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A CLASS BOOK OF PHYSICAL CHEMISTRY

BY

T. MARTIN LOWRY

C.B.E., M.A., D.Sc., F.R.S.

PROFESSOR OF PHYSICAL CHEMISTRY IN THE UNIVERSITY OF CAMBRIDGE

AND

SAMUEL SUGDEN

D.Sc., A.R.C.Sc. (LOND.), F.R.S.,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF LONDON
(UNIVERSITY COLLEGE)

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PREFACE

It was originally intended to make this *Class-Book of Physical Chemistry* an additional Part of Donington's *Class-Book of Chemistry*, to which sections dealing with the chemistry of the metals and with elementary organic chemistry have already been added. The present volume is, however, of wider scope than these supplementary volumes, and, although similar in arrangement, forms an independent introduction to the study of Physical Chemistry: it is, therefore, published separately. The subject has been presented so far as possible in a simple and elementary form, but for the sake of completeness two more difficult thermodynamic sections, § 20 *A* and *B*, have been added; these need not, however, be studied until the rest of the book has been read, if the student is content meanwhile to accept without proof the formulae which are there deduced.

The authors of a text-book on physical chemistry are faced at the present time with exceptional difficulties arising from the rapid development of the subject. The problem of atomic structure has not been included in the present volume, since it is more conveniently studied as a branch of general chemistry, or as a special subject; but the questions of molecular structure raised by the theory of complete ionisation have been considered in the light of current knowledge. An attempt has therefore been made to define the scope of this newer theory in relation to Arrhenius's older theory of reversible ionisation, and to take account of changing views in reference to the relative importance of ions and molecules in catalysis by acids and bases. Since, however, the normal scope of an elementary course of physical chemistry is already well defined, we have in the main been

content to keep within it, without trying to exploit unduly the more novel or personal points of view.

We are indebted to Sir Richard Gregory for much helpful advice, and to Dr. R. G. W. Norrish and Mr. A. J. V. Gale for reading the proofs and making a number of valuable suggestions.

T. M. LOWRY.
S. SUGDEN.

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CHAPTER I.

THE GASEOUS STATE.

1. The Gas Laws.

1. Boyle's Law.—(*a*) Select a round-bottomed flask of 250 c.c. capacity (Fig. 1). Fit it with a rubber stopper carrying a short capillary tube. The lower end of this tube should be flush with the cork and the upper end should project about 3 to 4 cm. Push the stopper in tightly, and make a mark on the neck of the flask (a scratch, or a piece of gummed paper can be used) so that the stopper can always be pushed in to the same distance. Fill the flask to this mark with water and determine its volume by pouring the water into a measuring cylinder.

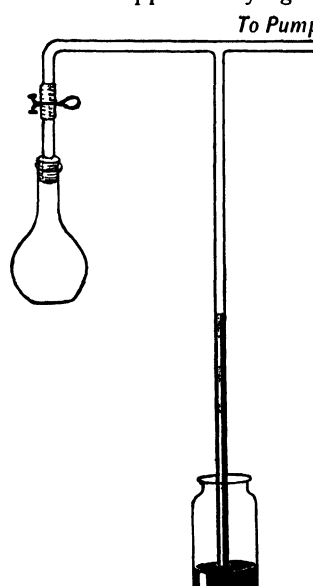


FIG. 1.—Apparatus for experiments on Boyle's Law.

Clean and dry the flask, insert the stopper and slip over the capillary tube a piece of rubber tubing about 5 cm. long with a clip. Slip the other end of the rubber tube over the side arm of a T-piece, with a vertical limb about 40 cm. long, carrying a scale and dipping into a bottle of mercury to form a mercury-gauge. Connect the other arm of the T-piece to a water-jet pump, by a rubber tube provided with a spring clip. Open both clips and start the pump.

When the mercury has risen about 20-30 cm. in the gauge, close the clip on the tube leading to the pump. Read off on the

gauge the height to which the mercury in the tube has risen above the level of the mercury in the bottle. Then close the clip on the tube connected to the flask, remove the rubber tubing from the gauge (taking care not to open the clip), invert the flask in a dish of water, so that the rubber tube is completely immersed, and open the clip. Water will rush into the flask.

After allowing a few minutes for the temperature to become steady, adjust the flask so that the level of the water inside and outside is the same, and close the clip. Measure the volume of water which has entered.

Let p_1 be the reading of the barometer and p the reading of the gauge; then the flask was filled with air under a reduced pressure of $p_2 = p_1 - p$.

Let v_2 be the volume of the flask; then, if x c.c. of water have entered, the volume of the air in the flask, when the pressure is raised to that of the atmosphere, is $v_1 = (v_2 - x)$.

If Boyle's Law is true, then

$$p_1 v_1 = p_2 v_2.$$

Express p_1 in millimetres and v_2 in litres and see how nearly this is true.

(*b*) Repeat the experiment with a different setting of the gauge. The flask may also be filled with coal gas or hydrogen in order to verify the fact that Boyle's Law holds for other gases as well as for air.

ii. **Charles's Law.**—(*a*) Take the flask used in Exp. i., with the stopper, tube and spring-clip, and immerse up to the stopper in a large vessel of boiling water, leaving the clip open. Close the clip, after heating the flask for five minutes, when the air in the flask should be at 100° C. Remove the flask. When it is cool enough to handle, immerse completely in a bath of cold water, and open the clip. When water ceases to enter, adjust the flask till the water is at the same level inside and out. Close the clip, remove the flask, and measure the volume of water which has entered. Let t be the temperature of the cold water. Then if v is the volume of the flask in c.c., and x c.c. of water enter on cooling, then $v - x$ c.c. of air must have expanded to v c.c. on heating from $t°$ to 100° C. If Charles' Law is true, then

$$\frac{v - x}{273 + t} = \frac{v}{273 + 100}.$$

Calculate these ratios and see whether your results verify this law.

(*b*) The experiment may be repeated after filling the flask with coal gas. It will be found that the same amount of water

enters, thus proving that this gas expands by the same amount as does air when heated through the same interval of temperature.

(*c*) The coefficient of expansion of the gas may be calculated from the formula :

$$\alpha = \frac{x}{100(v-x) - vt}.$$

Thus by definition $\alpha = \frac{1}{v_0}\frac{dv}{dt}$ where v_0 is the volume at 0° C.; but from the experiment we find $\frac{dv}{dt} = \frac{x}{100-t}$, and from the measured rate of expansion between t° and 100° we can deduce that

$$v_0 = (v-x) - x\frac{t}{100-t} = \frac{100(v-x) - vt}{100-t.}$$

$$\therefore \alpha = \frac{x}{100-t}\frac{100-t}{100(v-x) - vt} = \frac{x}{100(v-x) - vt}.$$

For all gases α is very nearly 0·00366.

iii. Determination of the density of air.—Place about 30-40 c.c. of water in the flask used in Expts. i. and ii. Insert the stopper, leaving the clip open, and boil vigorously over a wire gauze for 5 minutes. Then take away the flame and immediately close the clip on the rubber tube. When the flask is cold, suspend it on the balance and weigh carefully. Open the clip for a few seconds, when air will rush in to take the place of the condensed vapour ; then weigh again. The increase in weight gives the weight of air which has entered the flask. Take the temperature of the water in the flask and measure its volume. The volume of the air which has entered is obtained by subtracting this volume from the total volume of the flask. Read the barometer. The pressure of the air in the flask is given by the height of the barometer, minus the vapour-pressure of the water. (The vapour-pressures of water at different temperatures are given in Table 44, p. 180). The weight of a known volume of air at a known temperature and pressure has thus been obtained. Calculate the weight of 1 litre of air at 0° C. and 760 mm. pressure.

iv. Density of carbon dioxide.—Choose a light flask of about 200 c.c. capacity. Fit it with a rubber stopper carrying two right-angle tubes, one reaching to the bottom of the flask, and the other ending flush with the stopper (Fig. 2). Determine the volume of the flask by filling it with water up to the stopper and measure the volume of the water. Then clean and dry the flask.

Fit the outer ends of the two glass tubes with short lengths of rubber tubing each closed by a clip. Weigh the flask carefully. Then pass a stream of carbon dioxide (prepared in a Kipp apparatus and dried over sulphuric acid) through the longer tube until the gas issuing from the other tube extinguishes a taper. Pass the gas for a minute or two longer, then close the clips, starting with the one through which the gas enters the flask.

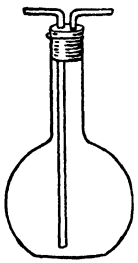


FIG. 2.—Flask for measuring density of gases.

Read the temperature of the air by means of a thermometer which has been hanging near the flask, and read the barometer. Weigh the flask again. The increase in weight *plus* the weight of air displaced gives the weight of the carbon dioxide. The weight of air displaced can be calculated from the volume of the air and its density as determined in Expt. 1, iii. Hence calculate the weight of 1 litre of carbon dioxide at 0° C. and 760 mm.

v. Density of hydrogen.—The same apparatus may be used to determine the density of hydrogen. The gas may be generated by the action of zinc on sulphuric acid in a Kipp apparatus and should be dried by bubbling it through sulphuric acid. The flask must be inverted whilst it is being filled with hydrogen. Invert a test-tube over the exit tube, and from time to time ignite the contents at a flame some distance away from the flask. When the gas in the test-tube burns quietly, the gas stream is allowed to flow for two minutes more, and the clips are then closed.

It will be found that the flask filled with hydrogen is lighter than when it was filled with air. The weight of the hydrogen is equal to the weight of air displaced, minus the decrease in weight on filling with hydrogen. Calculate the weight of 1 litre of hydrogen at 0° C. and 760 mm.

PROPERTIES OF GASES.

The three states of matter.—The three states of matter, solid, liquid and gaseous, can be defined as follows:

(i) **Solids** have a definite volume and a definite shape. They can be compressed or expanded: they can also be distorted; but force has to be exerted in order to change either the volume or the shape of a solid.

(ii) **Liquids** are fluids, which have a definite volume, but no definite shape. A liquid can be compressed, but the resistance to compression has to be overcome by the exercise of force. On the other hand, no force is required to make a liquid change its shape. The form of a liquid is therefore determined in the first instance by the form of the vessel in which it is contained. Thus when a liquid is at rest under the influence of gravity, it fills the lower part of the vessel, and the free upper surface is horizontal.

(iii) **Gases** are fluids which have no definite shape and no definite volume. They differ from liquids in possessing the power of expanding until they fill completely any vessel in which they are placed.

Gases and liquids are classed together as **fluids**, on account of their ability to flow under the influence of very small forces. Thus, gases (which were formerly described as **elastic fluids**) will flow under the influence of their own elasticity until the space in which they are confined is filled completely. Liquids will flow under gravity, but viscous liquids flow only slowly. **Plastic solids**, such as lead or sodium, can be made to flow under pressure, *e.g.* by squirting through a nozzle or die; but this flow does not take place until a minimum limiting pressure is applied.

The study of gases.—The majority of the common gases are transparent and colourless, and are therefore invisible under ordinary conditions. They can, however, be detected by means of other senses. Thus we are unconscious of the surrounding air when the weather is calm; but a breeze immediately demonstrates the existence of the atmosphere to the sense of touch. Whilst, however, the existence of the atmosphere, and the fact that air plays an essential part in breathing, has been known for many centuries, it is only within the last three hundred years that the existence of gases of other kinds has been recognised. The discovery and investigation of these gases has, however, led to results of great importance both in Chemistry and in Physics. Thus it was the investigation of the part played by gases in chemical changes such as combustion that led to the overthrow of the Phlogiston Theory and the establishment of the modern science of chemistry. On the other hand, the study

of the physical properties of gases was a principal factor in the establishment of the theory of molecules, and in particular of the kinetic theory which is described below (p. 11).

The properties of gases.—The behaviour of gases is in general much simpler than that of solids and liquids. Thus, whilst the physical properties of liquids and solids vary widely from substance to substance, and have to be studied individually, it is often possible to state a simple rule which will describe the properties or behaviour of all gases. This fact can be illustrated in connexion with the physical properties of **compressibility, expansion by heat,** and **combination by volume.**

(*a*) *Compressibility.*—If we take equal volumes of water, of alcohol and of ether, at one atmosphere pressure, and increase the pressure to two atmospheres, the liquids will all decrease slightly in volume; but the decrease will vary from substance to substance. Thus it is greatest for ether, which contracts by 0·0145 per cent., and least for water, which contracts only to the extent of 0·0049 per cent. If, however, we take a given volume of any gas, and double the pressure upon it, the volume is always approximately halved. Each liquid (or solid) has, therefore, its own characteristic compressibility, whilst all gases have approximately the same compressibility.

(*b*) *Expansion by heat.*—In the same way, if we study the expansion in volume when equal volumes of water, of alcohol and of ether are heated from 15° to 16°, we find that the increase of volume of water (0·015 per cent.) is much less than that of alcohol (0·11 per cent.), whilst ether (0·163 per cent.) expands more than either. Thus each liquid or solid has its own characteristic **coefficient of expansion.** On the other hand, all gases are found to expand to a similar extent when heated through the same interval of temperature. All gases have, therefore, approximately the same coefficient of thermal expansion.

(*c*) *Combining volumes.*—Another instance of the comparative simplicity of the properties of gases is to be found in the simple ratios in which they combine together, as expressed by Gay Lussac's *Law of Volumes.* This law states that

Gases always combine in the simplest proportions by volume when they act on one another.

or, in general, that

The volumes of gases entering into, or formed by, a chemical reaction, bear a simple numerical relation to one another.

No similar relation exists, however, between the combining volumes of liquids or solids.

Since gases behave in a much simpler manner than do solids or liquids, we shall commence the study of physical chemistry with a discussion of the properties of gases.

The gas laws.—The behaviour of gases, and especially the changes of volume which take place when the temperature and pressure are varied, can be expressed by means of three important laws. These three laws can also be combined in an equation, which gives a very useful summary of the physical properties of gases.

(*a*) **Boyle's Law**, which describes the behaviour of a gas under varying pressures, may be stated as follows:

The volume of a given quantity of a gas at constant temperature is inversely proportional to its pressure.

It may also be expressed algebraically by the equation

$$pv = k,$$

where p is the pressure, and v the volume of a fixed quantity of a gas at constant temperature; k is then a constant, the value of which depends upon (i) the quantity of gas considered, (ii) the temperature, and (iii) the units in which p and v are measured.

(*b*) **Charles's Law** describes the manner in which the volume of a gas varies when it is heated at constant pressure. It expresses the fact that all gases expand and contract uniformly and to a similar extent when the temperature is changed. Thus, the volume of all gases increases by about 37 per cent. between the freezing-point and the boiling-point of water. If this rate of expansion and contraction were maintained, the volume of the gas would diminish to zero at $-273°$ C.; this temperature is therefore called the **absolute zero**. At any other temperatures the volume of the gas would be proportional to the **absolute temperature**, *i.e.* to the temperature measured in Centigrade degrees, but from the absolute zero at $-273°$ C. instead of from 0° C. Charles's Law may therefore be stated as follows:

At constant pressure the volume of a given quantity of any gas is proportional to its temperature on the absolute scale.

If t is the temperature on the Centigrade scale then the absolute temperature T is equal to $t+273$. We may therefore write Charles's Law algebraically in the following manner:

$$v = k(273 + t) = kT.$$

The numerical value of the constant k depends upon (i) the quantity of gas considered, (ii) the pressure, and (iii) the units in which v and T are expressed.

(*c*) These two equations may be combined to give the relation:

$$pv = kT.$$

The constant k in this equation is the same for all values of the temperature, pressure or volume; but its value still depends upon the units in which p, v, and T are expressed, and upon the quantity of gas which is taken. We can, however, make this equation still more general by applying **Avogadro's hypothesis,** according to which *equal volumes of all gases at the same temperature and pressure contain the same number of molecules.* One gram-molecule of any gas at a given temperature and pressure will therefore occupy a definite volume, which will be the same for all gases. If, therefore, we always consider one gram-molecule of gas, the value of k in the equation $pv = kT$ will also be the same for all gases. This standard value of k is usually indicated by a special symbol R and is named the **gas constant.** The equation

$$\mathbf{pv = RT}$$

thus summarises the three important laws of gases and enables us to predict the behaviour of one gram-molecule of any gas when subjected to changes in volume, pressure and temperature. These predictions are only approximately true in the case of actual gases; the ideal gas, for which alone they would be mathematically exact, is described as a *perfect gas* (p. 24).

The gas-law $pv = RT$ also affords a practical method for the measurement of temperature, since we can find T by measuring the variations of p when v is constant, as in a **constant volume air thermometer,** or by measuring the variations of v when p is constant, as in the **constant pressure air thermometer.** In practice, an accurate scale of temperature has been constructed by using a constant volume nitrogen thermometer at temperatures above 100°; but below 100° hydrogen has been used. At very low

temperatures helium under reduced pressure is used, since the gas-law is only obeyed accurately when the gas is far from its point of liquefaction. The instruments used for this purpose are described in books on Physics.

The gas constant.—The value of the gas constant R has been determined by a careful study of the density of gases under known temperatures and pressures. If M is the molecular weight of a gas, d its density at a pressure p, and at an absolute temperature T, then the volume occupied by a gram-molecule is given by $V=\frac{M}{d}$, and $R=\frac{pV}{T}=\frac{Mp}{dT}$. By using this formula, the value of the gas constant R can be calculated from the results of measurements of the densities of gases, *e.g.* as described in Expt. I, iv and v.

The numerical value of the gas constant R, when deduced from the densities of different gases, is found to vary slightly. This is due to the fact that the gas laws are not obeyed strictly by any gas. At moderate pressures, however, and at temperatures much above the temperature of liquefaction, many gases obey the gas laws with a very close approach to accuracy, and therefore give concordant values for the gas constant R. Table I gives a summary of the most accurate determinations of the densities of a number of such gases, together with the volume in litres V_0 occupied by one gram molecule at 0° C. and 760 mm. pressure (*i.e.* at "normal temperature and pressure," or N.T.P.).

TABLE I. MOLECULAR VOLUMES OF GASES.

Gas.	Mol. Wt.	Density d (in grams per litre at N.T.P.).	Volume V_0 (in litres at N.T.P.).
Hydrogen - - -	2·016	0·08988	22·43
Oxygen - - -	32·000	1·4291	22·39
Nitrogen - - -	28·02	1·2507	22·40
Nitric Oxide - - -	30·01	1·34265	22·35
Carbon Monoxide - -	28·00	1·2507	22·44
Nitrous Oxide - -	44·02	1·9706	22·34
Methane - - -	16·04	0·71464	22·44
Ammonia - - -	17·07	0·7621	22·39

It will be seen that the molecular volume V_0 is not quite constant,

but varies a little from one gas to another. Since these variations become less as the pressure under which the gases are studied is reduced, it is supposed that they would disappear altogether at very low pressures.

