} + SO_4'' \rightarrow HSO_4'.$$

The anion of a strong acid is not a base because, on account of the strong acid being almost completely ionised in solution, the anion does not combine with proton to form acid.

The cation of a weak base, on the other hand, is to be regarded as an acid because it can yield proton and a base, *e.g.*, $NH_4^+ \rightarrow H^+ + NH_3$. Water is both an acid and a base. When it ionises according to the equation $H_2O \rightarrow H^+ + OH^-$ it gives up a proton and, therefore, is an acid ; and when it combines with a proton to form hydrated hydrogen ion (oxonium ion), $H^+ + H_2O \rightarrow H_3O^+$ it acts as a base. In aqueous solution, therefore, catalytic activity is shown, not only by hydrogen ion and hydroxyl ion, but by all these molecules and ions which according to the above definition act as proton donors and acceptors. Thus the hydrolysis of ethyl orthoacetate and ethyl orthopropionate is catalysed not only by hydrogen ion but by molecules of water, acetic acid [1] and similar evidence of the catalytic effects of uncharged acid molecules was obtained in the decomposition of nitramide in aqueous solution [2] and in the mutarotation of glucose.[3]

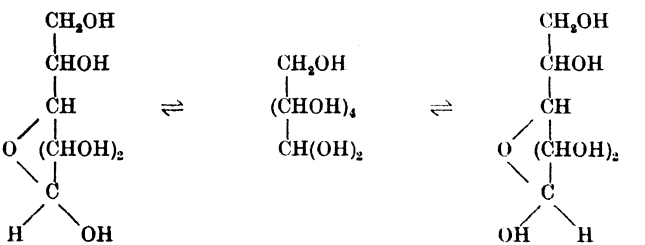
[1] Brønsted and Wynne-Jones, *Trans. Faraday Soc.*, 1929, **25**, 59.

[2] Brønsted and Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185, see also R. P. Bell, *The Kinetics of Acid Base Catalysis* (Oxford).

[3] Brønsted and Guggenheim, *J. Amer. Chem., Soc.* 1927, **49**, 2554.

The explanation of acid-base catalysis once again involves the formation of a transient complex, whose separate existence is not easy to prove, between the acid (or base) and the reactant R (*e.g.*, sucrose), and in equilibrium with both. The concentration of the reactant will thus be proportional to the product of the effective concentrations. It is further presumed that the complex breaks down at a comparatively slow rate, which is determined by the rate of transfer of a proton to the reactant. A rapid internal rearrangement then takes place with the formation of the product of the reaction and a return of the proton to form a molecule of the catalysing acid. Since in acid-base catalysis the concentration of hydrogen ion (at *p*H less than 7) plays a predominant role, then in the case of weak acids this concentration will be affected by the addition of anions of the acid. Such an effect, called the primary salt effect, will be governed by the laws of equilibria already discussed in Chapter XIV. In addition the effective concentration or activity of the hydrogen ion will also be affected by the ionic strength of the medium, that is, by the addition of neutral salts. This is the so-called secondary salt effect.

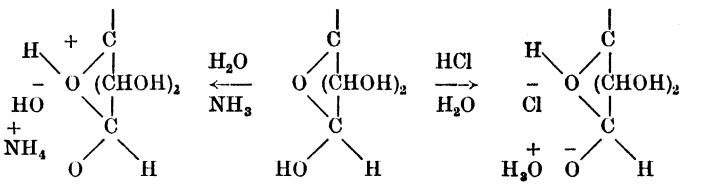
Further information about the more detailed mechanism of acid-base catalysis has been provided by studying the mutarotation (that is the change of optical rotation) of glucose and also tetramethyl glucose. This reaction, which is believed to occur as follows was investigated under a wide variety of conditions by Lowry.[1]



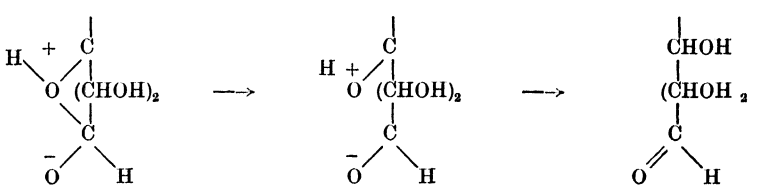
If the sugars are dissolved in dry pyridine no mutarotation is observed, but if twice its volume of water is added the rate is twenty times as fast as it is in pure water. Again, cresol is not active as a solvent. To explain these observations it has been suggested that mutarotation cannot take place in the pure substance because a proton cannot wander from one

[1] *J. Chem. Soc.*, 1925, **127**, 1371, 2883; 1927, 2554.

position to another in the sugar. To effect such a transfer a source of protons (*e.g.*, acids, water, cresol) must be present and an acceptor of proton (*e.g.*, bases, water, alcohol) into which a proton can escape from the sugar. Therefore, while water can act as a catalyst because it has the properties of acid and base, neither cresol nor pyridine is effective, but together they supply the necessary acid and base, or proton donor and proton acceptor. It will be seen from the scheme



that base plus water or acid plus water produce a salt of the same bipolar-molecule in which the $-OH$ and $-CHO$ groups are present, though joined by a bond. The ionisation of this bond provides the electric charges to neutralise those on the bipolar molecule



Enzymatic Catalysis.—Enzymes are bodies which act as catalysts for the processes that occur in the living cell. They are, for example, active in all fermentation processes. It was indeed in connection with fermentation processes that the term enzyme was first introduced by the German physiologist, W. Kühne, in 1878, from a recognition of the fact "that ἐν ζύμῃ (*en zyme*, in yeast) something occurs that exerts this or that activity, which is considered to belong to that class called fermentative." An enzyme may now be regarded as a catalyst elaborated in the living cell to act specifically so that certain reactions may be carried out smoothly.

As will be seen on p. 492 minute amounts of solid catalyst in heterogeneous systems cause a great deal of chemical

transformation. Enzymes are even more striking in their catalytic behaviour. For example, invertase which hydrolyses sucrose to glucose and fructose will hydrolyse without loss of activity 200,000 times its weight of sugar. Similarly, rennet can clot 400,000 times its weight of caseinogen. Even in homogeneous catalysis the enzyme is 5,000 times more effective than an equal weight of hydrochloric acid.

Specificity in enzyme action is probably better displayed than in any other kind of chemical reaction. Further, it is not yet known just what kind of structural change is necessary to give this high degree of specificity. Invertase hydrolyses sucrose, maltase hydrolyses maltose, peptin degrades proteins, emulsin hydrolyses only β-glucosides. Sometimes the specificity is not all exclusive. Thus emulsin will accelerate the hydrolysis of a number of glucosides, but the acceleration is not the same in all cases. Enzymes will also discriminate between stereoisomeric compounds. For example, when lipase attacks racemic ethyl mandelate the dextrorotatory ester is hydrolysed more quickly than the laevorotatory one.

Enzymes will also effect oxidation and reduction as well as hydrolysis. Even the products of an enzymatic reaction may be markedly modified by environment. Under normal conditions with yeast about three parts of glycerol are formed for a hundred parts of sugar fermented. On raising the *p*H value of the medium, as much as 30 to 40 parts of glycerol can be formed.

Although the precise nature of the enzyme is not known, it is a large molecule which cannot diffuse through permeable membranes. If, however, an enzyme solution is submitted to dialysis something does pass through the membrane, which results in the enzyme losing its activity. When the dialysate is added to the enzyme, activity is restored. The dialysable material is the so-called co-enzyme.

In conformity with the definition of a catalyst, an enzyme when present in small proportion does not alter the state of equilibrium in a reaction. Thus the hydrolysis of β-glyceryl glucoside $C_6H_{11}O_5 . C_3H_7O_2$ is accelerated by the enzyme emulsin, and similarly, the combination of glucose and glycerol is accelerated by emulsin, so that whether one starts with the glucoside and water or with glucose and glycerol, the same equilibrium point is reached in each case. A

similar result is obtained in the case of the hydrolysis of amyl butyrate to amyl alcohol and butyric acid, and in the synthesis of the ester from the acid and alcohol under the influence of lipase extracted from the pancreas. The same equilibrium point is reached from both sides.

Heterogeneous Reactions.—In all the reactions discussed above the seat of chemical transformation has occurred wholly in the gas phase or in the liquid phase. Such reactions are, therefore, termed homogeneous. On the other hand, it is often found that the shape of a reaction vessel markedly affects the rate, and in particular the rate may increase if the surface : volume ratio of the vessel is increased. In addition, it may happen that the introduction of solids of a great variety of types may induce reactions to occur whose velocity and course are quite different from that occurring in a homogeneous reaction. These experimental observations clearly show that the seat of reaction is connected with the presence of the gas-solid or liquid-solid interface. Furthermore, we shall see in Chapter XX that at the solid-gas (liquid) interface there is a tendency for molecules to concentrate. But the quite specific chemical reaction induced by the presence of solids clearly demonstrates that the reaction takes place wholly at the interface. These are, therefore, heterogeneous catalytic reactions for, in the majority of cases, the chemical composition of the surface of the solid is not changed by the occurrence of reaction upon it.

The aim in studying the velocity of these reactions is to attempt to describe chemically the course of events in a manner similar to that for homogeneous reactions, from the time the reactant molecules strike the surface until the products leave the surface. The variables that can be observed are the effect of concentration of molecules in the gas or liquid phases and the effect of temperature. The bulk chemical nature of the catalyst gives some clue to the chemical nature of the surface, and studies in adsorption give a measure of the amount of material that can be adsorbed by the surface.

The variety of reactions that can be brought about is without limit, but the most studied are probably hydrogenations and oxidations. While both hydrogenation and oxidation can occur homogeneously, the heterogeneous catalytic reaction will occur at much lower temperatures

and lead, therefore, to products which are too unstable to survive high temperature processes. With gas phase reactions the normal procedure is to pass the gas mixture at a known rate over the solid catalyst maintained at a suitable temperature and analyse the products of reaction. Alternatively, sometimes the catalyst in a finely divided form is blown through the gas mixture, and the gas and solid separated by suitable cyclones. This is the so-called "fluid catalyst" process, used only industrially on a large scale. For static experiments with metallic catalysts a simple fine wire filament serves as the catalyst.

In order to get the maximum activity at the lowest temperatures the specific surface of the catalyst (*i.e.*, the area of surface per gram of catalyst) must be large. Mechanical subdivision is sufficient in some cases, but two general methods provide the extensive surface usually required. The first is to deposit the solid catalyst on an inert body having a porous structure and very large specific surface. The second is to break up the surface of a massive catalyst by repeated oxidations and reductions. Again, it may be necessary to subject the substance to specific types of treatment before the necessary catalytic activity is developed.

Nature of Catalyst.—Heterogeneous catalysis is usually specific, but it is fortunately not quite so specific as to preclude the formulation of certain guiding principles in regard to the choice of catalyst for promoting a defined reaction. In the case of hydrogenation, for example, there is the general rule that a wide variety of metals—nickel, platinum, palladium, copper—are effective, but iron, gold silver, tungsten, molybdenum are not specially effective. Hydrogenation reactions not only include the interaction with oxygen, carbon monoxide and the hydrogenation of ethylene compounds but the break-up of hydrocarbons into simpler hydrocarbons. Hydrogenating catalysts are also effective in promoting exchange reactions between deuterium and hydrogen-containing molecules such as water, ammonia and hydrocarbons both saturated and unsaturated. There seems little doubt, therefore, that it is the hydrogen molecule that is brought into a state of reactivity, most probably by its dissociation into atoms which are held on the surface of the catalyst. The state of the adsorbed molecule which reacts with hydrogen is an important

fact in determining the velocity rather than the possibility of hydrogenation.

Similarly, if conditions are favourable, at a given temperature catalytic dehydrogenation may be carried out with the same types of catalyst. That this type of reaction is not normally observed is due to the fact that at low temperatures and with normal hydrogen pressures it is the fully hydrogenated state that is most stable.

It is hardly correct to cite as an example of hydrogenation the formation of ammonia from hydrogen and nitrogen, for a special type of catalyst consisting mainly of iron with promoters is necessary to maintain activity. Nickel molybdenum catalysts are also effective. These and other observations point to the fact that nitrogen must also be brought into a state of reactivity. One of the most striking cases of specificity is the catalytic interaction of hydrogen and carbon monoxide. If a nickel catalyst is used at temperatures from 200° to 400° C. and at 1 atmosphere the product is methane by the reaction $CO + 3H_2 = CH_4 + H_2O$. If, however, zinc oxide-chromium oxide catalysts are used at 200 atmospheres and 300° C. the product is methanol $CO + 2H_2 = CH_3OH$. If these oxide catalysts are modified by the addition of alkali oxides, higher aliphatic alcohols make their appearance. Still more surprising is the fact that returning to atmospheric pressure and using a cobalt-thoria-kieselguhr catalyst in a very limited temperature range around 190° C. the products are straight chain hydrocarbons and olefins containing up to as many as 20 carbon atoms. It would appear as if the carbon monoxide molecules are reduced to CH_2 radicals, a number of which join up together to give an olefin which may be reduced to the saturated hydrocarbon. Each of these reactions is of major industrial importance, the methane synthesis providing a method for raising the calorific value of water gas, the methanol synthesis being now the standard method of manufacture, and the hydrocarbon synthesis being the Fischer Tropsch process for the production of synthetic petroleum.

Oxidation processes are equally specific. With a platinum catalyst ethylene is oxidised to CO_2 and H_2O. With a specially prepared silver catalyst ethylene oxide can be obtained in good yield, but if conditions are slightly changed this may isomerise to acetaldehyde. Many more examples

of empirically discovered reactions could be cited. The main function, however, at present, is to see how study of the velocity of these reactions can provide some clue as to their mechanism. Unfortunately it must be conceded that the highly specific character of catalysis is difficult to explain, and unfortunately almost impossible to predict.

The measurables are the effect of the pressure of the reactants and of products, the temperature, and may be a knowledge of what factors affect the volume of gas taken up by the particular catalyst being used. The problem is to try and elucidate the mechanism of molecular transformations on the surface of the catalyst. The rate of reaction is not governed by the rate at which molecules strike the surface for, in general, this rate is exponentially dependent on temperature in precisely the same way as a homogeneous reaction. By analogy, therefore, some kind of activation process must be involved. Further, it must be concluded that the rate of reaction will be governed at least by the concentration of adsorbed molecules.

Decomposition of Ammonia on Tungsten.—Tungsten powder or tungsten filaments thermally decompose ammonia into hydrogen and nitrogen at temperatures from 500° C. upwards. At lower temperatures the rate of reaction does not depend very much on pressure, as shown in Fig. 142, in which the amount of ammonia decomposed is plotted as a function of time for initial pressures of 50, 100 and 200 mm. respectively. The slopes of these curves, *i.e.*, the rate of decomposition increases only slightly with pressure. This is the characteristic of a zero order reaction—a state of affairs very rarely met with in homogeneous reactions. Another characteristic of such a zero order reaction is that the time required for half the substance to react should be proportional to its concentration. This nearly holds for the ammonia reaction in which the relative times for half decomposition are in the ratio 1 : 1·92 : 3·52. Measurement of the temperature coefficient of the rate of decomposition gives an energy of activation of 45 kg.-cal. In this reaction added hydrogen or nitrogen has no effect on the reaction. Furthermore, at 856° C. and 100 mm. the pressure of ammonia present at equilibrium is quite negligible and the reaction virtually goes to completion. The interpretation of the mechanism is, therefore, as follows:

Ammonia is adsorbed so strongly that it covers all the available sites on the catalyst surface. Whether the molecule is adsorbed as such, or whether it is split up, say, into NH_2 and H is not known. When the system acquires an energy of at least 45 kg.-cal. a further chemical transformation takes place in such a way that molecular hydrogen and nitrogen are formed on the surface. Since these gases are not strongly adsorbed they evaporate rapidly, leaving an adsorption site available for another ammonia molecule. Unfortunately

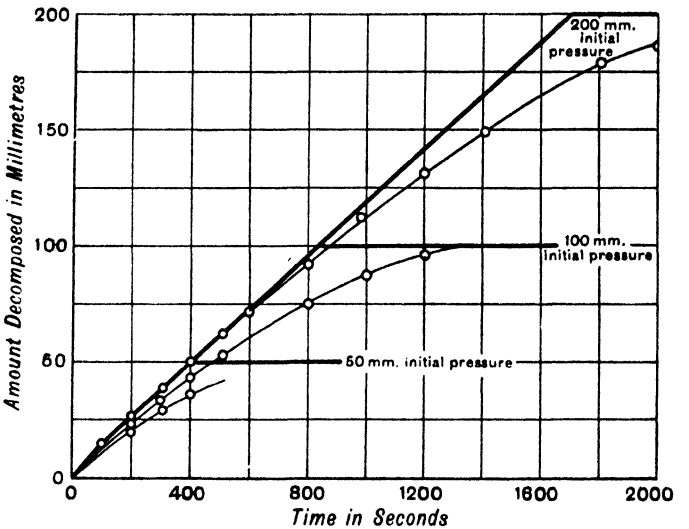


FIG. 142.

(Redrawn from Hinshelwood, *The Kinetics of Chemical Change*, by permission of Oxford University Press.)

nothing more can be said from the available data. It is a matter for speculation whether two adsorbed ammonia molecules react to give $N_2 + 3H_2$ or whether, say, NH_2 radicals interact to give $N_2 + 2H_2$, the remaining hydrogen evaporating. In view of these complexities in mechanism it is not possible to say what process requires the energy of activation of 45 kg.-cal. It is, therefore, an almost impossible task to correlate absolute rate and energy of activation as for homogeneous reactions. The important point, however, is that energetically it is easier to effect transformation at the surface than in the homogeneous gas phase, *i.e.*, the metallic catalyst provides the easier reaction path. It is

this particular function of catalysts that makes them so important chemically in lowering the temperature required for chemical transformation to occur.

First Order Heterogeneous Reactions.—Phosphine, like ammonia, is decomposed into red phosphorus and hydrogen by tungsten and also molybdenum. With the latter metal, and at high enough pressures, the reaction is very nearly zero order, and the energy of activation is 39·3 kg.-cal., thus indicating a mechanism similar to that for ammonia. But as the pressure is lowered the reaction becomes first order.

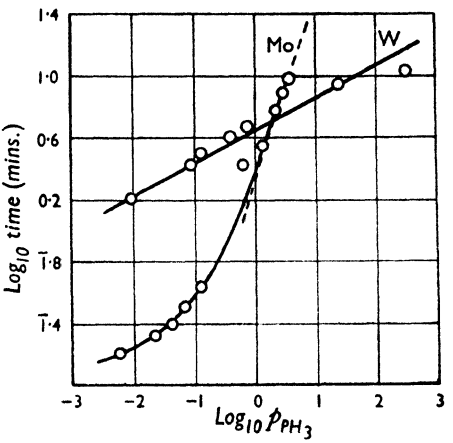


FIG. 143.

This is shown in Fig. 143, where it will be seen that the time for decomposition of half the phosphine gradually becomes independent of pressures—the characteristic of a first order reaction. At the same time the energy of activation drops to 15·1 kg.-cal. The reason for this change is that at the lower pressures the catalyst surface is not wholly covered by adsorbed phosphine molecules. The proportion of the surface covered then becomes proportional to the phosphine pressure. But since the rate of decomposition is, under these conditions, also proportional in the same way to the pressure, it must be presumed that whatever be the precise mechanism whereby the molecule decomposes, this is a process concerned with only one molecule at a time. Similarly, at low pressures, when the temperature of the catalyst is increased, two things happen: The number of molecules adsorbed on the surface will

decrease because heat is evolved on adsorption. The number will decrease in a manner proportional to $e^{+\lambda/RT}$ where λ is the heat of adsorption per mole. On the other hand, the rate of decomposition of these molecules remaining on the surface will increase at a rate proportional to $e^{-E/RT}$ where E is the true energy of activation. The apparent energy of activation will thus be $E - \lambda$, and is in this case 15·1 kg.-cal. In decomposition reactions of this kind it may be that one or other of the products of reaction is more strongly adsorbed than the reactant itself. Hence as the products accumulate the reaction rate will fall off at a greater rate than would otherwise occur.

State of the Adsorbed Molecule.—It will have been seen from the above discussion that an examination of the factors affecting velocity does not really give any clue to the way in which the molecule is adsorbed. The point at issue is whether the molecule is adsorbed as such or whether it is broken into fragments. The first possibility really corresponds to physical adsorption, but it must be recognised that the configuration of the adsorbed molecule is subject to a considerable amount of change so that its reactivity is increased. The second case corresponds to a chemical reaction between the gas and the adsorbing surface, in which the molecule is broken into fragments either atoms or radicals, each of which interacts chemically with the unsaturated valence forces existing at the surface.

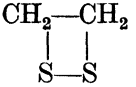
It is, for example, important to find how hydrogen is adsorbed so that its high reactivity in presence of catalysts may be explained. The experiments with hydrogen atoms (see p. 479) have shown that metals rapidly catalyse their recombination. Likewise it might be expected that the same metals would dissociate hydrogen molecules if they were adsorbed. Some information on this point can be gained by studying the reaction $H_2 + D_2 = 2HD$. The formation of HD molecules can be followed by measuring the small change in thermal conductivity that occurs during the reaction: alternatively the mass spectrograph may also be used for H_2^+ and D_2^+ will be accompanied by the ions HD^+ when HD molecules accumulate. When $H_2 - D_2$ mixtures are brought into contact with hydrogenating catalysts it is almost an invariable result that HD molecules are formed much more quickly than hydrogenation occurs. The easiest way of explaining this result is to suppose that when adsorp-

tion takes place there is the possibility that since the original molecules have lost their identity H and D combine and evaporate. Thus it is these adsorbed atoms that attack the molecule to be hydrogenated. Furthermore, the rate of formation of HD molecules ought to give the rate of production of adsorbed atoms. Since the rate of hydrogenation is, in general less, then it is the interaction of the adsorbed atom with the other molecule that determines the rate. While this mechanism probably does occur there unfortunately is another possibility, for HD molecules may be formed in quite another way. In discussing the interaction of bromine atoms with hydrogen molecules (p. 468) the mechanism is really a simple exchange process, $Br + H_2 \rightarrow BrHH \rightarrow BrH + H$. Precisely the same kind of process might occur in which, say, a deuterium *molecule* interacts with an adsorbed hydrogen atom thus $S-H+D-D \rightarrow S-D+HD$ (where S represents an adsorption site). Thus HD molecules may be formed by an exchange process with the intermediate formation of atoms for each transformation.

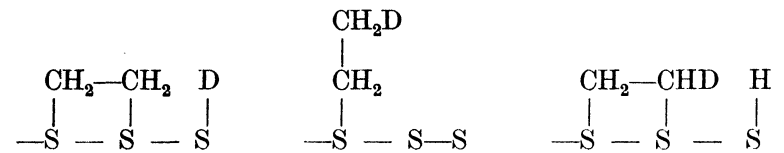
The use of isotopic tracer elements, of which the above is an example, can be extended to the other molecules. Again, using hydrogenating catalysts, it is found that reactions of the following type $D_2 + HX = DX + HD$ where X may be a group of atoms, *e.g.*, OH, NH_2, CH_3, etc. In, for example, the exchange reaction with methane the problem does arise with regard to the adsorbed methane molecule. In order to decide the matter we may use a mixture of CH_4 and CD_4. If the molecule is adsorbed as such and reacts in that form then when mixtures of these two gases are brought into contact with the catalyst no mixed molecules of the types CH_3D, CH_2D_2 and CD_3H should be formed. On the other hand, if exchange involves adsorption with dissociation, say, into methyl radicals and hydrogen atoms, then mixed molecules should be produced at the same rate as exchange occurs. This matter has been investigated, and it was found that exchange rates and mixed molecule formation rates are equal. Here the reaction was followed by examining the infra-red absorption spectrum of the hydrocarbon mixture.

The main interest in hydrogenation is, however, the attack of ethylenic molecules. Here there is a further possibility of, say, ethylene reacting with a surface. It may be that in adsorption the double bond is opened out

there being formed a cyclic compound with the surface thus

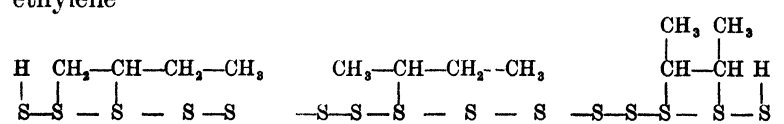


The surprising observation is that if hydrogenation is carried out with deuterium some of the ethylene undergoes exchange as well as hydrogenation. This might imply dissociation of the ethylene molecule to hydrogen and C_2H_3. A mixture of ethylene and tetra—deutero—ethylene does not, however, undergo exchange. Therefore, it would appear that dissociation does not occur. The exchange reaction with deuterium can, however, be explained in another way by means of the half-hydrogenated state. If a deuterium atom attacks the ethylene molecule thus



an adsorbed partially deuterated ethyl radical is formed. This may be further hydrogenated to ethane or, alternatively, it may dissociate again. There is, however, roughly an equal probability that either a hydrogen or deuterium atom is broken off. Hence a partially deuterated ethylene may remain.

This general kind of mechanism explains the phenomenon of double bond shift. For example, of the two molecules, butene-1 and butene-2, the latter is the more stable, and thus it should be possible in principle to obtain a catalyst which will effect this transformation. This double bond shift has been observed with hydrogenation catalysts, and it is especially marked if a small amount of hydrogen is present. The transformation can readily be explained if it is assumed that the double bond is opened out as with ethylene



Catalyst Poisoning.—One of the troubles experienced with active catalysts is their sensitivity to impurities present in

the reacting gases. The matter is simply explained, the poisons being much more strongly adsorbed than the reactants. In some cases a few parts per million are sufficient, and it would seem that not enough poison is present to cover completely the catalyst surface. Another relevant observation is that it often happens that a poison will strongly affect catalytic reactivity, but the volume of gas adsorbed is not affected. These observations imply that the activity of the surface is far from uniform and, in particular, that adsorption sites are not necessarily reaction sites. It is these specially active sites that are put out of action by very small amounts of poison.

CHAPTER XIX

INTERFACIAL AND RELATED PHENOMENA

Crystalloids and Colloids.—When one brings copper sulphate in contact with water it dissolves, and a blue solution is obtained in which, we may believe, the molecules of the dissolved substance (or its ions) are uniformly distributed throughout and among the molecules of water. The mixture is said to be *homogeneous*. If to the solution of copper sulphate one adds excess of ammonia, a liquid of a much deeper blue colour is produced, and in this case also the molecules of the dissolved substance, copper ammonia hydroxide, are distributed uniformly throughout the solution. Another dark blue liquid of similar appearance is obtained when one mixes dilute solutions (containing, say, 1 gram-molecule in 300 litres) of ferric chloride and potassium ferrocyanide, and one is therefore inclined to say that the blue liquid is a solution of Prussian blue in water. When, however, one studies more fully the properties of these two dark blue liquids, it is found that they differ in some very important respects.