Numerical value of the gas constant.—When allowance is made for the deviations of actual gases from the ideal gas laws, it can be calculated that the value of V_0 for a perfect or ideal gas would be 22·412 litres at 0° C. and 1 atmosphere pressure. We can use this figure in order to calculate the numerical value of R as follows. From the gas equation

$$R = \frac{pV}{T} = \frac{1 \times 22{\cdot}412}{273} = 0{\cdot}0821 \text{ litre-atmospheres.}$$

Since we have expressed p in atmospheres and V in litres, the number 0·0821 represents the value of R in a special unit of *litre-atmospheres.* This unit is a convenient one to use when the gas equation is applied to the calculation of the volumes of gases at different temperatures and pressures.

The real significance of the constant R will be seen when we consider the nature of the quantities of which it is made up. Pressure is force per unit area, whilst temperature is expressed by a pure number, hence

$$R = \frac{\text{pressure} \times \text{volume}}{\text{temperature}} = \frac{\text{force}}{\text{area}} \times \text{volume}$$

$$= \text{force} \times \text{length} = \text{work.}$$

We can therefore express R in absolute units of work. Thus in the centimetre-gram-second system (C.G.S. system) the value of R can be expressed in *ergs.* In order to do this, we must transform p and V into C.G.S. units. One atmosphere is the pressure of a column of 760 mm. of mercury at 0°. Since the density of mercury at 0° is 13·596 grams per c.c., the weight of a column of mercury 76 cm. in height and 1 sq. cm. in area is $76 \times 13{\cdot}596$ grams. To convert this pressure into absolute units we must multiply by the gravitational constant 980·6, which converts grams of weight into absolute units of force or dynes. The absolute value of an atmosphere of pressure is therefore

$$76 \times 13{\cdot}596 \times 980{\cdot}6 = 1{,}014{,}000 \text{ dynes per sq. cm.}$$

If we then express V_0 in cubic centimetres, instead of in litres, we have

$$R = \frac{76 \times 13{\cdot}596 \times 980{\cdot}6 \times 22{,}412}{273} = 83{,}150{,}000 \text{ ergs.}$$

Now work and heat are forms of energy which may be converted quantitatively into one another. We can, therefore, express the value of the gas constant R in units of heat instead of in units of work. For this purpose we must make use of the fact that the unit of heat, the *calorie* (*i.e.* the amount of heat required to raise 1 gram of water from 15° to 16° C., see p. 202), is equal to $4{\cdot}183 \times 10^7$ ergs. The value of R in calories is therefore

$$R = \frac{8{\cdot}315 \times 10^7}{4{\cdot}183 \times 10^7} = 1{\cdot}985 \text{ calories.}$$

The approximate figure, $R = 2$ calories, finds many applications in the discussion of problems concerning gases, and should be remembered.

THE KINETIC THEORY OF GASES.

Molecules in motion.—Many of the properties of gases suggest that the molecules of which they are composed are in rapid motion.

(*a*) *Expansion.*—Gases can expand indefinitely, in such a way that a small quantity of gas will fill completely any vessel, however large, in which it is placed. The first explanation of this expansion to suggest itself is that the molecules must repel one another, but this is not the case. On the contrary, we shall see later that molecules must attract one another, since it is the attraction of the molecules for one another which causes gases to condense to liquids at high pressures and low temperatures.

The indefinite expansion of a gas can, however, be accounted for equally well by assuming that the molecules are moving with considerable velocities, and continue to move in straight lines until they collide with other molecules or with the walls of the containing vessel. If we could place a swarm of gas molecules at the centre of a spherical vessel which was completely evacuated, then the outer molecules of the swarm would

meet no obstacle and would move away till they struck the wall of the vessel and then would rebound in a different direction.

The collisions between molecules and molecules, or between molecules and the walls of the vessel, are continually changing the direction of motion, so that we must think of molecules as moving at random in all directions. Thus, a particular molecule moves in a straight line until it collides with another molecule; but it then flies off in another direction, depending upon the angle at which the molecules were approaching one another before the collision occurred. This random distribution of velocities causes the molecules to arrange themselves so that, at a given moment, each cubic centimetre of the space within the vessel contains the same number of molecules; in other words, the gas placed originally at the centre becomes distributed uniformly throughout the vessel.

(*b*) *Diffusion.*—In addition to expanding into a vacuous space, gases will diffuse readily into one another. Thus, if two gas jars, the upper one containing hydrogen and the lower one carbon dioxide, are placed mouth to mouth, then the light hydrogen diffuses downwards into the heavy carbon dioxide, and the heavy carbon dioxide diffuses upwards into the lighter hydrogen, until both cylinders finally contain a uniform mixture of the two gases. This property of diffusion is very striking evidence in favour of the view that the molecules of a gas are in continuous motion.

(*c*) *Elasticity.*—Since the properties of a gas do not change with time, we must suppose that the molecules of the gas do not lose any energy in colliding with each other or with the walls of the containing vessel, but maintain a constant average velocity. The molecules of the gas must therefore behave like perfectly elastic spheres, which rebound after collision without any dissipation of energy in the form of heat. It is well known, of course, that molecules are not mere solid lumps of matter, but have a very complex structure. If, however, no chemical or physical change is produced by the impact, the interior arrangement of the molecules persists, and it is sufficiently accurate to regard them as behaving like hard, perfectly elastic spheres.

Gas pressure explained by the kinetic theory.—If we could follow the path of a single molecule in a gas, we should find that it moves in a straight line until it meets another molecule, when its direction suddenly changes. Its path would, therefore, be an irregular zigzag, made up of a series of straight lines. Not only must the direction of motion vary, but also the speed at which the molecule is moving, since at one moment it may be moving rapidly and then after a collision be brought almost to a standstill.

It can be shown by mathematical reasoning that it is sufficient to consider only the average velocity of the whole group of molecules, provided that this average is calculated in a special way. Suppose there are n molecules which at a given instant have velocities c_1, c_2, c_3, ... c_n; then this special kind of average, which is called the **root mean square velocity** is given by the formula:

$$c = \sqrt{\frac{1}{n}(c_1^2 + c_2^2 + c_3^2 \ldots + c_n^2)},$$

where the symbol c is used to signify this average velocity.

Since the gas molecules are perfectly elastic, the time occupied by a collision is negligible compared with the time in which the molecules are moving in a straight line. There is also a great deal of evidence to show that the volume of the molecules themselves is very small compared with the volume occupied by the gas. Thus 1 c.c. of water at 100° gives 1700 c.c. of steam at the same temperature, so that the volume of the water molecules is certainly less than 1/1700 of the volume occupied by the steam. Hence in discussing the effect of the gas molecules on the walls of the containing vessel, we can neglect the influence of the collisions between molecules in the interior of the vessel, and suppose that each molecule moves in a straight line from one wall to another, and is then reflected back again.

Suppose we have n molecules of gas contained in a cubical vessel of side l cm. Let the mass of each molecule be m, and let c be the root mean square velocity. This is represented in magnitude and direction by OK in Fig. 3. This velocity can be regarded as made up of three component velocities, x, y, and z,

parallel to the sides of the cube; and these are related to c by the equation:

$$c^2 = x^2 + y^2 + z^2.$$

Now suppose that the particle starts with a velocity x from the face $EFGH$. It will strike the face $ABCD$ and be reflected back again in the opposite direction. Just before colliding with $ABCD$ its momentum is mx; and after the collision it is $-mx$, since the particle is moving in the opposite direction. Hence the change of momentum during each collision is $2mx$. The force exerted on the walls is measured by the rate of change of momentum. Now the molecule is moving with velocity x, and no time is wasted in collisions, so that it will strike the face $ABCD$, or the opposite face, x/l times per second. Hence the change of momentum per second (which gives the force exerted on these two faces) is

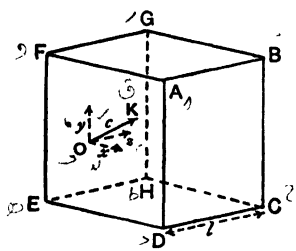


FIG. 3.—Diagram to illustrate the kinetic theory of gases.

$$2mx \times \frac{x}{l} = \frac{2mx^2}{l}.$$

Similarly, if the particle had only the component y of its velocity, it would exert a force of $2my^2/l$ on the faces $ABGF$ and $CDEH$; and if it had only the velocity component z, it would exert a force of $2mz^2/l$ on the faces $ADEF$ and $BCHG$. Adding these, the total force exerted by one molecule on all six faces of the cube is

$$f = \frac{2m}{l}(x^2 + y^2 + z^2) = \frac{2mc^2}{l}.$$

If n particles are present, we can, as we have seen, neglect the effect of interior collisions so far as effects on the wall are concerned, and suppose each particle to behave as if the others were not there. The *total force* on the walls due to n particles is therefore $\frac{2nmc^2}{l}$, where c is now the *root mean square* of all the individual velocities. Hence the pressure (or force per unit area) exerted by n molecules will be given by dividing this quantity by

the area of the six faces, $6l^2$. We thus obtain the fundamental equation

$$p = \frac{2nmc^2}{6l^2 \times l} \quad \text{or} \quad pv = \tfrac{1}{3}nmc^2. \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

since $l^3 = v$, the volume of gas in the cube.

The gas laws explained by the kinetic theory.—(*a*) *Boyle's Law.*—The quantities on the right-hand side of equation (1) are n and m, the number and mass of the gas molecules (which are constant) and the root mean square velocity c. If the gas is at constant temperature in a closed vessel, it neither gains nor loses energy, so that the mean square velocity c^2, and therefore the root mean square velocity c, must remain constant. Equation (1) may therefore be written

$$pv = \text{constant (at constant temperature).}$$

We have thus deduced **Boyle's Law** from the kinetic theory of gases.

(*b*) *Charles's Law.*—The average kinetic energy of the molecules is $\frac{1}{2}nmc^2$. Writing for this the symbol E, we have

$$pv = \tfrac{1}{3}nmc^2 = \tfrac{2}{3}E.$$

But $pv = RT$ for 1 gram-molecule ;

$$\therefore \; E = \tfrac{3}{2}RT,$$

or *the kinetic energy of the gas-molecules is proportional to the absolute temperature.* This is the interpretation of **Charles's Law** in terms of the kinetic theory, which therefore gives us a new definition of the **temperature** of a gas, as a quantity which may be measured by the average kinetic energy of the molecules.

(*c*) *Avogadro's hypothesis.*—If we take equal volumes of two gases at the same pressure and temperature, and allow them to mix together, there is in most cases no change of temperature. Hence the average kinetic energy of the molecules must be the same for each gas. If these equal volumes contain, in the case of one gas, n_1 molecules of mass m_1 and velocity c_1, and, in the case of the other gas, n_2 molecules of mass m_2 and velocity c_2, then, since the kinetic energies are the same

$$\tfrac{1}{2}m_1c_1^2 = \tfrac{1}{2}m_2c_2^2. \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Also since equal volumes at the same pressure were taken

$$p_1v_1 = p_2v_2$$

and therefore $\frac{1}{3}n_1m_1c_1^2 = \frac{1}{3}n_2m_2c_2^2$. .....(3)

Dividing (3) by (2), we find that

$$n_1 = n_2,$$

or that *equal volumes of different gases at the same temperature and pressure contain the same number of molecules*, which is **Avogadro's hypothesis.**

(*d*) *Graham's law of diffusion.*—The rate at which gases diffuse through a porous plug, or escape from a small orifice, was studied by Graham, who found that the rate of diffusion varied inversely as the square root of the density of the gas. It is obvious that the rate of diffusion will depend upon the velocity with which the molecules are moving.

Since $pv = \frac{1}{3}nmc^2$, it follows that $c^2 = \frac{3pv}{nm}$, and, since the density d is equal to the weight per unit volume,

$$d = \frac{nm}{v}; \quad \therefore c^2 = \frac{3p}{d} \quad \text{and} \quad c = \sqrt{\frac{3p}{d}}.$$

Thus, at constant pressure and temperature *the velocity of the gas molecules is inversely proportional to the square root of the density.* The kinetic theory of gases therefore accounts for **Graham's law of diffusion.**

(*e*) *Mean velocity of molecules.*—The mean velocity of the molecules of a gas can be calculated from this equation by putting in the values of p and d for a particular gas. To get the velocity in centimetres per second, we must express p and d in absolute units. Thus oxygen at 1 atmosphere pressure and 0° C. has a density of 1·429 grams per litre.

p = 1 atm. = 76 cm. of mercury
= 76 × 13·6 × 981 dyn./sq. cm.
= 1,014,000 dyn./sq. cm.

d = 1·429 gm./lit. = 0·001429 gm./c.c.

$$\therefore c = \sqrt{\frac{3 \times 1{,}014{,}000}{0{\cdot}001429}}$$

= 46,100 cm./sec.
= 0·3 miles per second.

Similarly the mean velocity of the hydrogen molecule at 0° is calculated to be 192,000 cm./sec. or 1·2 miles per second.

Specific heats of gases.—We have seen already (p. 15) that the kinetic energy of a gas molecule is proportional to the absolute temperature, and that the kinetic energy per gram molecule is given by $E = \frac{3}{2}RT$.

If therefore a gram-molecule of a gas is heated in a closed vessel from T to $T+1$ degrees, the kinetic energy increases from $\frac{3}{2}RT$ to $\frac{3}{2}R(T+1)$, an increase of $\frac{3}{2}R$ or 3 calories (since $R = 2$ calories approximately).

The **molecular heat** of a gas is defined as the amount of heat required to raise one gram-molecule through 1° C. If the effect of heat is only to increase the energy of translation of the molecules, then the **molecular heat at constant volume** C_v should be 3 calories for all gases. It must be remembered, however, that molecules are complex systems and consist in many cases of several atoms, which may possess other forms of energy, due to rotation of the molecules or vibrations of parts of the molecule. If this is the case, then an extra amount of heat will be used up in increasing the amplitude of these rotations or vibrations, or generally speaking in doing internal work on the molecules. If this amount of work is represented by x units of heat, then the molecular heat at constant volume will be

$$C_v = 3 + x,$$

where x will vary from one gas to another, and will be large for complex molecules.

If the gas is heated at *constant pressure*, instead of at *constant volume*, then it expands during the heating. If we imagine the gas to be in a vessel closed by a piston held down by a pressure p, the piston will be pushed up and an extra amount of work done by the gas.

Since $$V = \frac{RT}{p},$$

the expansion of one gram-molecule heated through 1° C. is $V/T = R/p$; and since the gas expands against a constant pressure p, the work done in expansion is given by the relation

$$\textit{work done} = \textit{pressure} \times \textit{increase of volume}$$

$$= p \times \frac{R}{p} = R = 2 \text{ calories.}$$

Hence the **molecular heat at constant pressure** C_p for one gram-molecule of an ideal gas is $3+2=5$ cal. As before, however, we have neglected the heat used up in doing internal work on the gas molecules, and more generally we should write

$$C_p = 5 + x \text{ calories.}$$

The ratio C_p/C_v of the heat-capacities of the gas at constant pressure and at constant volume is often indicated by the symbol γ, so that

$$\gamma = \frac{C_p}{C_v} = \frac{5+x}{3+x}.$$

If $x=0$, $\gamma = 5/3 = 1{\cdot}667$. As x increases, this ratio gets smaller and smaller, and, for very large values of x, γ becomes nearly unity.

Table 2 contains some of the experimental values found for the molecular heats of gases.

TABLE 2. MOLECULAR HEATS OF GASES.

Gas.	Formula.	C_p.	C_v.	C_p/C_v.
Helium	He	4·97	2·98	1·67
Argon	A	4·97	2·98	1·67
Hydrogen	H_2	6·86	4·87	1·41
Oxygen	O_2	7·04	5·04	1·40
Nitrogen	N_2	6·925	4·929	1·41
Carbon monoxide	CO	6·94	4·94	1·40
Chlorine	Cl_2	8·04	5·93	1·36
Carbon dioxide	CO_2	8·79	6·75	1·30
Ammonia	NH_3	8·74	6·67	1·31
Acetylene	C_2H_2	8·88	6·83	1·28
Ethylene	C_2H_4	10 25	8·20	1·25
Ethane	C_2H_6	11·47	9·40	1·22

It will be seen that the values of C_p and C_v for helium and argon agree closely with the predicted values of 5 and 3 calories respectively. The heat applied to raise the temperature of these gases is therefore expended in increasing the translational velocity of the molecules, and not in increasing their internal energy. Other monatomic gases such as the vapours of mercury and of the alkali metals behave in the same way. The diatomic gases have larger values of C_p and C_v, but the external work x

still amounts to about 2 calories; the ratio γ therefore falls, *e.g.* to $7/5 = 1{\cdot}40$, whilst for triatomic molecules the typical value is $8/6 = 1{\cdot}33$. For more complex gas molecules the value of γ tends towards unity, indicating that the heat expended within the molecule is very large compared with the external work done by the expanding gas.

According to Maxwell's principle of **equipartition of energy**, each degree of freedom calls for an equal increment of internal energy. A single atom, which behaves as a moving point, has only 3 degrees of freedom, corresponding to movement of *translation* along the axes, x, y and z; but a rigid diatomic molecule, behaving like a line joining two points, has also 2 degrees of freedom of *rotation*, making 5 in all. The heat expended within the molecule, which is 3 cal. per gram-molecule for 1° C. for a monatomic molecule, is therefore 5 cal. for diatomic molecules and rises to 6 cal. for triatomic molecules, with their 3 degrees of freedom of rotation. Higher molecular heats than this are attributed to degrees of freedom depending on intramolecular *vibration*, but this effect is small at low temperatures, when C_v tends towards a uniform value of 6 cal.

Number, mass, and dimensions of molecules.—The number of molecules in a gram-molecule of a gas is indicated by the symbol N, and is named the **Avogadro Number**. It has been determined with considerable accuracy by several different methods and has the value $0{\cdot}6062 \times 10^{24}$. It is difficult to obtain any idea of the significance of such an enormous number. Suppose we have a gas at a pressure of only a millionth of a millimetre of mercury (which is the vacuum attained in an electric light bulb), then each cubic millimetre of the attenuated gas still contains more than 30 million molecules.

In view of the extremely small size of atoms and molecules it is convenient to use a special system of units to describe their physical constants. Such a system can be based very conveniently on the **Ångström unit of length**, 1×10^{-8} cm., as used in measuring the wave-length of light. The Ångström unit of area is then 10^{-16} cm.^{2} and the unit of volume is 10^{-24} c.c. In this system the natural unit of mass is 10^{-24} grams.

The mass of a single molecule can be expressed very

conveniently in this system of units. Thus, from the known magnitude of the Avogadro number, 1 gram-molecule of any substance contains $0{\cdot}6062 \times 10^{24}$ molecules. The mass of a single molecule is therefore

$$\frac{M}{0{\cdot}6062 \times 10^{24}} \text{ grams} = 1{\cdot}65M \text{ Ångström units,}$$

where M is the molecular weight of the substance. In the same way the mass of a single atom is $1{\cdot}65A$, where A is the atomic weight of the element. Thus an individual atom of oxygen has a mass of $1{\cdot}65 \times 16 = 25{\cdot}4$; and a molecule of oxygen has a mass of $1{\cdot}65 \times 32 = 52{\cdot}8$ Ångstrom units.

Approximate values for the diameter of a molecule can be calculated from the density of a substance in the solid state. Thus solid oxygen has a density of 1·43 grams per c.c. at −225°C. Hence 32 gm. has a volume of $32 \div 1{\cdot}43 = 22{\cdot}4$ c.c. Dividing this by Avogadro's number, the volume of each molecule cannot be greater than $\frac{22{\cdot}4}{0{\cdot}6062 \times 10^{24}} = 37 \times 10^{-24}$ c.c. or 37 Ångström units of volume. If we take the cube root of this, the diameter of the oxygen molecule is approximately $3{\cdot}3 \times 10^{-8}$ cm. or 3·3 Å.U. This is obviously only a rough value; more accurate figures can be deduced from measurements of the viscosity of gases and the table below gives some of the values found in this way.

TABLE 3. MOLECULAR DIAMETERS.

Argon	A	$2{\cdot}9 \times 10^{-8}$ cm.
Krypton	Kr	2·69 ,,
Nitrogen	N_2	3·3 ,,
Oxygen	O_2	3·0 ,,
Hydrogen bromide	HBr	2·76 ,,
Seleniuretted hydrogen	H_2Se	2·93 ,,
Arsine	H_3As	3·17 ,,

From these numbers it will be seen that molecules are very small entities indeed. It would take 3 million nitrogen molecules placed side by side to form a line 1 mm. in length. The precision with which these minute dimensions are known may be contrasted with the rough illustration given by Lord Kelvin many years ago of the smallness of molecular magnitudes,

namely, that if a drop of water were magnified to the size of the earth, the molecules would appear to be larger than small shot but smaller than cricket balls.

QUESTIONS ON CHAPTER I.

1. What are the laws deduced from the behaviour of gases under varying conditions of temperature and pressure? How is this behaviour to be explained? (Inter. Sci., Sheffield.)

2. State Charles's Law. Describe an instrument that employs this principle to measure temperature and explain how it is used.

Chlorine for sterilising drinking water is supplied under pressure in steel cylinders. A medical text-book gives the pressure in such cylinders as 54 lb. per square inch at 32° F. and 216 lb. per square inch at 122° F. If this be so, does chlorine behave as a perfect gas? (Inter. Sci., Manchester.)

3. In what manner are the specific heats of gases affected according as the experiments are carried out at constant pressure or at constant volume? How is the ratio of the two specific heats connected with the atomicity of a gas? (Cambridge Schol.)

4. How may the states of matter be classified? Illustrate your answer by reference to sulphur and water. (Cambridge Schol.)

5. What is Graham's Law of Diffusion? Show how advantage is taken of this law in the determination of the relative densities of gases.

The speeds of diffusion of carbon dioxide and ozone were found by Soret to be as 0·29 is to 0·271. The relative density of carbon dioxide is 22 when H = 1. What is the relative density of ozone? (Inter. Sci., Bombay.)

6. "The molecular weight of a substance is numerically equal to the weight in grams of it which occupies in the state of vapour 22·4 litres at 0° and 760 mm."

Give the experimental facts and reasoning on which this statement is based.

(Oxford and Cambridge Schools Examination Board.)

7. Calculate the average velocity and kinetic energy of a molecule of carbon dioxide at 0° C. and 1000° C., given that $R = 0{\cdot}0821$ litre-atmospheres, and Avogadro's number

$$N = 0{\cdot}606 \times 10^{24}.$$

CHAPTER II.

LIQUEFACTION.

2. Liquefaction and Vaporisation.

i. Observation of critical phenomena.—Select a piece of soft glass tube about 15 cm. long and 3-4 mm. internal diameter. Seal and round off one end, taking care that the rounded end has even walls of the same thickness as the tube. Make a constriction about 5 cm. from the open end of the tube. Fill to above the constriction with ether and fit a short length of rubber tubing, closed by a spring clip, on to the open end of the glass tube (Fig. 4). Heat the lower part of the tube in a beaker of hot water so that the ether boils away gently. When the space below the constriction is rather more than half full of ether, close the clip, and seal off the glass tube at the constriction in a small blow-pipe flame. In this way a glass tube of sufficient strength containing only ether and its vapour is obtained.

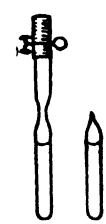


Fig. 4.—Apparatus for observing critical phenomena.

Support the tube vertically in a wire holder behind a glass screen and heat it gently by brushing a Bunsen flame up and down it. Note how the meniscus flattens as the temperature rises, and disappears suddenly when the critical temperature is reached. Allow to cool. When the temperature falls below the critical temperature, a cloud of mist suddenly appears in the tube, and rapidly settles to form a liquid layer.

ii. Preparation and use of solid carbon dioxide.—(*a*) Support a cylinder of carbon dioxide so that the nozzle is lower than the base of the cylinder. Make a cylinder of blotting paper about 4 cm. diameter and 40 cm. long and support this below the nozzle by means of a bag constructed of two dusters sewn together (Fig. 5). Open the valve rapidly so that the liquid

carbon dioxide escapes and cools itself by evaporation. In about a minute the paper cylinder will be found to contain a solid mass of carbon dioxide snow. (This simple device gives better results than the metal apparatus sometimes supplied for the purpose.)

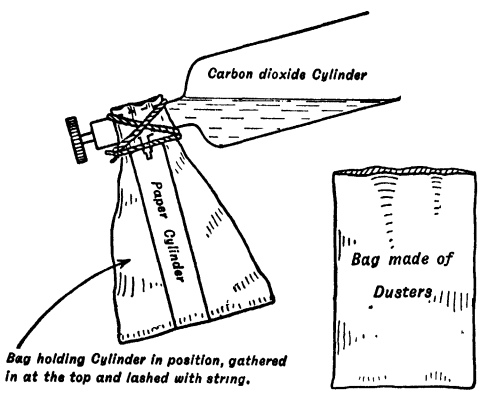


FIG. 5.—Preparation of solid carbon dioxide.

Transfer the snow by means of a wooden scoop to a beaker packed in cotton wool, to a thermos flask, or to a Dewar vessel provided with a vacuum-jacket. Temperatures down to $-70°$ or $-80°$ can be maintained for some time by half-filling a Dewar vessel with petrol, and then adding solid carbon dioxide till the desired temperature is attained. The gain of heat through the vacuum-jacket is so small that the temperature can be kept constant within $\pm 1°$ C. by adding a little more solid carbon dioxide from time to time. This type of cooling-bath is often employed in experiments on the properties of liquefied gases or on reactions at low temperatures.

The solid carbon dioxide may be handled lightly without any ill effects, since the rapid evolution of gas from its surface prevents any real contact with the skin; if, however, a piece of the solid is gripped firmly, it will cause a "burn," since it freezes the water in the surface-cells and thus damages the tissues.

(*b*) Pour ether or petrol on to the snow and stir with a glass or wooden rod until a paste is formed. Plunge into this paste a test-tube containing about 1 c.c. of mercury. In a few seconds the mercury will be frozen hard, and if the tube is struck with a hammer the glass will break away and the solid mercury can be hammered out to the form of a disc.

DEVIATIONS FROM THE GAS LAWS.

The ideal or perfect gas.—Accurate measurements of the volumes occupied by a gas at different temperatures and

pressures show that the laws of Boyle and Charles are only approximately true. The ideal gas, which would obey both of these laws exactly, is called a **perfect gas.** Two properties of this ideal gas may be specially noted.

(i) If a perfect gas were cooled at constant pressure, its volume would decrease continuously, and become zero at $-273°$ C. No known gas behaves in this fashion, since when cooled sufficiently all real gases contract suddenly to a much smaller volume and change into the liquid state.

(ii) Again, a perfect gas could be compressed (as well as expanded) to an indefinite extent in the manner predicted by Boyle's Law. Thus, every time the pressure was doubled the volume would be halved, however small it might already be. Real gases, however, are found to be less compressible when the volume is already small and the density high, than when the volume is large and the density small. They therefore show a marked deviation from Boyle's Law, quite apart from the fact that (if the temperature is not too high), the gas may change suddenly into a liquid when a certain pressure is reached.

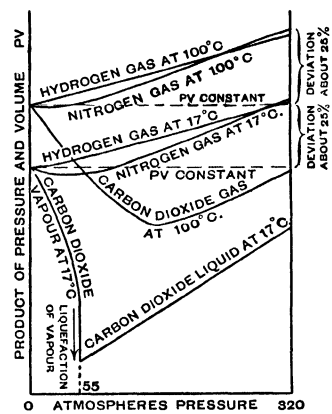


FIG. 6.—Deviations from Boyle's Law.

Deviations from the gas laws are specially marked when the conditions approach those at which liquefaction occurs, namely, at low temperatures and high pressures. On the other hand, most gases approximate in behaviour to a perfect gas at high temperatures and low pressures.

For a perfect gas at constant temperature, pv should have the same value at all pressures, as shown by the horizontal straight lines in Fig. 6, in which pv is plotted against p. All known gases, however, show deviation from Boyle's Law and consequently do not give a constant value for pv. The manner

in which pv varies with the pressure for some gases is shown by the curves in Fig. 6.

Deviations at moderate pressures.—(*a*) *Deviations from Boyle's Law.*—Let us consider first the nature of the deviations from Boyle's Law at pressures of a few atmospheres, as shown by the left-hand end of the curves. At very low pressures the deviations are negligible. At pressures of a few atmospheres the deviations are shown by the initial slope of the curves. Thus for hydrogen, pv increases as p increases, whilst for nitrogen and carbon dioxide pv decreases as p increases.

If therefore, we take equal volumes of a number of gases at a very low pressure (*i.e.* a pressure at which they behave as perfect gases), and then raise the pressure to one atmosphere, the gases will not all have the same volume. Some gases, like hydrogen, will occupy a greater volume than a perfect gas would at this pressure, whilst others, like nitrogen and carbon dioxide, will have a smaller volume.

Gases, such as nitrogen and carbon dioxide, which are more compressible than an ideal or perfect gas, are described as **under-perfect gases.** Gases like hydrogen, which are less compressible than a perfect gas, are described as **over-perfect gases.** The imperfectness of a gas can be expressed by means of a constant λ, which represents the initial slope of the curve in Fig. 6. Thus, the volume occupied by a gas at a pressure of 1 atmosphere will be $\frac{1}{1+\lambda}$ times the volume which a perfect gas would occupy. Table 4 gives the values of λ for a number of gases deduced from an accurate study of pv at low pressures.

TABLE 4. RELATIVE VOLUMES OF GASES AT NORMAL TEMPERATURE AND PRESSURE.

	λ	Relative Volumes at N.T.P.
Helium - - -	−0·00013	1·00013
Hydrogen - -	−0·00062	1·00062
Nitrogen - - -	+0·00051	0·99949
Oxygen - -	+0·00075	0·99925
Carbon monoxide -	+0·00077	0·99923
Carbon dioxide -	+0·00682	0·99322
Sulphur dioxide -	+0·02601	0·97465

(*b*) *Deviations from Avogadro's Law.*—The last column of Table 4 gives the relative volumes occupied by these gases if *equal* volumes were taken at a very low pressure and the pressure then raised to one atmosphere. From this table it can be seen that *Avogadro's hypothesis is only approximately true for gases at atmospheric pressure.* The statement that "equal volumes of gases at the same temperature and pressure contain the same number of molecules," is therefore strictly true only at those very low pressures at which real gases behave as perfect gases.

(*c*) *Deviations from Gay Lussac's Law of Volumes.*—Gay Lussac's *Law of Combining Volumes*, when accurately investigated, is also found to be only approximately true, since gases at ordinary pressures do not combine together in ratios which are exactly whole numbers. Thus Morley found that 2·00274 volumes of hydrogen at N.T.P. combine with 1 volume of oxygen to form water. This ratio could, however, be predicted from the data of Table 4, as follows. Suppose we took exactly two volumes of hydrogen and one volume of oxygen at some very low pressures at which the gas laws are strictly true, and then raised the pressure to one atmosphere. From the data in Table 4 the relative volumes become

$$\frac{2 \times 1{\cdot}00062}{1 \times 0{\cdot}99925} = 2{\cdot}00272.$$

This is, however, almost exactly the figure that Morley obtained experimentally at atmospheric pressure. Since the deviation from Gay Lussac's law is accounted for exactly by the deviations from Boyle's Law, we can assume that at very low pressures the law of combining volumes would be strictly true, like Avogadro's hypothesis, from which it can be deduced.

Deviations at high pressures.—It will be seen from the curves in Fig. 6 that pv for hydrogen increases continuously as the pressure rises. For nitrogen pv first decreases, then passes through a minimum, and rises again, until at about 300 atmospheres both hydrogen and nitrogen give values of pv which are 25 per cent. greater than that which would be given by a perfect gas. The effect of temperature on the form of the curve is

important. Thus at 17° the curve for nitrogen shows a more clearly marked minimum than at 100°. This effect is still more clearly seen in the case of carbon dioxide, which shows a deep depression at 100°, whilst at 17° a sudden decrease occurs at 55 atmospheres, at which pressure the gas liquefies.

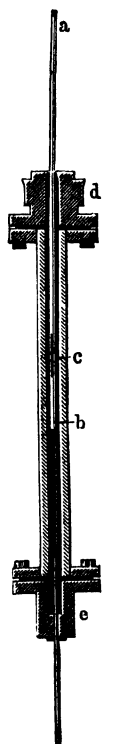


FIG. 7.—Andrews' apparatus for measuring the critical pressure of carbon dioxide

Thus the minimum becomes more clearly marked as the conditions under which liquefaction occurs are approached; and even gases such as hydrogen and helium, which at ordinary temperatures give a continuous increase of pv with p, if examined at very low temperatures, give curves of the same type as those shown for carbon dioxide at ordinary temperatures. The deviations from the gas laws are therefore intimately connected with the process of liquefaction of a gas.

The critical state.—The precise conditions under which a gas can be converted into a liquid were first defined by Andrews in 1869, as a result of a detailed study of the influence of pressure and temperature on the volume of carbon dioxide. Andrews' apparatus is shown in Fig. 7. The volume of the gas was measured in the strong capillary tube *a* in which it was confined by a mercury thread *c*. The lower end of the tube *b* opened into water contained in the outer water-tight case of the apparatus. By screwing in the plunger at *e* the water was compressed, and pressures up to 400 atmospheres could thus be applied to the gas in the tube. The pressure was measured by means of a similar tube, containing air, which was fitted into the same reservoir of water. Since pv for air was known accurately over a large range of pressures, the common pressure in the two tubes could be calculated from observations of the volume of the air. The upper part of the tube containing the carbon dioxide was surrounded by a bath maintained at a

suitable temperature and a series of observations of p and v at a number of temperatures was made.

The curves obtained by plotting pressure against volume for a fixed quantity of gas at one temperature are called **isotherms**. Fig. 8 shows a number of isotherms for carbon dioxide. For

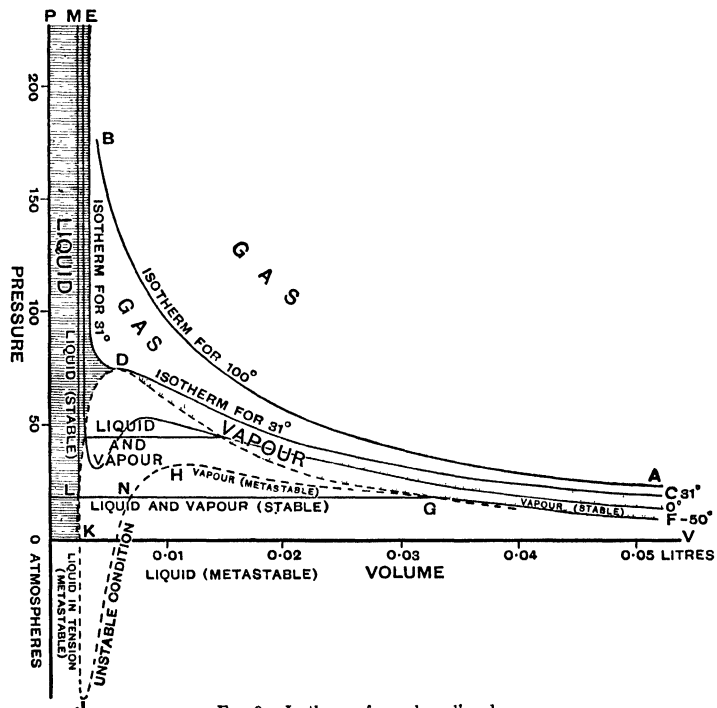


FIG. 8.—Isotherms for carbon dioxide.

a perfect gas at constant temperature pv is constant and hence the isotherm should be a rectangular hyperbola. At 100° carbon dioxide gives the isotherm AB which has nearly the correct shape. At lower temperatures the curve droops below the ideal hyperbola for large values of p and this drooping is more marked the lower the temperature. Above 31° no separation of liquid can be detected even at the highest pressure. At 31° the isotherm has the form CDE and at D the gas liquefies.

Below 31° the curves are no longer continuous, but exhibit sudden breaks which divide them into three portions. Thus *FG* represents the progressive decrease in volume as the gas is compressed at −50°. At *G* a liquid layer separates, and when further compression is attempted the only effect is to convert more of the gas into liquid. The pressure therefore remains constant until all the gas has been liquefied and a large contraction in volume has taken place. This large change of volume at constant pressure is represented by the horizontal line *GL*. Then, since liquids are not easily compressed, further contraction in volume is only brought about by the application of high pressures. The remainder of this isotherm, *LM*, is therefore a steeply ascending curve.