It has already been pointed out (p. 103) that substances in solution, like the molecules of a gas, possess the power of diffusion; and this diffusion of the molecules of a dissolved substance can readily be demonstrated in the following way :—

A 3·5 per cent. solution of gelatin is poured into a test-tube to a depth of 8-10 cm. and allowed to set to a jelly. If on the top of this jelly one now pours a solution of copper sulphate (say, 10 per cent.) or of copper ammonia hydroxide, it is found that in the course of a few hours the blue colour of the dissolved substance will have penetrated some distance into the gelatin layer; and in the course of twenty-four hours a blue band 1 cm. or more in depth will be produced.[1]

On carrying out a similar experiment with the apparently homogeneous dark blue liquid containing Prussian blue, the gelatin remains uncoloured. In this case, therefore, diffusion into the gelatin does not take place, or takes place

[1] It has been found that the presence of the gelatin reduces, only comparatively slightly, the rate of diffusion of the solute molecules.

incomparably more slowly than in the case of copper sulphate or of copper ammonia hydroxide. One is consequently led to the conclusion that the Prussian blue is not present in the molecular state in the blue liquid, but in the form of larger particles or aggregates.

This conclusion is borne out by another experiment. When the solution of copper ammonia hydroxide is poured into a "diffusion shell" or tube of parchment paper closed at one end, partially immersed in water, the blue colour very soon makes its appearance in the outside water; but when the same experiment is carried out with the Prussian blue, the outside water remains colourless. The molecules of the copper salt can pass through the parchment membrane, but the larger aggregates present in the liquid containing Prussian blue are retained.

This difference in behaviour forms, historically, the very basis of our knowledge of the *colloidal state*. The process of diffusion of dissolved substances through a parchment paper or animal membrane (such as pig's bladder), a process known as *dialysis*, was first made the subject of investigation by Thomas Graham in the sixties of last century. Into a dialyser such as is shown in Fig. 144, the bottom of which is formed by a membrane of parchment paper or of pig's bladder, solutions of different substances are poured, and the vessel is then suspended so that the membrane is below the surface of water. By testing the outside water it can be ascertained whether or not the dissolved substance has diffused through the membrane. In this way Graham found that whereas certain substances readily pass through the membrane, other substances either do not pass through at all, or pass through with very great slowness. Since the substances which can diffuse through parchment paper are such as generally crystallise well, *e.g.*, sucrose, sodium chloride, and other salts, whereas those which do not pass through, *e.g.*, starch, gelatin, glue, etc., are amorphous, and, as was thought, non-crystallisable, Graham divided substances into the two classes of *crystalloids* and *colloids* (from the Greek *kolla* = glue); and this distinction is one which was for long maintained. Appropriate, however, as Graham's classification of substances appeared to be at the time, it cannot any longer be regarded as suitable. The terms "crystalloid" and "colloid" can now no longer be employed to connote different kinds of substances, but only different states of matter. Not only have substances such as albumin and gelatin, which Graham regarded as distinctively colloid,

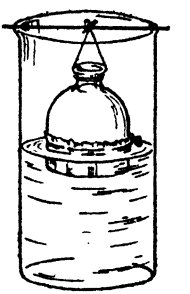


FIG. 144.

been obtained in the crystalline form, but even such definitely crystalloid substances as common salt have been obtained in the colloidal state. Although, therefore, the term " colloid " is still retained, it has acquired a new signification, and it is now recognised that *the colloid properties of matter depend on a particular state of aggregation or degree of subdivision of matter, intermediate between the comparatively gross matter which can be observed by means of a microscope and the molecular state.*

It may, perhaps, seem strange that this particular range of subdivision of matter should be singled out for special study, but the justification for this is found in the fact that matter in this state does possess properties which are not exhibited, or are exhibited in a much lower degree by molecularly dispersed matter or by the grosser microscopic particles. These properties, as will appear more clearly later, depend mainly on the enormous extent of surface exposed by a given mass of matter, so that surface forces play a predominant part in the behaviour of matter in the colloidal state.[1]

The magnitude of the increase in total surface produced by subdivision will be understood from the following figures : A cube of 1 cm. side has a total surface of 6 sq. cm. ; if this cube is subdivided into cubes of $\frac{1}{1000}$ mm. side, the total number of cubes will be one thousand billion (10^{15}), and the total surface will be 60 sq. metres ; and if the subdivision is carried farther so that the cubes have a side of one-millionth of a millimetre, the number of cubes will be one thousand trillion (10^{21}), and the total surface will be 6000 sq. metres, or 6×10^7 sq. cm. One cubic centimetre of activated charcoal used in gas masks was calculated to have a surface area of 1000 sq. metres.

The method of dialysis through parchment paper is one of great practical importance, because, on the one hand, it gives a means of distinguishing between a colloidal solution or colloidal *sol*, as it is called, and a true or crystalloid solution (in which the dissolved substance is in the molecular state) ; and, on the other hand, it gives a means of preparing a colloidal sol free from crystalloids (or substances present in true solution).

It will be clear that a colloidal sol is *heterogeneous*, and that it is a system in which the particles of a *disperse phase* are distributed in a continuous *dispersion medium*. According to Wolfgang Ostwald, a coarsely disperse

[1] For a fuller treatment of the subject, see W. D. Bancroft, *Applied Colloid Chemistry* ; H. Freundlich, *The Elements of Colloidal Chemistry*, trans. by G. Barger ; H. R. Kruyt, *Colloids*, trans. by van Klooster ; E. A. Hauser, *Colloidal Phenomena* (McGraw-Hill) ; A. W. Thomas, *Colloid Chemistry* (McGraw-Hill).

system is one in which the particles of the disperse phase can be seen by the naked eye or with the aid of a microscope; a colloidally disperse system is one that requires the ultra-microscope (p. 507) to detect the particles of the dispersed phase; a molecularly disperse system, being homogeneous, is a true solution. From this viewpoint Freundlich [1] classified the possible combination of phases in the following table, the first named being the dispersion medium; the second the disperse phase.

	Examples.
Gaseous—Liquid	Mist.
Gaseous—Solid	Smoke.
Liquid—Gaseous	Foam.
Liquid—Liquid	Emulsion.
Liquid—Solid	Suspension.
Solid—Gaseous	Solid Foam.
Solid—Liquid	Solid Emulsion.
Solid—Solid	Solid Suspension.

Of these the emulsions and suspensions are the most important; and particularly those systems with water as the dispersion medium.

The Size of the Colloid Particles.—Although a true solution, in which the solute is in the molecular state, is classed as homogeneous and a colloidal sol as heterogeneous, there is no sharp division between the two, and it is possible to pass gradually and continuously from true solutions to suspensions. Further, the dispersed material may be in the molecular (or ionic) state and yet be of colloidal dimensions, *e.g.*, in soap solutions. The following table, which is due to Zsigmondy, gives the sizes of particles in different systems and the variation of properties with the size of the particle.[2]

0·1 $m\mu$.	1 $m\mu$.	10 $m\mu$.	100 $m\mu$.	1 μ.	10 μ.	100 μ.	1 mm.
True solutions	Colloidal solutions			Suspensions and emulsions			
Ultra-microscopic region				Microscopic region			
Particles pass through ordinary filter paper.				Particles are retained by filter paper			
Particles show increased solubility				Particles show ordinary solubility			
Particles show Brownian movement				Particles do not show Brownian movement			

[1] *Colloid and Capillary Chemistry*, Eng. Trans., 1926, p. 3.

[2] A micron, represented by μ, is equal to one-thousandth of a millimetre (0·001 mm.), and a millimicron, represented by $m\mu$, is equal to one-thousandth of a micron, or equal to one-millionth of a millimetre.

Methods of Determining the Size of Particles.—(1) *The Ultra-microscope.*—This method of examining a colloidal sol is due to Faraday,[1] who wrote of the red gold sols : " When in their finest state [they] often remain unchanged for many months and have all the appearances of solutions. But they are never such, containing, in fact, no dissolved but only diffused gold. The particles are easily rendered evident by gathering the rays of the sun (or a lamp) into a cone by a lens and sending the part of the cone near the focus into the fluid. The cone becomes visible, and though the illuminated particles cannot be distinguished because of their minuteness, yet the light they reflect is golden in character." The method was afterwards (1869) applied more fully by the English physicist, John Tyndall (1820-93), and the production of the beam due to scattered light is called the *Tyndall phenomenon.*

If a beam of light is passed through pure water or through a solution of salt, the path of the beam is invisible; the liquid is "optically empty." [2] If, however, a beam of light be passed through a colloidal sol of, say, arsenious sulphide or of mastic, obtained by pouring an alcoholic solution of the resin into water, the path of the beam is traced by a diffused light, like the sunbeam in a darkened room. By means of the Tyndall phenomenon, therefore, one can detect the presence of particles too small to be seen in the ordinary way, if only the light reflected or dispersed by the particles, and not the direct rays from the source of light, are allowed to enter the eye. And it will be clear that if, instead of the unaided eye, one employs a microscope to examine the reflected light, one can extend still farther one's range of vision, so that one can detect, although not actually see in their own shape and colour, particles which are much smaller than can be seen when the microscope is used in the ordinary way. On the basis of this principle there has been devised an arrangement known as the *ultra-microscope*, due more especially to the German physicist, H. Siedentopf, and German chemist, R. Zsigmondy, by means of which not only the heterogeneity of colloid sols can be detected but also the number of particles in a given volume

[1] *Phil. Trans.*, 1857, **147**, 145.

[2] Owing to the presence of floating particles even in filtered water, the Tyndall phenomenon will be observed with ordinary pure water. Special precautions must be adopted to free the water from all suspended particles.

of the sol can be determined. This arrangement is shown diagrammatically in Fig. 145. A powerful beam of light is sent horizontally into the liquid under investigation, at right angles to the line of vision through the microscope, and the point of focus of the beam examined. If the liquid under examination is optically empty the field of view in the microscope will appear dark; but if particles are present in the liquid, minute points of light will be observed against the dark background. These points of light will be seen to be in more or less rapid movement (Brownian movement; p. 59). The points or discs of light are due to the diffraction of the rays of light by small particles called *submicrons*; and a diffuse light may also be observed due to the presence of still smaller particles, not distinguishable as individuals, called *amicrons*.

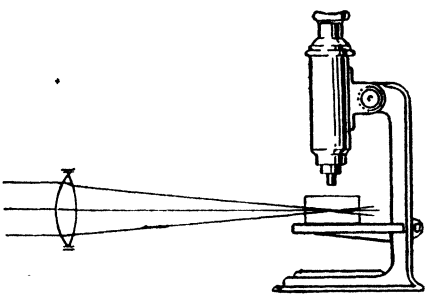


FIG. 145.

For most purposes one may also use a dark-ground condenser in place of the ultra-microscope just described.[1]

By means of the ultra-microscope it is possible to detect the presence of particles having a diameter of not less than about six-millionths of a millimetre ($\frac{6}{1000000}$ mm.) or 6 millimicrons (6 $m\mu$), whereas the smallest particle directly observable by a microscope in the ordinary way has a diameter of about $\frac{2}{10000}$ mm. or 0·2 μ. Failure, however, to detect the presence of particles by means of the ultra-microscope does not necessarily mean that the liquid is homogeneous. It may be that the particles are present as amicrons, or it may be that the refractive index of the particles is too near to that of the dispersion medium for them to be distinguished.

The size of colloid particles was determined by Siedentopf and Zsigmondy by using a small cell with an engraved scale. By analysis, the total mass m of the dispersed phase in unit

[1] For a description of the apparatus and methods of ultra-microscopic examination, see E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy* (Wiley).

volume of the sol was determined. The number of particles n in unit volume of the sol was obtained by a direct count of the number of particles in the illuminated volume of the sol in the ultra-microscope. This volume was fixed by the depth of the illuminating beam and by the area of the field. The volume of a particle was then calculated from the expression $v = \frac{m}{n \cdot d}$, where d is the density of the substance. Assuming the particles to be spheres (which is plausible only in certain cases) the diameter could then be calculated from the volume of the particle.

Some idea of the dimensions of colloidal particles will be obtained from the statement that the diameter of human red blood corpuscles is about 7·5 μ, micrococci have diameters of the order of 1μ, while the particles of a colloidal gold sol have diameters of 7–15 $m\mu$. The molecule of hydrogen has a diameter of about 0·1 $m\mu$, that of sodium chloride a diameter of about 0·26 $m\mu$, and that of cane sugar a diameter of about 0·7 $m\mu$, or about one-tenth of the dimensions of the smallest particles detectable by means of the ultra-microscope.

2. *Sedimentation.*—According to Stokes' law, the radius of a spherical particle falling with constant velocity v, in a medium of viscosity η, is given by the expression

$$r = \sqrt{\frac{9}{2} \cdot \frac{\eta v}{(d_p - d_l)g}},$$

where g is the gravitational constant, d_p the density of the particle, and d_l the density of the liquid. The rate of sedimentation is determined from the movement of a boundary between the sol and the pure medium, or by the use of the ultra-microscope to count the particles periodically. In the case of very small particles (*e.g.*, gold particles of radius less than 50 $m\mu$) no settling is observed under the action of gravity, but the method can still be used if a force greater than gravity is applied by means of a centrifuge (p. 524).

3. *Ultra-filtration.*—That the particles of colloidal sols vary in size is shown by the fact that it is possible not only to separate colloids from crystalloids by dialysis, or diffusion through parchment paper and other membranes, but also to separate different colloids from one another by the use

of membranes of different porosity. Such membranes have been prepared, more especially by J. H. Bechhold,[1] who employed filter paper impregnated with gelatin hardened with formaldehyde, or with collodion prepared by dissolving guncotton in glacial acetic acid. By using solutions of different concentrations, membranes of different porosity can be obtained. Filtration through such membranes is called ultra-filtration, and is carried out under pressure.

By the use of ultra-filters of different porosity it is possible to classify colloidal sols according to the mean size of the particles present in them, and a list of such systems with particles varying in dimensions from those present in suspensions to those present in true solution has been drawn up by Bechhold :

Suspensions	Hæmoglobin (1 per cent.)
Prussian blue	Serum albumin
Colloidal platinum (Bredig) . . .	Diphtheria toxin
Colloidal ferric hydroxide . . .	Protalbumoses
Casein (in milk)	Colloidal silicic acid
Colloidal arsenious sulphide . . .	Lysalbic acid
Colloidal gold (about 40 $m\mu$) . . .	Deuteroalbumoses
Colloidal bismuth oxide (Paal) . . .	Litmus
Colloidal silver (collargol)	Dextrin
Gelatin (1 per cent.)	*Crystalloids*

By means of ultra-filtration it is possible to separate colloids from one another, *e.g.*, albumin from its decomposition products, the albumoses, and so obtain information regarding changes which may occur in colloidal sols. In using the ultra-filter for the purpose of determining the size of colloidal particles, however, the possibility of adsorption must be borne in mind.[2] Thus, in filtering a mixture (green) of Prussian blue and hæmoglobin a red filtrate of the finer hæmoglobin is obtained, but if arsenious sulphide is substituted for hæmoglobin all the particles are retained even when using a filter which normally passes arsenious sulphide. The retention is due to adsorption of arsenious sulphide on the Prussian blue.

[1] *Z. physikal. Chem.*, 1907, **60**, 257. See also G. S. Walpole, *Biochem. J.*, 1915, **9**, 284; J. Manning, *J. Chem. Soc.*, **1926**, 1127; Ferry, *Chem. Rev.*, 1937, **18**, 373

[2] That great care must be exercised in interpreting the action of a membrane merely as a sieve is clear from the fact that whereas Congo red with a molecular weight of 696 is retained by a collodion membrane, amylodextrin with a molecular weight of 20,000 passes through. See also H. Reinboldt, *Kolloid-Z.*, 1925, **37**, 387; A. Grollman, *J. Gen. Physiol.*, 1926, **9**, 813; A. Augsberger, *Biochem. Z.*, 1928, **196**, 276.

In recent years ultra-filtration has become of increasing importance and can be used not only as a test for the existence of substances in the colloidal state, but also for the study and control of filter-passing viruses. For these purposes, membranes of cellophane have been recommended.[1] By suitable treatment the size of the pores can be reduced and the cellophane membrane converted into a molecular sieve; and the permeability for different solvents, *e.g.*, alcohol, benzene, etc., can be altered.

Filters having pores of 0·02 μ have also been obtained by the deposition of successive thin layers of carborundum of graded particle size on a layer of sintered glass.[2]

4. *Absorption and Scattering of Light.*—With regard to the dispersion of light by very small colloid particles, it may be mentioned that the shorter waves of light—the blue of the spectrum—are scattered more than the longer waves which make up red light. Consequently, when the path of a beam of light is observed from the side, against a dark background, the scattered light waves which enter the eye are mainly those of shorter wave-length, and so the sensation of blue is obtained. If, however, the colloidally dispersed matter is viewed by transmitted light, the colour appears red. The very fine smoke rising from a wood fire, for example, appears of a blue colour when it is illuminated from the side and when it is viewed against a dark background; but when one views the smoke against a background of white clouds, that is, by transmitted light, the smoke appears reddish-brown in colour.

The relation between the size of the particles and the colour of a sol can be seen by coagulating a red gold sol prepared by adding 5-10 ml. of alcohol to 100 ml. of a boiling 0·001 per cent. gold chloride solution. This sol is very sensitive to electrolytes because no protective agent is present; addition of a drop of dilute hydrochloric acid or sodium chloride solution causes a change of colour to blue in a few seconds. Examination with the ultra-microscope proves that the blue sol has larger particles than the red sol (see "gold number," p. 530).

Production of Colloidal Sols.—In the case of emulsoid or reversible colloids, the production of a colloidal sol takes place, as in the case of a true solution, by bringing the dry substance, *e.g.*, gelatin, in contact with water or other dispersion medium under suitable conditions. In the case of suspensoid or irreversible colloids, however, special methods must be adopted. In preparing such sols one may proceed from matter in the molecular state (in solution) and pass to the larger particles of the colloid state; or one may start with

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[1] J. W. McBain and S. S. Kistler, *J. Gen. Physiol*, 1928, **12**, 187; *J. Physical Chem.*, 1931, **35**, 130.

[2] Amat and Duclaux, *J. Chim. Phys.*, 1938, **35**, 379.

gross matter and, by subdividing it sufficiently, also obtain the colloid state of aggregation.

1. *Methods of Dispersion.*—Dispersion of metals can be effected by the Bredig method.[1] An arc is formed under the liquid between thick wires of the metal, *e.g.*, silver, platinum, etc. The metal is dispersed and a dilute colloidal sol is obtained. Svedberg and others have extended and improved the method by using high frequency alternating current.[2] Dispersion of solids may also be effected in special mills. The Plauson colloid mill, for example, consists of two discs rotating in opposite directions. The liquid medium and coarse particles of the solid are introduced into the narrow space between the two discs, and the coarse particles are thus disintegrated to colloidal particles.

2. *Methods of Condensation or Aggregation.*—The aggregation of molecules to colloid particles can be brought about:

(a) *By cooling.* An ice sol in pentane is formed by cooling a solution of water in pentane. A smooth ice cream contains colloidal particles of ice "protected" by gelatin.

(b) *By lowering of solubility.* When an alcoholic solution of resin is poured into water, an opalescent sol is obtained. Similarly, a colloidal sol of palmitic acid is obtained by pouring a hot, concentrated solution of the acid in alcohol into water.

(c) *By chemical reaction.* A sol of *arsenious sulphide* is obtained by passing hydrogen sulphide into a solution of arsenious oxide in distilled water. Excess of hydrogen sulphide is removed by means of a stream of hydrogen. *Ferric hydroxide*: To a half-saturated freshly prepared solution of ferric chloride, add, in drops and with stirring, an approximately 2N solution of ammonium carbonate, until the precipitate formed just ceases to be dissolved. Filter, if necessary, and dialyse the liquid in a tube of parchment paper against distilled water until only a trace of chloride can be detected in the outer water. Or, one may add a 2 per cent. solution of ferric chloride to boiling water. Colloidal ferric hydroxide is formed by hydrolysis *Gold sol*: To 100-150 ml. of carefully distilled water are added 1 ml. of a 1 per cent. solution of gold chloride and 3 ml. of N/5 solution of pure potassium carbonate. The solution is heated to boiling and then 2·4 ml. of a solution of formaldehyde are gradually, but fairly rapidly, added. In a short time the liquid assumes a pure ruby-red colour. For demonstration purposes a ruby-gold sol can be most easily obtained in the following manner. To 100 ml. of distilled water contained in a flask are added a few drops of a 1 per cent. solution of gold chloride, carefully neutralised with sodium carbonate, and then a few drops of a 0·1 per cent. solution of tannic acid. The liquid is then heated. In a short time a pink colour develops, and by adding further small quantities of the gold and tannic acid solutions a deep ruby-red sol of gold is obtained. In this preparation the gold chloride is reduced by the tannic acid, which also acts as a "protective" agent (p. 530). *Platinum sol*: A colloidal platinum sol can readily be obtained by adding 2·4 ml. of 33 per cent. acrolein to 500 ml. of a boiling-hot solution of platinic chloride (1 g. in 1000 ml.), previously rendered slightly alkaline with potassium carbonate.

Electrical Properties of Colloids.—When a solid is introduced into a liquid of different dielectric constant the solid becomes electrically charged. Thus the particles of a suspension of clay or of peat fibres are negatively charged, and if two electrodes connected with the poles of a high-tension battery are introduced into the suspension, the suspended particles are found to move towards the positively

[1] *Z. Elektrochem.*, 1898, **4**, 514.

[2] Svedberg and Kraemer, *J. Amer. Chem. Soc.*, 1924, **46**, 198; Miyamoto, *Kolloid-Z.*, 1934, **67**, 284.

charged electrode. This is the phenomenon of *electrophoresis*. Similarly, when oil or other liquid is shaken up with water, the droplets of the emulsion are also electrically charged. Thus the negatively charged particles of rubber suspended in the latex of the rubber plant are carried, in an electric field, towards the positively charged anode, and moulds of any desired form, or fabric or wire may thus be coated with a layer of rubber.

This electrification, which is found in the case of coarse suspensions or emulsions, is also found in the case of the more finely subdivided colloidal particles. Whence, then, do these fine suspensions and colloid particles derive their electric charge? On this point complete certainty has not yet been reached. According to one view, the origin of the charge is the same as that of frictional electricity, and it is a significant fact that the charge on the particle depends, as a rule, on the difference in the value of the dielectric constant of the medium and of the dispersed material. When the dielectric constant of the medium is higher than that of the dispersed material (as is generally the case), the particle will become negatively charged relatively to the medium. Although one does, indeed, find that most colloids become negatively charged in water, positively charged colloids are also obtained, *e.g.*, ferric hydroxide. It must therefore be concluded that the value of the dielectric constant is not the only factor which determines the sign of the charge. In some cases the charge seems undoubtedly to be due to a process of ionisation with production of a colloidal ion, as in the case of silicic acid; and in other cases it is probable that the charge is due to the taking up of positively or negatively charged ions from the medium—either hydrogen or hydroxide ions from water, or ions from impurities originally present in the water or formed in the process of formation of the colloids. This is borne out by the fact that the charge on the colloid may vary with the nature of the medium in which the colloid is formed. Thus, albumin in an acid medium is positively charged, whereas in an alkaline medium it is negatively charged. In the case of suspensoid colloids, also, the sign of the charge can be altered. Thus, as Svedberg and others have shown, if a solution of aluminium sulphate is cautiously added to a silver or gold sol the negative charge on the colloid particles is first reduced and then converted into a positive charge by adsorption of the

aluminium ions. "The charge on the colloid is determined by the environment of the colloid particles at birth."

The existence of an electric charge on the colloid particles can readily be demonstrated by the following experiment :—

Into the bend of a U-tube A (Fig. 146), the limbs of which are about 15 cm. long and 1·5 cm. diameter, is sealed a short length of tubing B, of about 0·4 cm. bore. This tube is loosely plugged with cotton-wool, previously well washed, and then connected with a piece of rubber tubing and a funnel. On the rubber tubing, near B, is placed a spring clip. Into the funnel pour a colloidal sol of arsenious sulphide, so as to fill the rubber tube without air-bubbles. Carefully open the spring clip so as to allow the sol almost to fill the tube B. Into the U-tube pour 6-7 ml. of distilled water, so as to fill the bend of the tube. Lower the reservoir funnel to the level of B, open the spring clip carefully, and raise the funnel very slowly. The sol will in this way be made to rise in the limbs of the U-tube, lifting the water with it. When the water has been raised to about 1 cm. from the mouth of the tube, close the spring clip, insert the corks carrying the platinum electrodes in the U-tube, and connect the electrodes with the lighting circuit (100-200 volts, direct current). The lower edge of the platinum electrodes should be only 2-3 mm. above the surface of the arsenious sulphide sol. After a short time, 10-15 minutes, a distinct movement of the yellow sulphide sol towards the anode should be observed. This shows that the arsenious sulphide sol is negatively charged.

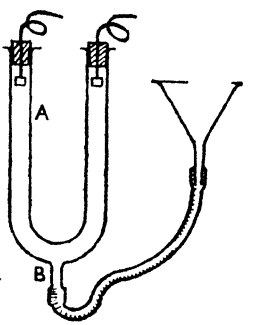


FIG. 146.

By a study of the electrophoresis of different colloids one can classify them into electro-positive and electro-negative colloids. Thus, we have :

Electro-positive.	Electro-negative.
Ferric hydroxide.	Gold, silver, and platinum.
Aluminium hydroxide.	Arsenious sulphide.
Hæmoglobin.	Silicic acid.
Night blue (dye).	Alkali blue (dye)
	Congo red acid.
	Caseinogen.
	Mastic.
	Suspensions of kaolin, charcoal, etc.

If the water between two charged electrodes is separated into two parts by means of a clay diaphragm, water is forced by the current towards the cathode, the relative motion of clay and water being the same as in electrophoresis of clay particles. In *electro-osmosis*, as this phenomenon is called, the direction of flow of the water depends on the diaphragm and on the electrolytes present. Hittorf found that with

cadmium chloride present water flows to the anode through animal membranes and towards the cathode through earthenware. Using a diaphragm of insoluble chromic chloride, Perrin found that dilute alkalis flowed to the cathode and dilute acids to the anode. The "reversal" of flow is due to the presence of strongly adsorbed ions; the diaphragm becomes positively charged in acid and negatively charged in alkaline solution.