Above 31° liquid is never formed, no matter how great the pressure, whilst below this temperature liquid is formed at some definite pressure and the isotherms exhibit a horizontal portion, representing the change from the gaseous to the liquid state. At low temperatures the pressure at which liquefaction occurs is low, and the contraction in volume when the gas is liquefied is large. As the temperature increases the pressure at which liquefaction occurs becomes greater. At the same time the difference in density (or in molecular volume) of the liquid and its saturated vapour becomes steadily less, mainly because of a progressive increase in the density of the saturated vapour. The length of the horizontal portion of the isotherm therefore diminishes steadily as the temperature is increased. Finally, at 31° the length of the horizontal portion of the isotherm is reduced to zero, so that the isotherm is only horizontal for a moment at *D*.* The isotherms for higher temperatures, at which no liquefaction takes place, show no horizontal portion.

For carbon dioxide, then, 31° is the upper limit of temperature at which the gas can be liquefied by pressure. Other gases behave in the same manner, and for each gas there is a special temperature above which it cannot be liquefied by any pressure

* At this point, a horizontal line would form an " osculating tangent " to the curve, *i.e.* it would pass through *three* consecutive points on the curve at *D*, just in the same way as an ordinary tangent passes through *two* consecutive points.

however great. This temperature is called the **critical temperature**; the pressure required to cause liquefaction at the critical temperature is called the **critical pressure**; and the volume of one gram-molecule of the substance at the critical temperature and pressure is the **critical volume.** These three critical constants play a very important part in the theoretical discussion of the properties of liquids and gases. The constants for some gases which have been studied accurately are therefore given in Table 5, in which the critical temperature, pressure and volume are indicated by the symbols T_c, P_c, and V_c.

TABLE 5. CRITICAL CONSTANTS.

Substance.	T_c°C.	P_c atm.	V_c litres.	$\frac{RT_c}{P_cV_c}$.
Helium - -	−268°	2·26	0·061	3·04
Hydrogen - -	−241°	13·4	0·061	3·21
Nitrogen	−146°	34	0·087	3·52
Oxygen - - -	−118°	50	0·074	3·44
Carbon dioxide -	+31°	73	0·096	3·56
n-Pentane - -	197°	33	0·310	3·77
Carbon tetrachloride	283°	45	0·276	3·67
Benzene - -	288°	48	0·256	3·75
Chlorobenzene -	359°	45	0·308	3·75
Methyl alcohol -	240°	78	0·117	4·61
Water - - -	374°	218	0·056	4·35
Acetic acid - -	322°	57	0·171	5·01

Determination of critical constants.—(*a*) **Critical temperature.**—An approximate value for the critical temperature can be found by sealing up a quantity of liquid and vapour in a strong glass tube and heating it in a suitable bath. At the critical temperature the surface between liquid and vapour flickers and disappears. If the tube is then cooled again to the critical temperature, a turbidity appears in the gas, which is quickly dispersed by the settling of liquid to the bottom of the tube and the reappearance of the meniscus. (Expt. 2, i.)

(*b*) **Critical pressure.**—The critical pressure may also be determined by a modification of this experiment due to Cagniard de la Tour, in which the liquid occupies one limb of a strong closed U-tube (Fig. 9), and is separated from a quantity of

air in the other limb by a column of mercury. From observations of the volume of the air in the left-hand limb when the critical temperature is reached, the pressure within the tube (*i.e.* the critical pressure) can be calculated.

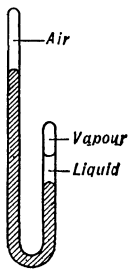


FIG. 9.—Apparatus for measuring critical pressure

(*c*) **Critical volume.**—The accurate determination of the critical volume is a much more difficult matter, since at the critical temperature a small change in pressure causes a large change in volume. The best method of determining this constant is due to Amagat. It makes use of the fact that the mean of the densities of the liquid and of its saturated vapour varies much less rapidly than the individual values of these two densities. The experimental method depends, therefore, on measuring the densities of liquid and vapour at a series of temperatures approaching the critical temperature, and plotting these two densities against the temperature.

Amagat found that when lines were drawn connecting the points which represent the density of liquid and vapour at the same temperature, the middle points usually fell on a straight line, which was termed by Amagat the **rectilinear diameter** of the curve. By extending this line to the critical temperature, and reading off the corresponding value of the density, the critical density and therefore the critical volume can be determined.

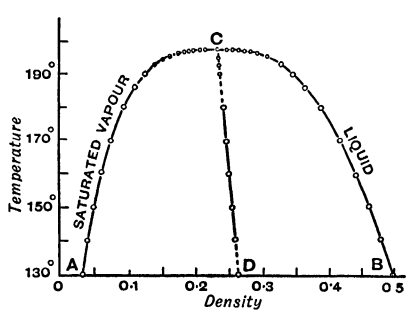


FIG. 10.—Diagram to illustrate the determination of critical volumes.

In Fig. 10 the densities of the liquid and vapour of *n*-pentane are plotted against the temperature. The left-hand branch *AC* of the curve shows the density of the saturated vapour, which increases as the temperature rises. The right-hand branch *BC*

shows the decrease in the density of the liquid as the critical point is approached. The two curves meet at the critical point, since the liquid and its saturated vapour then become identical in all respects, and must, therefore, have the same **critical density.** This critical density is given by the intersection of the rectilinear diameter DC with the continuous curve ACB, or, more simply, by extrapolating the rectilinear diameter to the known critical temperature of the substance.

CONTINUITY OF STATE.

Identity of the liquid and gaseous states at the critical temperature.—At the critical temperature, the density of the liquid becomes the same as that of the saturated vapour. All the other properties that can be examined in the two states also become identical at the same point. We can therefore assert that *at the critical temperature the liquid and vapour become identical in all respects.*

One characteristic property of a liquid is its surface tension (see Chap. III.). This property tends to diminish the free surface of a liquid, and therefore to draw the liquid together into round drops. It also causes the liquid to rise in a capillary tube which is wetted by the liquid, or to be depressed if (like mercury) it does not wet the tube. Since the surface tension of a liquid decreases as the temperature rises, the "meniscus" or curved surface of the liquid gets flatter and flatter as the temperature is raised. Moreover, since very little work has to be done in increasing the surface between the two layers, the boundary becomes unsteady and irregular as the critical temperature is approached. Finally, when the critical temperature is reached, the surface tension becomes zero and the meniscus which forms the boundary between liquid and vapour disappears completely.

Continuity of liquid and gaseous states.—In the series of changes described above, liquid and vapour both pass at the critical temperature into a permanent gas, which cannot be liquefied by pressure alone. In this process they become identical, but without any abrupt change in the properties either of the liquid or of the vapour. It is therefore possible,

by making use of a suitable series of changes, to convert a liquid entirely into vapour or vice versa, *without any separation into two layers or any discontinuity in physical properties.*

Thus, suppose we have liquid carbon dioxide at $-50°$ and 230 atmospheres (point M in Fig. 8, p. 29). This material is undoubtedly in the liquid state, for if we lower the pressure to about 20 atmospheres without altering the temperature, a layer of vapour begins to separate from it at the point represented by L. If, however, we keep the pressure constant at 230 atmospheres and raise the temperature to 100° C., the resulting change must be represented by a horizontal movement on the diagram from M to a point on the prolongation of the curve AB. This change of conditions, therefore, produces an increase of volume, but it is not accompanied by any abrupt change in any of the physical properties of the material. If, however, the pressure is now lowered, after increasing the temperature to 100° C., the substance expands continuously along BA and at A is found to have all the properties of gaseous carbon dioxide.

We have, therefore, converted a liquid into a gas without at any stage producing an abrupt alteration of properties, or causing the material to separate into two distinct layers. Obviously, by reversing these processes, we could convert a gas into a liquid in such a way that it would be impossible to detect at what point (if any) the material had changed from one state to the other.

This phenomenon is described as **continuity of state.** In practice, we generally describe as **vapour** any gas which can be liquefied by pressure alone, without lowering the temperature. Gases which cannot be so liquefied are described as **permanent gases.** We can, therefore, say that at 31° the *liquid* and *vapour* of carbon dioxide both become *gas*, and that whilst the change from liquid to vapour is always abrupt (except at the critical temperature), there is no physical change involved in the conversion of liquid or vapour into gas on raising the temperature through the critical point, or in the conversion of gas into liquid or vapour on cooling the material through the critical point. This distinction is illustrated in Fig. 8 by dividing the diagram into areas labelled "gas," "vapour," "liquid," and "liquid and vapour."

Van der Waals' equation of state.—The kinetic theory of gases outlined in the previous chapter involves two assumptions which are nearly true at low pressures and high temperatures. It is supposed (i) that the volume of the molecules is very small compared with the volume occupied by the gas, and (ii) that the molecules do not attract or repel one another.

(i) When a gas is compressed, the volume occupied by the molecules becomes an appreciable fraction of the total space occupied by the gas. The space in which the molecules can move about is therefore less than the total volume V occupied by the gas. Van der Waals allowed for this diminution of the free space by writing the gas-equation

$$p(V-b)=RT,$$

where b is a function of the volume of the molecules and is assumed to be constant for a particular gas. This correction then merely substitutes for the volume V a diminished volume, $V-b$, which represents the free space between the molecules instead of the total space occupied by them.

(ii) Since every known gas can be condensed to a liquid or solid, *e.g.* by cooling or compression or both, it is evident that there must be a force of attraction between the molecules. Indeed, apart from the existence of such a force, we should be quite unable to explain why a gas should break up on cooling into a denser layer of liquid and a lighter layer of vapour, instead of remaining homogeneous. The cohesion of solids also shows clearly that molecules which are close together attract one another, and require a considerable force to separate them.

Very little is known of the laws which govern the variation of molecular attraction with distance ; but this attraction certainly falls off very rapidly indeed as the molecules are separated from one another. Thus, it has been suggested, as a rough approximation, that the force varies inversely as the *tenth* power of the distance. The attraction between molecules which are separated by a distance greater than their diameter is therefore very small ; and in discussing the effect of this attraction on the pressure and volume of a gas, it is only necessary to consider the behaviour of adjacent molecules.

Consider a molecule at some little distance from the walls of the containing vessel. It will be acted upon by all the surrounding molecules which are near enough to attract it; but, since it is completely surrounded by other molecules, these attractions neutralise one another and do not tend to move the molecule in any definite direction. A molecule near the wall of the container is not surrounded completely by gas molecules, and has more molecules tending to pull it inwards than outwards. Hence the effect of the mutual attraction of the molecules is equivalent to an increase of pressure, since it tends to cause a contraction in volume. This extra pressure is sometimes termed the **internal pressure** of the gas. Van der Waals supposed that the internal pressure was proportional to the square of the density. He therefore corrected it by adding a term $\frac{a}{V^2}$ to the pressure, where a is a constant for a given substance and measures the force of attraction between the molecules. In this way **van der Waals' equation** assumed its final form, as follows:

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

Isotherms of van der Waals' Equation.—The isotherms deduced from the simple gas equation $pV = RT$ are rectangular hyperbolas, *i.e.* when p is plotted against V for a number of different temperatures a series of rectangular hyperbolas is obtained. If we multiply out the factors in van der Waals' equation (1), and rearrange in powers of V, we have

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

This is a cubic equation in V. When a b and T have suitable values this gives the type of isotherm shown in Fig. 8 by the dotted curve $MLKJNHGF$. This differs from the isotherm obtained experimentally in that there is no sudden break at L or G, where layers of liquid and vapour are formed, since these two points are joined by a continuous loop.

Supersaturated vapour and superheated liquid.—Parts of van der Waals' theoretical loop can be realised experimentally as follows;

(i) When a saturated vapour which is free from dust particles is cooled, it does not at once deposit liquid, since the moisture can persist, at least for a short time, in the form of a **supersaturated vapour.** If, however, nuclei of dust, etc., are present, liquid forms and the pressure drops to the vapour pressure. Since the pressure of the supersaturated vapour is greater than that at which condensation normally occurs at the temperature produced by cooling, this precarious condition, although actually produced by a change of temperature, *i.e.* by a transference from one isothermal to another, is similar to that which would be produced by an extension of the isothermal beyond G towards H.

(ii) Conversely, a liquid does not always begin to boil as soon as the normal boiling-point is reached, but may rise to a higher temperature as a **superheated liquid.** The introduction of a piece of porous material charged with air, however, leads at once to the formation of bubbles of vapour, and the temperature falls to the normal boiling-point. Since the atmospheric pressure is less than the normal vapour-pressure of the liquid when superheated, this phenomenon may be compared with the condition which would be produced by a prolongation of the isothermal in the direction of lower vapour-pressures from L towards $\mathcal{J}$.

(iii) The region $\mathcal{J}H$ represents an unstable condition, in which pressure and volume increase together, and has never been realised experimentally.

Liquids under tension.—A liquid can persist not only (along LK) at pressures less than its normal vapour-pressure, but also (along $K\mathcal{J}$) under negative pressures. The condition of a **liquid under tension** is sometimes realised when a long barometer-tube filled with mercury is inverted over mercury, since the mercury sometimes clings to the tube and does not fall to the normal barometric height until it is tapped.

Stable, metastable or labile, and unstable states.—The phenomena described above can be used to illustrate the principal types of equilibrium.

(i) **Stable equilibrium** represents a state in which there is no tendency to change, since any alteration of conditions sets up a

resistance which opposes any further change. A ball lying at the bottom of a basin is in this condition. A liquid and vapour sealed up together in a tube are also in stable equilibrium.

(ii) **Metastable or labile equilibrium** is a state, intermediate between stable and unstable equilibrium, in which the system is stable to minute disturbances, but unstable towards larger ones. A ball resting in a tiny cup on the top of a support from which it can easily fall, or a pencil standing precariously erect on a flat end, are mechanical examples of this condition. In physical chemistry this type of equilibrium may be illustrated by the properties of a supersaturated vapour or superheated liquid.

(iii) An **unstable state** is one which is too precarious to persist, since no disturbance at all is needed to initiate a process of change towards a more stable condition. A pencil standing on its point falls over as soon as it is released, and is thus in an unstable state. A condition in which pressure and volume increase together is most certainly of this impossible type. Thus in the region JH of Fig. 8, part of the material would condense immediately to a denser liquid, thus allowing the remainder to expand to the normal density of a saturated vapour, and this condition would be produced spontaneously without waiting for the intervention of particles of dust.

Solutions of van der Waals' Equation.—Since this is a cubic equation, it can have three roots, *i.e.* a given value of p may correspond to three values of V, as at the points L, N and G of Fig. 8. If a and b are fixed, then for low values of T the loops LJN and NHG (which should be equal in area) are large, and the three values of V differ widely from one another. As T becomes larger the loops become smaller; and finally there is one particular value of T at which the loops just vanish, and the three values of V become identical. For still higher values of T there is only one real root of the equation; the other two values of V are described mathematically as "imaginary" quantities and have no physical significance.

This feature of the theoretical isotherms of van der Waals' equation corresponds closely to the change in the form of Andrews' experimental isotherms as the temperature rises, when the horizontal portion LG of the isotherms becomes shorter and

shorter at higher temperatures and vanishes when the critical temperature is reached. Obviously the **critical isotherm** is the one which for a particular value of p, namely, the critical pressure P_c, gives three equal values of V, all equal to the critical volume V_c. Expressed algebraically, this means that at the critical point van der Waals' equation (1) must become identical with the particular solution represented by equation (3).

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

For the purpose of comparing the two equations, we must expand equation (3), as in (4),

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0. \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

We must also insert the special values $T = T_c$ and $p = P_c$, in the expanded form (2) of van der Waals' equation, which then assumes the form

$$V^3 - \left(\frac{RT_c}{P_c} + b\right) V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0. \quad \ldots\ldots\ldots\ldots\ldots (5)$$

We can now equate coefficients of equal powers of V in equations (4) and (5), and so deduce the following relations:

Equating the coefficients of V^2:

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

Equating the coefficients of V:

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

Equating the coefficients of the terms not containing V:

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

From these three equations the values of the critical constants in terms of a and b can be deduced as follows:

(i) Dividing (8) by (7),

$$V_c = 3b, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

i.e. the **critical volume** is equal to $3b$; or conversely, van der Waals' constant b is 1/3 of the critical volume.

(ii) Substituting this value of V_c in (7), we find that we can express the **critical pressure** in terms of the two constants of van der Waals' equation as follows:

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

(iii) Finally, by substituting for P_c and V_c in (6), it is found that the **critical temperature** is given by the expression

$$T_c = \frac{8a}{27Rb}. \quad \text{.....(11)}$$

Hence, if a and b are determined from measurements on compressed gases, they can be used to predict the critical constants. The converse process can also be used in order to deduce the values of a and b from the critical constants as measured experimentally. Thus, from (9), (10) and (11), it is readily shown that

$$b = \tfrac{1}{3}V_c = \frac{RT_c}{8P_c}$$

and

$$a = 3P_cV_c^2 = \frac{9RV_cT_c}{8} = \frac{27R^2T_c^2}{64P_c}. \quad \text{.....(12)}$$

Van der Waals' Equation not numerically exact.—An important general relation is revealed when the values of the critical constants given by equations (9), (10) and (11) are used to calculate the ratio RT_c/P_cV_c, thus:

$$\frac{RT_c}{P_cV_c} = \frac{R \times 8a \times 27b^2}{27Rb \times 3b \times a} = \frac{8}{3} = 2{\cdot}67.$$

If, therefore, van der Waals' equation gives a true representation of the transition from the liquid to the gaseous state, this ratio should be constant for all substances and should have the value 2·67. It will be seen from the last column of Table 5 (p. 31) that this ratio is nearly constant for many substances, but that it usually has a value 3·7, which is much larger than the figure predicted by van der Waals' equation. There are two groups of substances which give abnormal values. The ratio for hydrogen and helium is lower, but it is difficult to determine the value of V_c for these substances. Water, the alcohols, and acetic acid all give values higher than 3·7. They all belong to the group of "associated" liquids (Chap. III. p. 61), and high

values for the ratio RT_c/P_cV_c are probably characteristic of this group.

The principle of corresponding states.—It has been found experimentally that, in the neighbourhood of the critical point, all gases give the same type of isotherm as carbon dioxide. The actual position of the critical isotherm varies with the critical constants of the gases studied; but the similarity is great enough to suggest that, if we could choose for each different gas a suitable scale of pressure, temperature and volume, we could superimpose all the critical isotherms on one another. If this were done for the critical isotherms, it is probable that all the other isotherms would coincide. We should then have one isothermal diagram, and one fundamental equation, for all gases.

The scale which immediately suggests itself is one in which the pressure, temperature and volume are expressed as fractions of the critical pressure, temperature and volume. If we write

$$\pi = \frac{p}{P_c}, \quad \phi = \frac{V}{V_c} \quad \text{and} \quad \theta = \frac{T}{T_c},$$

then π, ϕ and θ are termed the **reduced pressure**, the **reduced volume** and the **reduced temperature** respectively. If now in van der Waals' equation we replace p, V and T by πP_c, ϕV_c, and θT_c, we have

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c.$$

Expressing P_c, V_c and T_c by the functions of a and b given in equations (9), (10) and (11), we have

$$\left(\frac{\pi a}{27b^2} + \frac{a}{\phi^2 9b^2}\right)(3\phi - b) = \frac{8aR\theta}{27Rb},$$

which reduces to

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta. \quad \text{.....(13)}$$

This is the fundamental equation we are seeking. The quantities a and b, P_c, T_c, V_c, which are characteristic for any given gas, have all cancelled out, and equation (13) should predict the form of the isotherms for any gas whatsoever. Thus if we take any two substances at the same reduced pressure and

the same reduced temperature, they should have the same reduced volume. The data in Table 6 show that this is nearly true for many substances with respect to the volume in the liquid state and in the state of saturated vapour.

TABLE 6. CORRESPONDING STATES.

$\pi = 0{\cdot}08846$. $\theta = 0{\cdot}73$.

Substance.	ϕ (liquid).	ϕ (vapour).
Benzene	0·4065	28 3
iso-Pentane	0·4085	27·7
n Pentane	0·4061	28·4
n-Hexane	0 4055	29·1
Chlorobenzene	0 4028	28·5
Ether	0·4030	28·3

When two substances are at the same reduced temperature and the same reduced pressure they are said to be in **corresponding states.** It is obvious that if we wish to make comparisons between physical properties which are altered by changes in pressure or temperature, the comparison should be made when the substances are in corresponding states. When a property of a liquid or solid is concerned, pressure has usually little effect, and it is sufficient to use corresponding temperatures. As an approximation, liquids at their boiling points are roughly at corresponding temperatures, since it has been found that the boiling-point on the *absolute* scale of temperature of a liquid under a pressure of 760 mm. is approximately 2/3 of the critical temperature (Table 7).

TABLE 7. BOILING-POINTS AND CRITICAL TEMPERATURES.

Substance.	Boiling-point T_b.	Critical Temperature T_c.	T_b/T_c.
Benzene	353°	561°	0·629
iso-Pentane	303°	468°	0·647
n-Pentane	313°	470°	0·666
n-Hexane	342°	508°	0·673
Chlorobenzene	405°	632°	0·641
Ether	308°	467°	0·661

Limitations of van der Waals' equation.—Whilst van der Waals' equation accounts qualitatively (and approximately quantitatively) for the pressure-volume-temperature relations of gases and liquids, it does not predict accurately the form of the isotherms. At temperatures above the critical temperature and for moderate pressures, there is good agreement between the observed and theoretical curves. At lower temperatures and higher pressures, van der Waals' curves differ appreciably from the observed curves, though they have the right shape. Further, the law of corresponding states only holds approximately (Table 6), and the experimental values of the ratio RT_c/P_cV_c are much higher than the value 2·67 predicted by van der Waals' equation (Table 5). These and other similar discrepancies show that van der Waals' equation, whilst it is a great advance on the simple gas laws, gives only an approximate account of the behaviour of liquids and gases.

Dieterici in 1898 deduced an equation of state, which differs from van der Waals' equation in that an allowance is made for a gradient of density at the boundary of the gas as the internal pressure diminishes to zero. In this equation, instead of replacing p by $p+\frac{a}{V^2}$, we replace it by $pe^{\frac{a}{RTV}}$, and therefore write

$$pe^{\frac{a}{RTV}}(V-b)=RT.$$

The ratio RT_c/P_cV_c now has the theoretical value $\frac{1}{2}e^2=3{\cdot}695$, and agrees closely with the typical ratio 3·7 of the simple organic compounds of Table 5; but even in this equation the ratio V_c/b, which should be equal to 2 for all gases (but 3 when van der Waals' equation is used), has the value 2·80 for hydrogen, 1·89 for air, 1·86 for carbon dioxide and 1·41 for argon. We therefore conclude that no simple equation of state has yet been found which will cover effectively the whole process of liquefaction; and van der Waals himself certainly did not suppose that this could be done.

THE LIQUEFACTION OF GASES.

Liquefaction by cooling and compression.—If the critical temperature of a gas lies below the atmospheric temperature, the gas cannot be liquefied by pressure alone and is therefore described as a **permanent gas.** All other gases can be liquefied by the application of sufficient pressure, but the liquefaction is much easier if the gas is cooled in addition to being compressed. Thus Faraday in 1823 liquefied chlorine, sulphur dioxide, carbon dioxide, cyanogen, ammonia, and hydrochloric acid by preparing the gas at one end of a bent sealed tube, and cooling the other end in a freezing mixture. The cooling agents chiefly employed in the laboratory at the present time for purposes such as these are solid carbon dioxide ($-80°$) and liquid air ($-180°$).

Since the critical temperature of carbon dioxide at 31° C. is above the atmospheric temperature, cylinders of compressed carbon dioxide actually contain liquid. This liquid does not quite fill the vessel unless it has been over-filled. The vessel therefore also contains some vapour, and the pressure on the liquid is its normal vapour-pressure, *e.g.* 35 atmospheres at 0°, 46 atmospheres at 10° and 59 atmospheres at 20° C. If the cylinder is upright it delivers gas from the nozzle, and the liquid slowly evaporates or boils away into the vapour-space above it. If, however, a cylinder of the compressed gas is tilted, so that the nozzle is at the lowest point, the liquid escapes; but this evaporates so rapidly in the air that part of it is frozen into a white snow-like mass (Expt. 2. ii). When this **carbon dioxide snow** is made into a paste with ether or petrol it gives a convenient bath which can be maintained at about $-80°$ and used to cool gases whose critical temperatures lie between 0° and $-80°$.

Liquefaction by adiabatic expansion.—The methods used in the liquefaction of air (and of gases which are still more difficult to liquefy) depend upon the property possessed by many gases of cooling themselves when expanded through a jet or a porous plug. We have already seen, when discussing the kinetic theory of gases (Chap. I. p. 15), that the *average kinetic energy* of the gas molecules is given by

$$E = \tfrac{1}{2}mc^2 = \tfrac{3}{2}pV = \tfrac{3}{2}RT.$$

The average kinetic energy of the molecules is therefore proportional to pV. If we allow a gas to expand suddenly, *e.g.* by pushing back a piston, it will be cooled, since it gives up some energy in pushing back the piston. If, however, we allow it to flow through a jet into an empty space, so that the streams of gas from the jet give up their energy to the expanded gas which they strike, then no energy will be given up to surrounding bodies or taken from them. Under these conditions the total energy in the compressed gas is equal to the total energy in the expanded gas. For a perfect gas it is found that $p_1V_1 = p_2V_2$, and the temperature of the gas is not changed by expansion, *i.e.* the kinetic energy of the gas molecules is the same before and after expansion. Real gases, however, also possess *potential energy*, owing to the mutual attraction between the molecules, and, when a gas expands, work has to be done to separate the molecules. The potential energy of an expanded gas is then greater than that of a compressed gas. Since the total energy is unchanged this must mean that the kinetic energy decreases, *i.e.* that $p_1V_1 > p_2V_2$, and that the gas is cooled on passing through the jet.

It will be seen from Fig. 6 (p. 25), that for most gases pV at 100 atm. is less than pV at 1 atm. on account of the relatively large attraction between the molecules, as presented by a in van der Waals' equation. Gases such as air or nitrogen are therefore cooled when expanded through a jet, *e.g.* from 100 atmospheres to 1 atmosphere. The effect of the finite size of the molecules (the b of van der Waals' equation) is in the opposite direction, and tends to make pV at high pressures greater than pV at low pressures. For hydrogen this effect is greater than the effect of the molecular attraction, and pV increases steadily with pressure. Hydrogen at atmospheric temperatures is therefore heated instead of cooled by expansion through a jet. At lower temperatures, however, hydrogen gives the same kind of curve as air and can be cooled by expansion through a jet. The magnitude of the cooling produced by the adiabatic expansion of a gas was determined by Joule and Thomson, who allowed the compressed gas to escape through a porous plug and measured the temperature on either side of the plug. The magnitude

of the **Joule-Thomson effect** for some common gases is shown below.

COOLING OF GASES BY EXPANSION AT 0° C.

Carbon dioxide	1·46° per atm.	Nitrogen	0·31° per atm.
Oxygen	0·326° ,,	Hydrogen	−0·03° ,,

The actual cooling per atmosphere of expansion at 0° is shown in Table 8, where it is seen that under-perfect gases are cooled to an extent which is greater for the easily liquefied gas, carbon dioxide, than for nitrogen and oxygen, which are much more difficult to liquefy. Hydrogen, on the other hand, as an over-perfect gas, gives a negative effect, and is slightly heated by expansion. For air and similar gases the cooling, starting at ordinary temperatures, is not large and amounts only to 12° for air at 20° when the pressure falls from 50 atmospheres to 1 atmosphere; but the cooling becomes larger at lower temperatures, so that by arranging a continuous circulation of the gas, lower and lower temperatures can be obtained, until liquid air is produced.

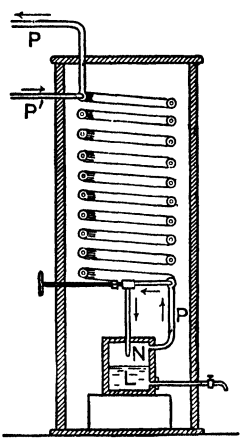


FIG. 11.—Apparatus for liquefaction of air by adiabatic expansion.

Liquid air is now manufactured on a large scale by means of an apparatus based on this principle and devised by Linde and Hampson (Fig. 11). The compressed gas enters through P' and flows through the innermost of the concentric copper tubes, until it reaches the jet N, where it expands and is cooled. The cooled gas now circulates through the outer tube, P, thus cooling the incoming compressed gas, which is still further cooled by expansion. The cooling is thus progressive, and finally the air escaping from the nozzle N is obtained as a liquid. The whole apparatus is very carefully "lagged" in order to minimise the inflow of heat from surrounding bodies, and the liquid air is stored and handled in vacuum-jacketed vessels.

By means of this type of apparatus, all gases except hydrogen and helium can be liquefied. Dewar found that when compressed hydrogen was cooled with liquid air before expansion it behaved like other gases, and was cooled instead of heated when expanded through the jet. In this way he first prepared liquid hydrogen in quantity. Later Kammerlingh Onnes succeeded in liquefying helium in a similar manner, by first cooling the compressed gas in liquid hydrogen, and then expanding it in an apparatus of the Linde-Hampson type.

QUESTIONS ON CHAPTER II.

1. The equation $pV = RT$ represents the behaviour of a perfect gas. Give some account of the deviations from this equation which are observed experimentally. How are these deviations accounted for by van der Waal's equation ? (Cambridge Schols.)

2. What do you understand by " continuity of state " ? Give an account of experimental work bearing on this subject.

3. Is Avogadro's hypothesis exact or approximate ? What other data besides the gas or vapour density are required for the exact determination of molecular weight ?
(B Sc. Hons., Manchester.)

4. How would you determine, directly or indirectly, the critical constants of ether ? (B.Sc , Sheffield.)

5. Describe qualitatively the changes in volume which would be observed if the pressure on a given mass of carbon dioxide were gradually increased from 1 to 1000 atmospheres at each of the following temperatures: 25°, 32°, 40°, 50°, 100° C. The critical temperature and pressure of carbon dioxide are 31° C. and 73 atmospheres. (B.Sc., Sheffield.)

6. Of the three critical constants, the critical volume is the most difficult to determine with accuracy. Explain the reason for this and describe the methods actually employed.
(B.Sc., Hons., Manchester.)

7. Discuss the law of Avogadro with reference to (*a*) the kinetic theory of gases, (*b*) the equation of state of van der Waals.
How far is it possible to obtain accurate values for the molecular weights of gases from observations of their density ?
(Trinity College, Senior Schol.)

8. Discuss the deviations gases show from simple gas laws. Explain how this behaviour is useful in the method introduced by Linde for liquefying gases. (B.A., Bombay.)

CHAPTER III.

THE LIQUID STATE.

3. Vapour-Pressure.

i. Measurement of vapour-pressure: Barometric method.—Fill four barometer-tubes, about a metre long, with mercury, and invert in a bath of mercury. The first tube is left empty to act as a barometer. By means of bent pipettes, introduce about 1 c.c. of water, alcohol, and ether respectively into the remaining tubes. After a minute or two, measure by means of a cathetometer the difference in level between the mercury in the first tube and in the other tubes. The lowering of the mercury surface below the level at which it stands in the first tube gives the vapour-pressure of the liquid.

ii. Measurement of vapour-pressure: Ramsay and Young's method.—Fit up the apparatus shown in Fig. 12. *A* is a stout boiling tube. It is closed by a rubber stopper carrying a thermometer, a tap funnel, and an exit-tube. The bulb of the thermometer is covered with a very thin layer of cotton-wool, tied on with thread; and the lower end of the tap-funnel is bent round so as to touch the cotton-wool. *B* is a pressure gauge, consisting of a vertical tube, provided with a scale and dipping into mercury. *C* is a large empty bottle, which serves to increase the capacity of the apparatus and to minimise the effect of leaks. To the side tube *D* is attached a tube drawn out to a long fine capillary, so that when the tap *D* is opened, air is admitted slowly to the apparatus.

First test for leaks by evacuating to about 30 mm. by means of the water-pump and closing *E*. The gauge should show no change in pressure in 10 minutes. When all the joints are tight, admit a little chlorobenzene through the tap-funnel, heat the water-bath surrounding *A* to about 50° and watch the thermometer in *A*. It will record a lower temperature than that in the outer bath, and will finally become steady at the temperature

at which the vapour-pressure of chlorobenzene is equal to the pressure in the apparatus. If it has initially a higher temperature than this, some liquid will evaporate and cool the bulb, while, if its temperature is too low, the surrounding vapour will condense upon it and warm the bulb. When a steady temperature is attained, read the thermometer and the pressure-gauge. The latter reading, when subtracted from the height of

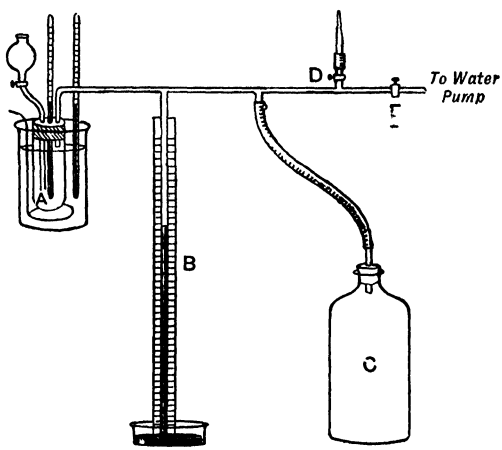


FIG. 12.—Ramsay and Young's apparatus for the measurement of vapour-pressure.

the barometer at the time of the experiment, gives the vapour-pressure at the temperature of the thermometer in *A*. The temperature of the outer bath should be maintained about 5° higher than that recorded by this thermometer.

Next admit air cautiously, by opening *D*, until the gauge falls about 50 mm.; raise the temperature of the outer bath until it is 5° higher than the steady reading of *A*, and repeat the measurements. Repeat the observations at higher temperatures up to 95°. Plot the observed vapour-pressures against temperature and compare with the standard pressures given in Table 8 (p. 52).

iii. Measurement of vapour-pressure of water: Method of Smith and Menzies.—The apparatus required is the same as that used in Ramsay and Young's method, except that the boiling-tube *A* is fitted with a cork bored with only two holes for thermometer and exit-tube. A small bulb-tube, of the shape shown in Fig. 13, is attached to the thermometer by a thread and partly filled with water. The boiling-tube *A* is partly filled with high-boiling

medicinal (B.P.) paraffin, and the temperature of the outer bath is raised to about 30°.

When the apparatus is evacuated, air bubbles will issue from the bulb-tube, followed by vapour as the water boils. After a minute or two close the tap *E*, and adjust the pressure in the apparatus by cautiously opening the tap *D* until bubbles just cease to issue from the tube. Read the pressure-gauge and the thermometer. The difference between the reading of the gauge and the height of the barometer gives the vapour-pressure. This pressure must, however, be increased by adding a correction for the depth of immersion of the bulb-tube in the oil, the density of which may be taken as 0·9. Raise the temperature by intervals of 10° to 100° and repeat the observations. The results should be plotted and compared with the standard figures in Table 8 (p. 52).

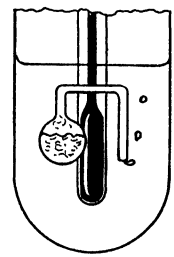


FIG. 13.—Apparatus of Smith and Menzies for measurement of vapour-pressure.

Vapour-pressure.—Many liquids evaporate when exposed to the air, and are converted into vapour. Marked differences are observed between different liquids with respect to this property. Thus ether evaporates at the ordinary temperature much more rapidly than water, whilst mercury does not evaporate to any appreciable extent. If the evaporation takes place into a closed space, it is found that evaporation at a given temperature ceases when the space contains a definite pressure of vapour. If the liquid is allowed to evaporate into the vacuum above a barometer, as in Experiment 3, i. the vapour-pressure can be measured by comparing the height of the mercury in the tube containing vapour with the height of the barometer.

It will be remembered that Andrews found, when compressing a vapour at a constant temperature below the critical temperature, that liquid appeared at a definite pressure, and that, when further compression was attempted, the pressure remained constant until all the vapour was converted into liquid. This pressure, corresponding to the horizontal portion of the isotherms in Fig. 8 (p. 29), is the **vapour-pressure** of the liquid.

The existence of a definite vapour-pressure is readily accounted for by the kinetic theory. In a liquid, the molecules are held

together by their mutual attraction, and their movements are much more restricted than in a vapour. At the surface of the liquid this attraction tends to pull the molecules inwards, and is sufficiently strong to prevent most of them from escaping as gas. A few molecules, however, which have acquired by collision a velocity greater than the average, will approach the surface at such a speed that they are able to overcome the attractive force and to escape into the space above the liquid.

As molecules of vapour accumulate in this space, some of them will begin to strike the surface of the liquid and be recaptured. The number which return in this manner will obviously depend on the concentration of molecules in the vapour, *i.e.* on its pressure. The process will go on until an equilibrium is reached at which in a given time each unit of area of the liquid surface loses as many molecules by evaporation as it gains by recapturing molecules from the vapour. The pressure at which this occurs is the vapour-pressure, and is thus the pressure of a vapour in equilibrium with the liquid. Vapour at this pressure is often referred to as **saturated vapour**, whilst when the pressure is less it is described as **unsaturated vapour.**

As the temperature rises, the molecules move more swiftly, and the number which have a sufficient velocity to escape from the surface increases rapidly. Hence the vapour-pressure becomes greater at higher temperatures. Thus the vapour-pressures of water and of chlorobenzene are found to increase between 0° and 100° in the manner shown in Table 8.