By the adsorption of ions on the surface of the colloid particle, a diffuse zone[1] of oppositely charged ions is established in the surrounding medium, and a potential difference is thereby set up. When electrophoresis takes place, a layer of the dispersion medium adheres to the colloid particle and there is therefore a movement, not between the actual surface of the colloid particle and the main body of the liquid, but between the liquid layer adhering to the colloid particle and the main liquid. The total drop in potential between the surface of the particle and the liquid medium is spoken of as the "Nernst" potential, while the fall of potential between the liquid adhering to the particle and the movable liquid is known as the "electrokinetic" or "zeta" (ζ) potential. It is on this zeta potential that the stability of a hydrophobic colloid mainly depends.

Mutual Precipitation of Colloids.—When two colloids of opposite electric charge are mixed, the charge of one is neutralised by the charge of the other; aggregation of the particles and flocculation or precipitation of the colloids then take place. In order that this mutual precipitation may be complete, the two colloids must be mixed in certain proportions *within rather narrow limits*. There are, in fact, certain optimum amounts of the two colloids which bring about precipitation, and if these proportions are considerably exceeded, on either side, no precipitation at all may take place. To illustrate this, the following experiment may be performed :—

Prepare solutions of arsenious sulphide and of ferric hydroxide of 0·5 per cent. concentration (expressed as As_2O_3 and Fe_2O_3). By means of graduated 10 ml. pipettes mix, in a series of test-tubes, 1 ml. As_2S_3 sol and 9 ml. $Fe(OH)_3$ sol; 3 ml. As_2S_3 sol and 7 ml. $Fe(OH)_3$ sol, etc. Thoroughly mix and allow to stand for one hour. Ascertain the relative concentrations at which complete

[1] The older conception of a double layer as consisting of two parallel layers of oppositely charged ions, one molecular diameter apart, has been abandoned.

precipitation occurs, as shown by the absence of colour from the supernatant liquid. In the above case the optimum amounts will be found to be about 9 ml. As_2S_3 sol and 1 ml. $Fe(OH)_3$ sol. Vary the proportions by fractions of a millilitre on either side of the approximate optimum point.

To illustrate the mutual precipitation of colloids one may also use Congo red (−) and night blue (+) in 0·1 per cent. solutions.

The behaviour observed in the above experiments indicates that precipitation is due to the mutual neutralisation of electric charges, and the optimum condition is obtained when the proportions of the two colloids are just sufficient to produce uncharged masses, or when the two opposite charges are equivalent. The particles then coalesce and undergo precipitation. It may be concluded, therefore, that in the case of any two colloids the optimum amounts will be definite and the " adsorption complex " will therefore simulate a compound. This conclusion is in harmony with experimental results in the case, for example, of tannin and gelatin, tannin and basic dyes, basic and acid dyes, etc.

No precipitation takes place when colloids having charges of the same sign are mixed.

Precipitation of Suspensoids or Lyophobic Colloids by Electrolytes.—One of the most notable facts in connection with the behaviour of suspensoid sols is that, although non-electrolytes are without effect on the sols, precipitation of the colloid readily takes place on addition of electrolytes. This fact was known to Faraday, who observed that gold is precipitated from a ruby gold sol by addition of salts, and is readily demonstrated by adding hydrochloric acid to arsenious sulphide sol or to a ruby gold sol. In the latter case the red particles first aggregate together to form the larger blue particles and then separate out as a precipitate. This precipitation is intimately connected with the electrical charge on the colloid particle.

It has been shown that for colloid particles of different kinds, the potential difference between the particles and water is approximately 0·05 volt. By the addition of electrolytes to the colloid sol this potential difference is diminished, and the point of maximum instability of the colloid has been found to lie at or very near the point of electric neutrality, the *iso-electric point*, as it has been called. How is this action of electrolytes to be explained ?

Solutions of electrolytes contain positively and negatively charged ions, and when these ions are added to a colloidal sol the particles of the latter adsorb the ions of opposite

charge, and the potential difference between the colloid and the medium is thereby diminished. One would expect, therefore, that the greater the electric charge on the ion (the higher the valency of the ion) the more effective will the electrolyte be in diminishing the potential difference and in bringing about the precipitation of the colloid. In other words *the precipitating effect of an ion—of a positive ion on a negative colloid and of a negative ion on a positive colloid—depends on the valency of the precipitating ion.* This is known as the *Hardy-Schulze* law. The numbers in the following table, giving the concentration (in thousandths of a gram-molecule per litre) of different electrolytes required to bring about the precipitation of an arsenious sulphide sol, illustrate the rule. (1 ml. of the electrolyte solution was added to 10 ml. of the sol, the mixture shaken and allowed to stand for two hours.)

PRECIPITATION OF ARSENIOUS SULPHIDE SOL

	Concentration.
(a) *Univalent Cations*—	
LiCl	58·0
NaCl	51·0
KNO_3	50·0
KCl	50·0
HCl	30·8
(b) *Bivalent Cations*—	
$BaCl_2$	0·67
$MgCl_2$	0·72
$MgSO_4$	0·81
$CaCl_2$	0·65
$Sr(NO_3)_2$	0·67
$ZnSO_4$	0·81
(c) *Tervalent Cations*—	
$AlCl_3$	0·093
$Al(NO_3)_3$	0·095
$\frac{Ce_2(SO_4)_3}{2}$	0·092

The Hardy-Schulze law, however, is no more than a guide, for the precipitating efficiency of an ion depends not only on its valency but also on its chemical nature, as is shown by the fact that ions of the same valency may vary in their efficiency, as the numbers in the above table prove. Hydrogen and hydroxide ions, and the ions of the heavy metals, *e.g.*, silver ions, are specially efficient as precipitants. This behaviour depends on the readiness with which the ions are adsorbed by the colloid.

In studying the precipitating effect of salts one must consider not only the adsorbability of the ion of opposite sign to that of the colloid, but that also of the ion of like sign. Adsorption of the ion of like sign will stabilise the colloid. Thus, hydrogen ion will stabilise a positive sol and hydroxide ion will stabilise a negative sol, as the following figures indicate :—

	Precipitating Concentration (mg.-mol. per Litre).
Platinum Sol (negative)—	
NaCl	2·5
NaOH	130
Ferric Oxide Sol (positive)—	
NaCl	9·25
KCl	9·0
HCl	400

Precipitation of a colloid by an electrolyte is the end-point of a process marked by an increase in the size of the colloid particles. This is sometimes clearly indicated by a change in the colour of the sol. Thus, addition of appropriate small quantities of salts will cause a yellow silver sol to become red, a red gold sol to become blue, and a Congo-rubin sol to show various shades between red and blue.[1]

In accordance with the Fajans-Hahn law, those ions are preferentially adsorbed which can be incorporated in the lattice structure of the colloid.

In connection with the precipitation of suspensoids by electrolytes, several points must be borne in mind. The precipitating action of an electrolyte differs according as it is added all at once or in small portions at a time. When the electrolyte is added in small portions the colloid becomes " acclimatised " or tolerant to the electrolyte, and a much larger total concentration of the latter is required to produce precipitation. Further, it should be noted that if one adds a much larger amount of electrolyte than is required for precipitation, no precipitation at all may occur, owing to the reversal of the sign of charge on the colloid by the added electrolyte. As has been pointed out, small additions of aluminium sulphate will cause the precipitation of a silver or gold sol, but if excess of aluminium sulphate is added, aluminium ions are adsorbed, and a *positively* charged silver or gold sol is obtained. Similarly, if increasing amounts of ferric chloride are added to negatively charged platinum sols, flocculation of the negative colloid is first brought about, then a stable but positively charged sol is produced, and lastly, when sufficiently large amounts of ferric chloride are added, complete precipitation of the positively charged colloid is effected.

[1] Wo. Ostwald, *Kolloid-Z.*, 1919, **24**, 67.

Since flocculation of a suspensoid by an electrolyte is brought about by the neutralisation of the colloid charge by adsorption of an ion, it follows that the adsorbed ion must be carried down by the precipitated colloid. Thus, when arsenious sulphide sol is precipitated by barium chloride, the barium ion is adsorbed and carried down by the precipitate, and it is held so firmly by it that it cannot be removed by washing with water. The precipitation is *irreversible*. In some cases, however, the adsorbed ion can be removed by washing, so that the precipitate may, on washing with water, pass back again into a sol. Thus, when an electropositive sol of copper is precipitated by means of the chloride ion, the latter can be removed by washing with water, and a sol is again obtained. If precipitation is carried out by the sulphate ion, however, the latter is not removed by washing with water, and the precipitate appears to be irreversible. By washing the precipitate with sodium chloride solution, the sulphate ion is replaced by the chloride ion, and this can then be removed by washing.

It was previously stated that addition of an electrolyte to a colloidal sol diminishes the potential between the colloid and the dispersion medium. If, however, the concentration of the electrolyte is below a certain value the potential is not lowered but *raised*, so that minute traces of electrolytes may, owing to adsorption of an ion, increase the stability of a colloidal sol. For this reason a trace of sodium bicarbonate is added to the water in the preparation of colloidal platinum sol by the Bredig method (p. 511).

Peptisation.—Not only may a small trace of electrolyte stabilise a suspensoid, but it may also facilitate the dispersion of a substance and produce a colloidal sol. This process of deflocculation, which is the reverse of flocculation or precipitation, is often spoken of as *peptisation*, on account of its superficial resemblance to the process of conversion of insoluble protein into soluble peptone. This peptising action is due to the preferential adsorption of one of the ions of the electrolyte, which then gives to the colloid particle a positive or negative charge, according to the charge on the adsorbed ion. Peptisation, however, is the result not only of adsorption but also of the lowering of the surface tension on the water side of the adsorbed film.

Many examples of the peptising action of ions could be given. Freshly precipitated silver chloride, for example, can be peptised by shaking with dilute solutions of silver nitrate or of potassium chloride. In the former case, silver ion is adsorbed strongly, and, in the latter case, chloride ion.

In the case of emulsoids, peptisation can be produced by water alone.

Peptisation and the stabilising action of small amounts of electrolytes are related phenomena, and so it is found that hydrogen ion peptises positive colloids and hydroxide ion negative. Use is frequently made of peptising agents in the preparation of colloidal sols. Thus, aluminium hydroxide sol can be obtained by shaking aluminium hydroxide with water to which a small amount of aluminium chloride or of hydrochloric acid has been added. In the former case

aluminium ion acts as the peptiser and in the latter case hydrogen ion. Similarly, a colloidal sol of graphite can be obtained by grinding graphite with a solution of tannin. The tannin peptises and stabilises the graphite.

Solutions of High Molecular Weight Substances.—Besides the colloidal solutions described above there is another class of solution which has similar characteristics in that diffusion of the dissolved particles is slow and membranes act as a barrier to their passage. At that point the resemblance ceases. These substances, many of which occur naturally, for example, gelatine, starch, rubber, go into solution spontaneously when brought into contact with a suitable solvent. Conversely they are not precipitated from solution unless large amounts of precipitant are added, or in the case of aqueous solution of such large quantities of salts, that there is no resemblance to the phenomenon of precipitation with ordinary colloidal solutions. Again such solutions do not scatter light in the same way as, say, a gold solution in which each particle is clearly observed in the ultramicroscope. The viscosity of ordinary colloidal solutions is not greatly different from that of the suspension medium, but the above-mentioned solutions are often highly viscous. The substances that give rise to such phenomena are now known to be comprised of molecules of high molecular weight (high polymers) ranging up to values of several millions, and all the properties of the solutions must be ascribed to this fact. With colloidal solutions of gold there is no question that, although the suspended particles are small, there is a definite interface in the system, and it is the presence of that interface that gives rise to most of the phenomena observed. While there is theoretically no limit to the size of the gold particle, the practical limit is set approximately by the sensitivity of the electron microscope. Hence we may truthfully say that such solutions are heterogeneous and, therefore, really very fine suspensions of gold particles in water. With solutions of high molecular substances it must be conceded that the molecules are in true solution, and even with the highest molecular weight substances no definite interface exists between the dissolved molecules and the solvent. It should be pointed out, however, that such high molecular weight substances can be precipitated from a solvent by the addition of a precipitant when the individual molecules will have a separate though transitory existence before they unite into larger aggregates,

Besides the naturally occurring high polymers there is now a great variety of synthetic high polymers with molecular weights ranging from a few hundreds up to many millions, whose general physical properties are quite similar to the naturally occurring substances.

General Structure of High Polymers.—It is outside the province of this book to deal in detail with the structure of high polymers, but from the point of view of understanding their physical properties and those of their solutions it is necessary to indicate briefly the general kinds of structure. For example, if an ω-hydroxy acid in which the number of carbon atoms exceeds 6 is heated, then instead of getting intra-molecular reaction to give a lactone, intermolecular condensation occurs with the building up of linear chains of atoms thus

$$n(\mathrm{HO}\,.\,(\mathrm{CH_2})_x\,.\,\mathrm{COOH}) \downarrow$$

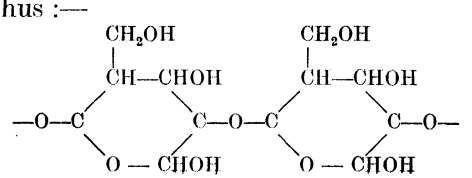
$$\mathrm{HO}\,.\,(\mathrm{CH_2})_x.\mathrm{CO}\,.\,\mathrm{O}\,.(\mathrm{CH_2})_x.\mathrm{CO}\,.\mathrm{O}\,.(\mathrm{CH_2})_x.\mathrm{COOH} + (n-1)\mathrm{H_2O}$$

where $n = 3$.

Alternatively, ethylene glycol $\mathrm{HOCH_2}\,.\,\mathrm{CH_2OH}$ and a dibasic acid such as adipic acid $\mathrm{HOOC(CH_2)_4COOH}$ may esterify, in which the repeating unit is—$\mathrm{CH_2CH_2}\,.\,\mathrm{O}\,.\,\mathrm{CO(CH_2)_4CO}\,.\,\mathrm{O}$–. Again, ω-amino acids such as amino-caproic acid will condense in the same way, the repeating unit being —$\mathrm{NH.(CH_2)_nCO}$—. Proteins are built up from α-amino acids

$$\mathrm{NH_2}\,.\,\underset{\mathrm{R}}{\mathrm{CH}}\,.\,\mathrm{COOH} \text{ to give repeating units } —\mathrm{NH}\,.\,\underset{\mathrm{R}}{\mathrm{CH}}\,.\,\mathrm{CO}—$$

Synthetic methods have given molecules of a molecular weight of 25,000, but the proteins exceed this comfortably, the maximum being 6,000,000 (see Svedberg, *The Ultra-Centrifuge*). Even ethylene glycol can be induced to form linear polymers, the unit being —$\mathrm{CH_2}\,.\,\mathrm{CH_2}\,.\,\mathrm{O}$—. The naturally occurring counterpart is cellulose where glucose units are joined together with the elimination of water molecules thus :—



The other general method of making large molecules is the combining together of ethylenic molecules by the opening of the double bond. Thus ethylene gas at high pressures and temperatures polymerises to polyethylene, $n(CH_2=CH_2) \rightarrow (-CH_2 \,.\, CH_2-)_n$. The groups of atoms attached to the end of the polymer are determined by the conditions for polymerisation. By substituting for one of the hydrogen atoms a polar group such as Cl, CN, etc., polymerisation occurs more easily. Dienes, *e.g.*, butadiene, can also be polymerised thus :—

$$n(CH_2=CH-CH=CH_2) \longrightarrow (-CH_2-CH=CH-CH_2-)_n$$

In natural rubber and in guttapercha the same kind of unit, namely isoprene, is involved, *i.e.*, $-CH_2-C(CH_3)=CH-CH_2-$. Thus with all these polymers which are soluble the molecule consists of single chains of atoms running into thousands. The physical properties of solutions of such substances are, therefore, bound to differ very markedly from those of small molecules.

Molecular Weight Determination.—According to common usage high polymers usually have molecular weights exceeding 10,000. In a 10 per cent. solution by weight the ratio of solute to solvent molecules of molecular weight, say 100, would thus be 10^{-4}. Assuming Raoult's Law to hold the relative lowering of the vapour pressure $1-\frac{p\text{-solution}}{p\text{-solvent}}=10^{-4}$. Such a small decrease in vapour pressure simply could not be measured by any apparatus. Similarly, the effect on the boiling-point and freezing-point of liquids is so small that the Beckmann thermometer is not nearly sensitive enough, apart altogether from the difficulty of maintaining the temperature of the system to close limits. Fortunately the osmometer can be used, provided certain precautions are taken. The type of osmometer needed for the measurement of low osmotic pressures—a few millimetres of mercury is quite a high value—has been described in Chapter VIII. A high surface : volume ratio of the cell is achieved in such a design so that the minimum amount of solvent need diffuse through the diaphragm to establish equilibrium. As it is, the time required for a close approach, *e.g.*, 2 per cent. to equilibrium may take as long as twenty-four hours. If the osmotic pressure (π) of such

solutions is plotted against concentration (c), no linear relation is obtained; instead there is a curve sloping steeply upwards as the concentration is increased (Fig. 147). As will be seen, this happens at quite low concentration. Similarly, if the value of π/c is plotted against c, the deviation of ideal behaviour is shown by the line having a finite slope

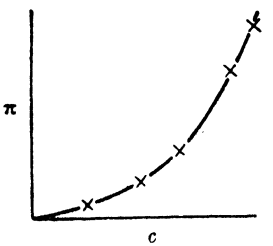


FIG. 147.

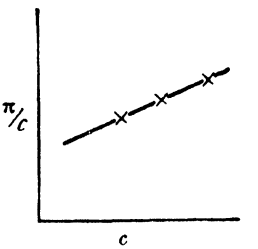


FIG. 148.

(Fig. 148). In all such determinations it is, therefore, necessary to extrapolate the curve in Fig. 148 to $c=0$. Since $\pi=\frac{c}{M}$. RT in very dilute solution, the limiting value of π/c as $c\rightarrow 0$ will give RT/M whence M may be calculated. Values of M up to 10^6 may be measured with an accuracy of ± 5 per cent.

Osmotic Pressure of Polyvalent Electrolytes.—Some of the high polymers are soluble in water and are multivalent electrolytes in the sense that they dissociate into multiple charged ions of high molecular weight and a number of small ions equal in charge to the polyvalent ion. This can happen with proteins which can acquire a positive or negative charge, depending on the pH of the solutions owing to their being amphoteric. Again, on the synthetic side, polyacrylic acid $(—CH_2-CH(COOH)—)_n$ will behave as a polycarboxylic acid. A similar behaviour also is observed with certain molecules like soaps and certain dyestuffs which have the property of aggregating together into so-called micelles, the binding force being due to secondary valence forces contrasted with the primary valence force in high polymers. Congo red (disodium salt of diphenyl bisazo naphthylamine sulphonic acid) when dissolved in water is highly ionised, forming a micellar anion which cannot pass through a membrane of parchment paper. This kind of system will therefore behave in quite a different way from the

solutions illustrated in Fig. 147. If a solution of Congo red is placed in an osmometer with water on the other side of the membrane, the sodium ion will diffuse into water. The process will soon stop, owing to the creation of a potential difference across the membrane because of the separation of the sodium and polyvalent ions. A membrane potential is thus developed.

If the Congo red solution is allowed to stand in the osmometer, the osmotic pressure falls. This is due to hydrolysis. The sodium ion accompanied by hydroxyl ions can then diffuse out through the membrane. Sodium hydroxide can be continually removed, and hydrolysis proceeds with the eventual precipitation of Congo red acid. This phenomenon is known as *membrane hydrolysis*.

When a readily diffusible electrolyte, *e.g.*, sodium chloride, is added to the colloidal electrolyte, Congo red, or to the water on the other side of the membrane, the added electrolyte does not distribute itself uniformly throughout the solutions. It is found that, at equilibrium, the concentration of sodium chloride is less in the cell containing the Congo red than in the other cell. This is shown by the figures in the following table (NaR = Congo red).

Original Concentration of NaR in Cell.	Original Concentration of NaCl in Outside Liquid.	Equilibrium Concentration in Cell.		Equilibrium Concentration in Outside Liquid [NaCl].	Ratio of [NaCl] in Outside Liquid to [NaCl] in Cell.
		[NaR].	[NaCl].		
0·01	1·0	0·01	0·497	0·503	1·01
0·1	1·0	0·1	0·476	0·524	1·1
1·0	1·0	1·0	0·33	0·66	2·0
1·0	0·1	1·0	0·0083	0·0917	11·0
1·0	0·01	1·0	0·0001	0·0099	99·0

The theory of membrane equilibria, first put forward by F. G. Donnan, can account for the observed behaviour. According to this theory a colloidal electrolyte with a non-diffusible anion drives the sodium chloride into the solvent on the other side of the diaphragm. The same distribution of sodium chloride would take place even if it were all initially present with the Congo red. Hence the membrane behaves as if it were permeable to sodium chloride in one

direction only. In presence of other electrolytes the effect of the Donnan membrane equilibirum is to lower the osmotic pressure exerted by the colloidal electrolyte.

When to the solution of Congo red is added an electrolyte with no common ion, *e.g.*, KCl, the non-diffusible anion attracts the cation (K^+) and repels the anion of the added electrolyte. At equilibrium, therefore, the concentration of the potassium ion is greater in the compartment containing the colloidal electrolyte.

The Ultra-centrifuge.—We have already seen that the size of microscopic and even submicroscopic particles may be measured by observing the rate of their sedimentation under the influence of a gravitational field. In addition, we have seen that if the particles become too small they exhibit Brownian movement to such an extent that they do not settle under gravity. The only way then to achieve sedimentation is to use centrifugal force, for it is fortunate that by mechanical means it is possible to rotate bodies at such a rate that the centrifugal force may attain 500,000 times that of gravity. The machine that allows such centrifugal field to be applied to a solution and also allows of the observation of the rate of sedimentation is called an ultra-centrifuge, developed to a high degree of precision by Th. Svedberg.

The simple theory of the instrument may be developed in the following manner. The rate of sedimentation is given by the equation

$$\frac{ds}{dt} = c\omega^2 x M(1 - V\epsilon)/f,$$

where c is the concentration of dissolved material in gm./100 c.c., ω is the angular velocity of rotation, x the distance from the centre of rotation at which sedimentation is observed, M is the molecular weight of the substance, V is the partial specific volume of the dissolved substance given by $V = w - (1 - x)/\epsilon h$, where w is the weight of the solvent, h the weight of dissolved substance, ϵ is the density of the solvent. f is the frictional force exerted by the sedimentation of a gram-molecule of dissolved substance. The numerator of the above expression, therefore, represents the driving force for 1 g. mol. Unfortunately it cannot be assumed that the particles are in fact spherical, and, therefore,

the Stokes relationship will not necessarily hold. However, it can be shown that f is given by

$$f = \frac{RT}{D}$$

where D is the diffusion coefficient of the dissolved substance. The value of M may be computed from the equation

$$M = \frac{ds/dt \,.\, RT}{c\omega^2 x(1 - V\epsilon)D}$$

D, the diffusion coefficient of the substance, may be measured by separate experiments.

If the centrifugal force is not too high, the dissolved particles will not be thrown to the bottom of the cell ; instead the concentration gradient set up by the field will tend to make the particles diffuse back in the opposite direction just as happens in Perrin's experiment. In time an equilibrium will be set up. The rate of diffusion in the direction opposite to sedimentation is given by

$$\frac{ds}{dt} = RT\frac{dc}{dx} \cdot f^{-1}.$$

Hence equating the above expressions

$$RT\frac{dc}{dx} \cdot \frac{1}{f} = c\omega^2 x M(1 - V\epsilon)/f,$$

or

$$\frac{dc}{c} = \frac{M(1 - V\epsilon)\omega^2 x \, dx}{RT},$$

on integration

$$M = \frac{2RT \log c_2/c_1}{(1 - V\epsilon)\omega^2(x_2^2 - x_1^2)},$$

where c_1 and c_2 are the concentration measured at distances x_1 and x_2.

A diagrammatic illustration of one type of ultra-centrifuge is shown in Fig. 149. The rotor which contains the cells holding the solution can be rotated at high velocity by means of a small oil turbine. The rotor is contained in a strong steel case provided with windows through which a beam of light may be directed. The concentration of dissolved substance may be calculated by measuring the amount of light absorbed, and the movement of the boundary

between pure solvent and solution by determining the position of the refractive index gradient by a number of methods. The range of the instrument is extremely wide reaching from a molecular weight of 100 to over 10^6.

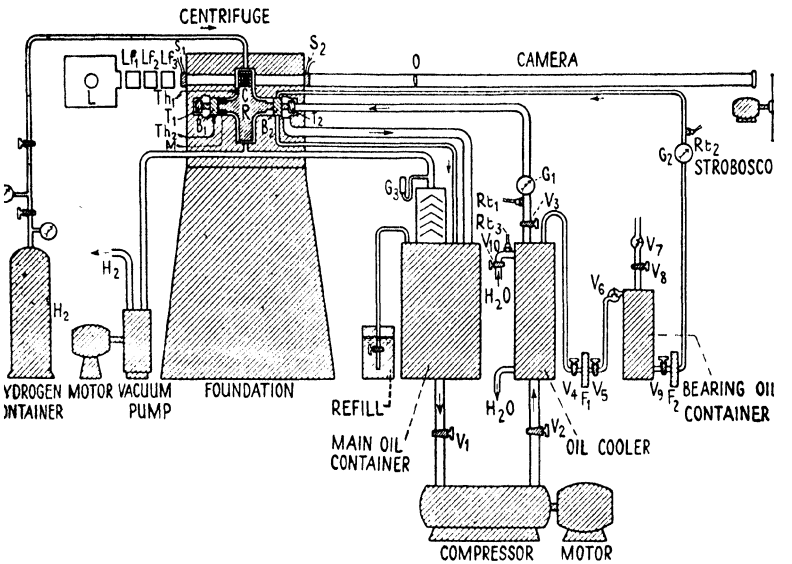


FIG. 149.

L. Lamp.	Th_1, Th_2. Thermocouples.
Lf_1, Lf_2, Lf_3. Light filters.	M. Magnetic speedometer.
S_1, S_2. Shutters.	G_1, G_3. Pressure gauges.
R. Rotor.	Rt_1 to Rt_3. Resistance thermometers.
C. Cell.	V_1 to V_{10}. Valves.
B_1, B_2. Bearings.	F_1, F_2. Oil filters.
T_1, T_2. Turbines.	O. Objective.

(From Svedberg and Pedersen, *The Ultra-centrifuge*, by permission of Oxford University Press.)

Light Scattering.—When a beam of light is passed through the solution of a high polymer there is well-marked scattering of the light only in the path of the beam. On examination of the solution by an ultra-microscope no individual sources of light can be seen as with an ordinary colloidal solution, say of gold. This is partly due to the fact that the particles do not scatter enough light to be seen individually. The reason for the scattering is, however, rather different. Scattering of light is due to fluctuations in density of a medium. It occurs to an observable extent even in a highly

purified liquid free from suspended matter. It is much more marked with high molecular weight substances, especially if the molecules are long chains of atoms. These chains execute a violent wriggling type of movement in solution, and the density fluctuations are more marked than with small molecules. Qualitatively a method is thus available for obtaining particle sizes. Such scattering reduces the intensity I_0 of a beam of light incident on a solution, and it emerges after traversing a path length x with an intensity I, the two being related by the equation

$$I = I_0 e^{-z \cdot c \cdot x}.$$

where z is an extinction coefficient and can be computed from the fraction of the light scattered. It is, however, possible to calculate what relation exists between z and molecular weight M. It has the form $z = A \cdot M \cdot c\left(\frac{dn}{dc}\right)^2$ where $\left(\frac{dn}{dc}\right)^2$ can be computed from the variation of refractive index (n) with concentration of the solution; A is a constant.

Viscosity of High Polymer Solutions.—One of the most striking properties of solutions of high polymers is their high viscosity at quite low concentrations. If the concentration of the solution is increased one obtains quite rigid gels, the most familiar example being that of gelatine in water. The viscosity of the solution depends on factors other than concentration. The nature of the solvent has some effect, the viscosity increasing the better the solvent for a given concentration. The most important influence is the size of the molecule, as measured by the methods described above. As a result of much empirical work the following general relationship holds for very dilute solutions—less than 0·1 per cent. weight concentration.

$$\frac{\eta_{\text{solution}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}} = K \cdot M^a,$$

where η is the viscosity, K is a constant depending on the nature of the high polymer and the solvent, c is the concentration usually of polymer per 100 gm. solvent, M is the molecular weight of the high polymer and a is another constant dependent on both solute and solvent. The quantity on the left-hand side is called the *specific viscosity*,

often denoted by η_{sp}, while the limiting value of η_{sp}/c as c approaches zero is called the intrinsic viscosity and denoted by $[\eta]$. Thus, if for a substance of unknown molecular weight a measurement of η_{sp} is made, calculation of the molecular weight is possible, provided the value of K and of a have already been obtained by a sufficient number of measurements on polymers of known molecular weight. The above form of the equation in which $a=1$ was first suggested by H. Staudinger, and proposed by him as a simple method of estimating molecular weight.

A number of values of K and of a are given in the following table. It will be seen that a has values not far from unity.

TABLE OF VALUES OF K AND OF a

(Concentration in basic g. mol. lit^{-1})

Substance.	Solvent.	K.	a
Decamethlyene adipate	Chlorobenzene	$3{\cdot}3 \times 10^{-5}$	1·00
Polyisobutene	Di-isobutene	$3{\cdot}6 \times 10^{-4}$	·64
Cellulose acetate	Acetone	$1{\cdot}04 \times 10^{-2}$	0·67
Polystyrene	Solvene	$6{\cdot}6 \times 10^{-3}$	0·80

No general rule can, however, be formulated. Similarly, it will be seen that the values of K do not vary a great deal. These facts suggest there is some underlying principle at work controlling viscosity, but its precise significance has so far eluded thorough investigation.

Some long time before the nature of high polymers was known, A. Einstein deduced a relationship for the viscosity of suspensions of small spherical particles in a liquid. This would of course correspond approximately to colloidal solutions of the kind described on p. 506. The relation can be written $[\eta]=2{\cdot}5$. Thus it will be seen that $[\eta]$ is independent of the solute, solvent, and of the molecular weight. This equation has been experimentally verified, using finely divided spherical particles. The striking difference between the two equations is now explained by supposing that with linear polymers the molecules are more or less stretched out in a good solvent. It is the entanglement of these long chains that gives rise to high viscosities

and to gelling. Naturally the higher the molecular weight the more important does this entanglement become.

In order to keep colloidal solutions for long periods of time it is essential to add a protective agent. When this is done it is possible to evaporate the solution to dryness and add water, when the colloid goes back into solution without difficulty. For example, in Paal's method of preparing colloidal silver the following procedure is adopted: Silver nitrate solution is added to an alkaline solution of sodium protalbate [1] (1 gm. in 15 ml. water).

The protective action of high polymers can also be used to colloidal solutions which are normally so unstable that their existence is only transitory. For example, when dilute solutions of silver nitrate and potassium bromide are mixed an immediate precipitate of silver bromide is formed and separates out. If, however, say, 1 per cent. of gelatine is added to the solutions, no precipitate is formed on mixing. An opalescent solution results, and no precipitation ever occurs. The particles of silver bromide are of colloidal dimensions, the gelatine acting as the protective agent. In fact, this is the basis of forming the photographic "emulsions"; the latter inaccurate name (see below) has become standard photographic practice. (The gelatine also exerts certain other specific actions in rendering the emulsion sensitive to visible light.) In a similar way the so-called Purple of Cassius, obtained by reducing gold chloride solution with stannous chloride, consists of gold particles intimately mixed with the protecting stannic acid.

Gels.—When the solvent is removed from a solution of a high polymer the solution becomes more and more viscous until a gel is formed. With aqueous solutions a gel may be precipitated by the addition of an inorganic salt. The function of the salt is to remove water associated with the high polymer. A secondary effect may be the removal of, or at least modification of, the charge in the dissolved molecules, since the electrolyte may also be carried down with the precipitated polymer. This latter effect is especially important with proteins which, in virtue of their structure,

[1] This is made by partial hydrolysis of egg albumin with sodium hydroxide until a precipitate is formed; the precipitate is then dissolved by addition of sodium hydroxide. The mixture is heated on a water bath until reduction of the silver oxide is complete and the solution dialysed. The silver solution is evaporated to dryness. On adding water the solid goes into solution as a yellow or brown colloidal solution of silver.

behave as amphoteric electrolytes. At a certain *p*H the net charge on the protein molecule can be shown by electrophoresis experiments to be at a minimum. Under this condition, the so-called isoelectric point, the protein is most easily precipitated.

Protective Action of High Polymers.—High polymeric materials, in virtue of their relatively high stability, can prevent the precipitation of colloidally dispersed particles when electrolytes are added. This is the *protective* action of high polymers, first discovered by Faraday in connection with the precipitation of gold sols. The protective effect varies among the water-soluble high polymers, hence it is necessary to attempt to define some quantitative measure of protective action. Zsigmondy proposed the following empirical definition. The " gold number " of the substance is the weight in milligrams of the protective agent, which fails to prevent the change from red to blue (due to aggregation) in 10 ml. of a gold sol when 1 ml. of 10 per cent. solution of sodium chloride is added. If this definition is to be used in an absolute sense, it is of course necessary to specify clearly the method of preparation and concentration of the colloidal gold solution. The following table gives some representative figures :—

Substance.	Gold Number.
Gelatin . .	0·005 . 0·01
Casein . . .	0·01
Hæmoglobin .	0·03 . 0·07
Gum arabic . .	0·15 . 0·25
Dextrin . .	6 . 20
Albumin . .	0·1 . 0·2

Precipitation of High Polymers from Solution.—High polymers can be readily precipitated from solution by adding a non-solvent. With those substances which are soluble in organic solvents it is most convenient to add a precipitant that is miscible with the solvent. For example, methyl alcohol is almost universally useful in this connection. By carrying out precipitation slowly it is possible to separate a high polymer into a number of fractions of increasing molecular weight, the higher polymers being less soluble than the lower. The separation is never complete, but by refractionation procedures fairly narrow cuts may be obtained.

With those high polymers that dissolve in water the phenomena are rather more complex, for not only can substances like alcohol function as precipitants in much the same way as mentioned above, but electrolytes, when added in large proportion, also cause precipitation. The latter effect is of a quite different order of magnitude from that with colloidal solutions. For example, an arsenious sulphide solution is precipitated by the tervalent lanthanum ion at a concentration of only 5×10^{-5} molar, whereas egg-albumin is precipitated from aqueous solution when the concentration of the ion reaches $1{\cdot}6 \times 10^{-3}$ molar.

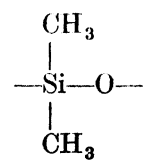
The effect of the nature of electrolytes is quite marked, and it is possible to arrange a series of ions in order of their precipitating power, which order does not depend on the nature of the dissolved polymer. For example, with egg-albumin, lecithin, the order is citrate, tartrate, sulphate, acetate, chloride, nitrate, iodide, thiocyanate. With univalent cations the differences are not pronounced, the order being lithium, sodium, potassium. This phenomenon was first recognised by F. Hofmeister, and the series of ions is referred to as the *Hofmeister series*. These series turn up in a number of physico-chemical phenomena, especially in solubility. The explanation simply is that these ions are more or less hydrated and that they act as weak dehydrating agents. A transparent gel is formed which continues to lose solvent, shrinking until a sample of pure high polymer is obtained having all the properties of a rigid solid. There is, therefore, a continuous transition from a mobile liquid to a solid. The same kind of transition can occur in the opposite direction if a transparent high polymer, *e.g.*, polymethyl methacrylate (perspex) $(CH_2 - C(Me)COOMe)_n$, is heated. It becomes plastic and flows like a liquid at a temperature of 150° C. A gel is thus an ill-defined stage between a solid and a liquid, and has the mechanical properties of both states of matter, depending on the deformation and temperature to which it is subjected.

In general, gels may be divided into two classes : (*a*) those which can go back into solution readily after precipitation, *i.e.*, reversible gels ; and (*b*) those that when precipitated by heating, or even by isothermal removal of the solvent, cannot be got back into solution simply by adding solvent. Gels of silicic acid, aluminium hydroxide and other metallic hydroxides belong to this category. Here precipitation

involves drastic *chemical* changes in the nature of the dissolved molecules. These changes cannot be reversed. For example, silicic acid could be finally dehydrated until the empirical formula for the residual solid is simply SiO_2. In silica, however, SiO_2 units do not exist by themselves. They are linked together into a network of silicon and oxygen atoms of no definite molecular weight. In order to obtain a solution of silicic acid in water it is necessary to break the silicon-oxygen bonds and to add progressively the elements of water to the system. This does not happen spontaneously.

Another peculiar property of gels is *syneresis*. If a gel is allowed to stand the system may separate into two phases, a gel and a mobile fluid. The process of expulsion of fluid was termed by Thomas Graham syneresis.

When certain gels are shaken violently they liquefy, and on standing the liquid sets to a gel again. In a similar way more dilute solutions of high polymers exhibiting high viscosity show a decrease in viscosity when the solution is subjected to high rates of shear, for example, by being forced through a capillary tube at high rates of flow. These phenomena are known as *thixothropy* (from the Greek, meaning to change by touching). Even aqueous suspensions of the mineral bentonite exhibit thixotropy. The reverse type of behaviour, namely increase of viscosity varying with rate of shear, is also exhibited by certain systems containing high polymer substances. This is most strikingly shown by a silicon polymer containing the repeating unit



These polymers range from mobile liquids up to rubber-like substances, depending on the degree of polymerisation. When these polymers lying within a suitable molecular weight range are mixed with a filler like clay a putty-like mass is obtained. This material flows like putty, and can be almost poured out of beakers. A ball of it on being allowed to stand loses its form entirely and forms a pool-like thick oil. If, however, the ball is dropped on a hard floor it bounces like a rigid ball, say, of glass. This latter property

shows that on sudden shock the material behaves like a rigid solid, and it is colloquially referred to as " bouncing putty." The phenomenon is known as *dilantancy*.

Precipitation of High Polymers by Electrolytes.—Such colloids are much less sensitive than suspensoids to electrolytes, and are precipitated by neutral alkali salts, for example, only when these are added in large amount. The effect, therefore, is comparable with that known as " salting out." Moreover, the precipitation is *reversible*, so that on washing away the precipitating salt the colloid passes again into a sol. With multivalent ions, it is true, precipitation is effected by a comparatively small concentration, but the concentration is much greater than in the case of suspensoids. Thus, whereas arsenious sulphide sol is precipitated by the tervalent lanthanum ion in a concentration of 0·00005 molar, egg-white is precipitated only when the concentration is increased to 0·0016 molar.

In the precipitation of emulsoids by salts, the nature of the ion and *its power to alter the distribution of water (or other dispersion medium) between the internal and the external phase* [1] play an important part. Thus in the precipitation of egg-white, lecithin, etc., the efficiency of different anions is in the order : citrate>tartrate>sulphate>acetate>chloride >nitrate>iodide>thiocyanate ; and in the case of the univalent cations, although the differences are much less pronounced, the order is : lithium>sodium>potassium. Since the effect of different anions on the precipitation of egg-white was first observed by Franz Hofmeister, the series given above is generally referred to as the *Hofmeister series*. The same order of anions is met with in a number of different physico-chemical and physiological processes (*e.g.*, influence on the solubility of slightly soluble substances), and can be explained, in the case of aqueous solutions, as due to differences in the hydration of the ions or to their effect on the equilibrium between the different molecular states of liquid water. By the addition of these salts to a hydrophilic colloid the water-content of the colloid is diminished until at last the particles resemble those of a hydrophobic colloid and are precipitated, the charge on the colloid being neutralised by the electrolyte. As in the case of hydrophobic colloids, so in the case of hydrophilic colloids, precipitation

[1] The dispersed phase is sometimes called the internal phase, and the dispersion medium the external phase.

is the end-point of a process, so that addition of electrolytes, even in a concentration insufficient to effect precipitation, may produce notable alterations of the colloid. This fact is of much importance in the living organism where there is a constant interaction between hydrophilic colloids and electrolytic ions leading to variations in the state of the colloids.

It is of interest and importance to note that the Dutch chemist, H. R. Kruyt, has, in certain cases, demonstrated the existence of hydration and electric charge as two contributory factors to the stability of hydrophile colloids. Thus, by adding alcohol to an agar sol, free from electrolytes, the stability due to hydration was destroyed, and the colloid could then be precipitated by electrolytes as in the case of hydrophobic colloids. Or the electric charge could first be neutralised by electrolytes, and precipitation of the colloid then brought about by addition of alcohol (dehydration).

Imbibition. — One of the most important properties possessed by a number of gels is that of taking up or "imbibing" water and swelling. This property is also shown by most animal and vegetable tissues. In the case of gelatin the property is one with which every one is familiar, the increase of volume of the gelatin being very considerable when the gelatin is left for some time in contact with water. Conversely, the pressure to which this process of imbibition can give rise, or the pressure which must be exerted in order to squeeze out the water from the gel, is very great, as is shown by the following table, which applies to a species of *Laminaria* (seaweed) :—

Pressure (Atmospheres).	Volume of Water taken up by 100 Volumes of Dry Gel.
1·0	330
3·2	205
7·2	97
21·0	35
41·0	16

From these numbers it is seen that, even when subjected to a pressure of 41 atmospheres, the dry seaweed was able to take up water to the extent of 16 per cent. of its volume.

The swelling of gels is more or less markedly affected by the presence of electrolytes, and in the case of gelatin, fibrin and other proteins, acids and alkalis are especially powerful. Thus, fibrin which swelled to 8 mm. in water swelled to 48 mm. in 0·02-normal HCl. In more dilute and in more concentrated acid the swelling was less. In 0·02-normal NaOH the fibrin swelled to 77 mm. In these cases the great effect of acids and alkalis is probably due to the amphoteric character of the colloids ; addition of acids or alkalis leads to the formation of salts which give rise to hydrated ions. In presence of neutral salts the swelling in acid and alkaline solution is diminished.

The swelling of gels is also influenced by the presence of neutral salts alone, in dilute solution, and it is found that different ions influence the swelling of gels in different ways and in different degree.

Emulsions.—When two immiscible liquids are brought together there will, in general, be developed a certain interfacial tension ; and the tension on the two sides of the interface will be different. The interfacial surface will therefore be curved, with its concave surface towards the side of greater surface tension, and the liquid on this side will tend to form drops in the other liquid.

When one shakes pure water and benzene, or pure water and olive oil together, the oil or benzene is broken up into drops, the energy required to bring about the dispersion of the oil or the increased area of interface between the two liquids being considerable. The emulsion which is thus produced with pure liquids is, however, not stable, unless the oil content is less than about 1 in 10,000. Such very dilute emulsions are often met with in engine condenser water. On allowing more concentrated emulsions of pure liquids to stand, the globules unite and separation into two liquid layers takes place. In order that a permanent emulsion may be produced, a stabilising agent or emulsifying agent must be present. In the case of dilute emulsions (up to about 2 per cent.), stabilisation may be effected by adsorption of ions from water or traces of added electrolyte. The dispersed droplets thus acquire an electric charge, similar to the particles of a lyophobe colloid, and the emulsion behaves in many respects like a colloidal sol. More generally, however, stabilisation of an emulsion is effected by means of an emulsifying agent, such as albumin, gelatin, or an alkali soap,

which forms an interfacial film between the two liquids.[1] A decrease [2] of the interfacial tension is thereby produced and the work which must be done in increasing the surface of the dispersed liquid, by breaking it up into small drops, is diminished.

The energy required for the production of an emulsion may be added to the system by hand or mechanical shaking, by mechanical mixers of various kinds, by homogenisers which force the liquid mixture under pressure through small holes, or by high-frequency ultrasonic waves [3] of from 100,000 to 500,000 vibrations per second.[4]

The production and treatment of emulsions is of great importance in the food, drug, and other industries.[5]

Inversion or Reversal of Emulsions.—A phenomenon of much importance is the inversion or reversal of emulsions. Under certain conditions, oil and water may exist as an oil-in-water emulsion, with the oil as the dispersed phase, and under other conditions as a water-in-oil emulsion, with water as dispersed phase. Thus, when soaps are used as emulsifiers, the nature of the emulsion depends on the nature of the cation present in the soap solution. When sodium oleate is used as an emulsifier, an oil-in-water emulsion is formed; but if a soap with a bivalent or polyvalent cation *e.g.*, magnesium oleate or calcium oleate, is used, a water-in-oil emulsion is formed. If to an oil-in-water emulsion, stabilised with sodium oleate, a calcium salt is added, the emulsion becomes unstable when the ratio of calcium to sodium reaches a certain value. When this critical point is passed, inversion of the type of emulsion takes place.[6] It would appear that inversion of the oil-in-water emulsion by polyvalent ions applies only to those cases where the interfacial film can react with the added electrolyte.[7]

An adsorption-film theory of emulsions, based on earlier

[1] Stabilisation of emulsions may, however, also be effected by substances which do not decrease the interfacial tension.

[2] Mayonnaise is an oil-in-water emulsion in which yolk of egg acts as emulsifying agent.

[3] These are sound waves of a frequency so high that they cannot be detected by the human ear.

[4] R. W. Wood and A. L. Loomis, *Phil. Mag.*, 1927, (vii), **4**, 417

[5] See W. Clayton, *Emulsions and their Technical Treatment* (Churchill)

[6] G. H. A. Clowes, *J. Physical Chem.*, 1916, **20**, 407; S. S. Bhatnagar, *J. Chem. Soc.*, 1920, **117**, 542; 1921, **119**, 61, 1760; L. W. Parsons and O. G. Wilson, *Ind. Eng. Chem.*, 1921, **13**, 1116.

[7] King and Wrzeszinski, *Trans. Faraday Soc.*, 1939, **35**, 741.

work by F. G. Donnan, was put forward by W. D. Bancroft,[1] and put to the test of experiment by Clowes [2] and by Bhatnagar.[3] According to this theory, an emulsifying agent is adsorbed into the surface separating the two liquids and there forms a coherent film. This film, if in contact with two phases, oil and water, will have two surface tensions, and will tend to curve towards the side having the higher surface tension. The dispersed liquid is on the side of the film having the higher surface tension. Since soaps of univalent cations are readily dispersed in water but not in oil, they form a film which is wetted more readily by water than by oil. Consequently, the surface tension is lower on the water side than on the oil side, and the film tends to curve so that it encloses globules of oil in water. Thereby the area of the side of the film of higher surface tension is reduced compared with that of lower surface tension. Soaps of divalent and trivalent cations, however, are freely dispersed in oil, but not in water, and the film is wetted more easily by the oil than by the water. Thereby the formation of globules of water in oil is favoured. According to this theory the preferential wetting of the adsorbed film by water or by oil is an important factor.

It is probable that the molecules of the adsorbed film of emulsifying agent are orientated in a definite manner [4]; and the stability of an emulsion depends on the strength and completeness of the adsorbed film. Such a stabilised emulsion resembles a protected lyophobe colloid.[5]

Fine powders may also act as emulsifying agents,[6] and the nature of the emulsion will depend on the nature of the powder used. Thus, by using carbon black, emulsions of the water-in-oil type are obtained,[7] whereas with silica, oil-in-water emulsions are formed. By using a suitable mixture of carbon black and silica, no emulsion is obtained.[8]

[1] *J. Physical Chem.*, 1915, **19**, 275; Bancroft and Tucker, *ibid.*, 1927, **31**, 1681.

[2] *Loc. cit.*

[3] *Loc. cit.* See also Ghosh and Dhar, *J. Physical Chem.*, 1926, **30**, 294.

[4] See, for example, Harkins, Davies, and Clark, *J. Amer. Chem., Soc.* 1917, **39**, 541; Finkle, Draper, and Hildebrand, *ibid.*, 1923, **45**, 2780.

[5] For a general discussion of the oil-water interface, see *Trans. Faraday Soc.*, 1941, **37**, 117.

[6] S. U. Pickering, *J. Chem. Soc.*, 1907, **91**, 2001.

[7] A. U. M. Schlaepfer, *J. Chem. Soc.*, 1918, **113**, 522.

[8] T. R. Briggs, *Ind. Eng. Chem.*, 1921, **13**, 1008.

The action of these powders seems to depend on the fact that they form a layer in the interface of the two liquids, and contraction of the interface cannot take place without crowding these particles together and ultimately forcing them into one or other of the liquids, a process which involves an increase in the free energy of the system.[1]

[1] N. K. Adam, *Physics and Chemistry of Surfaces* (Oxford University Press).

CHAPTER XX

ADSORPTION

It has already been mentioned on p. 117 that the effect of certain substances in decreasing the surface tension of water is most readily explained by supposing that the dissolved substance tends to congregate at the air-liquid interface. The phenomenon of this accumulation of a component at an interface is called *adsorption*. It is not confined to air-liquid interfaces, although it is most readily demonstrated at such an interface. Adsorption is well exhibited at the gas-solid, the liquid-solid and the liquid-liquid interfaces. We shall deal in this chapter with gas-solid and gas-liquid systems where the phenomenon of adsorption has been most studied.

Adsorption of Gases on Solids.—From the time of Scheele in 1777 the property of finely divided or porous solids of taking-up gases has been well known, charcoal especially displaying this property. Similarly, glass is known to be covered with a film of water which can only be removed by heating *in vacuo*. It is now known, however, that if any solid is produced in a finely divided form it is possible to demonstrate that gases will be taken up to a greater extent from a surrounding gas phase. The volume of gas taken up is naturally proportional to the specific surface, *i.e.*, the area of the interface in $cm.^2/g$. It depends on the precise nature of the surface exposed, *e.g.*, different crystal surfaces adsorb to different extents. It depends on the nature of the gas, its pressure, temperature and the presence of other gases in a mixture. The interaction may merely be physical or it may sometimes be chemical. It may be reversible or irreversible.

The order of magnitude of the phenomena can be illustrated by the figures in the following table, which shows how a variety of gases is adsorbed by an active charcoal, previously evacuated :—

ADSORPTION OF GASES BY CHARCOAL

Gas.	Volume of Gas in Cubic Centimetres adsorbed by 1 c.c. of Charcoal at	
	0° c.	−185° c.
Hydrogen . .	4	135
Nitrogen . .	15	155
Oxygen . .	18	230
Argon . . .	12	175
Helium . .	2	15
Carbon monoxide .	21	190

The adsorption here is reversible except with oxygen. Some of the adsorbed oxygen reacts chemically with the active charcoal with the production of carbon monoxide which can be pumped off. It will be seen that oxygen, nitrogen, argon and carbon monoxide fall into a class, hydrogen is much less strongly adsorbed and helium less so. If the temperature is lowered to −185° then uniformly the volume of gas adsorbed is increased. According to the principle of Le Chatelier, this result implies that heat is given out when adsorption occurs.

Again, the volume of gas adsorbed increases with increasing pressure, as shown by the following figures for carbon dioxide and charcoal :—

ADSORPTION OF CARBON DIOXIDE BY CHARCOAL

Pressure in millimetres of mercury (p).	4·1	25·1	137·4	416·4	858·6
Vol. of CO_2 adsorbed per gram of Charcoal (x/m).	0·38	0·77	1·45	2·02	2·48

When x/m is plotted against p the curve is seen in Fig. 150 to be concave towards the pressure axis. Again this is a general experience. That is, the amount of gas adsorbed increases at first linearly with the pressure, but at higher pressures the additional amount adsorbed gradually falls off and the curve would seem to tend to maximum value. This curve is called the *adsorption isotherm.* A simple empirical relationship first suggested by H. F. Freundlich, namely,

$$x/m = Kp^{1/n},$$

where K and n are constants, will describe the course of the isotherm without, however, giving any clue as to the nature of the interaction of the gas with the solid so that the basis of the equilibrium may be understood.

The first satisfactory picture of adsorption processes was given by Irving Langmuir. When a solid is subdivided to produce an adsorbent then in the actual process of subdivision the bonds holding the solids together are severed. Depending upon the nature of the solid, these bonds may involve forces between molecules — intermolecular forces, or they may be interatomic forces. An example of the first class would be white phosphorus, in which P_4 units make up the crystal; in the second class is diamond, in which carbon-carbon bonds are broken when the crystal is divided. Interionic, that is electrostatic, forces are involved when ionic crystals like sodium chloride are subdivided. Langmuir suggested that the cause of adsorption was the interaction of these unsatisfied fields of force with the gaseous molecules bombarding the solid surface. This interaction may thus involve different kinds of bonds so that adsorption may be essentially physical in character in the case of intermolecular forces, but chemical in character if interatomic forces are involved. The important point, however, is that just as in a crystal these forces are short range in character, *i.e.*, a few angströms, so the fields of force are short range. Once the fields of force are satisfied by adsorption, the new surface so created has much less power of attracting another layer of molecules on top of these forming the first layer. In this way Langmuir put forward the idea that adsorbed films tended predominantly to be only one molecule in depth.

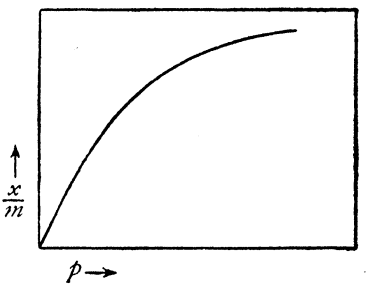


FIG. 150.

In those cases where intermolecular forces are operative the adsorbed molecules remain adsorbed as molecules, although of course their shape may be altered to some extent. With interatomic forces, on the other hand, there is the possibility of chemical interaction with the adsorbed molecule, which may be split into atoms or radicals. For example, when oxygen is adsorbed by tungsten it is certain

that a surface layer of oxygen atoms is formed. Similarly, it is believed that molecular hydrogen is likewise dissociated when adsorbed on clean metal surfaces.