TABLE 8. VAPOUR-PRESSURES OF WATER AND OF CHLOROBENZENE.

t.	Vapour-pressures in mm. Hg.		*t.*	Vapour-pressures in mm. Hg.	
	Chlorobenzene.	Water.		Chlorobenzene.	Water.
0	2·6	4·6	60	64·8	149·5
10	4·9	9·2	70	98·2	233·8
20	8·8	17·5	80	144·9	355·5
30	15·4	31·8	90	208·4	526·0
40	25·7	55·3	100	292·8	760·0
50	41·5	92 5			

When the vapour-pressure becomes equal to the atmospheric pressure, vapour is also produced by the formation of bubbles within the liquid itself, and the liquid is then said to boil. The **boiling-point** of a liquid is therefore the temperature at which the vapour-pressure is equal to the atmospheric pressure. If the pressure above a liquid is reduced it will boil at a lower temperature. Distillation under reduced pressure is therefore often used in order to purify substances which would decompose if distilled at ordinary pressure, and consequently at a higher temperature. On the other hand, the temperature at which water boils is raised when the pressure is increased, as in the boiler of a steam engine.

TABLE 9. VAPOUR-PRESSURE OF WATER ABOVE 100°.

t.	*p.*	*t*	*p.*
100° C.	1·000 atm.	260° C.	46·22 atm.
120°	1·960	280°	63·17
140°	3·567	300°	84·58
160°	6·097	320°	111·2
180°	9·885	340°	143·8
200°	15·33	360°	183·5
220°	22·86	374°	217·0
240°	32·98	(Crit. temp.)	

The vapour-pressure of water for different temperatures above 100° is shown in Table 9. The maximum value is reached at the critical temperature, 374° C., when water exerts a critical pressure of 217 atmospheres. Beyond this temperature the term vapour-pressure has no significance, since only "gas" can exist, whether the pressure is high or low, and it is therefore impossible for any liquid to appear in the system.

Latent heat of vaporisation.—When a liquid boils, a considerable quantity of heat has to be supplied to convert it into vapour at the same temperature. Thus, when 1 gram of water at 100° is converted into steam at 100°, 538 calories are absorbed. Since this quantity of heat produces no rise in temperature, it is regarded as hidden or "latent" in the vapour and is termed the **latent heat of vaporisation.** When a vapour condenses, this heat is given out, so that the condensation of 1 gram of steam at 100° will raise the temperature of 538 grams of water by 1°.

Table 10 gives the latent heats of vaporisation of some common liquids at their boiling-points. It will be seen that the value for water is much larger than the value of this constant for other liquids.

TABLE 10. LATENT HEATS OF VAPORISATION AT THE BOILING-POINT.

Substance	Boiling-point.	Latent Heat.
Water - - -	100°	538 cal.
Phosphorus - -	287°	130
Sulphur - - -	316°	362
Mercury - - -	358°	68
Chloroform - -	61°	58
Methyl formate	33°	110·5
Benzene - - -	80°	95·5

Liquids also absorb heat when allowed to evaporate at temperatures lower than their boiling-point. Thus an obvious cooling is produced by the rapid evaporation of water or of ether in a draught. The latent heat of evaporation is, however, not the same at all temperatures, and in general it decreases as the temperature rises. Some examples of the variation of latent heat with temperature are given in Table 11. It will be seen that acetic acid is an exception to the general rule, since its latent heat first rises and then falls as the temperature rises. At the critical temperature, where vapour and liquid have identical properties, the latent heat of vaporisation is zero.

TABLE 11. VARIATION OF LATENT HEAT OF VAPORISATION WITH TEMPERATURE.

Temperature C.	Latent Heat.			
	Ether.	Benzene.	Ethyl Alcohol.	Acetic Acid.
0	92·5	—	220·9	—
40°	82·8	—	218·7	87·0
80°	73·5	95·5	206·4	91·6
120°	62·2	86·6	184·2	94·4
160°	46·1	78·9	156·9	89·6
200°	19·4(190°)	68·8	116·6	85·6

Trouton's rule.—An important relation between the latent heat, the molecular weight and the boiling-point was discovered by Trouton and is usually known as **Trouton's Rule.** This is expressed by the formula

$$\frac{Ml}{T} = \text{constant},$$

where M is the molecular weight, l the latent heat of vaporisation and T the boiling-point on the absolute scale. Table 12 gives these quantities for a number of liquids. For many substances Trouton's ratio has a value of about 20 units, but a number of anomalous cases have been found in which this ratio is less than 20 (*e.g.* hydrogen and acetic acid), or more than 20 (ethyl alcohol and water).

TABLE 12. TROUTON'S RULE.

Substance.	Ml (cals.).	T (abs.).	Ml/T.
Nitrogen	1,362	77·5	17·6
Oxygen	1,664	90·6	18·6
Ether	6,466	307	21·1
Benzene	7,497	353	21·2
Propyl acetate	8,310	375	22·2
Aniline	10,500	457	23·0
Hydrogen	248	20·4	12·2
Acetic acid	5,400	391	13·8 (27·6)
Ethyl alcohol	9,448	351	26·9
Water	9,650	373	25·9

The low value for acetic acid is probably due to molecular association of the vapour, since it is found that the molecular weight of the vapour is nearly double the normal value. If M in Trouton's formula refers to the vapour, so that $M = 120$ instead of 60, the true value of the ratio for acetic acid is 27·6, which brings it into line with other associated liquids.

Hildebrand's modification of Trouton's rule.—A more accurate form of Trouton's rule has been suggested by Hildebrand. This modification depends on the fact that, although the pressure at the boiling-point is the same for all liquids, the number of

molecules of vapour in unit volume varies with the temperature, and is less for a liquid boiling at a high temperature than for one boiling at a low temperature. Hildebrand eliminates this difference by calculating the latent heat *at a temperature at which each vapour contains the same number of molecules in a unit volume.* He then finds that Ml/T is very nearly constant, as shown in Table 13, where values are given for a concentration of 0·005 mol. per litre in the vapour.

TABLE 13. HILDEBRAND'S RELATION.
(C = 0·005 mol. per litre.)

	T.	Ml/T.
Nitrogen	55° A.	27·6
Chlorine	194°	27·8
Hexane	294°	27·0
Stannic Chloride	329°	27·2
Mercury	560°	26·2
Cadmium	988°	26·4
Zinc	1130°	26·4
Ammonia	200°	32·4
Water	325°	32·0
Ethyl alcohol	307°	33·4

This relationship holds for normal liquids over a wide range of temperatures. For associated liquids higher values are found, as is shown by the data for ammonia, water and ethyl alcohol.

Clapeyron's equation.—The latent heat of vaporisation is related closely to the change of vapour-pressure with temperature. By thermodynamical arguments (see p. 228) it was shown by Clausius that

$$l = T\frac{dp}{dT}(V - V').$$

In this equation, the ratio dp/dT of a minute increment dp of pressure to the minute increment of temperature dT by which it is produced, is a measure of the rate of change of vapour-pressure with temperature at an absolute temperature T, whilst V and V' are the volumes occupied by one gram of vapour and liquid at this temperature. Thus, water has a vapour-pressure of 746·52 mm. at 99·5°, and of 773·69 mm. at 100·5 ; the average

rate of change of vapour-pressure with temperature at 100° is therefore $773{\cdot}69 - 746{\cdot}52 = 27{\cdot}17$ mm. per degree $= 0{\cdot}03570$ atmospheres per degree. Measurements of the density of saturated steam at 100° give $V = 1{\cdot}674$ litres, whilst the volume of a gram of water is still given approximately by $V' = 0{\cdot}001$. Hence

$$l = 373 \times 0{\cdot}03570 \times 1{\cdot}673$$
$$= 22{\cdot}29 \text{ litre-atmospheres}$$
$$= 22{\cdot}29 \times 24{\cdot}19 = \mathbf{539{\cdot}1 \text{ calories.}}$$

In general, V' is very small compared with V and can therefore be neglected. Further, if it is assumed that the gas laws hold for the vapour, it follows that

$$V = \frac{RT}{Mp},$$

where M is the molecular weight. Hence L, the **molecular latent heat** is given by

$$L = Ml = \frac{RT^2}{p}\frac{dp}{dT} = RT^2 \frac{d \log_e p}{dT},$$

since, by the formulae of the " differential calculus "

$$\frac{d \log_e p}{dT} = \frac{1}{p}\frac{dp}{dT}.$$

This formula can be used to calculate latent heats from observations of vapour-pressures, since the line obtained by plotting $\log_e p$ against temperature has only a small curvature, and the value of its slope can be determined without difficulty. This calculation can also be made by an algebraical instead of by a graphical method. Thus, if the vapour-pressures are considered over a small range of temperatures it may be assumed that l does not vary appreciably, and by the mathematical process of " integration " the preceding equation can be transformed into

$$L = Ml = \frac{RT_1T_2}{T_2 - T_1} \log_e \frac{p_2}{p_1}.$$

where p_1 and p_2 are the vapour-pressures at temperatures T_1 and T_2. Since $R = 1{\cdot}985$ cal. and $\log_e x = 2{\cdot}303 \log_{10} x$ this becomes

$$L = Ml = 1{\cdot}985 \times 2{\cdot}303 \frac{T_1T_2}{T_2 - T_1} \log_{10} \frac{p_2}{p_1}.$$

For benzene $p = 389$ mm. at 60° and 754 mm. at 80°.

$\therefore$ when $T_1 = 333$ and $T_2 = 353$, $p_1 = 389$, $p_2 = 754$, $M = 78$;

$$\therefore l = \frac{1{\cdot}985 \times 2{\cdot}303}{78} \frac{333 \times 353}{20} \log_{10} \frac{754}{389}$$

$$= 344{\cdot}5 \times \log_{10} \frac{754}{389}$$

$$= 344{\cdot}5 \times 0{\cdot}2875$$

$$= \mathbf{99{\cdot}1 \text{ calories.}}$$

This gives the average latent heat over the interval 60° to 80°.

4. Surface-Tension.

i. Experiments on surface-tension.—Half-fill a narrow test-tube with benzene, and another with clean mercury. Note the difference in the form of the surfaces. Pour out the liquids and note whether a film is left on the glass or not. Take a piece of narrow glass tube, open at both ends; dip the lower end into a basin of mercury, and notice whether the level of the mercury in the tube is higher or lower than in the basin. Repeat this experiment with benzene, taking care first to plunge the tube into the benzene so that the interior is wetted by the liquid.

ii. Measurement of surface-tension.—Clean a length of thermometer-tubing, of about $\frac{1}{2}$ mm. bore and 15 cm. long, by passing through it a solution of chromic acid, then water, and finally dry air. Draw up a column of mercury into the tube, measure its length in two or three positions in the tube, run into a weighed vessel and weigh. Calculate the radius of the tube by the formula

$$r = \sqrt{w/13{\cdot}6\pi l}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where w is the weight of the mercury and l is the length of the column. Attach a mm. scale to the tube, and support it vertically so that the lower end dips into benzene contained in a small beaker. Raise and lower the tube a few times so as to wet the surface of the glass, then read the height h to which the liquid rises above the level in the beaker and note the temperature of the liquid. The surface tension may then be calculated by the formula

$$\gamma = \tfrac{1}{2} rhgd, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where d is the density of the liquid.

Origin of surface-tension.—The mutual attraction of the molecules of a liquid gives special properties to the surface-layer. In the bulk of the liquid, the molecules are attracted equally in all directions; but in the surface-layer the attraction is all on one side, and tends to pull the molecules towards the interior of the liquid. Liquids therefore behave in much the same way as if they were bounded by a stretched elastic skin, which tends to contract in order to make the surface-area as small as possible. It is this tension of the surface-layer which causes drops and bubbles to assume a spherical form and is responsible for the rise (or fall) of liquids in capillary tubes.

The latter phenomenon depends also upon the ability of the liquid to "wet" the material of which the tube is made. Water and most organic liquids wet glass and are drawn upwards in a capillary tube, since in this way the area of the wet surface is diminished. The liquid is therefore bounded by a concave surface or **meniscus**, the edges of which are continuous with the film on the wet surface of the glass. Mercury does not wet glass, and tends to withdraw from a capillary tube, in order to diminish the surface-area as much as possible. The surface of the liquid is therefore convex in the tube; but it does not meet the surface of the glass tangentially, as in the case of water, since the surface of the mercury intersects the surface of the glass at a definite **angle of contact**, which is about 140°. Water on a greasy surface, or in contact with certain minerals, behaves in the same way as mercury on glass.

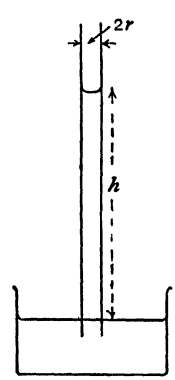


FIG 14.—Measurement of surface-tension by 'capillary rise.'

Surface-tension, which is usually indicated by the symbol γ, is defined as the tension in dynes along a line of 1 cm. length on the surface. When the liquid wets a piece of glass, the surface film is continued on the surface of the glass, and the surface-tension at the edge of the liquid acts in a direction parallel to the surface of the glass. The surface-tension of a liquid, such as benzene, which wets glass, can therefore be deduced from the **capillary rise** in a narrow

tube, by equating the weight of the column of liquid against the forces which hold it up, as follows. The perimeter of the tube is $2\pi r$; the tension supporting the column is therefore $2\pi r\gamma$. The weight of the column of liquid supported by this tension $= \pi r^2 hd$, where h is the height of the column and d is the density of the liquid (Fig. 14). Expressing this in dynes, we have

$$2\pi r\gamma = \pi r^2 hgd,$$

or $$\gamma = \tfrac{1}{2} rhgd, \text{ where } g = 981 \text{ cm./sec.}^2$$

Table 14 gives the density and surface-tension of benzene at laboratory temperatures.

TABLE 14. SURFACE-TENSION OF BENZENE.

Temperature.	Density (grams per c.c.).	Surface-tension (dynes per cm.).
10°	0·890	30·2
15°	0·884	29·5
20°	0·879	28·9
25°	0·874	28·2

Influence of temperature on surface-tension.—The surface-tension of a liquid decreases as the temperature rises, and becomes zero at the critical temperature. If the surface-tension is plotted against temperature, the graph is not a straight line, but shows a decided curvature. It was shown by Ramsay and Shields that a straight line is obtained if, instead of the surface-tension γ, we plot the quantity $\gamma\left[\frac{M}{D}\right]^{\frac{2}{3}}$ (where M is the molecular weight and D is the density of the liquid). Moreover, these lines have very nearly the same slope for many different liquids.

The quantity $\frac{M}{D}$ is termed the **molecular volume**, and $\left[\frac{M}{D}\right]^{\frac{2}{3}}$ is a measure of the surface area of the molecules. Ramsay and Shields called the quantity $\gamma\left[\frac{M}{D}\right]^{\frac{2}{3}}$ the **molecular surface energy**, and expressed the variation of this quantity with temperature by the equation

$$\gamma\left[\frac{M}{D}\right]^{\frac{2}{3}} = k(T_c - t - 6). \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Here k is a constant giving the slope of the graph, T_c is the critical temperature, and t is the temperature of observation. The accuracy with which the Ramsay-Shields Law holds for a typical liqud is shown in Table 15, which gives the data for carbon tetrachloride.

TABLE 15. MOLECULAR SURFACE ENERGY OF CARBON TETRACHLORIDE.

$\gamma V^{\frac{2}{3}} = 2{\cdot}106(T_c - t - 6)$. $T_c = 288{\cdot}5°$ $(V = M/D.)$

t	$\gamma V^{\frac{2}{3}}$ (obs.).	$\gamma V^{\frac{2}{3}}$ (calc.).	Diff.
80°	425·1	425·1	0
110°	361·9	362·9	+1·0
140°	298·8	299·0	+0·2
170°	235·7	235·2	−0·5
200°	172·5	172·5	0
230°	109·0	110·1	+1·1
260°	46·3	48·6	+2·2

The third column is calculated by putting $k = 2{\cdot}106$ and $T_c = 288{\cdot}5$ in equation (3). The figures thus obtained are in good agreement with the observed values.

Molecular association.—For many liquids k has a value of approximately 2·12, that is, the rate of change of molecular surface energy with temperature is constant for a large number of substances. In some cases, however, notably with water, methyl and ethyl alcohol, and acetic acid much lower values of k are obtained. The liquids which give low values of k are also found to give anomalous results when other physical properties are studied. They give higher values than usual for the ratio RT_c/P_cV_c (see Chap. II.), and have very high latent heats of evaporation and high dielectric constants. Further, when the molecular weight of such liquids (dissolved in a suitable solvent) is determined, by the methods described in Chap. VIII., much higher figures are often obtained than would be expected from their chemical formulae. For these reasons it is usually supposed that in the liquid state the molecules are combined together to form larger molecules, and liquids of this type are termed **associated liquids.**

If this is the true explanation of the low values of the Ramsay-

Shields constant k, then by replacing the molecular weight M in equation (3) by xM (where x is the number of molecules which are associated together to form the larger molecules), we should get the normal value 2·12 for k. Conversely we can calculate x from the observed value of k by the equation

$$x = \left[\frac{2{\cdot}12}{k}\right]^{\frac{3}{2}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The number x is termed the **degree of association**, and the method of Ramsay and Shields is the most important method yet devised for determining the molecular weight or degree of association of a substance *in the liquid state*. Table 16 gives the values of k found for a number of liquids and in the last column the values of x calculated by equation (4).

TABLE 16. CONSTANTS IN RAMSAY AND SHIELDS' EQUATION.

Substance.	k.	x.
Benzene	2·10	1·01
Nitrobenzene	2·23	0·93
Ether	2·01	1·08
Carbon tetrachloride	2·21	0·94
Water	1·04	2·91
Methyl alcohol	0·93	3·44
Ethyl alcohol	1·08	2·75
Acetic acid	0·98	3·18
Benzophenone	2·90	0·63
Tribenzylamine	3·50	0·47
Amyl stearate	3·82	0·41
Tristearin	5·95	0·21

The first four liquids in this table are normal substances, since x is approximately unity, indicating that the molecular weight in the liquid state is the same as in the state of vapour. The second group consists of four associated liquids, which (if the assumptions of Ramsay and Shields are correct) are chiefly composed of triple molecules. The last four substances give results which are difficult to account for, since by applying formula (4), we get fractional values for x. This should mean that these substances are *dissociated* in the liquid state; but

since they are all stable substances this is very unlikely. It is, therefore, necessary to admit that the Ramsay-Shields constant can have higher values than 2·12 for normal liquids. Since, however, the effect of chemical composition on the Ramsay-Shields constant has not been studied in detail, no definite conclusion can be drawn and the values found for x by this method can therefore only be regarded as a qualitative indication of the existence of association in the liquid state.