These conceptions lead to another conclusion, namely, that there are a finite number of adsorption sites corresponding to a regular two-dimensional lattice. This two-dimensional lattice in practice is by no means uniform in the forces causing adsorption. From what has been said about the solid state (Chapter VI.), it is evident that different faces of a crystal contain different densities of packing of atoms. Thus the surface forces will vary on this account alone. Again, such crystal facets are seldom atomically smooth and, therefore, on an individual face there may be a great variation in the strength of these surface forces. These complexities make it difficult to formulate precise quantitative theories of adsorption phenomena. The following quantitative treatment is sufficiently rigorous provided the simplifying premises are remembered. It will be presumed that there are a finite number of adsorption sites of precisely similar type and that the adsorption of one molecule occurs on one site. It will also be assumed that the filling of a fraction of the adsorption sites will not affect the activity of other sites to adsorb molecules. Suppose at the equilibrium pressure p a fraction θ of the adsorbed sites is filled, then we have to consider the system in a state of dynamic equilibrium in which the rate at which molecules are adsorbed is equal to the rate at which they evaporate. Considering 1 cm.^{2} of adsorbing surface, the rate of adsorption is equal to

$$K_1(MT)^{-\frac{1}{2}}p,$$

where K_1 is a constant that can be calculated from the kinetic theory of gases if it is assumed each molecule that strikes a site is taken up, M is the molecular weight and T the absolute temperature. This expression only holds if the surface is not covered, *i.e.*, $\theta = 0$. If, as postulated, a fraction of the sites is occupied, then adsorption can only occur on bare sites, the fraction being $(1 - \theta)$. The rate of adsorption per cm.^{2} at equilibrium is therefore

$$K_1(MT)^{-\frac{1}{2}}p\ (1 - \theta).$$

The calculation of the rate of evaporation is more difficult. It will be proportional to the fraction of the surface covered.

It will also be proportional to the probability that a molecule will overcome the surface forces holding it to the solid. This factor will be given by an expression of the type

$$K_2 e^{-\lambda/RT},$$

where λ is the magnitude of the binding energy in calories per mol and K_2 is a constant whose precise value cannot always be calculated. This expression is, of course, analogous to that for the evaporation of solids and liquids.

Therefore, at equilibrium,

$$K_1 (MT)^{\frac{1}{2}} p(1-\theta) = K_2 \theta e^{-\lambda/RT}$$

and

$$\theta = \frac{K_1 (MT)^{\frac{1}{2}} p}{K_1 (MT)^{\frac{1}{2}} p + K_2 e^{-\lambda/RT}}.$$

If A is the effective area of the adsorbent and n mols are adsorbed/cm.^{2} when $\theta = 1$, then the number of mols of gas adsorbed x is given by

$$x = \frac{nAK_1 (MT)^{\frac{1}{2}} p}{K_1 (MT)^{\frac{1}{2}} p + K_2 e^{-\lambda/RT}}.$$

There are two extreme cases that may readily be considered. If p is low the first term in the denominator is small compared with the first, hence

$$x = \frac{nAK_1 (MT) e^{\lambda/RT} p}{K_2}.$$

The volume of gas adsorbed will increase linearly with pressure, and it will, for a given pressure, exponentially decrease with increasing temperatures, as would be expected from Le Chatelier's principle.

The second extreme occurs when the pressure is high. Now the first term in the denominator is much larger than the second and, therefore,

$$x = nA$$

Experimental Verification of the Theory.—The experimental method for measuring the adsorption of gases on solids is in principle simple (Fig. 151). It consists of a bulb containing the adsorbent. Attached to the bulb are, (*a*) a gas pipette of known volume which can be filled with gas at a measured pressure; (*b*) a manometer; (*c*) a pump for exhausting the system. It is necessary also to know the volume of space not occupied by the adsorbent. This is

most conveniently done by measuring the pressure in the adsorbent bulb of a known quantity of gas admitted from the pipette, the gas being chosen so that it is not appreciably adsorbed. Helium is suitable for this purpose. When a gas is adsorbed the pressure registered on the manometer will be smaller. This corresponds then to the amount of gas adsorbed.

For a full investigation of the matter it is also necessary to know the area of the surface exposed to the gas. If the

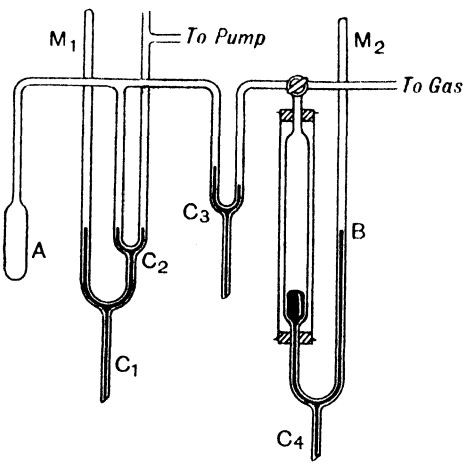


FIG. 151.

(Redrawn from Smithell's *Bases and Metals*, by permission of Chapman & Hall Ltd.)

adsorbent consists of a fine powder this measurement is difficult. If the particles are not submicroscopic, *i.e.*, exceed 2×10^{-4} cm. considerably, then the only satisfactory method is laboriously to examine microscopically a representative sample and assess the area from the external shape on the assumption there are no internal cracks or crevices. If the particles are submicroscopic an electron microscope capable of detecting particles as small as 5×10^{-7} cm. may be used. If internal cracks are suspected of being present, or if the solid is obviously porous, such as charcoal, an estimate of internal volume may be obtained if the apparent volume of the solid can be measured, for example, with liquid mercury, it being presumed that mercury cannot penetrate the pores. This, together with the measurement of dead space in the

system, will provide an approximate measure of pore volume. Langmuir overcame the difficulty by using microscope cover slips whose superficial area could be measured. With gases, such as nitrogen at 90° K, it was in fact found that a mono-molecular layer of gas was formed at high enough pressures. Many measurements subsequently made have confirmed the general form of the adsorption isotherm, but naturally exact agreement cannot be expected unless the assumptions used in its derivations are compiled with in practice. With nearly all real systems it is doubtful whether this state of affairs is ever reached.

Adsorption from Liquids.—In a gas mixture those components most strongly adsorbed will be selectively removed. Similarly, in a mixture of liquids, one component may be removed. The important point is that selective adsorption is well marked to such an extent that the presence of the solvent, suitably chosen, does not appear to interfere with the accumulation of a readily adsorbable substance at the liquid-solid interface.

In fact, a general behaviour similar to that of gaseous adsorption is generally observed and adsorption isotherms of a similar shape are also observed. The practical applications are extensive. The most striking perhaps is the development of efficient fractionation procedures of difficultly separable substances. This is accomplished by passing the solution through a column of adsorbent when the most easily adsorbable component is taken up by the first layers, which thus become saturated. The next layer takes up the second most strongly adsorbed component and so on. There is, therefore, produced a series of bands of adsorbed molecules. By mechanical subdivision of the column these adsorbed substances can then be recovered by suitable extraction processes. This general method is now referred to as *chromatography*, since it was first practised with coloured substances like chlorophyll and other plant pigments. The method is, however, of general applicability and depends wholly upon the slight differences in adsorbability of the dissolved substances.

Adsorption Indicators.—Extensive use is now made in volumetric analysis of the phenomenon of selective adsorption.[1] When silver nitrate is added to the solution of a

[1] Fajans and Hassel, *Z. Elektrochem.*, 1923, **29**, 495; Fajans and Wolff, *Z. anorgan. Chem.*, 1924, **137**, 221.

chloride in presence of a small amount of fluorescein, the silver chloride, which is precipitated preferentially, adsorbs chloride ion; and this adsorbed chloride ion is completely removed only when a very slight excess of silver has been added to the solution. The organic anion is then adsorbed and forms a complex on the surface of the silver chloride with the first trace of excess of silver. This complex is of a well-marked pink or red colour and shows up distinctly against the greenish-yellow colour of the solution. The fluorescein acts as an *adsorption indicator*. In very dilute or in acid solution, dichlorofluorescein, bromophenol blue, or bromocresol purple should be used in place of fluorescein.

The adsorption indicator must be such that it is less readily adsorbed than one of the ions of the precipitated salt. Thus, eosin cannot be used with chlorides because it is too strongly adsorbed, but can be used with bromides, as the bromide ion is more strongly adsorbed than the chloride ion. Eosin can also be used in the titration of iodides, but di-iododimethyl-fluorescein is better.

Many other adsorption indicators are used in titrations involving the formation of precipitates.

Adsorption at the Air-Liquid Interface.—The study of adsorption phenomena at this interface has revealed more about the behaviour of two-dimensional matter than any other system. In fact, it may be said that there is an exact analogy between the behaviour of two-dimensional and three-dimensional matter: indeed, with two-dimensions there happens to be a greater variety of observable states. If a drop of oil is allowed to float on water it may or may not spread. The criterion for spreading is laid down in a very simple way. Consider a lenticular drop floating on the surface (Fig. 152), then there are three surface active forces in operation, γ_1 is the interfacial tension for the air-oil interface, γ_2 that for the oil-water interface and γ_3 that for the air-water interface. If the sum of the resolved components of γ_1 and γ_2 in the direction of γ_3 is greater than γ_3, the oil will remain as a lenticular mass. If γ_3 is greater than the resolved components, the drop will spread. The question, therefore,

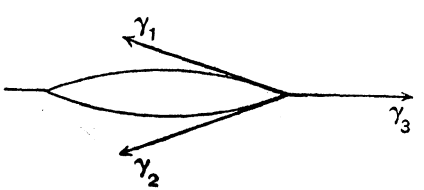


FIG. 152.

arises as to the ultimate thickness of the oil film. This in turn raises the question of detecting the presence of the film. The spreading of oil invariably lowers the surface tension at the liquid-air interface, hence it is a matter of devising a special type of interfacial tension apparatus. This was first done by Irving Langmuir, though the properties of such films had been examined by Lord Rayleigh and Miss Pockels. The instrument has now been elaborated but its essential principles are shown in Fig. 153. A shallow

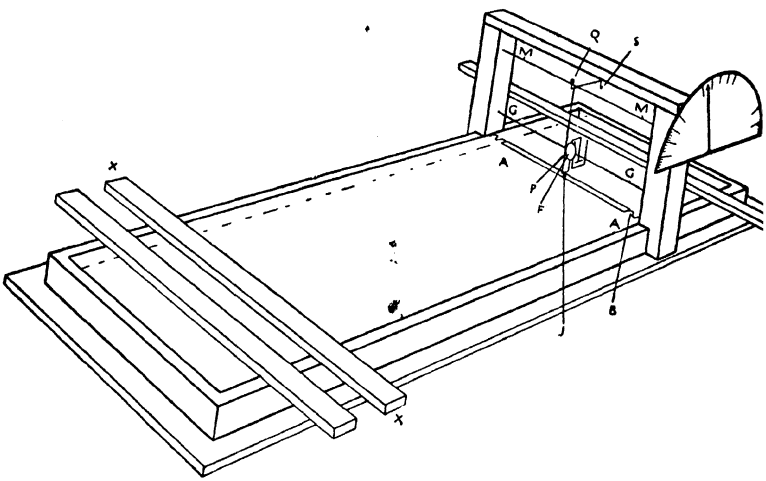


FIG. 153.

(From Adam, *The Physics and Chemistry of Surfaces*, by permission of Oxford University Press.)

trough is filled brimful with water. Floating on the surface is a boom A, generally of mica. This is supported by a torsion wire M. The position of the boom can be accurately measured by the movement of the mirror P. Attached to the boom are waxed threads, the other ends of which are stuck to the sides of the trough. Paraffin-waxed glass slides X rest on the other end of the trough. If a drop of a spreading oil is placed on the water the barrier X and the boom confine the film to a known area. As the edge of the film comes into contact with the boom, the latter will be subjected to a certain pressure, which is numerically $\gamma_3 - (\gamma_1 + \gamma_2)$. In order to maintain the position of the beam the torsion wire must be rotated. By calibration the actual force exerted on the boom can readily be calculated. These forces can be

quite large. It is not uncommon to find the surface tension of water reduced to, say, 35 dynes/cm. The boom may be 10 cm. long. Roughly, therefore, a force of 250 dynes or 0·38 grams is exerted on the barrier. This is the surface pressure of the film.

Further investigation has shown that a great variety of substances have the property of spreading in this way. The most suitable consists of a long straight chain of CH_2 groups terminated by a suitable polar group such as COOH, stearic acid being a good example. Such a molecule is not soluble in water, unless of course the water is made alkaline. It has a strong tendency to accumulate at the surface, because the hydrocarbon chains have so little affinity for water that they tend to aggregate; on the other hand, the COOH group tends if possible to reach such an aqueous environment. The result is a compromise, in that by accumulating and orienting at the interface the carboxyl group may still be in the right environment and the hydrocarbon chains may associate together.

With a three-dimensional gas we have the relationship $pv=kT$, where p is the pressure exerted by one molecule in a volume v at absolute temperature T. If we stretch the analogy to two dimensions, we would have $FA=kT$, where F is the pressure measured in the surface balance and A is the area of the film. Very sensitive balances can detect surface pressures as low as 10^{-3} dynes/cm. Hence F can be measured and, using a known weight of a substance, the number of molecules comprising the film may be calculated. If the analogy is exact we should, therefore, be able to calculate the numerical value of k. If the unit of area is square Angströms $k=1{\cdot}37$. The experimentally observed value is 1·4, when each molecule occupies an area of the order of 10,000 A^2. As the film is compressed from these large areas the pressure exerted is somewhat less than that predicted for an ideal two-dimensional gas as shown in Fig. 154. At quite a well-defined point the pressure suddenly ceases to increase, but is maintained constant to point C when it once more increases. At areas between B and C two-dimensional condensation takes place, a two-dimensional vapour co-existing in equilibrium with a two-dimensional liquid. As the film area is made smaller the proportion of the liquid film grows until at C the film is wholly liquid. The pressure represented by BC is the vapour pressure of

the liquid. If the temperature of the substances is raised the length of BC decreases, and in fact tends to zero at a critical temperature. It is difficult in many cases to reach

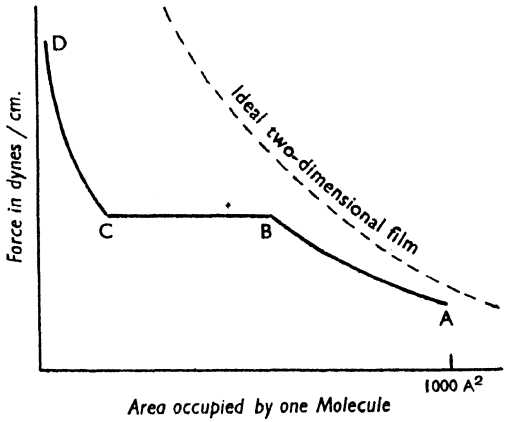


FIG. 154.

this point, since naturally there is a practical limit in working with an aqueous substratum. As the area of the film is reduced below C there is a very rapid rise in pressure with a break in the curve at D, followed by a steeply linear portion DE. At E the pressure abruptly ceases to rise. At this point it could readily be argued that this wide range of transition had all occurred, that a monomolecular layer had in fact been completed and, therefore, any further compression would simply involve piling another layer on top of the first, the latter naturally having the greatest effect in changing the interfacial tension. If the line ED (Fig. 155), is extrapolated back to zero pressure, the area so obtained, namely 20·5 A², is that occupied by a single molecule as closely packed as possible in such a monomolecular layer.

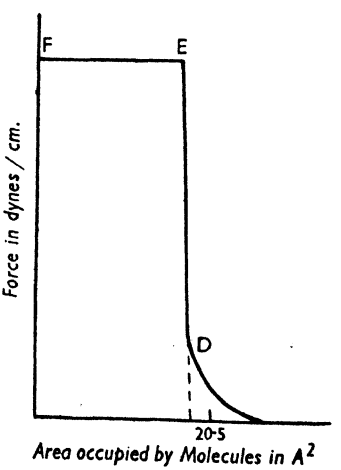


FIG. 155.

This area in addition gives considerable amount of information on the state of orientation of the molecule. Suppose we consider the molecules of stearic acid—$C_{17}H_{33}COOH$, then, if this molecule were stretched out parallel to the interface, it would be about 4 A. wide and about 22 A. long, occupying an area of nearly 90 A.^{2}. The measured area is only 20·5 A., and all the above phenomena point to the completion of a compact monomolecular layer at this area. The only explanation that is tenable is to suppose that the molecule is oriented perpendicular to the interface, with the carboxyl group adjacent to or may be dissolved in the aqueous substratum. The chain of methylene groups then is turned towards the atmosphere. From the X-ray analysis of solid fatty acids it is known that the cross-section of a chain of methylene groups is about 20 A., which is, in fact, in agreement with the surface area measurements and consequently quantitatively supports the above picture. In the vapour state of this film it is of course more likely that the hydrocarbon chain lies parallel to the surface. The reason for this supposition can be obtained by considering the deviation of gaseous films from ideal behaviour. From the van der Waals theory of three-dimensional gases it is possible to obtain from the value of b some indication of the actual volume occupied by the molecules. In the same way, it is possible to calculate, approximately, the area occupied by the molecules at these very low surface pressures. Such an area comes out to be of the order of 100 A.^{2}.

The above type of behaviour is common to all long chain molecules possessing terminal polar groups, provided such molecules are non-miscible with water. Even esters conform. For example, with glyceryl tripalmitate the area occupied per molecule in the highly compressed state is exactly three times that of palmitic acid itself. More surprising still is the fact that esters made from pentaerythritol $C(CH_2OH)_4$ occupy four times the area of the acid from which they were derived. This means that one of the hydrocarbon chains has to bend round in order that it may align itself with the others. It is, therefore, forced out of the aqueous medium as a result of its non-miscibility.

Multilayers.—It has been seen that at high enough pressures multilayers may be built up. There is, however, another way of building multilayers on a solid substratum devised by Miss K. Blodgett. If a clean strip of chromium-

plated metal is pushed through a monolayer of, say, stearic acid and withdrawn, a monolayer of acid can be deposited on the metal surface. By a series of operations of this type layer upon layer of acid may be built up until the layer is thick enough to exhibit optical interference colours. In fact, by this optical method it is possible to measure the thickness of the multimolecular film. The measurements point to the building of one on the top of the other of oriented acid molecules, each layer having a thickness corresponding to that existing with a compressed film in an aqueous substratum.

APPENDIX

TABLE OF CONSTANTS

R—Gas constant per gram-molecule—

$=0{\cdot}082055$ (0·0821) l.-atm. per degree.

$=82{\cdot}055$ (82·1) ml.-atm. per degree.

$=62{,}362$ ml.-mm. Hg. per degree.

$=8{\cdot}315 \times 10^{7}$ ergs per degree.

$=1{\cdot}9866$ g.-cal. per degree.

R—Rydberg's constant for hydrogen $=109{,}677{\cdot}76$ cm.$^{-1}$

N—Avogadro's number $=6{\cdot}031 \times 10^{23}$.

F—Faraday's constant $=96{,}494$ (96,500) coulombs.

J—Mechanical equivalent of heat—

1 g.-cal. $=4{\cdot}185 \times 10^{7}$ ergs $=4{\cdot}185$ joules (*j*.).

$=42{,}670$ g.-cm.

$=0{\cdot}04130$ l.-atm.

1 joule $=1$ volt-coulomb $=0{\cdot}2390$ cal.

1 l.-atm. $=24{\cdot}21$ cal.

c—Velocity of light *in vacuo* $=2{\cdot}998 \times 10^{10}$ cm./sec.

e—Electronic charge $=4{\cdot}802 \times 10^{-10}$ e.s.u.

h—Planck's constant $=6{\cdot}62 \times 10^{-27}$ erg-sec.

k—Boltzmann's constant, or gas constant per molecule $=\boldsymbol{R}/\boldsymbol{N}=1{\cdot}3787 \times 10^{-16}$.

Absolute zero of temperature $=-273{\cdot}16°$ C.

Gram-molecular volume at N.T.P. $=22{\cdot}414$ l.

QUESTIONS AND PROBLEMS

CHAPTER I

1. State the periodic law of the elements as expressed by Mendeléeff. Point out the main imperfections of the Mendeléeff classification.

2. Give a short account of the development of modern views regarding the constitution of the atom, noting, more especially, the contributions made by J. J. Thomson, R. A. Millikan, W. Ramsay, and Lord Rutherford.

3. Write short notes on the nature and origin of *electrons, positrons, neutrons, protons, alpha rays, beta rays, gamma rays.*

4. What is meant by the atomic number of an element? Give a short account of Moseley's determinations of atomic numbers.

5. Being given that the α-line of the X-ray spectrum of chromium has the wave-length $\lambda = 2{\cdot}301 \times 10^{-8}$ cm., and that the corresponding line in the case of iron has $\lambda = 1{\cdot}946 \times 10^{-8}$ cm., calculate the wave-length of the α-line of the X-ray spectrum of manganese. [$2{\cdot}111 \times 10^{-8}$ cm.]

6. In the case of ytterbium and of tungsten the L_{a1} lines in the X-ray spectra were found to have the wave-lengths $1{\cdot}6678 \times 10^{-8}$ and $1{\cdot}4734 \times 10^{-8}$ cm. respectively. In the case of two other elements, the wave-lengths of the corresponding lines were found to be $1{\cdot}6155 \times 10^{-8}$ and $1{\cdot}5661 \times 10^{-8}$ cm. respectively. What are the atomic numbers of these elements? [71; 72]

7. Define the term *isotopes.* By whom was the term introduced? How can the existence of isotopes be experimentally demonstrated? Explain the principle of the mass spectrograph.

8. Discuss the significance of the *packing fraction* of an element.

9 State the number of protons and neutrons in the nuclei of the isotopes of (*a*) lithium, (*b*) silicon, (*c*) zinc.

10. Calculate the wave-lengths of the first three Balmer lines in the hydrogen spectrum.

11. Give a short account of the arrangement of the extranuclear electrons in the elements of the two short periods and the first long period. Explain the terms electrovalency, covalency, co-ordinate covalency, dipole.

CHAPTER II

1. A certain mass of oxygen was found to occupy a vol. of 250 ml. at 15° and under a press. of 755 mm. What vol. would the gas occupy at 30° and under a press. of 765 mm.?

If the vol. were kept constant, what would be the press. in the vessel at 30°? [259·5 ml.; 794·2 mm.]

2. Give a short account of the deviation of gases from Boyle's law at high pressures. How are the deviations affected by change of temp.?

3. Discuss the validity of Dalton's law of partial pressures.

4. 15·803 l. of air, measured at N.T.P., were passed through water at 25°, the bar. press. being 742·2 mm. The water vapour carried off by the air weighed 0·4203 g. What is the v.p. of water at 25°? [23·75 mm.]

5. If n_2 represents the number of g.-mol. of a gas bubbled through water at 25° and under a bar. press. P in mm., and if n_1 represents the number of

g.-mol. of water vapour absorbed in a drying tube through which the moist gas is passed, calculate, from the numbers in the following table, the v.p. of water at 25° :—

n_2	0·69220	0·59636	0·65353	0·76095
n_1	0·02294	0·01985	0·02192	0·02533
P	740·4	737·5	731·9	737·4

[23·75, 23·76, 23·75, 23·76 mm.]

6. What weight of acetone would be evaporated by passing a vol. of air equal to 20 l. at N.T.P. through the liquid at 15°, the bar. press. being 755 mm. ? The v.p. of acetone at 15° is 147·1 mm. [12·54 g.]

7. The value of the g.-mol. vol., calculated from the equation $v = RT/p$, varies in the case of different gases. Why ?

8. Assuming the validity of the equation $pv = nRT$, calculate the vol. which will be occupied at N.T.P. by 5·096 g. of the vapour of a substance the mol. wt. of which is 114·3. [1 l.]

9. The weights of 1 l. of sulphur dioxide and of nitrous oxide at N.T.P. are 2·9265 g. and 1·9777 g. respectively. Assuming the validity of Boyle's law, calculate the value of the gas constant R and also of the g.-mol. vol.

[R = 0·080065 ; 0·081477 ; v = 21·871 ; 22·256 l.]

10. The mass of 1 l. of CO at N.T.P. is 1·25010 g. The coeff. $\lambda = 0{\cdot}00050$. Assuming that the g.-mol. vol. for an ideal gas is 22·414 l., calculate the mol. wt. of CO and the at. wt. of carbon. [28·006 ; 12·006]

11. In the case of nitrous oxide the following values of pv were obtained :—

Press. (in atm.)	1	0·66	0·5	0·33
pv	1·00000	1·00294	1·00416	1·00559

Find, by a graphic method (or by calculation, assuming that pv varies linearly with the press.), the value of pv at zero press., and so obtain the value of $1 + \lambda$. Being given that the mass of 1 l. of N_2O at N.T.P. is 1·9804 g., calculate the at. wt. of nitrogen. [$1 + \lambda = 1{\cdot}0085$; N = 14·007]

12. The following densities (g./l.) at 0° C. have been determined :—

Press. (atm.)		1	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{3}$
Density :	CO	1·25000	...	0·62487	...
,,	C_3H_6	1·9149	1·2681	0·9478	...
,,	NH_3	0·77169	0·511815	0·382925	0·254607

Determine, for each gas, the density per unit press., the limiting density $(d/p)_0$, and the value of $1 + \lambda$; and calculate the mol. wt. of the compounds and the at. wt. of carbon and nitrogen. (The limiting density of oxygen is 1·42767).

$[(d/p)_0$:	CO = 1·24950 ;	C_3H_6 = 1·8764 ;	NH_3 = 0·75989
$1 + \lambda$:	1·00040	1·0205	1·0205
M :	28·006	42·058	17·032
A :	C = 12·006	C = 12·003	N = 14·008]

13. The densities per unit pres. at 0° of methyl fluoride at 760, 506·67, and 253·33 mm. were found to be 1·54507, 1·53576, and 1·52665 respectively. Calculate the mol. wt. of CH_3F and the at. wt. of fluorine. [34·025 ; 19·00]

14. At 0°, the density per unit press. of CH_3Cl has the following values —

Press. (atm.)	1·00	0·667	0·500	0·333	0·250
d/p	2·3074	2·2895	2·2802	2·2714	2·2664

Find the value of the limiting density and calculate the mol. wt. of CH_3Cl.

[$(d/p)_0$ = 2·2527 ; M = 50·492]

15. On determining relative densities by the buoyancy method, the following balancing press. in mm. were obtained :—

p_{O_2}.	p_{N_2O}.	p_{O_2}.	p_{CO_2}.	p_{O_2}.	$p_{C_2H_4}$.	p_{O_2}.	p_{CF_4}.
418·612	303·796	418·281	303·622	428·133	486·552	484·225	176·009
229·137	166·430	234·464	170·3196	234·918	267·408	252·760	91·898

Find, in each case, the limiting ratio of press. and calculate the mol. wt. of the four gases. [r_0 = 1·37542 ; 1·37532 ; 0·876735 ; 2·74971
M = 44·0135 ; 44·010 ; 28·056 ; 87·991]

16. The buoyancy press. for xenon and oxygen were found to be : 152·937 and 627·82 mm. in one case, and 80·38 and 329·85 mm. in another. The ratios, corrected for change in the vol. of the bulb, were 4·1049 and 4·1035 respectively. Find the at. wt. of xenon. [r_0 = 4·1020 ; X = 131·26]

17. Given that the limiting density of oxygen at 0° is 1·42767, calculate the value of R and the g.-mol. vol. of an ideal gas. [R = 0·082055 ; 22·414 l.]

18. Given that the densities of oxygen and of hydrogen at N.T.P. are 1·42894 and 0·08988 respectively, and that the coeff. of compressibility are +0·00094 and −0·00054, calculate the values of the limiting densities and the mol. wt. of hydrogen (O_2 = 32·000). [1·42760 ; 0·089929 ; 2·0157]

19. A liquid was vaporised at 150° in a Dumas bulb of 526·6 ml. capacity, the bar. press. being 745 mm. The weight of vapour was found to be 1·7096 g. Find the mol. wt. of the compound. [114·9]

20. When 0·1008 g. of $CHCl_3$ was vaporised in a V. Meyer apparatus filled with dry air, 22·0 ml. of air, measured over water at 16·5° and 707·5 mm., were expelled. Calculate the approximate mol. wt. of $CHCl_3$. The v.p. of water at 16·5° = 14·08 mm. [119·3]

21. What vol. of dry air at 15° and under a press. of 770 mm. would be expelled by the vaporisation in a V. Meyer apparatus of 0·2350 g. of benzene ? [70·3 ml.]

22. 0·4068 g. of a volatile liquid was vaporised in a V. Meyer apparatus filled with air of which the humidity was 75 per cent. The vol. of expelled air, measured over water at 15° and under a bar. press. of 740 mm., was 45·3 ml. Calculate the approximate mol. wt. of the compound. The v.p. of water at 15° = 12·7 mm. [219]

23. The v.d. of sulphur was found to be 0·110 g./l. at 250° and 14 mm. ; 0·332 g./l. at 450° and 85 mm. ; 0·0777 g./l. at 850° and 85 mm. Interpret these data with reference to the mol. formula of sulphur.

24. 0·0870 g. of $CHCl_3$ was vaporised at 100° in Lumsden's apparatus and the excess press. produced was 15·2 mm. 0·0526 g. of a liquid A and 0·0448 g. of a liquid B were separately vaporised in the same apparatus at 100°, and the excess press. produced were 14·0 and 16·1 mm. respectively. Find the approximate mol. wt. of A and B. [78·5 ; 58·1]

25. From the data given in the text calculate the mean kinetic energy of a hydrogen molecule at 0°. [$5·649 \times 10^{-14}$ erg.]

26. What will be the press. and temp. of a gas in 1 ml. of which there are present 4×10^{19} mol. with a mean kinetic energy of $5·96 \times 10^{-14}$ erg ? (g = 981 cm./sec.^{2}) [$1·59 \times 10^6$ dynes/cm.^{2} or 119·1 cm. Hg ; 288·1° K.]

27. Given that the masses of 1 ml. of O_2 and of CO at N.T.P. are 0·001429 and 0·001250 g. respectively, calculate the mean velocity of the molecules. [46,222 and 49,313 cm. per sec.]

28. Under a const. press. a given vol. of H_2 escaped through a fine perforation in 26 sec., whereas an equal vol. of CO_2 required 122 sec. Find the density of CO_2 relatively to that of hydrogen. [22·02]

29. A hydride of silicon, containing 90·29 % of silicon, diffuses with two-thirds the velocity of nitrogen. What is the formula of the compound ? [Si_2H_6]

30. What is meant by the Avogadro number ? How may its value be determined ? How many mol. would there be in a bulb of 200 ml. capacity which had been evacuated at 15° to a pressure of 0·001 mm. ? [$6·75 \times 10^{15}$]

31. What relation exists between the spec. ht. of a gas at const. press, and at const. vol. ? Calculate the difference between the mol. ht. at const. press. and at const. vol.

The mol. ht. of H_2 at const. vol. is, at 0°, 4·85 cal./degree. What is the value of the ratio of sp. ht. ? [1·41]

32. In determining the sp. ht. of nitrogen tetroxide by the method of

McCollum the following data were obtained: During a period of 5,040 sec. 0·7560 g. of nitrogen tetroxide at 45·20° were allowed to flow through a tube immersed in a bath at 45·20° + 1·398°. The fall of potential across the heating coil was 0·1330 volt, and the fall of potential across a resistance of 2·1965 ohm, in series with the heating coil, was 0·1070 volt. By a special experiment it was found that when no N_2O_4 was flowing there was a heat loss of 0·001202 cal./sec. Calculate the sp. ht. per g. of N_2O_4. [1·66 cal./degree]

33. Gas at a definite temp. is allowed to flow at a rate of m g. per sec. over a wire heated by an electric current, whereby the temp. of the gas is raised by $\Delta t°$. The electrical energy supplied to the heating wire is W j. per sec. From the following data calculate the value of c_p for the given gases. (1 j. = 0·2390 cal.)

	m.	W.	$\Delta t°$.	[c_p calc.] cal./g.
Air . . .	0·1105	0·5211	4·662	0·2418
Argon . .	0·06279	0·1733	5·101	0·1293
CO_2 . . .	0·1047	0·4496	4·910	0·209
N_2O . . .	0·07148	0·2591	4·105	0·211
NO . . .	0·05150	0·2231	4·223	0·2452

34. In determinations of the ratio of the sp. ht. (γ) by means of a Kundt's tube, the following data were obtained:—

	Air.	A.	N_2.	HCl.	CO_2.	SO_2.	
λ .	112·12	103·4	114·02	99·60	86·98	70·74	mm.
d .	1·2928	1·784	1·2507	1·6398	1·9768	2·9266	g./l.

Taking the value of γ for air as 1·405, calculate the value of γ for each of the other gases and state the conclusions you draw regarding the mol. complexity of the gases. [1·65; 1·406; 1·404; 1·294; 1·266]

35. Gases at a temp. $T_1°$ K. and under a press. p_1 mm. were allowed to expand adiabatically, whereby the temp. and press. fell to $T_2°$ and p_2 mm. respectively. From the following data calculate the ratio of the sp. ht.:—

	T_1.	T_2.	p_1.	p_2.	[γ cals.]
Air .	287·03°	280·40°	825·3	760·6	1·396
O_2 . .	289·21°	279·25°	856·94	757·5	1·392
CO_2 .	288·01°	277·08°	894·77	755·4	1·294
H_2 . .	290·32°	279·99°	855·27	754·6	1·401

CHAPTER III

1. Discuss the theoretical foundations of the methods employed for the liquefaction of gases.

2. Calculate the fall of temp. which would be produced when air at 15° and under a press. of 5 atm. is allowed to expand adiabatically into a space at atm. press. [107·6°]

3. Ignition of a mixture of hydrogen and oxygen takes place when the mixture, at 20°, is compressed adiabatically from atmospheric press. to a press. of 36·9 atm. What is the ignition temp.? ($\gamma = 1·4$.) [821° K.]

4. How may the crit. temp., press., and vol. of a liquid be determined?

From the following values of the density of liquid and vapour find the crit. vol. of n-heptane. The crit. temp. is 266·9°.

	200°.	220°.	240°.	250°.	260°.
D_{liquid} . .	0·4952	0·4616	0·4177	0·3877	0·3457
D_{vapour} . .	0·0330	0·0489	0·0745	0·0946	0·1287

[4·266 ml./g.]

5. Deduce a relationship between the crit. constants of a gas and the constants a and b of the van der Waals equation.

6. The van der Waals equation for ethylene is

$$\left(p+\frac{0{\cdot}00786}{v_2}\right)(v-0{\cdot}00224)=0{\cdot}0037(272{\cdot}5+t).$$

the constants being expressed in Amagat units. Calculate the crit. temp. and crit. press. of the gas. [$p_c=58{\cdot}03$ atm.; $t_c=8{\cdot}5°$]

7. From the following values of crit. press. and crit. temp. calculate the van der Waals factor b for the substance mentioned. (Unit of vol. = ml. per g.-mol. at N.T.P.)

	Hydrogen.	Ether.
p_c (atm.) . .	12·8	35·6
T_c	33·2° K.	466·9° K.
		[0·001187; 0·006004]

8. Given the following values for the constants a and b of the van der Waals equation (units: 1 g.-mol., ml., atm.), calculate in each case the crit. temp. and crit. press.:—

	a.	b.	T_c° K.	p_c (atm.).
Acetone . .	$13{\cdot}92\times10^6$	99·4	505·8°	52·2
Ammonia . .	$4{\cdot}17\times10^6$	37·08	406°	112·3
Argon . .	$1{\cdot}348\times10^6$	32·30	150·8°	52·9
Nitric oxide .	$1{\cdot}29\times10^6$	26·0	179·1°	70·67

9. From the following values of the crit. constants, calculate the values of the van der Waals constants a and b (ml., atm.):—

	Oxygen.	CO_2.	He.
T_c° K. . .	154·38°	304·1°	5·30°
p_c (atm.) . .	50·8	73·0	2·26
[a . . .	$1{\cdot}36\times10^6$	$3{\cdot}609\times10^6$	$0{\cdot}0325\times10^6$]
[b . . .	31·87	42·75	23·42]

10. From the data given in the preceding question calculate the mol. diameters of oxygen, carbon dioxide, and helium.

[2·93, 3·24, 2·65, $\times10^{-8}$ cm.]

11. By means of the van der Waals equation, in which $a=3{\cdot}6\times10^6$, $b=42{\cdot}75$ (g.-mol., ml., atm.), calculate the press. corresponding to a series of values of v and obtain therefrom the vol. of 1 g. of carbon dioxide at 50° and under a press. of 160 atm. [1·78 ml.]

12. Being given that for CO_2, $T_c=304{\cdot}1°$ K. and $p_c=73{\cdot}0$ atm., write the van der Waals equation for this gas, expressing the vol. as a fraction of the mol. vol. in ml. at N.T.P. From the equation so obtained calculate the vol. in ml. of 1 g.-mol. of CO_2 at the crit. point. [$v_c=128{\cdot}25$ ml.]

13. In the case of acetic acid, $v_c=2{\cdot}457$ ml.; $p_c=57{\cdot}1$ atm.; and $T_c=595°$ K. Calculate the approx. mol. wt. of acetic acid at its crit. temp. [94·1]

14. At N.T.P., 1 l. of CO_2 weighs 1·9768 g. The crit. temp. and press. are 304·1° K. and 72·9 atm. Calculate the mol. wt. of carbon dioxide. [44·001]

15. The normal densities of ammonia and of nitric oxide at 0° are 0·7717 and 1·3402 g./l. respectively. The crit. press. are 112·3 and 65 atm., and the crit. temp. 406° and 179·2° K. Calculate the mol. wt. of ammonia and of nitric oxide and the at. wt. of nitrogen. (H = 1·008.)

[17·110; 14·086; 30·02; 14·02]

16. The normal density of oxygen at 0° is 1·4290 g./lit., and the crit. temp. and crit. press. are 154·38° K. and 50·8 atm. respectively. Calculate the value of the gas constant R and the g.-mol. vol. at N.T.P. Calculate also the value of R, assuming the validity of Boyle's law.

[82·038 ml.-atm.; 22·41 lit.; 81·979 ml.-atm.]

17. The normal density of N_2 is 1·25049 g./l., and its crit. temp. and press. are 125·96° K. and 33·49 atm. Calculate the mol. wt. ($R=0{\cdot}082055$ l.-atm.)

[28·02]

18. At 0° the density of argon is 1·78364 g./l. under atm. press., and 0·59419 g./l. under 1/3 atm. In the case of ammonia the density is 0·77169 g./l. under atm. press. and 0·38293 g./l. under 0·5 atm. Calculate the mol. wt. of the two gases and the at. wt. of N_2. [39·94; 17·037; 14·013]

CHAPTER IV

1. Describe how the v.p. curve of a liquid may be determined experimentally.

2. From the data given on p. 92 plot the values of log p against $1/T$ for water and ethyl alcohol, and obtain the values of the v.p. at 50°. Determine the constants of the equation: $\log p = A - B/T$.

3. At the abs. temp. 343·2°, 327·4° and 293·1° the v.p. of ethyl formate is 1,300, 760, and 200 mm. respectively. At 392·2° K. the v.p. of propyl acetate is 1300 mm. At what temp. will the v.p. be 760 and 200 mm.? [374·1° and 335·0° K.]

4. The v.p. of carbon disulphide and of water is 50 mm. at 254·0° K. and at 311·3° K., and 400 mm. at 300·8° K. and 356·0° K. respectively. Given that the v.p. of CS_2 at 283·2° K. is 200 mm., at what temp. will the v.p. of water have this value? [339·6° K.]

5. A current of 1·085 amp. was passed for 20 min. through a spiral immersed in ethyl alcohol at its b.p. (78·4°). The fall of potential in the spiral was 5·14 volts. 7·397 g. of alcohol were vaporised. Calculate the heat of vaporisation. [216·3 cal.]

What conclusion do you draw concerning the mol. complexity of the liquid alcohol?

6. The amounts of liquid hydrogen fluoride vaporised at its b.p. by the given amounts of electrical energy are as below. Calculate the heat of vaporisation.

Time (min.).	Volts.	Amp.	Wt. vaporised (g.)
30	2·52	0·175	1·9727
30	2·15	0·150	1·4011

[96; 99 cal.]

7. What weight of ether would be evaporated if a current of 1·074 amp. were passed for 20 min. through a platinum spiral of 5·535 ohm resistance, immersed in ether at its b.p., if the heat of vaporisation of ether is taken as 84·68 cal./g. [21·63 g.]

8. Given that the heat of vaporisation of ethyl propionate at its b.p., 99·0°, is 80·12 cal. and that the densities of the liquid and of the vapour at the b.p. are 0·7958 and 0·0033 respectively, calculate the variation of the v.p. with the temp. [22·4 mm. per degree]

9. The normal b.p. of ethyl formate is 54·5°. The value of dp/dt at the b.p. is 27 mm. What is the heat of vaporisation per gram? [102·4 cal.]

10. The v.p. of acetone at 15° is 147·1 mm. and at 25°, 229·2 mm. Calculate the mean mol. ht. of vaporisation between 15° and 25°. [7570 cal.]

11. The mean mol. ht. of vaporisation of ethyl alcohol at 20° is 10,005 cal. and the v.p. at 15° is 32·2 mm. What is the v.p. at 25°? [57·9 mm.]

12. The heat of vaporisation of n-propyl alcohol at its b.p., 97·2°, is 164·5 cal. What conclusion do you draw regarding its mol. complexity?

13. The heat of vaporisation of ethyl ether at its normal b.p., 34·6°, is 83·89 cal. Find the b.p. under a pressure of 700 mm. [32·2°]

14. The v.p., in mm., of H_2O_2 at different temp. is represented by the equation $\log_{10} p = -\frac{0{\cdot}05223 \times 48530}{T} + 8{\cdot}853$. Calculate the mol. heat of vaporisation. [11,590 cal.]

15. Butyl chloride has the following v.p.:—

$t°$ C.	12·5	25·0	31·0	42·0	59·0	65·0	71·0	73·0	77·5
p (cm.)	5·65	10·2	12·8	20·4	39·6	48·8	60·3	65·0	76·0

Plot $\log_{10} p$ against $1/T$ and find the constants of the expression $\log p = A - B/T$. Calculate also the mol. ht. of vaporisation. [8090 cal.]

16. The v.p. of divinyl ether (C_4H_6O) at 301° K. and 303° K. are 750·2 and 807·3 mm. respectively. Calculate the mean mol. ht. of vaporisation at 302° K. [6660 cal.]

The v.p. of divinyl ether at 27·85° C. is 743·9 mm. and at 28·85° it is 771·8 mm. The sp. vol. of the liquid at 28·35° is 1·3098 and of the vapour 334·0 ml. Calculate the heat of vaporisation at 28·35°. [89·3 cal./g.]

17. The v.p. of a liquid at 25° is 8·6 mm. Given that the mean mol. ht. of vaporisation is 12,970 cal., find the v.p. at 75°. [200 mm.]

18. Ether boils at 35° under atm. press., and its mol. ht. of vaporisation is 6,640 cal. Calculate the v.p. of ether at 30°. [635 mm.]

19. The density of chlorobenzene at its b.p., 132·0°, is 0·9814 g./ml., the density of the vapour is 0·00359 g./ml., and the heat of vaporisation is 73·43 cal./g. Calculate the rate of change of v.p. with the temp. at the b.p. [20·5 mm./1°]

20. At 20° the times of outflow of water and of ethyl alcohol in an Ostwald viscosimeter were 85·2 and 187·1 sec. respectively. The densities of water and of alcohol at 20° are 0·9982 and 0·7893. If the viscosity of water at 20° is 0·01008 poises, what is the viscosity of alcohol ? [0·0175 poises]

21. A steel ball having a diameter of 0·1588 cm. took 19·4 sec. to fall a distance of 15 cm. through castor oil in a tube 2 cm. in diameter, the temp. being 20°. The height of liquid was 25·4 cm., the density of the oil was 0·96, and the density of the ball, 7·65. Find the coeff. of viscosity of the oil ($g = 981$). [9·88]

22. In a capillary tube of radius 0·01843 cm., water rose 8·10, 7·96, and 7·82 cm. at 0°, 10°, and 20° respectively. The density at these three temp. is 0·9999, 0·9997, and 0·9983. What is the association factor of water ? [3·81 ; 3·68]

23. At 14·8° acetylchloride ($d = 1·124$) ascends to a height of 3·28 cm. in a capillary tube of radius 0·01425 cm. At 46·2°, in the same tube, the height was 2·85 cm. and the density 1·064. Find the crit. temp. Mol. wt. of acetylchloride = 78·5. [234·9°]

24. What must be the radius of a capillary so that at 20° ethyl alcohol ($d = 0·7893$, $\gamma = 22·27$ dynes/cm.) may rise to a height of 3·50 cm. ? [0·01643 cm.]

25. A liquid ($d = 1·264$) rose at 19·4° to a height of 4·20 cm. in a capillary tube of radius 0·0129 cm. What is the surface tension of the liquid ? [33·58]

26. In the case of a certain liquid, the mol. surface energy at 19·4° is 515·4, and at 46·1° it is 461·4 ergs. What conclusion do you draw with regard to the mol. complexity of the liquid ?

27. Show from the following data that the molecules of formic acid are associated in the liquid state but that the degree of association diminishes with rise of temp. Radius of capillary = 0·01425 cm.

Temp.	16·8°	46·4°	79·8°
Height	4·442	4·205	3·90 cm.
Density	1·207	1·170	1·129

28. Drops of benzene falling from a stalagmometer weighed 35·239 mg. and 26·530 mg. at 11·4° and at 68·5° respectively. The densities at these temp. are 0·888 and 0·827. Find the crit. temp. of benzene. [288·4°]

29. The densities of heptane, of amylalcohol, and of acetone at their b.p. are 0·6150, 0·7115, and 0·7522 respectively. Find their molar volumes and compare the values with those calculated from the data in the text.

30. From the data given in the text calculate the mol. vol. and the density of propylchloride, C_3H_7Cl, at its b.p. [92·4 ; 0·8498]

31. At 20° the surface tension of ethylene oxide, C_2H_4O, is 24·3 dynes per cm., and the densities of liquid and vapour are 0·8707 and 0·0029 respectively. Calculate the value of the parachor and show that it indicates the presence of a three-membered ring. [P = 112·6]

CHAPTER V

1. At 20° the refractive index of allylacetone, $C_6H_{10}O$, for the D-line is 1·4213 and the density 0·84702. Calculate the mol. refractivity and compare the value found with that calculated by means of the at. refractivities given in the text. [$[R]_L = 29·38$]

2. If the refractive index of allylacetone (previous problem) were determined in a Pulfrich refractometer using a prism with refractive index $N = 1·6217$, what would be the angle of emergence ? [51° 21′]

3. A symmetrical unsaturated aliphatic ketone, $C_9H_{14}O$, was found to have the mol. refractivity 45·39. What conclusions do you draw regarding the constitution of the compound ?

4. The mol. refractivity for the D line of acetoacetic ester, $C_3H_5O.COOC_2H_5$, has the value 32·00. What conclusions do you draw regarding the constitution of the ester ?

5. At 20° the refractive index of acetone for the D line is 1·3641, and its density is 0·8005. Calculate the mol. refractivity. [16·15]

6. At 20° in a tube 0·9992 dm. long, nicotin ($d = 1·0110$) gave the rotation $\alpha_D = -165·65°$. What is its spec. rotation ? [$-164·00°$]

7. In a 2·1979 dm. tube at 20°, a 29·97 % sol. of turpentine in alcohol gave a rotation for the D-line of $-20·29°$. The density of the solution was 0·8127. Calculate $[\alpha]_D^{20}$ for turpentine. [$-37·90°$]

8. Solutions of cane sugar containing 5·087, 10·382, and 18·144 g. in 100 ml. of solution, gave, in a tube 2 dm. in length, $\alpha_D^{20} = 6·776°$, 13·824°, and 24·128° respectively. The densities of the three solutions were: 1·0179, 1·0382, and 1·0678. Calculate the value of $[\alpha]_D^{20}$. [66·61°, 66·57°, 66·45°]

9. For aqueous solutions of cane sugar, $[\alpha]_D^{20} = 66·510°$. What is the percentage composition of a solution of cane sugar ($d = 1·1037$) which gives $\alpha_D^{20} = +36·67$ in a 2 dm. tube ? [24·98]

10. State Beer's law of the absorption of light by a solution, and define the term *molecular extinction coefficient.*

11. Under a pressure of 10 atm., the dielectric constant of carbon dioxide at 35°, 70°, and 100° is 1·00971, 1·00831, and 1·00753 respectively. The mol. vol. in ml. is 2352, 2728, and 2991. Calculate the molar polarisation at the three temperatures and determine the dipole moment of carbon dioxide. [7·588, 7·536, 7·485 ml. ; $\mu = 0$]

12. From the following data, determine the dipole moment of ammonia (measurements carried out under press. of 20 atm.) :—

$t°$ C.	100°	125°	150°	175°
$(\epsilon - 1) \times 10^4$	940	822	713	638
Mol. vol. (ml.)	1385	1512	1636	1753

[$\mu = 1·44$ D.]

13. The molar polarisation, P, of water vapour at $T = 393·0°$, 423·0°, 453·0°, and 483·0° K. is equal to 57·4, 53·32, 50·04, 47·17 ml. respectively. Plot the values of P against $1/T$ and of PT against T and find the values of a and b in the expression $P = a + b/T$. Calculate the dipole moment.

Given that the molar volume is 43,090 ml., calculate the dielectric constant at 423·0° K. [$a = 3·756$; $b = 20,967$; $\mu = 1·84$ D. ; $\epsilon = 1·00372$]

14. The dielectric constant of ethyl ether vapour was determined at the temperatures shown and under different pressures. The following values were obtained :—

$T°$ K.	313·0°	353·0°	393·0°	433·0°
$(\epsilon - 1) \times 10^5$	495·0	470·0	450·7	431·0
Mol. vol. in ml.	31,610	31,420	31,290	31,230

Calculate the molar polarisation at each temp. and determine the value of the dipole moment. [1·14 D.]

CHAPTER VI

1. In what respects does the crystalline state differ from the amorphous state? How would you define the melting-point of a crystalline solid?

2. The change of volume $(v_2 - v_1)$ on melting is $-0{\cdot}00342$ ml./g. in the case of bismuth and $+0{\cdot}0904$ in the case of benzophenone. Under atm. press. the m.p. of the former is 270·9° and of the latter 47·8°. The latent heats of fusion are 12·5 and 23·90 cal. respectively. What will be the approx. m.p. of the two substances under a press. of 100 atm.? [270·54°; 50·74°]

3. The m.p. of tin (504° K.) and of naphthalene (353·3° K.) are raised by 0·328° and 3·50° respectively by an increase of pressure of 100 atm. On melting there is an increase of vol. of 0·03894 and 0·1458 ml./g. respectively. Calculate the latent heat of fusion of the two substances. [14·48, 35·64 cal./g.]

4. How does the velocity of crystallisation of a supercooled liquid vary with the degree of supercooling?

5. Assuming the validity of the Neumann-Kopp law, calculate the sp. ht. of a glass having the composition: Si = 24·5, Zn = 27·5, K = 7·5, B = 2·8, O = 37·7, the atomic heats of these elements being 3·8, 6·4, 6·4, 2·7, and 4·0 respectively. [0·173 cal./g.]

6. How may the deviations of solid elements from Dulong and Petit's law be explained?

7. What are the Miller indices of a crystal face which makes intercepts $3a : \frac{3}{2}b : c$ on the A, B, and C axes? What are the Miller indices if the intercepts are $2a : \frac{3}{2}b : c$?

8. First order reflexion maxima for X-rays of wave-length 0·581 A. were given for the (100), (110), and (111) planes of a cubic crystal at the angles 6° 57′, 4° 54′, and 12° 14′ respectively. Find the values of d_{100}, d_{110}, and d_{111} and deduce the crystal lattice type. [1 : 1·416 : 0·572]

9. For X-rays of a definite wave-length, first order reflexion maxima for the (100), (110), and (111) planes of a cubic crystal were obtained when the angles of incidence were 7·7°, 11·03°, and 6·7°. What type of cubic lattice has the crystal?

10. Crystals of potassium bromide have a face-centred cubic lattice and in the unit cell there are the equivalent of four molecules. Being given that the density of the crystal is 2·76, find the length of the edge of the unit cell and the distance between the planes parallel to the d_{100} face. [6·588 A.; 3·295 A.]

11. A first order reflexion maximum of X-rays from the (100) face of KBr was obtained at $\theta = 5° 3'$. From the result obtained in the previous problem find the value of λ.

CHAPTER VIII

1. What is meant by the osmotic pressure of a solution? How may its value be determined experimentally? How does the osmotic pressure of a dilute solution vary with the concentration and the temperature?

2. What distinction should be drawn between isotonic and isosmotic solutions?

3. The osmotic press. of a sol. containing 32·6 g. of sucrose per lit. was found to be 2·43 atm. at 0°. What would be the osmotic press. at 20° of a sol. containing 90·1 g. of sucrose per lit.? [7·21 atm.]

4. At 20° solutions of sucrose containing 0·098, 0·282, and 0·452 g.-mol. per lit. were found to give osmotic press. of 2·59, 7·61, and 12·75 atm. respectively. What are the calculated values according to the theory of van't Hoff? [2·34, 6·74, 10·81 atm.]