A much more precise relation between surface-tension and temperature was discovered by MacLeod in 1923, namely

$$\gamma = C(D-d)^4.$$

Here γ is the surface-tension, D is the density of the liquid and d the density of its saturated vapour, all measured at the same temperature. C is then found to be constant for a given liquid from its freezing-point up to within 30° of its critical temperature. Unlike Ramsay and Shields' equation, this relation represents the surface-tension as falling to zero at the critical point where $D=d$ and $D-d=0$. Some important applications of this relation to the study of molecular volumes are described below (p. 73).

5. Viscosity.

1. Comparison of viscosities.—Procure a viscometer (Fig. 15). Clean it with chromic acid, wash with water and dry. Charge the viscometer with benzene, clamp it vertically in a bath at constant temperature, and adjust the volume of the benzene to coincide with the marks AB. When the liquid has attained the temperature of the bath, it is sucked up the left-hand limb until it has attained the level of the mark C. The time z taken to fall from this mark to the mark D below the bulb is then determined by means of a stop-watch. Repeat the experiment with water. The viscosity η of the liquid can then be calculated by the formula

$$\text{Relative viscosity} = \frac{\eta}{\eta_w} = \frac{Dz}{D_w z_w},$$

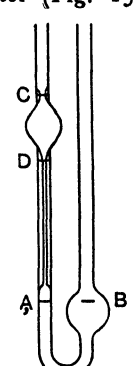


Fig. 15.—Viscometer.

where D is the density of the liquid and z is its time of flow, and η_w, D_w, z_w, are the corresponding numbers for water under the

same conditions. The viscosity of water at different temperatures is shown in Table 17 (p. 66).

ii. Measurement of viscosity of castor oil from velocity of fall of a sphere: method of Gibson and Jacobs.

The rate of fall of a sphere through a liquid soon reaches a constant value, which is given by **Stokes's law**, as follows:

$$\text{Limiting velocity } v = \frac{\text{force}}{6\pi\eta r} = \frac{\frac{4}{3}\pi r^3(S-D)g}{6\pi\eta r} = \frac{2}{9}gr^2\frac{S-D}{\eta},$$

where v = the limiting velocity in cm. per second, $g = 981$ cm./sec.^{2}, r = radius of the sphere, S = density of the sphere, and D = the density of the liquid. This equation is only strictly true when the sphere falls through a large mass of liquid. If the sphere is falling axially through a tube of radius R, the equation becomes

$$v = \frac{2}{9}gr^2\frac{S-D}{\eta(1+2{\cdot}4r/R)}$$

(a much smaller correction for "end" effect can be neglected). This relationship can be used in determining the viscosity of very viscous liquids such as castor oil.

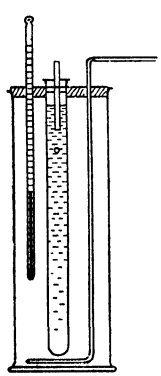


Fig. 16.—Measurement of viscosity by velocity of fall of a sphere.

The apparatus required is shown in Fig. 16. The inner tube containing the castor oil is 2 cm. in diameter and 30 cm. long. It is supported in a tall glass jar filled with water and fitted with a thermometer and stirrer. On the central tube two horizontal lines are etched, with an interval of about 15 cm. The cork closing this tube carries a piece of quill tubing, dipping 2-3 cm. into the liquid and pierced with a small hole above the level of the liquid.

Procure some steel ball-bearings of 0·15 cm. diameter. Measure the diameter of these with a screw micrometer. Also measure the inner radius of the tube R. Fill the inner tube with castor oil and insert in the water-jacket at about 20°. After half an hour, drop one of the steel balls into the quill tube. It will pass slowly through and move more rapidly when it reaches the wider tube. Determine with a stop-watch the time which the ball occupies in passing between the two horizontal lines and repeat with other balls. Note the temperature of the bath. Since $v = 15/t$ where t is the time-interval for 15 cm., the viscosity can then be calculated by formula (2), where $S = 7{\cdot}65$, $D = 0{\cdot}96$.

Viscosity and fluidity.—The rate of flow of a liquid depends, not only upon the forces acting upon it, but also upon a specific property of the liquid itself, which determines whether it will flow quickly or slowly. The property which retards the flow of the liquid is described as its **viscosity**; and the reciprocal of the viscosity is described as the **fluidity** of the liquid. Liquids differ enormously in their viscosities; *e.g.* ether shows very little "internal friction," whilst glycerine and treacle are very viscous. Liquids which have a very high viscosity behave in many respects like solids. Thus, if a lump of pitch is left at ordinary temperatures for some weeks, it slowly sinks to form a pool; it will also flow through a funnel, although very slowly indeed; but at atmospheric temperatures the pitch is hard and brittle, and is readily broken by a sharp blow. **Viscous liquids** such as pitch differ from **plastic solids** such as lead or sodium (which can be squirted through an orifice) in that they will flow slowly under the influence of very small forces, whereas plastic solids are only deformed by forces in excess of a minimum value.

The viscosity of a liquid is measured (in much the same way as the rigidity of a solid), as a resistance to change of shape without change of volume. Thus, rigidity is measured by the static force which resists the "shearing" of the solid by the opposite movement of two parallel planes. The coefficient of viscosity of a liquid is defined in a somewhat similar manner as *the force required to move a layer of unit area at unit velocity past a parallel stationary layer at unit distance away.* Absolute values for the viscosity of a liquid can be deduced from the resistance experienced when two concentric cylinders, separated by a layer of the liquid, are rotated in opposite directions relatively to one another. This method is only suitable for very viscous liquids and is not often used for exact measurements.

The absolute viscosity of a liquid can also be calculated from the time required for a given volume of the liquid to flow through a capillary tube, either under gravity (when the forces acting on the liquid are proportional to its density) or under a given manometric pressure. The formula used is

$$\eta = \frac{\pi p r^4 z}{8lv},$$

where p is the pressure causing flow, r the radius and l the length of the capillary, whiist v is the volume of liquid which flows through in a time z.

In order to get a true value for the viscosity, it is necessary to use a capillary of uniform bore, and of accurately circular section throughout, and to determine its dimensions with great exactness. For most purposes, however, it is sufficient to be able to compare the viscosities of two liquids, and this can be done most easily by measuring the ratio of the time of flow of two liquids in a **viscometer**, the capillary tube of which need not then be either of accurate form or of accurately known dimensions. If, then, the absolute viscosity of one of the liquids is known, the absolute viscosity of the other can be calculated from the ratio of the two times of flow, with or without a correction for the densities of the liquids. The liquid which is used most frequently as a standard is water, which has a viscosity, $\eta_{15} = 0{\cdot}0134$ c.g.s. units, where η_{15} is a symbol used to represent the viscosity at 15° C. An example of a liquid of high viscosity is glycerine, for which $\eta_{15} = 2{\cdot}34$.

Influence of temperature on viscosity.—The viscosity of water and benzene at a series of different temperatures is shown in Table 17.

TABLE 17. VISCOSITY OF WATER AND OF BENZENE AT DIFFERENT TEMPERATURES.

Temperature.	Viscosity η	
	Water.	Benzene.
0° C.	0·01793	0·009060
20°	0·01006	0·006537
40°	0·00657	0·004981
60°	0·00469	0·003980
80°	0·00356	0·003358
100°	0·00284	0·003358

The viscosity of a liquid decreases rapidly as the temperature rises and is often halved by an increase in temperature of 40° C. This large temperature-coefficient renders it difficult to trace any relation between the chemical constitution and viscosity of liquids. The use of corresponding temperatures (p. 41) as

temperatures of comparison has not proved very successful, and, whilst other methods of comparing viscosities have been suggested, no general relationships between chemical constitution and viscosity have yet been discovered.

Viscosity of solutions.—The viscosity of a mixture appears to depend on the average diameter of the molecules. The viscosity of a liquid is therefore altered greatly by small quantities of a colloid, the particles of which are much larger than the molecules of the solvent. Measurements of viscosity are therefore frequently employed in the study of colloidal solutions (Chap. XV.).

6. Molecular Volume.

1. Determination of density and molecular volume of a liquid.—Procure or construct a pyknometer of the type shown in Fig. 17. The stem is of about 2 mm. diameter, so that the bulb can readily be filled by means of a funnel drawn out to a long and thin capillary.

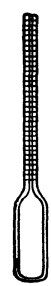


Fig. 17.—Graduated pyknometer.

(*a*) *Calibration.*—Weigh the clean and dry pyknometer. Fill with boiled distilled water to a mark in the lower part of the scale, immerse in a bath of water at about 20° and read the level of the water. Clean, dry and weigh. Repeat with a little more water in the pyknometer, so that the reading is in the upper part of the scale. From these weights calculate

(1) the ratio $\frac{\text{volume of one scale division}}{\text{volume of bulb to zero mark}}$;

(2) the volume in c.c. of the bulb to the zero mark at the temperature used.

With a weighed amount of water in the pyknometer read the volume on the scale at 80°. From this and the previous result calculate the change in volume of the bulb per degree. Table 18 gives the density of water from 0° to 100° to be used in these calculations.

Table 18. Density of Water.

0	0·9999	60	0·9832
10	0·9997	70	0·9778
20	0·9982	80	0·9718
30	0·9957	90	0·9653
40	0·9922	100	0·9584
50	0·9881		

The weight of liquid should be corrected for the buoyancy of the displaced air by the formula

$$w_v = w_a\left(1 + 0{\cdot}0012 - \frac{0{\cdot}00014}{D}\right),$$

where w_v is the weight in vacuo, w_a is the weight in air, and D is the density of the liquid. The results of the calibration should be expressed in the following form:

Example. $\begin{cases} 1 \text{ scale division} = 0{\cdot}0333 \times \text{volume of bulb}, \\ \text{volume of bulb} = 3{\cdot}110(1 + 0{\cdot}000024t). \end{cases}$

(*b*) *Density of benzene.*—Clean and dry the pyknometer and weigh, first empty and then filled with benzene to the lower part of the scale. The increase gives the weight of benzene. Place the pyknometer in a beaker of water and read the level of the benzene at 20°, 40°, and 60°, keeping the temperature constant for 10 minutes before taking a reading. Calculate the volume corresponding to these readings and hence the density of benzene at these temperatures.

ii. Molecular volumes at the boiling-point.—(*a*) *Benzene, toluene and chlorobenzene.*—The density of benzene at the boiling-point may be determined by plotting the results obtained in Experiment 6, i., and extrapolating to 80°; or by sealing off the tube above the scale and suspending the bulb in the neck of a distilling flask in which benzene is distilled. Read the volume after immersion in the vapour for ten minutes, and from this calculate the density and the molecular volume of benzene at the boiling-point. Repeat the experiment with toluene and with chlorobenzene. Calculate the molecular volumes and compare with those predicted by using the constants on p. 71.

(*b*) *Methyl and ethyl acetates.*—Determine the molecular volumes of these two liquids at 20° and at the boiling-point by this method. Repeat the experiment with other carefully purified esters, and deduce values for the increment CH_2.

Physical properties and chemical constitution.—One of the objects of physical chemistry is to trace the relationship between the physical properties of substances and the composition and structure of their molecules. Thus, when the laws governing the magnitude of a given property have been determined, we can not only predict the properties of new compounds of given structure, but may also be able to decide which of two possible constitutional formulae should be ascribed to a particular

compound of doubtful structure. From this point of view three types of physical property are usually distinguished.

(1) **Colligative properties** are those which are determined only by the *number of molecules* present, and are independent of their nature. An example of this type of property is the volume of a gas (at N.T.P.), which is fixed within very narrow limits (p. 26) by the number of molecules present per unit volume, whatever their mass or chemical properties.

(2) **Additive properties** are those which are determined only by the *nature and number of the atoms* (or radicals) in the molecule, and not by the way in which they are arranged or united together. Thus, the mass of a molecule is strictly additive, since (in accordance with the law of conservation of mass) it can be predicted accurately by adding together the masses of its constituent atoms. Many other physical properties which are roughly additive (*e.g.* molecular volume) are affected to some extent by changes in chemical constitution, and therefore belong strictly to the third group of properties.

(3) **Constitutive properties** are those which depend on the arrangement as well as on the number of the atoms in the molecule. These properties are affected profoundly by changes in chemical constitution, and are of special value in the study of molecular structure. As examples of this type of property we may take (i) *absorption spectra*, which depend almost entirely on the nature of the bonds by which the atoms are united, (ii) *optical rotatory power*, which depends on a dissymmetric arrangement of the atoms, and (iii) *refractivity*, which depends on the number and nature of the atoms in the molecule, but also on the character of the bonds between them.

Influence of pressure and temperature on physical properties.—Most physical properties are altered by changes in pressure and temperature. In the case of gases, *pressure* is of great importance; but when liquids or solids are considered the effect of pressure is small and can generally be neglected. The effect of *temperature* has, however, to be allowed for, even in the case of liquids and solids, before the physical properties of a number of substances can be compared fairly with one another. Two methods are usually employed.

(i) The first is to measure the physical property which is to be studied at corresponding temperatures, *i.e.* at temperatures which are equal fractions of the critical temperatures (p. 41) of the liquids under investigation. This is, in effect, the method used by Kopp in the study of molecular volumes (p. 70).

(ii) The second method consists in finding a function of the property studied which does not vary with temperature. This constant can then be used in comparing the magnitude of the property in different compounds. An example of this method will be found in the discussion of refractive index (p. 84).

Molecular volumes.—The **molecular volume** is *the volume in cubic centimetres occupied by one gram-molecule of a substance.* It is obtained by dividing the molecular weight by the density, and is therefore defined by the relation

$$V = \frac{M}{D}.$$

Since liquids expand on heating, the molecular volume varies with the temperature and a standard temperature must be chosen. Kopp, who discussed the subject in 1855, suggested that the boiling-point was a natural temperature for comparison; and by comparing molecular volumes *at the boiling-point* he discovered many regularities. If these boiling-points had been determined at equal fractions of the critical pressures of the liquids, instead of at atmospheric pressure, Kopp's method would have given a comparison of the molecular volumes of the liquids in corresponding states (p. 41). Since, however, the boiling-points at atmospheric pressure are *approximately* equal fractions of the critical temperatures, Kopp's method can be regarded as a practical approximation to this ideal condition.

The molecular-volumes of the members of a homologous series at their boiling-points were shown by Kopp to differ by a nearly constant increment for the addition of each CH_2 group. This is illustrated in Table 18.

From a large number of these differences Kopp deduced an average value of 22·0 c.c. for the increment for CH_2. Since the

TABLE 18. MOLECULAR VOLUMES AT THE BOILING-POINT.

Substance.	Formula.	Molecular Volume.	Diff.
Methyl iodide - -	CH_3I	64·1	
			21·6
Ethyl „ - -	C_2H_5I	85·7	
			21·1
Propyl „ - -	C_3H_7I	106·8	
			21·7
Butyl „ - -	C_4H_9I	128·5	
Methyl ethyl ether -	C_3H_8O	84·0	
			22·1
Diethyl „ -	$C_4H_{10}O$	106·1	
			21·7
Ethyl propyl „ -	$C_5H_{12}O$	127·8	
			22·3
„ butyl „ -	$C_6H_{14}O$	150·1	
Methyl formate -	$C_2H_4O_2$	62·7	
			21·9
Ethyl „ - -	$C_3H_6O_2$	84·6	
			21·6
Propyl „ - -	$C_4H_8O_2$	106·2	
			21·4
Butyl „ - -	$C_5H_{10}O_2$	127·6	

molecular volumes of butane, C_4H_{10}, and of benzene, C_6H_6, were equal, Kopp assumed that the volume of the carbon atom was twice that of the hydrogen atom, from which it follows that $C = 2H = 11$; $\therefore H = 5{\cdot}5$. By using these values, atomic volumes can be calculated for other elements. Thus methyl ethyl ether, C_3H_8O, gives $V = 84{\cdot}0$. Subtracting

$$3C + 8H = 33 + 44 = 77,$$

we find that the oxygen atom in this compound has an atomic volume of $84 - 77 = 7$ units. Working in this way Kopp compiled the list of atomic and structural constants which is set out in Table 19 below.

TABLE 19. KOPP'S ATOMIC VOLUMES.

C = 11·0	Cl = 22·8	O′ in OH or in ethers = 7·8
H = 5·5	Br = 27·8	O″ in >CO = 12·2
	I = 37·5	

These numbers may be used to predict molecular volumes, as follows:

Propyl iodide, C_3H_7I.		Acetic acid, $C_2H_4O''O'$.	
3C =	33·0	2C =	22·0
7H =	38·5	4H =	22·0
I =	37·5	O″ =	12·2
		′O′ =	7·8
V(calc.) =	109·0 c.c.	V(calc.) =	64·0 c.c.
V(obs.) =	106·8 c.c.	V(obs.) =	63·5 c.c.

It will be seen that the relation is not strictly additive, since different values are assigned to oxygen when singly linked and when doubly linked to carbon. Moreover, investigation has shown that the molecular volume of a compound is affected by other constitutional factors. Thus, if it were a strictly additive property isomeric substances would have identical values of V; but Table 20 shows that there are considerable deviations from this rule, and that the structure of the molecule does influence the value of the molecular volume. Molecular volumes are therefore roughly "additive" but are affected appreciably by "constitutive" factors.

TABLE 20. MOLECULAR VOLUMES OF ISOMERS.

Substance.	Formula.	Molecular Volume.
Acetaldehyde	C_2H_4O	56·9
Ethylene oxide	,,	52·4
Allyl alcohol	C_3H_6O	74·2
Acetone	,,	76·8
Propyl alcohol	C_3H_8O	81·3
Methyl ethyl ether	,,	84·0
Anisole	C_7H_8O	125·2
o-Cresol	,,	121·5

Surface tension and molecular volume.—The irregularities found in the study of molecular volumes at the boiling-point can be ascribed to three causes.

(i) Boiling-points are not exactly corresponding temperatures (cf. Table 7, p. 42).

(ii) The attraction between the molecules gives rise to a large internal pressure which is not the same for all liquids, even at corresponding temperatures; the unequal compression of the molecules under these unequal internal pressures will therefore introduce irregularities into the molecular volumes.

(iii) Kopp's method of calculating the atomic volumes of carbon and hydrogen ignores the structural differences between C_4H_{10} and C_6H_6, and therefore gives erroneous values.