5. Assuming the validity of the van't Hoff laws of dilute solutions calculate the osmotic press. at 0° of solutions containing in 1 l. (1) 33·93 g. of sucrose ($M = 342·2$), (2) 99·8 g. of glucose ($M = 180·1$), (3) 100 g. of mannitol ($M = 182·1$). [2·22; 12·42; 12·31 atm.]

6. A solution containing 100·5 g. of glucose per lit. has at 0° an osmotic press. of 13·21 atm. Calculate the approx. mol. wt. of glucose. [170·6]

7. At 20° a solution containing 18·0 g. of mannitol per lit. gave an osmotic press. of 2·39 atm. Calculate the mol. wt. of mannitol. [181·2]

8. Calculate the osmotic press. at 20° of a solution containing 0·6 g.-mol. of solute in 1000 g. of water, the solution being regarded as ideal. The spec. vol. of water at 20° = 1·0018. [14·3 atm.]

CHAPTER IX

1. State Raoult's law of the lowering of the v.p. of a solvent by a non-volatile solute.

2. An aqueous solution obtained by dissolving 21·24 g. of a substance in 100 g. of water had at 0° a v.p. of 4·432 mm., the v.p. of water being 4·620 mm. Calculate the mol. wt. of the solute? [93·9]

3. At 40° the v.p. of a solution containing 0·284 g. of solute in 100 g. of acetic acid is 34·69 mm., the v.p. of acetic acid at the same temp. being 34·77 mm. Calculate the mol. wt. of the solute. [74·1]

4. At 20°, 36·004 g. of mannitol dissolved in 1000 g. of water lowered the v.p. by 0·0614 mm. Being given that the v.p. of water at 20° is 17·539 mm. and its density 0·9982, calculate the mol. wt. of mannitol and the osmotic press. of the solution. [185·1; 4·67 atm.]

5. Given that the v.p. of water at 25° is 23·752 mm., find the concentration of a sol. of mannitol ($M = 182·1$) which would have the v.p. of 23·583 mm. [72·0 g./1000 g.]

6. When 6 g. of a compound ($M = 60·6$) is dissolved in 100 g. of water, the relative lowering of the v.p. is 0·01783. What will be the v.p. of a sol. containing 3·6 g. of a compound ($M = 182$) in 100 g. of water if the v.p. of water at the given temp. is 17·539 mm.? [17·477 mm.]

7. The v.p. at 25° of a sol. containing 1 g.-mol. of sucrose in 1000 g. of water was found to be 23·283, the v.p. of water being 23·752 mm. Assuming that the sol. is ideal, calculate the osmotic press. The mol. vol. of water at 25° = 18·054 ml. [26·8 atm.]

8. A solution of 8·28 g. of a substance A in 100 g. of ether was found to have the same v.p. as a solution of 7·32 g. of benzoic acid in 100 g. of ether. What is the mol. wt. of A? [138]

9. A current of dry air was passed through a series of bulbs containing a sol. of 3·458 g. of a substance in 100 g. of ethyl alcohol, and then through a series of bulbs containing pure alcohol. The loss of weight in the former series of bulbs was 0·9675 g. and in the latter series 0·0255 g. Calculate the mol. wt. of the solute. [60·4]

10. Air was drawn through a sol. containing 38·00 g. of solute in 100 g. of water and then through pure water, both at the same temp. The loss of weight of water was 0·0551 g., and the total weight of water absorbed in a sulphuric acid tube was 2·2117 g. What is the mol. wt. of the solute? [274·5]

11. At 20° the v.p. of water is 17·539 mm. What will be the v.p. of an aqueous sol. of 10·00 g. of glycerol in 100 g. of water? [17·196 mm.]

12. What will be the relative lowering of the v.p. produced by dissolving 0·4 g.-mol. of a substance in 1000 g. of water? [0·00715]

13. The b.p. of a sol. of 0·1050 g. of a substance in 15·84 g. of ether was higher than that of the pure solvent by 0·100° What is the mol. wt. of the solute? [139·8]

14. A sol. of 0·832 g. of mannitol ($M = 182·1$) in 20·55 g. of water boiled 0·114° higher than pure water. What is the mol. elevation of the b.p. of water ? [513]

15. 0·5042 g. of a substance dissolved in 42·02 g. of benzene raised the b.p. of the solvent by 0·175° Being given that the latent heat of vaporisation of benzene at its b.p., 80·2°, is 94·4 cal., calculate the mol. wt. of the solute. [179·8]

16. A solution of 0·976 g. of benzil ($M = 210$) in 100 g. of aniline boils 0·154° higher than the pure solvent. Calculate the heat of vaporisation of aniline at its b.p. 184°. [125·3 cal./g.]

17. A sol. of 0·300 g. of camphor ($C_{10}H_{16}O$) in 25·20 g. of chloroform boils at 61·299°, the b.p. of the solvent being 61·0°. Calculate the mol. elevation of the b.p. and the heat of vaporisation of chloroform. [3818 ; 58·07 cal./g.]

18. A solution containing 0·622 g. of solute in 40·0 g. of water froze at −0·510°. Calculate (1) the mol. wt. of the solute, (2) the osmotic pressure of the solution, (3) the relative lowering of the v.p. [56·7 ; 6·14 atm. ; 0·00494]

19. A solution of 0·1605 g. of naphthalene ($C_{10}H_8$) in 26·06 g. of benzene has a f.p. 0·245° lower than that of the pure solvent (5·40°). What is the latent heat of fusion of benzene ? [30·25 cal.]

20. 0·7320 g. of chloroform dissolved in 25·0 g. of benzene lowered the f.p. by 1·250°. What is the mol. wt. of chloroform ? [120]

21. What weight of mannitol ($M = 182·1$) would have to be dissolved in 15·00 g. of water in order to give a solution which freezes at −0·743° ? What would be the molar fraction of the solute in this solution ? [1·093 g. ; $n_2 = 0·00715$]

22. An intimate mixture of 0·4246 g. of a substance with 9·6871 g. of camphor had a f.p. 12·3° lower than that of camphor. Given that the mol. wt. of the substance is 139, calculate the mol. lowering of the f.p. of camphor. [39,000]

23. A solution containing 0·2965 g. of benzoic acid, $C_6H_4.COOH$, in 20·27 g. of benzene was found to freeze at 0·317° below the f.p. of the solvent. Calculate (1) the apparent mol. wt. of benzoic acid, and (2) the degree of association, assuming the formation of double molecules. [236·2 ; 0·968]

CHAPTER X

1. A sol. of 1·000 g. of $AgNO_3$ in 50·00 g. of water was found to freeze at −0·348°. Calculate the value of i. [1·59]

2. A sol. containing 0·0627 g.-mol. of NaCl in 1000 g. of water freezes at −0·221°. Calculate the value of i. [1·889]

3. How much electricity must be passed through a sol. of $AgNO_3$ in order that 1·350 g. of silver may be deposited ? [1207·5 coulombs]

4. A current of electricity was passed through a series of cells containing solutions of $AgNO_3$, $CuSO_4$, and H_2SO_4 for a period of 25 min. The wt. of Ag deposited was 0·5324 g. What was the wt. of Cu deposited and what was the vol. of H_2 collected over water at 15° (v.p. = 12·8 mm.) and barometric press. = 750 mm. liberated by the current ? What was the strength of the current, assuming that it remained constant ? [0·1569 g. ; 60·14 ml. ; 0·3174 amp.]

5. What wt. of iodine would be liberated if a current of 0·155 amp. were passed for 15 min. through a sol. of KI ? For how long would the current have to be passed through a sol. of $CuSO_4$ in order to give a deposit of 0·252 g. of copper ? [0·1835 g. ; 82·2 min.]

6. A mixture of hydrogen and oxygen is evolved when a dilute sol. of NaOH is electrolysed. How many g.-mol. of mixed gases would be liberated by a current which deposited 20·9742 g. of silver ? [0·14582]

7. A mixture of hydrogen and oxygen, liberated by the passage of an electric current through a series of six cells containing a sol. of NaOH was passed, in separate experiments, through solutions which contained 0·4 and 0·6 g.-mol. of KCl and of mannitol respectively, at a temp. of 25°. The amount of electricity was determined from the wt. of silver, W_s, deposited in a coulommeter, and the weight of water carried off, W_w, was determined. The v.p. of water at 25° = 23·752 mm. P is the atm. press. From the following data calculate the lowering of the v.p. and the value of i for the sol. of KCl:—

KCl	W_s.	W_w.	P.	Mannitol.	W_s.	W_w.	P.
0·4 M. .	21·3610	0·52467	740·82	0·4 M. .	21·4427	0·52757	744·08
0·6 M. .	15·5702	0·37712	745·04	0·6 M. .	15·8026	0·38792	742·76

[i = 1·86; 1·77]

8. At 20° the v.p. of a 0·1 M. sol. of mannitol is 0·0311 mm. less than that of water, and the v.p. of a 0·1 M. sol. of KCl is 0·0574 mm. less than that of water. What is the value of i? [i = 1·846]

9. The equiv. conductivity of a sol. of acetic acid containing 1 g.-equiv. in 1000 l. is 41·0 mhos at 18°. Being given that the ionic conductivities of hydrogen ion and acetate ion are 315 and 35, calculate the degree of ionisation of the acid. [0·117]

10. The equiv. conductivity of a 0·01 N sol. of NH_4OH at 18° is 9·6 mhos. For NH_4Cl, Λ_∞ = 129·8, and the ionic conductivities of OH′ and Cl′ are 174 and 65·5 mhos respectively. Calculate Λ_∞ for NH_4OH and the degree of ionisation in the above solution. [238·3; 0·040]

11. The equiv. conductivity at 25° of a 0·01 N sol. of KCl is 141·2, and the equiv. conductivity at infinite dilution is 148·8. Calculate the Arrhenius coefficient. What would be the f.p. of this solution?

[α = 0·949; Δ = 0·0362°]

12. A 0·02 M. sol. of K_2SO_4 freezes at −0·0952°. What is the value of i and of the Arrhenius coefficient? [2·56; α = 0·78]

13. The f.p. of sol. of KCl and $MgSO_4$ containing 0·01 and 0·03 g.-mol./l. are −0·0360° and −0·1055° for KCl, and −0·0266° and −0·0742° for $MgSO_4$. What are the values of the osmotic coefficient, g?

[0·031, 0·053; 0·283, 0·334]

14. The conductivity of a sat. sol. of AgCl at 19·95° is $1·33 \times 10^{-6}$ mhos. Given that the ionic conductivities of silver ion and of chloride ion are 56·9 and 68·4 respectively, calculate the solubility of AgCl.

[$1·06 \times 10^{-5}$ g.-equiv./l.]

15. At 18° a sat. aqueous sol. of $BaSO_4$ was found to have a conductivity of $3·648 \times 10^{-6}$, that of the water being $1·25 \times 10^{-6}$ mhos. What is the solubility of $BaSO_4$? The ionic conductivities are: $\frac{1}{2}Ba = 55$, $\frac{1}{2}SO_4 = 68·3$.

[$2·076 \times 10^{-3}$ g./l.]

16. A sat. sol. of gypsum at 19·94° has the conductivity $19·68 \times 10^{-4}$ mhos. Given that Λ_∞ = 125·9, find the total conc. of $CaSO_4$ in the sol., the degree of dissociation being 0·524. [2·034 g./l.]

17. At 20·15° the conductivity of a sat. sol. of thallous iodide is $26·18 \times 10^{-6}$ mhos. The equiv. conductivity at infinite dilution is 138·0. The degree of dissociation is 0·989. What is the total concentration of the salt?

[$1·92 \times 10^{-4}$ g.-equiv./l.]

18. A sol. of $AgNO_3$ having the composition 28·435 g. of H_2O, 0·2099 g. of $AgNO_3$ was electrolysed, using silver electrodes. The current passed deposited 0·000792 g.-equiv. of silver. At the conclusion of the electrolysis the sol. around the anode was found to have the composition 28·435 g. of H_2O, 0·2874 g. of $AgNO_3$. Calculate (1) the relative velocities of migration of the silver ion and nitrate ion, (2) the transport number of the nitrate ion.

[u_c/u_a = 0·737; n_a = 0·576]

19. During the electrolysis of a sol. of $CuSO_4$ in which 5·0473 g. of $CuSO_4$ were dissolved in 94·953 g. of H_2O, 1·548 g. of silver were deposited in a coulommeter placed in series with the copper sulphate sol. After the electrolysis,

137·7422 g. of the anode sol. was found to contain 7·7022 g. of $CuSO_4$. What is the transport number of the sulphate ion ? [0·693]

20. A sol. consisting of 99·399 g. of H_2O and 0·6011 g. of NaCl was electrolysed, using a cadmium anode. The silver deposited in a coulommeter weighed 0·745 g. After electrolysis, 130·59 g. of anode sol. contained 0·6229 g. of chlorine. Calculate the transport number of the chloride ion. [0·607]

21. A sol. containing 0·2010 g. of $AgNO_3$ in 23·8110 g. of sol. was electrolysed between silver electrodes. After electrolysis, 23·8823 g. of the anode sol. contained 0·2723 g. $AgNO_3$. In a coulommeter 0·0247 g. of copper was deposited. What is the transport number of the silver ion ? [0·461]

22. A sol. of KCl containing 24·044 g. H_2O and 0·9553 g. KCl was electrolysed, using a cadmium anode. In a silver coulommeter, 0·4176 g. Ag was deposited. After electrolysis, 25·211 g. of the anode sol. contained 0·5240 g. of chlorine. What is the transport number of the chloride ion ? [0·504]

23. 0·024 g. of copper was deposited in a coulommeter in series with a transport number cell containing N/20 $AgNO_3$ between silver electrodes. Calculate (*a*) the change in weight of the silver electrodes ; (*b*) the change in weight of silver in the solutions surrounding (i) the anode, (ii) the cathode ; (*c*) the duration of the electrolysis assuming a constant current of 0·01 amp. The transport number of the silver ion is 0·47.

[(*a*) 0·0815 g. ; (*b*) 0·0431 g. ; (*c*) 7280 sec.]

24. The equiv. conductivity of a very dilute sol. of $NaNO_3$ at 18° is 105·2 mhos. Being given that the ionic conductivity of nitrate ion in the same sol. is 61·7, calculate the transport number of this ion. [0·587]

25. The equiv. conductivity of KCl at infinite dilution is 130·1 mhos. The transport number of potassium ion in such a sol. is 0·496. Calculate the relative mobilities of K· and Cl′ and their absolute velocities under unit fall of potential.

[$u_c/u_a = 0·984$; $u_c = 6·69 \times 10^{-4}$, $u_a = 6·79 \times 10^{-4}$ cm./sec.]

26. In a dilute sol. of sodium bromide at 18° the transport number of sodium ion is 0·392. Given that the ionic conductivity of sodium ion is 43·5, calculate the equiv. conductivity of sodium bromide at infinite dilution.

[111 mhos.]

27. At 18° the equiv. conductivity of silver nitrate at infinite dilution is 116·0 mhos. The transport number of silver ion is 0·471. What is the velocity of silver ion under unit fall of potential ? [$5·66 \times 10^{-4}$ cm./sec.]

CHAPTER XI

1. Calculate the work done, in litre-atm., gram-millilitres, and in calories when the vol. of a gas increases at const. temp. against atm. press. from 500 ml. to 1000 ml. [0·5 ; 516,650 ; 12·11]

2. What is meant by the heat-content of a system ? What relation exists between the change in heat-content and the change in total energy of a system ?

3. If 32·7 g. of zinc were dissolved in excess of dilute hydrochloric acid at 15°, (*a*) in an open vessel, (*b*) in a closed vessel, what would be the difference between the heats evolved in the two cases ? [286·3 cal.]

4. Water and benzene boil at 100° and at 80·2° respectively. Calculate the external work done, in litre-atm. and in cal., against the atmosphere, when 100 g. of each liquid is vaporised at the b.p.

[170 and 37·14 l.-atm. ; 4116 and 899·3 cal.]

5. At 182° PCl_5 dissociates in the vapour state to the extent of 41·7 %. What would be the work done, in cal., on vaporising 100 g. of PCl_5 at the above temp. ? [615 cal.]

6. Being given that the heat of vaporisation of water and of benzene is 539·5 and 94·4 cal. per gram respectively, calculate the values of q, ΔH and ΔU associated with the vaporisation of 1 g.-mol. of the liquids.

[9723, 7375 cal. ; 9723, 7375 cal. ; 8982, 6673 cal.]

7. Calculate the heat of formation of potassium chloride from the following data :—

$$KOH\ aq. + HCl\ aq. = KCl\ aq. + H_2O + 13{\cdot}7\ kg.\text{-}cal.$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68{\cdot}4\ kg.\text{-}cal.$$
$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 + aq. = HCl\ aq. + 39{\cdot}3\ kg.\text{-}cal.$$
$$K + \tfrac{1}{2}O_2 + \tfrac{1}{2}H_2 + aq. = KOH\ aq. + 116{\cdot}5\ kg.\text{-}cal.$$
$$KCl + aq. = KCl\ aq. - 4{\cdot}4\ kg.\text{-}cal.$$

[105·5 kg.-cal.]

8. From the following data, calculate the heat of formation of anhydrous Al_2Cl_6 :—

$$2Al + 6HCl\ aq. = Al_2Cl_6\ aq. + 3H_2 + 239{,}760\ cal.$$
$$H_2 + Cl_2 = 2HCl + 44{,}000\ cal.$$
$$HCl + aq. = HCl\ aq. + 17{,}315\ cal.$$
$$Al_2Cl_6 + aq. + Al_2Cl_6\ aq. + 153{,}690\ cal.$$

[321,960 cal.]

9. Calculate ΔH for the reaction $Hg_2Cl_2 + 2KOH = 2KCl + Hg_2O + H_2O$, being given the following heats of formation in kg.-cal. : Hg_2Cl_2, 63·01 ; KOH aq., 114·85 ; KCl aq., 99·88 ; Hg_2O, 21·5 ; H_2O, 68·4. [3·05 kg.-cal.]

10. Calculate the heat of formation of a dilute sol. of nitric acid from nitrogen, oxygen, and water from the following data :—

$$HNO_3\ aq. + NH_3 = NH_4NO_3\ aq. + 20895\ cal.$$
$$NH_4NO_3 + aq. = NH_4NO_3\ aq. - 6325\ cal.$$
$$NH_4NO_3 = N_2 + 2H_2O + \tfrac{1}{2}O_2 + 49450\ cal.$$
$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3 + 11010\ cal.$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68350\ cal.$$

[14,845 cal.]

11. Calculate the heat of formation of ethyl acetate from ethyl alcohol and acetic acid, being given that the heat of combustion of ethyl alcohol is 34,000 cal., of acetic acid 21,000 cal., and of ethyl acetate 55,400 cal.

[−400 cal.]

12. Given that the heats of formation of H_2O (liq.), CO_2, and C_3H_8 are 68,400, 94,400, and 33,850 cal. respectively, calculate the heat of combustion of propane at constant press. and at constant vol. (Assume experimental temp. to be 15°.) [522,950 cal. ; 521,233 cal.]

13. Being given that the heats of formation of Fe_2O_3 and Al_2O_3 are 195·6 and 381·0 kg.-cal. respectively, calculate the heat of reduction of Fe_2O_3 by Al.

[185·4 kg.-cal.]

14. Calculate the heat of neutralisation from the following data : 250 ml. of 1·390 N/2-HCl was poured into 250 ml. of 1·478 N/2-NaOH. At the commencement of the experiment the acid had a lower temperature than the alkali by 1·132° The rise of temperature on mixing was 4·195°. The weight of the calorimeter was 74 g. and the specific heat of the material was 0·057. Similarly, the weight of the stirrer was 33 g. and the specific heat 0·095. The water equivalent of the thermometer was 1·155. (It may be assumed that the specific heat of the solution is equal to the specific heat of water.)

[13·9 kg.-cal. per g.-equiv.]

15. From the following data, determined at the ordinary temperature and at constant pressure, calculate the heat of formation of methane at constant pressure : heat of formation of carbon dioxide = 94·3 kg.-cal. ; heat of formation of water = 68·3 kg.-cal. ; heat of combustion of methane = 213·8 kg.-cal.

[17·1 kg.-cal.]

16. Calculate the heat of combustion of amylene, $CH_3 . CH_2 . CH_2 . CH : CH_2$.

[807·8 kg.-cal.]

17. Being given that the heat of formation of PbI_2 is 41,850 cal., and the heat of formation of $PbCl_2$ 83,900 cal., calculate the heat of the reaction : $PbI_2 + Cl_2 = PbCl_2 + I_2$. [42,050 cal.]

18. At 18° the heat of the reaction $C + CO_2 = 2CO$ is −41,950 cal. The mean atomic and molar heats of carbon, carbon dioxide, and carbon monoxide are 2·496, 9·066, and 6·791 cal. respectively. Calculate the heat of the above reaction at 50°. [−42,015 cal.]

19. At 20° the heat absorbed in the reaction $CaCO_3 \longrightarrow CaO + CO_2$ is, at constant pressure, 42,900 cal. What is the heat of dissociation at constant volume at 20° ? Being given that the mean molar heat capacities of CaO, $CaCO_3$, and CO_2 between 20° and 600° are 12·27, 26·37, and 7·3 cal. respectively, calculate the heat of dissociation at 600°. [42,317 cal. ; 38,956 cal.]

CHAPTER XII

1. A mixture of 6·22 moles of hydrogen and 5·71 moles of iodine were heated at 357° C., and the amount of free iodine in the equilibrium mixture was found to be 0·91 mole. Calculate the equilibrium constant of the reaction, $2HI = H_2 + I_2$. [0·0140]

2. Hydrogen and iodine in the ratio of 1 mole of the former to 4·103 moles of the latter were heated at 357° C. until equilibrium was established. Being given that the equilibrium constant of the reaction is 0·01494, calculate how much hydrogen iodide would be formed for each mole of hydrogen initially present. [1·963 moles]

3. The degree of decomposition, x, of HI at different temperatures is given by the expression $x = 0{\cdot}13762 + 7{\cdot}22 \times 10^{-5}t + 2{\cdot}5764 \times 10^{-7}t^2$. What is the value of the equilibrium constant, K_c, at 500° of the reaction, $2HI = H_2 + I_2$? [0·0244]

4. Under atm. press. 9·20 g. of N_2O_4 occupy a vol. of 2·95 l. at 27°. To what extent are the N_2O_4 mols. dissociated ? [19·8 %]

5. At 35° the degree of dissociation of N_2O_4 is 0·27 under a press. of 1 atm. Calculate the volume of the equilib. constant K_p and the degree of dissociation under a press. of 2 atm. [0·3147 ; 0·195]

6. At 26°, under a pressure of 1 atm., the vapour density of nitrogen tetroxide is 38·0, referred to that of oxygen = 16. Calculate the degree of dissociation (α) into NO_2 molecules, and the proportion of N_2O_4 to NO_2 molecules in the equilibrium mixture. [$\alpha = 0{\cdot}21$; $N_2O_4 : NO_2 = 79 : 42$]

7. From the value of α obtained in the preceding question, calculate the value of α under a pressure of 2 atm. [0·150]

8. At 52·90° the degree of dissociation of N_2O_4 under a pressure of 783·3 mm. is 0·448. Calculate the value of K_p and K_c. [$K_p = 1{\cdot}033$; $K_c = 0{\cdot}0386$]

9. The equilibrium mixture obtained by heating 1 vol. of N_2 with 3 vol. of H_2 to 350° under a press. of 50 atm. contains 25·11 % of NH_3. What is the value of K_p ? [$7{\cdot}6 \times 10^{-4}$]

10. Given that the degree of dissociation of PCl_5 at 523° K. under atm. press. is 0·798, calculate the values of K_p and K_c. Given that the value of K_p at 503° K, is 0·833, find the heat of dissociation. [1·75 ; 0·0409 ; −19,420 cal.]

11. The v.d. of $Ni(CO)_4$ at 63° is 83·3 and at 100° is 70·8, relative to that of oxygen = 16. Calculate the percentage dissociation at these two temperatures. [0·56 ; 6·54]

12. At 2033° and at 2580° K. the equilib. constants of the reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ are 0·0161 and 0·0539 respectively. What is the heat of the reaction ? [−20,850 cal.]

13. When 1 g.-mol. of PCl_5 was heated at constant temp. in a previously evacuated vessel the degree of dissociation was found to be 0·70. What would be the degree of dissociation if 1·13 g.-mol. of chlorine were present initially in the vessel ? [0·5]

14. What will be the amount of NO (in percentage by volume) in the equilibrium mixture obtained by heating 60 % of nitrogen and 40 % of oxygen at 2675° K. ? The value of K_c for the equilibrium, $N_2 + O_2 \rightleftharpoons 2NO$ is $3{\cdot}5 \times 10^{-3}$. [2·8 %]

15. 1 g.-mol. of acetic acid was mixed with 3 g.-mol. of ethyl alcohol at 25°. Being given that the equilibrium constant of the reaction is 4, calculate the proportion of acid which will undergo esterification. [90·3 %]

CHAPTER XIII

1. On what does the maximum efficiency of a heat engine depend? Why is a gas engine theoretically more efficient than a steam engine?

2. If 1000 cal. are supplied to a steam boiler at 130° C., and if the temperature of the condenser is 25°, what is the maximum work (in calories) obtainable? [260·5 cal.]

3. Being given that the latent heat of fusion of nitrobenzene is 22·46 cal. per g. at its m.p. (5·67°), by how much will the f.p. be depressed if 1 mole of a substance is dissolved in 1000 g. of nitrobenzene? [6·875°]

4. The equilibrium constant, $K_1 = p_{H_2O}/p_{H_2}$, for the reaction $CoO + H_2 = Co + H_2O$, is 67 at 450° C., and at the same temperature the equilibrium constant, $K_2 = p_{CO_2}/p_{CO}$, for the reaction $CoO + CO = Co + CO_2$ is 489·6. Calculate the equilibrium constant $p_{CO_2} \cdot p_{H_2}/p_{CO} \cdot p_{H_2O}$ for the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$, and the free energy of the reaction at the above temperature. [$K = 7{\cdot}31$; $-\Delta G = 2861$ cal.]

5. At 505° C. the equilibrium constant for the reaction $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$ is 0·037. What is the free energy of the reaction? [-5101 cal.]

6. At 25° the e.m.f. of the cell Pb | $PbCl_2$ – solution of KCl – HgCl | Hg is 0·5357 volt. Calculate the free energy change of the reaction $Pb + 2HgCl = PbCl_2 + 2Hg$. [$-\Delta G = 24{,}720$ cal.]

7. At 25° the e.m.f. of the cell As | As_2O_3 – solution of $HClO_4$ | Pt(H_2) is 0·2340 volt. (1) Find the free energy of the cell reaction $2As + 3H_2O = As_2O_3 + 3H_2$. (2) Being given that in the case of the reaction $3H_2 + \frac{3}{2}O_2 = 3H_2O$, $\Delta G = -169{,}680$ cal., calculate the free energy of formation of As_2O_3 from arsenic and oxygen at 25°. [32,400 cal.; $-137{,}300$ cal.]

8. In the cell $Pt(H_2) \left| \begin{matrix} \text{N-KCl saturated} \\ \text{with calcite} \end{matrix} \right\| \left. \begin{matrix} \text{N-KCl saturated} \\ \text{with aragonite} \end{matrix} \right| Pt(H_2)$ the calcite electrode is positive. The e.m.f. at 25° is 0·009 volt. Find the free energy of transformation of aragonite into calcite at 25°. [-414 cal.]

9. Being given that the equilibrium constant, K_v, for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is 44·04 at 480° and 38·06 at 520°, calculate the heat of formation of HI at constant volume. [$+2170$ cal.]

10. The heat of dissociation of nitrogen tetroxide at constant pressure is $-13{,}600$ cal. Being given that the equilibrium constant at 100° is 13·33, calculate the value of the constant at 50°. [0·782]

11. Given that in the reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ the velocity coefficients (at constant pressure) of the dissociation of ethane and of the combination of ethylene and hydrogen respectively are such that $\log_{10} k_1 = -73{,}170/2{\cdot}303RT + 15{\cdot}2$ and $\log_{10} k_2 = -43{,}150/2{\cdot}303RT + 8{\cdot}457$, find the value of the equilibrium constant and of the heat of dissociation of ethane at 600° K. [$K = 6{\cdot}5 \times 10^{-5}$; 31,360 cal.]

12. The equilibrium constant of the reaction $2Cu_2O + O_2 \rightleftharpoons 4CuO$ is given by $\log_{10} K = -13261/T + 12{\cdot}4$. Calculate the heat change at constant pressure accompanying the formation of 4 mols. of CuO at 1000° K.

13. The ionic product of water at 0° is $(0{\cdot}34 \times 10^{-7})^2$ at 50° $(2{\cdot}35 \times 10^{-7})^2$. Find the mean value of the heat of ionisation of water between 0° and 50°. [$-13{,}500$ cal.]

14. Given that the heat of reaction $H_2 + \frac{1}{2}O_2 = H_2O$ (*g.*) is 57,800 cal. and of the reaction $CO + \frac{1}{2}O_2 = CO_2$ is 67,960 cal., find the equilibrium constant of the reaction, $H_2O + CO = H_2 + CO_2$ at 1200° K., being given that the value of K at 1000° K. is 3·26. Find also the affinity of the reaction at 1200° K. [$K = 1{\cdot}39$; 7634 cal.]

CHAPTER XIV

1. Calculate the degree of electrolytic dissociation of monobromacetic acid from the following data :—

v . . .	32	128	∞
Λ_v . . .	73·2	130·4	385·9

What is the affinity constant of the acid ?

[$\alpha = 0{\cdot}19,\ 0{\cdot}34$; $K = 1{\cdot}38 \times 10^{-3}$]

2. The equiv. conductivity of a 0·01 N sol. of NH_4OH at 18° is 9·6 mhos. For NH_4Cl, $\Lambda_\infty = 130$, and the ionic conductivities of OH' and Cl' are 174 and 66 mhos respectively. Calculate Λ_∞ for NH_4OH, the degree of ionisation in the above sol. and the affinity constant. [$K = 1{\cdot}7 \times 10^{-5}$]

3. Being given that the affinity constant of salicylic acid is $1{\cdot}00 \times 10^{-3}$, calculate the value of the degree of dissociation in a 0·001 N solution.

4. Being given that the degree of ionisation of acetic acid in N/1024 solution at 25° is 0·127, what will be the approximate degree of ionisation of lactic acid in a solution of the same concentration ? ($K_A = 1{\cdot}8 \times 10^{-5}$; $K_L = 1{\cdot}38 \times 10^{-4}$.) [0·351]

5. What must be the concentration of a solution of lactic acid so that when mixed with a centinormal solution of acetic acid no change in the ionisation of either acid occurs ? ($K_A = 1{\cdot}8 \times 10^{-5}$, $K_L = 1{\cdot}38 \times 10^{-4}$.) [0·0013 normal]

6. Calculate the concentration of hydrogen ion, in g.-equiv./l., in a solution of decinormal acetic acid to which one-twentieth of a g.-mol. of sodium acetate has been added. [$0{\cdot}36 \times 10^{-4}$]

7. At what concentration will a sol. of glycolic acid ($K = 15{\cdot}2 \times 10^{-5}$) be isohydric with a 0·1 molar sol. of acetic acid ($K = 1{\cdot}8 \times 10^{-5}$) ? [0·01184 molar]

8. Explain how you would prepare a solution the hydrogen ion concentration of which is $4{\cdot}5 \times 10^{-6}$ g.-equiv. per litre, by means of acetic acid and sodium acetate.

9. Being given that the affinity constant of ammonium hydroxide is $1{\cdot}9 \times 10^{-5}$, how would you proceed to make up a solution the hydroxide ion concentration of which is $6{\cdot}34 \times 10^{-6}$ normal ?

10. To a litre of a molar solution of acetic acid ($K = 1{\cdot}8 \times 10^{-5}$), sodium acetate is added. How much (in g.-mol.) of the dry salt must be dissolved in order to decrease the conc. of hydrogen ion to 0·1 of its previous value ? [0·0421]

11. At a given temperature, 1 litre of a saturated solution of $AgBrO_3$ contains 0·0081 mole of salt. Calculate the solubility in a solution containing 0·0085 mole of $AgNO_3$ per litre. [0·0049 mole per litre]

12. 100 c.c. of water at 100° dissolve 0·12 g. of AgCNO. How much AgCNO will be dissolved at this temperature by 100 ml. of a solution containing 1 g. of $AgNO_3$? The silver salts may be regarded as completely dissociated. [0·00107 mole]

13. In a decinormal solution of KCN at 25°, the concentration of hydroxide ion owing to hydrolysis was found to be $9{\cdot}5 \times 10^{-4}$ g.-equiv. per litre. Being given that the ionic product for water is $1{\cdot}2 \times 10^{-14}$, calculate the affinity constant of HCN. [$1{\cdot}33 \times 10^{-9}$]

14. From the data in Q. 13 and the calculated value of the affinity constant of HCN, calculate the degree of hydrolysis and hydrolytic constant of KCN. [$x = 9{\cdot}5 \times 10^{-3}$; $K_h = 9{\cdot}113 \times 10^{-6}$]

15. At 25° and at the dilution of 1 mole in 99·2 litres, the equivalent conductivity of aniline hydrochloride is 118·6 mhos. When excess of aniline is present in the solution the conductivity is 103·6. The equivalent conductivity of HCl in the same dilution is 411. Find the degree of hydrolysis of aniline hydrochloride and the constant of hydrolytic dissociation. [$x = 0{\cdot}0488$; $K_h = 2{\cdot}52 \times 10^{-5}$]

16. In a decinormal solution at 25°, KCN is 0·91 per cent. hydrolysed. Being given that the affinity constant of HCN is $1·32 \times 10^{-9}$, find the value of the ionic product of water. $[1·1 \times 10^{-14}]$

17. The hydrolysis constant of NaCN in a molar solution at 25° is 0·000049. What is the approximate molar concentration of free base and free acid in the solution ? [0·007]

18. The affinity constant of cinnamic acid at 25° is 0·0000345, and its solubility in water is 0·00331 mole per litre, the ionisation being 9·84 %. In a 0·01 molar solution of aniline the solubility is increased to 0·00804 mole per litre. The salt formed is ionised at this dilution to 93 % and $K_w = (1·09 \times 10^{-7})^2$. What is the value of the constant $K = [B^{\cdot}][OH']/[BOH]$ for aniline ? $[5·3 \times 10^{-10}]$

19. The concentration of hydrogen ion in a solution is $2·265 \times 10^{-8}$ g.-equiv. per litre. What is the pH of the solution ? What is the concentration of hydrogen ion in a solution the pH of which is 5·23 ? $[p\text{H} = 7·64$; $5·89 \times 10^{-6}$ normal$]$

20. Why is a sharp end-point not obtained when acetic acid is titrated with ammonium hydroxide ?

21. Given that the affinity constant of acetic acid is $1·8 \times 10^{-5}$, find the pH value of a solution of the acid which has been half neutralised by addition of NaOH. [4·74]

22. Explain how one can determine the concentration of hydrogen ion by means of indicators. What considerations must guide one in the selection of an indicator in acid-alkali titrations ?

23. When a dilute sol. of formic acid and of benzoic acid were titrated with NaOH, it was found that when half the acid had been neutralised the pH of the sol. was 3·68 and 4·21 respectively. What are the affinity constants of the acids ? $[2·1 \times 10^{-4}$; $6·2 \times 10^{-5}]$

CHAPTER XV

1. The cell Ag | AgBr, N/100KBr || N/100KCl, AgCl | Ag has, at 23·1°, an e.m.f. of 0·1514 volt, and the temp. coefficient of e.m.f. is −0·000241. The current flows in the cell from left to right. What is the reaction taking place in the cell ? Calculate (1) the heat of the reaction, (2) the free energy. [5140 cal. ; 3492 cal.]

2. The cell Ag | AgI, N/10KI || AgCl, N/10KCl | Ag has, at 15°, an e.m.f. of 0·3727 volt. The temp. coefficient of e.m.f. is −0·00014. Calculate the heat of the reaction taking place in the cell. [9524 cal.]

3. Using the data given in the text, state the e.m.f. at 25° of the following cells. The ions have in all cases unit activity. Which is the positive pole of the cell ? (1) Zn | $Zn^{\cdot\cdot}$ || $Cu^{\cdot\cdot}$ | Cu ; (2) Ni | $Ni^{\cdot\cdot}$ || $Ag^{\cdot}$ | Ag ; (3) $Pt(H_2)$ | $H^{\cdot}$ || OH' | $Pt(H_2)$; (4) $Pt(Cl_2)$ | Cl' || Br' | Pt | (Br_2).

4. Calculate the e.m.f. of the cell, Cd | 0·5M-$Cd(NO_3)_2$ || 0·1N-$AgNO_3$ | Ag, at 25°, assuming that the activity coefficients of $Cd(NO_3)_2$ and $AgNO_3$ in the above solutions are 0·38 and 0·72. Which is the positive pole of the cell ? [+1·153 volt ; Ag]

5. At 23·1° the e.m.f. of the cell Cu | CuBr, N/100KBr || N/100KI, CuI | Cu is 0·2041 volt. The temp. coefficient is −0·000305. Calculate the heat of the cell reaction. [13,580 cal.]

6. At 25·1° the e.m.f. of the cell Pb | PbI_2, N/100KI || N/100K_2SO_4, $PbSO_4$ | Pb is 0·0084 vol and the temp. coefficient is $+5·14 \times 10^{-4}$. Calculate the heat of the cell reaction and the free energy. [−6641·9 cal. ; 388·1 cal.]

7. At 25° and at 35° the e.m.f. of the cell Li | LiI in propylamine | Li-amalgam, in which the amalgam contains 0·0350 % Li is 0·9457 volt and 0·9489 volt respectively. Find the heat of solution of 1 g.-equiv. of lithium in a large quantity of the amalgam. [19,605 cal.]

8. The e.m.f. of the cell Cl_2 | fused $PbCl_2$ | Pb is given by $E = 1·786 - 0·000679T$ volt. Calculate the heat of formation of $PbCl_2$ at 498°. [82,400 cal.]

9. The cell Ag | AgBr, 0·05M-KBr || 0·05M-$AgNO_3$ | Ag has, at 25°, an e.m.f. of 0·570 volt. If the activity coefficient of $AgNO_3$ and of KBr in the above solutions is 0·90, calculate the solubility of AgBr in pure water at 25°. [$6·71 \times 10^{-7}$ g.-equiv. per litre]

10. The cell Ag | AgI, 0·05M-KI || 0·05M-$AgNO_3$ | Ag has, at 25°, an e.m.f. of 0·788 volt. If it be assumed that the activity coefficient of $AgNO_3$ and of KI in the above solutions is 0·90, calculate the solubility of silver iodide in pure water at 25°. [$9·73 \times 10^{-9}$ g.-equiv./l.]

11. Calculate the e.m.f. of the concentration cell, Cu || 0·001M-$CuSO_4$ | 0·01M-$CuSO_4$ | Cu at 25°, being given that the transport number of $Cu^{\cdot\cdot}$ in the above solutions is 0·38. The activity of the $Cu^{\cdot\cdot}$ in the two solutions is 0·00404 and 0·00069 respectively. [0·0141 volt]

12. Calculate the e.m.f. of a concentration cell containing N/100 and N/1000 thallous nitrate at 18°, being given that the transport number of the nitrate ion in the above solutions is 0·484. The activity coefficients of thallous nitrate are 0·92 and 0·98 respectively. [0·05735 volt]

13. A hydrogen electrode in a solution gave, when combined with a saturated calomel electrode, an e.m.f. at 18° of 0·5622 volt. What is the *p*H of the solution? [5·4]

14. A hydrogen electrode dipping in a N/32 solution of aniline hydrochloride when combined with a normal calomel electrode gave an e.m.f. of 0·4655 volt at 25°. Calculate the degree of hydrolysis of the salt. The potential of the calomel electrode is +0·281 volt. [0·021]

15. The cell Tl(amal.) | TlCl in KCl soln. || TlSCN in KSCN soln. | Tl(amal.), in which the ratio of concentrations [Cl′]/[SCN′] = 1·50 has at 39·9° an e.m.f. of −0·0141 volt. Find the equilibrium constant of the reaction $TlCl + SCN' = TlSCN + Cl'$. Given that the temperature coefficient of e.m.f. is −0·00044, calculate the heat of reaction. [0·88; 31,800 cal.]

16. The cell Pb(amal.) | $PbSO_4$, N/5Na_2SO_4 || PbI_2, N/20NaI | Pb(amal.) has at 25° an e.m.f. of 0·028 volt. Find the equilibrium constant of the reaction $PbI_2 + Na_2SO_4 \rightleftharpoons PbSO_4 + 2NaI$. [0·26]

17. Find the free energy of the reaction $2Ag + Cl_2 = 2AgCl$ at 25° and under atm. pressure, from the following data: normal potential of the silver electrode = +0·798 volt, normal potential of chlorine electrode = 1·359 volt, solubility product of AgCl at 25° = $1·56 \times 10^{-10}$. [53,630 cal.]

18. The potential of a platinum electrode in a 0·1N-HCl containing equal concentrations of ferric and ferrous salts is +0·770 volt. Calculate the potential when the acid solution contains (*a*) 0·01M $FeCl_2$ + 0·09M $FeCl_3$, and (*b*) 0·09M $FeCl_2$ + 0·01M $FeCl_3$.

19. From the values of the electrode potentials given on p. 373, find the equilibrium constants of the reactions $Zn + CuSO_4 \rightleftharpoons Cu + ZnSO_4$, and $Zn + FeSO_4 \rightleftharpoons Fe + ZnSO_4$. [$3·09 \times 10^{37}$; $7·41 \times 10^{10}$]

20. Given that the normal electrode potentials Pt | ($Fe^{\cdot\cdot\cdot}$/$Fe^{\cdot\cdot}$) and Pt(Cl_2) | Cl′ are +0·743 and +1·359 volt respectively at 25°, find the equilibrium constant of the reaction $2Fe^{\cdot\cdot} + Cl_2 \rightleftharpoons 2Fe^{\cdot\cdot\cdot} + 2Cl'$. [$7·59 \times 10^{20}$]

21. The e.m.f. of the cell, N-calomel electrode || M/64 $AlCl_3$ | Pt(H_2) at 25° is 0·4655 volt, the potential of the calomel electrode being +0·2812 volt. If it is assumed that $AlCl_3$ hydrolyses in accordance with the equation $AlCl_3 + H_2O \rightleftharpoons AlCl_2(OH) + HCl$, and that the HCl produced is ionised to the extent of 90 %, find the degree of hydrolysis of $AlCl_3$ in the above solution. [0·0542]

CHAPTER XVI

1. From the data on p. 399 determine the heat of dissociation of $CaCO_3$ by a graphic method.

2. Given that the dissociation pressure of $CaCO_3$ is 25·3 mm. at 700° and 168 mm. at 800°, calculate the mean heat of dissociation between these temperatures. [−39,300 cal.]

3. From the data on p. 399 find the dissociation pressure of $CaCO_3$ at 905°. Calculate the weight left undissociated when 14 g. of $CaCO_3$ are heated in an evacuated 2-lit. flask at 905°. (The vol. occupied by the solids to be neglected.)

4. The dissociation pressure of the system $AgCl.NH_3 \rightleftharpoons AgCl + NH_3$ is 240 mm. at 42° and 613 mm. at 59°. What is the heat of dissociation ? [−11,480 cal.]

5. On being heated, $CdCO_3$ dissociates into CdO and CO_2. At 330° the pressure of CO_2 is 190 mm. and at 340° 330 mm. Calculate the heat of combination of CdO and CO_2. [43,630 cal.]

6. The dissociation pressure of NH_4HS at 24·7° is 479 mm. If it be assumed that the vapour is dissociated practically completely into NH_3 and H_2S, calculate the total pressure produced when solid NH_4HS is vaporised at 24·7° in a vessel in which ammonia is present at a pressure of 400 mm. Calculate also the partial pressures of NH_3 and H_2S at equilibrium.
[624 mm. ; $p_{NH_3} = 512$ mm., $p_{H_2S} = 112$ mm.]

7. The dissociation pressure of $NH_2.COONH_4$ at 34·89° is 174·9 mm. Calculate the equilibrium constant. Assuming that the carbamate is practically completely dissociated into $2NH_3 + CO_2$, calculate the total pressure produced when the salt is vaporised at 34·89° in an atmosphere of NH_3 of pressure 143·5 mm. Calculate also the partial pressures of NH_3 and CO_2 at equilibrium.
[$K = 7{\cdot}92 \times 10^5$; $P = 265{\cdot}2$, $p_{NH_3} = 188{\cdot}4$, $p_{CO_2} = 22{\cdot}5$ mm.]

8. If ammonium carbamate is vaporised at 30° in a closed vessel containing ammonia under a pressure of 169 mm., the total pressure rises to 194 mm., whereas if the vessel contains CO_2 under a pressure of 169 mm., the total pressure rises to 227 mm. Show that these experimental results are in agreement with the law of mass action and calculate, in each case, the partial pressures of NH_3 and CO_2.

9. At 16° the dissociation pressures of pure NH_4HS and pure $NH_2(CH_3)_2HS$ are 276 and 83 mm. respectively. Calculate the pressure which would be exerted by a system in which both hydrosulphides are present. [284 mm.]

10. The concentrations of chlorine gas C_1, in millimoles per litre over a chlorine solution in CCl_4 of concentration C_2 at 0° are :—

C_1 . . .	0·1109	0·2666	0·5365	0·8800
C_2 . . .	8·908	22·46	44·14	75·09

What is the molecular state of chlorine in solution ? [Cl_2]

11. Acetic acid was shaken with water and CCl_4, and the following concentrations, in moles per litre, were found in the two solutions :—

Conc. in CCl_4 . .	0·292	0·725	1·41
Conc. in H_2O . .	4·87	7·98	10·70

Assuming that acetic acid has normal molecular weight in water, what is its molecular weight in CCl_4 ? [$(CH_3COOH)_2$]

12. An aqueous solution of citric acid and acetic acid containing insufficient base for complete neutralisation was shaken with $CHCl_3$. At equilibrium the latter was found to contain 0·007 g.-equiv. of acetic acid per litre, and the water layer contained 0·3 g.-equiv. NaOH, 0·3049 g.-equiv. acetic acid, and 0·3015 g.-equiv. citric acid per litre. For acetic acid the distribution ratio $C_{H_2O}/C_{CHCl_3} = 26{\cdot}4$. Calculate the ratio in which the acids compete for the base.

13. After shaking an aqueous solution of NH_3 with $CHCl_3$ the concentration of NH_3 in the aqueous layer was 5·211 g. per litre, that in the chloroform layer being 0·1686 g. per litre. On shaking an aqueous ammoniacal 0·1N solution of $CuSO_4$, the corresponding concentrations were 6·688 and 0·1153 g. per litre. Find the ratio $CuSO_4$: fixed NH_3.

14. Phenol distributes itself between water and chloroform in the following ratios :—

Conc. in H_2O .	0·094	0·163	0·247	0·436
Conc. in $CHCl_3$.	0·254	0·761	1·85	5·43

What are the relative molecular weights of phenol in the two solutions ?

CHAPTER XVII

1. The specific volume of α-rhombic ammonium nitrate at 32·3° is 0·5826 ml. per g., and that of the β-rhombic form is 0·6046 ml. per g. The transition point is 32·3° and the heat of transformation 4·99 cal. per g. Find the effect of increase of pressure by 1 kg. per sq. cm. on the transition point. [$\Delta T = 0{\cdot}0315°$]

2. Starting with the compound AgCl, $3NH_3$ in a closed vessel under pressure control and containing only NH_3 in addition, what changes will take place on reducing the pressure at constant temperature? Illustrate by means of a diagram.

3. The freezing-points of molten mixtures of metal A and B are as follows:—

Atoms of B, %	0	10	20	30	40	50	60	70	80	90	100
Freezing-point	65°	60°	50°	35°	50°	55°	50°	35°	20°	30°	35°

Draw and interpret the freezing-point curve, and explain what happens when molten mixtures containing 20 and 70 atoms % of B are cooled down.

4. Propyl alcohol and water and formic acid and water are miscible in all proportions. The vapour-pressure curve of mixtures of propyl alcohol and water shows a maximum for a mixture containing 80 % of alcohol by weight. The vapour-pressure curve of mixtures of formic acid and water shows a minimum for a mixture containing 73 % of formic acid. Describe how solutions containing 50 % of propyl alcohol and of formic acid respectively will behave on distillation.

5. The solubility of benzoic acid in toluene at different temperatures is as follows:—

Temperature	30°	40°	50°	60°	70°	80°
Molar fraction of solute	0·0891	0·1270	0·1790	0·247	0·333	0·439

Calculate the heat of solution in cal. per mole of solute. Confirm your result by a graphic method. [$L = 6700$ cal]

6. In the steam distillation of nitrobenzene ($M = 123$) the distillate is found to contain 20 % of nitrobenzene. The external pressure on the boiling liquid is 760 mm. Calculate the partial pressure of water and of nitrobenzene in the distilling flask. [$p_n = 26{\cdot}8$; $p_w = 733{\cdot}2$ mm.]

7. When aniline ($M = 93$) is steam distilled, the distillate is found to contain 26·5 % by weight of aniline. What is the approximate vapour pressure of aniline at the temperature of the distillation? [496 mm.]

8. The transition point of rhombic to monoclinic sulphur lies at 95·5° and is raised 0·04° by an increase of pressure of 1 atm. Given that the passage from rhombic to monoclinic sulphur is accompanied by an increase of volume of 0·01395 ml. per g., calculate the heat of transformation per g. [3·122 cal.]

9. Toluene and water are distilled together under a barometric pressure of 755 mm. The v.p. of the two pure liquids are given below. Calculate (*a*) the b.p. of the mixture, and (*b*) the composition of the distillate.

Temp.	83°	84°	85°	86°
V.p. of water	400·1	416·3	433·0	450·3 mm.
V.p. of toluene	321·7	332·7	344·7	355·7 mm.

CHAPTER XVIII

1. In the case of a unimolecular reaction, show that the time required for 99·9 % of the reaction to take place is ten times that required for half the reaction.

2. Being given that the disintegration constant of radon is $1{\cdot}25 \times 10^{-4}$, when time is measured in minutes, what fraction of the original material will be left after 3·58 days? [0·5]

3. The disintegration constant of radium A is $3{\cdot}85 \times 10^{-3}$ when the time is measured in seconds. How long will it take for half the initial amount of radium A to disintegrate ? [3 min.]

4. Given that the period of half-life of radon is 3·85 days, find what proportion of radon will remain after 14 days. [0·0805]

5. From a solution of methyl acetate in dilute hydrochloric acid, 2 ml. were withdrawn at intervals of t min. and titrated with baryta solution. From the following data calculate the velocity coefficient of hydrolysis :—

t (min.)	0	20	75	119	∞
Ml. baryta	19·24	20·73	24·20	26·60	42·03

Determine the value of k also by a graphic method. [0·00331]

6. When malonic acid is heated it undergoes decomposition in accordance with the equation : $CH_2(COOH)_2 \longrightarrow CH_3 . COOH + CO_2$. The velocity of decomposition was determined at 136·4° by measuring the increase of pressure produced in a closed vessel. From the following data calculate the velocity coefficient :—

t (min.)	10	15	20	35	56	64	∞
Pressure (mm.)	37·0	53·0	67·0	108·0	155·0	171·0	302·0

After what time would half the malonic acid have undergone change ? [0·0128 ; 54·1 min.]

7. A given volume of a solution of hydrogen peroxide when titrated at intervals of time t decomposed x ml. of permanganate solution. From the ollowing data show that the decomposition of hydrogen peroxide is a unimolecular reaction :—

t (min.)	0	10	20
x	22·8	13·8	8·25

8. In the inversion of sucrose in presence of an acid the following polarimetric readings were obtained :—

t (min.)	0	30	90	150	330	630	∞
α	46·75°	41·00°	30·75°	22·00°	2·75°	−10·00°	−18·75°

Determine by calculation and by a graphical method the value of the velocity coefficient. What time would be required for half the sucrose to be inverted ? [$k = 0{\cdot}00313$]

9. For the decomposition of nitrous oxide on a gold wire at 990° C., the following values of percentage decomposition were obtained :—

t (min.)	15	30	53	65	80	100	120
% decomposed	16·5	32	50	57	65	73	78

Show that the reaction is one of the first order.

10. When heated, nitrous oxide undergoes decomposition, and for different initial pressures the times required for half decomposition are as given below. What is the order of the reaction ?

Pressure (mm.)	360	290	278	139	114	52·5
Half life (sec.)	212	255	300	470	490	860

[Second]

11. The decomposition of arsine into solid arsenic and hydrogen may be followed by measuring the press. at const. vol. At 310° the press. p were obtained at times t.

t (hours)	0	5·5	6·5	8
p (mm.)	733·3	805·8	818·1	835·3

Find the order of the reaction.

12. The reaction $CH_3I + Na_2S_2O_3 = NaS_2O_3 . CH_3 + NaI$ was followed by titrating 10 ml. of the mixture at 25° with 0·0101 N-iodine. The following results were obtained :—

t (min.)	0	4·75	10	20	35	55	∞
Titration (ml.)	35·35	30·5	27·0	23·2	20·3	18·6	17·1

What is the value of the velocity coefficient ? [1·97]

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