A method of comparing molecular volumes, in which allowance is made for the effect of internal pressure, has been worked out by Sugden. This depends on using MacLeod's relation between surface tension and density (p. 63). Since

$$\gamma = C(D-d)^4, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

it follows that $C^{\frac{1}{4}} = \gamma^{\frac{1}{4}} \div (D-d)$ is constant and therefore that the quantity

$$[P] = \frac{M}{D-d}\gamma^{\frac{1}{4}} = MC^{\frac{1}{4}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

(where M is the molecular weight), will be constant over the range of temperatures within which MacLeod's relationship is valid. Since d is small compared with D, $[P]$ is practically equal to the molecular volume, multiplied by the fourth root of the surface tension, so that if two liquids are examined under such conditions that their surface tensions are equal, their molecular volumes will be proportional to the values of the constant $[P]$. The constant $[P]$ is therefore a measure of the *molecular volume at temperatures at which different liquids have the same surface tension.* This constant is named the **parachor** (from παρά = by the side of, and χώρα = space), signifying comparative volume.

Atomic and molecular parachors.—The parachor is an additive property, *i.e.* the value for a given molecule can be calculated as the *sum* of a series of atomic and structural constants. The atomic parachors for carbon and hydrogen, which are of fundamental importance in the study of organic compounds, can be

deduced from the " molecular parachors " of a series of paraffin hydrocarbons, as given in Table 21.

TABLE 21. PARACHORS OF THE PARAFFINS.

	[P] obs.	Diff.	39n.	2H.
C_2H_6 -	110·5		78·0	32·5
		40·3		
C_3H_8 -	150·8		117·0	33·8
		40·1 × 3		
C_6H_{14} -	270·1		234·0	36·1
		39·2		
C_7H_{16} -	309·3		273·0	36·3
		35·7		
C_8H_{18} -	345·0		312·0	33·0
	Mean	39·3	Mean	34·2

The differences (column 3) between successive members of this and other homologous series are nearly constant, the average increment for CH_2 being 39·0. The value for 2H can then be obtained by subtracting

$$n \times CH_2 = 39n$$

from the parachor for the compound C_nH_{2n+2}. The magnitude of this residue as calculated from successive members of the homologous series is given in the last column of the table, the average value being $H_2 = 34·2$, or $H = 17·1$. Combining this with the value $CH_2 = 39·0$ it follows that

$$C = 39·0 - 2 \times 17·1 = 4·8.$$

When the values for carbon and hydrogen are fixed, the atomic parachors for other elements can be determined in a similar manner. It is then found that the parachor can be expressed as the sum of a series of atomic and structural constants *which do not vary from compound to compound.* Thus the same constant can be used for oxygen in ethers and in ketones (there is a small anomaly in esters); and the increment for a double bond is the same in the groups C=C, C=O, C=N, C=S, and N=O. The most important atomic and structural constants are quoted in Table 22; in general the atomic parachors vary with the atomic weight in much the same way as Lothar Meyer's atomic volumes.

TABLE 22. PARACHOR CONSTANTS.

H = 17·1	Triple bond - - -	46·6
B = 14·0	Double bond - -	23·2
C = 4·8	3-membered ring - -	17·0
N = 12·5	4 ,, ,, - -	11·6
O = 20·0	5 ,, ,, - -	8·5
F = 25·7	6 ,, ,, - -	6·1
Si = 12·0	Single bond - - -	0·0
P = 37·7	Semi-polar double bond -	−1·6
S = 48·2	O_2 in esters - - -	60·0
Cl = 54·3		
Br = 68·0		
I = 91·0		

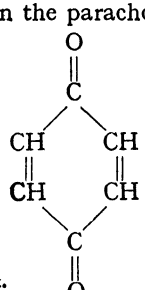
Parachors of isomeric compounds.—The additive nature of the parachor can be tested by comparing the values recorded for a series of isomerides, such as the esters in the following table:

	[P] obs.		[P] obs.
iso-Amyl formate -	293·6	Ethyl butyrate -	293·6
iso-Butyl acetate -	295·1	Ethyl isobutyrate -	293·9
n-Propyl propionate -	295 3	Methyl valerate -	292·5

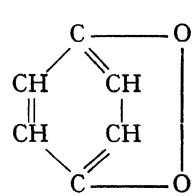
It will be seen that six compounds having the formula $C_6H_{12}O_2$ give a parachor which is constant within the limits of experimental error and is very close to the calculated value

$$[P] = 294{\cdot}0.$$

On account of its additive character, the parachor cannot be used to detect differences of structure in a series of isomeric esters; and, since the structural constant for a triple bond is exactly twice as great as for a double bond, the parachors would be the same for methyl cyanate $CH_3O \cdot C \equiv N$ and methyl isocyanate $O : C : N \cdot CH_3$. If, however, two isomerides differ by the change from a double bond to a ring structure, as in the case of the two formulae I. and II. suggested for quinone, a difference in the parachor would be produced.



[P] calc. = 236·1.
I.



[P] calc. = 218·7.
II.

Measurements of the surface tension and density of this substance give $[P]$ obs. $= 236{\cdot}8$, which points clearly to I. as representing more accurately the constitution of this substance.

Influence of double bonds.—The parachor is of special interest on account of the evidence that it provides of the existence of two different kinds of double bond. This is shown in Table 23, where the difference between the sum of the atomic parachors $\Sigma[P]$ and the experimental value $[P]$, is a measure of the influence of the double bonds. In the first three compounds this difference corresponds to an increment of about $+23$ for each double bond, but in the last three compounds a small decrement (about $-1{\cdot}6$) is observed.

TABLE 23. NON-POLAR AND SEMI-POLAR DOUBLE BONDS.

		[P] obs.	Σ[P].	Diff.
Ethylene	$CH_2=CH_2$	99·5	78·0	21·5
Acetone	$(CH_3)_2C=O$	161·7	137·0	24·7
Carbon disulphide	$S=C=S$	144·7	101·2	21·8 × 2
Phosphorus oxychloride	$Cl_3P\rightleftharpoons O$	217·6	220·6	−3·0
Thionylchloride	$Cl_2S\rightleftharpoons O$	174·5	176·8	−2·3
Methyl sulphate	$(MeO)_2S\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$	238·9	240·4	−0·8 × 2

An explanation of these differences is found in the newer theories of valency, in which two kinds of linkage are recognised. The first is the ordinary symmetrical or "non-polar" bond of compounds such as $Cl-Cl$ or $CH_3 \cdot CH_3$, which is sometimes distinguished as a "covalence." The second type of valency is the "polar" link which is characteristic of salts such as $\overset{+}{Na}\ \overset{-}{Cl}$, in which the atoms carry opposite electric charges, and are held together by the electrostatic attraction between them. This kind of linkage is termed a polar valency or "electro-valence."

From these considerations it follows that a double bond can consist of two covalences, or of two electrovalences, or of one of each. It is then found that a "non-polar" double bond, consisting of two covalences, gives rise to an *increase* of 23 units in the parachor. If, however, the double bond is composed of one covalence and one electrovalence, the "semi-polar" double

bond, represented by symbols such as $\overset{+}{S}Cl_2-\overset{-}{O}$ or $SCl_2{=}O$, causes a small *decrease* in the parachor. The third kind of double bond, consisting of two electrovalences, is probably present in compounds such as $\overset{++--}{Mg}\,O$ or $\overset{++--}{Ca}\,S$, but data for compounds of this type are not yet available.

7. Optical Properties.

1. Measurement of the refractive index of a liquid.—Many of the most convenient instruments for measuring refractive indices depend upon the method of total reflexion; a text-book of physics should be consulted for a detailed description. The Pulfrich refractometer, illustrated in Fig. 18*a*, depends on this principle. The essential part of the instrument is a right-angled glass prism (Fig. 18*b*), with a small cell containing the liquid mounted upon the upper horizontal surface. A beam of monochromatic light *AB* *at grazing incidence* follows the path *ABCD* and is observed in a telescope at *D*. If the telescope is moved to make an angle with the horizontal which is less than *i*, no light can reach

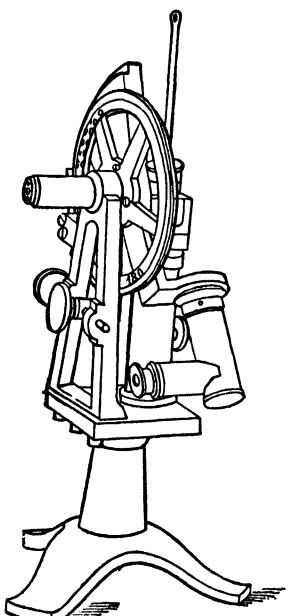


Fig. 18*a*.—Pulfrich refractometer.

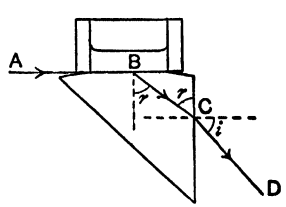


Fig. 18*b*.—Optical system of Pulfrich refractometer.

it; a very accurate determination can therefore be made of the angle *i*, at which a sharp boundary between a dark and light field is seen in the field of view.

If *r* is the critical angle

$$\sin r = \frac{n}{N},$$

where n is the refractive index of the liquid and N is that of the glass prism. Also

$$\frac{\sin i}{\cos r} = N; \quad \therefore \cos r = \frac{\sin i}{N};$$

$$\therefore \sin r = \sqrt{1 - \frac{\sin^2 i}{N^2}} \quad \text{and} \quad n = N \sin r = \sqrt{N^2 - \sin^2 i}.$$

A table of refractive indices corresponding to each value of i is usually supplied with the instrument. The value of N can also be determined by making an observation with pure water.

In some forms of refractometer the prism is fitted with an arrangement for circulating water at a known temperature around it. For the experiments described below it is sufficient to work at room temperature (which should be noted), leaving the specimens of liquid in the neighbourhood of the refractometer and thermometer for half an hour before taking measurements.

A sodium flame can be used as a source of monochromatic light. A Mecker burner, with a small piece of pumice soaked in fused common salt and mounted on the grid of the burner, is a convenient apparatus to use for this purpose.

ii. Refractive index of water.—Place a little distilled water in the cell and move the telescope until the cross-wires coincide with the boundary between the dark and light regions. Read the angle i on the graduated circle, and, by reference to the tables, obtain the corresponding value of the refractive index. If the instrument is adjusted correctly, the value for n_D will be in agreement with the numbers given in Table 24.

TABLE 24. REFRACTIVE INDEX OF WATER.

Temperature.	n_D.
0°	1·3328
10°	1·3329
20°	1·3330

iii. Molecular refractivities.—In the same way, determine the refractive index of benzene, toluene, chlorobenzene, methyl acetate, ethyl acetate. The densities of these substances at the temperature of observation can be obtained from the results of Expt. 6, i. and ii., p. 68.

Calculate the molecular refractivities of each substance by the formula

$$R = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$$

From the molecular refractions, tabulate the increments for CH_2 and for replacement of H by Cl, etc.

iv. Measurement of optical activity.—(*a*) *The polarimeter.*—Fig. 19 illustrates a type of half-shade polarimeter which can be used for the following experiments. Monochromatic light from a sodium flame (compare Expt. 7, i) falling on a *diaphragm* 7 is rendered parallel by a *condensing lens* 6, before passing through the *polarising prism* 5, made of doubly-refracting Iceland spar. In this prism the light is broken up into two rays, vibrating in two perpendicular directions, which are therefore said to be "polarised" in a horizontal and a vertical plane.

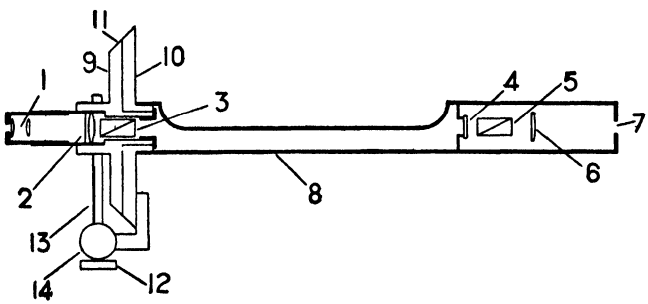


FIG. 19.—Diagram of half-shade polarimeter.

1. Eyepiece.
2. Object-glass.
3. Analysing prism.
4. Half-wave plate of mica or quartz.
5. Polarising prism.
6. Condensing lens.
7. Diaphragm.
8. Trough.
9. Scale.
10. Back plate carrying centre fitting.
11. Vernier.
12. Slow-motion clamp.
13. Rod to clamp slow motion adjustment.
14. Slow-motion tangent screw.

The "ordinary ray," which is polarised in a vertical plane, is totally reflected by a film of Canada balsam running diagonally through the prism, whilst the "extraordinary ray," which is polarised in a horizontal plane, passes on to the *analysing prism* 3, which can be rotated about the horizontal axis of the instrument. If these two prisms are set in "parallel" positions, the polarised light from the "polariser" is transmitted freely by the "analyser"; but if they are "crossed" (*i.e.* set in positions at right angles to one another), the light from the polarising prism is thrown out by the analysing prism, and the beam passing through the apparatus is extinguished. If an "optically-active" medium is introduced between the two prisms, the plane of polarisation is twisted, and the beam is once more transmitted. The angle through which the plane of polarisation has been rotated in its transit from one prism

to the other, can be determined by measuring the angle through which the analysing prism must be rotated in order once again to extinguish the light; but since the extinction of the light takes place only gradually as the analyser is rotated, this method is not very sensitive. A "half-shadow" device is therefore introduced, whereby the setting is made to depend on equalising the brightness of two feebly-luminous areas, instead of extinguishing completely the light from either of them.

The device used for this purpose is a *half-wave plate* 4 of quartz (or mica) covering half the aperture of the polarising prism, *e.g.*, the shaded part of the circle in Fig. 20. This plate is made by cutting a quartz crystal parallel to its principal axis, which we will suppose to occupy the vertical position AB. Light

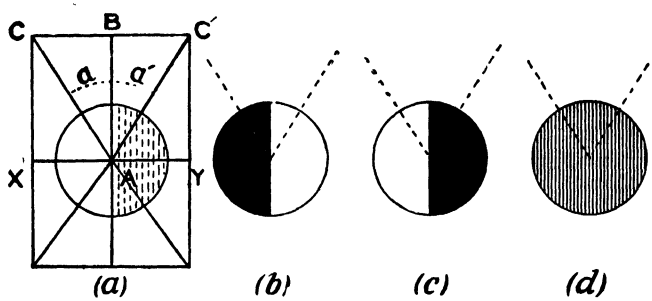


FIG. 20.—Diagram to illustrate "half-shadow."

polarised in the direction AC will then be resolved by the plate into an "ordinary ray" polarised in the plane AB and an "extraordinary ray" polarised in the plane XY. If the thickness of the plate is adjusted so that the extraordinary ray is retarded by half a vibration relatively to the ordinary ray, the vibrations AB, AX will become AB, AY, and the beam emerging from the plate will be polarised in the plane AC', where $CBA = C'BA$. If therefore the light coming from the polarising prism is polarised in the direction AC, the light which has passed through the plate will be polarised in the plane AC', at an equal inclination to the vertical plane. When the *eyepice* 1 (Fig. 19) is focussed on the sharp edge of the half-wave plate, the field of view will be divided by a vertical line into two halves of unequal brightness. Thus, if the polariser and analyser are crossed (by setting the analyser in a direction perpendicular to AC) the light in the left-hand part of the field will be extinguished completely as in Fig. 20 (*b*), whilst the right-hand part

of the field will remain relatively bright, since the light (polarised in the plane AC') which has passed through the half-wave plate will not be extinguished. If, however, the analyser is perpendicular to AC', the right-hand part of the field will be dark, and the left-hand part will be light, as in Fig. 20 (*c*). Finally, if the analyser is set parallel to AB, neither half of the field will be completely dark, but both halves will be illuminated equally as in Fig. 20 (*d*).

The angle CAC' is called the "half-shadow angle," and can be varied by rotating the polarising prism relatively to the half-wave plate; the sensitiveness of the instrument depends on *making* this angle as small as possible, whilst still providing sufficient light to enable the fields to be equalised readily. It will be found that there are two positions 90° apart in which the two halves of the field are equally illuminated; in one the amount of light passing through is small and the change-over is sharp, and this setting should be used for all measurements. The apparatus should be set up in a dark room and a screen used to prevent light from the sodium flame reaching the eye directly.

(*b*) *Measurement of the rotatory power of turpentine.*—Fill the polarimeter tube with water and insert in the instrument. Make five settings of the analysing prism; the mean value gives the zero of the instrument. Clean and dry the tube and fill with oil of turpentine. It will be found that the two halves of the field have the same intensity when the analysing prism is moved to a new position. Read the angle through which the prism has been turned, and note whether the rotation is clockwise (+) or anticlockwise. If α_D is this angle, the specific rotatory power (p. 89) $[\alpha]_D$ for sodium light is given by

$$[\alpha]_D = \frac{\alpha_D}{ld},$$

where l is the length of the tube in *decimetres* and d is the density of the liquid examined. This must be determined by means of a pyknometer or specific gravity bottle.

(*c*) *Measurements of the specific rotatory power of cane-sugar.*—Prepare solutions of cane-sugar containing 5, 10 and 20 grams in 100 c.c. of solution. Determine the rotatory powers of these solutions and in each case calculate the specific rotation of cane-sugar by the formula

$$[\alpha]_D = \frac{\alpha_D}{lc},$$

where c is the concentration in grams of sugar per 100 c.c. of solution.

(*d*) *Measurements of the specific rotatory power of camphor.*—In the same way determine the specific rotations of 10 per cent. solutions of camphor in (*a*) alcohol, (*b*) benzene. The specific rotatory power can be calculated by the formula given for cane sugar above.

(*e*) *Calculation of molecular rotations.*—Calculate the molecular rotations of cane-sugar and of camphor from the formula

$$[M]_D = M[\alpha]_D \div 100.$$

Additive and constitutive properties.—Properties which are strictly additive (in the same sense as that in which the molecular weight of a compound is the sum of the atomic weights of the constituent atoms) are extremely rare. They can be recognised by the fact that the numerical values of the property are identical in pairs or groups of isomeric compounds; but since in practice nearly all the properties of isomeric compounds (except optical isomerides) are found to differ to a larger or smaller extent, it follows that constitutive factors are already making their influence felt. The molecular volume, when corrected for internal pressure by using the parachor, is perhaps the best example now known of an additive property, since it is subject only to the constitutive factor that a double bond produces a definite increment, just like an atom, *e.g.* of hydrogen or of carbon. It will now be shown that the optical properties of organic compounds provide an excellent illustration of the transition from purely additive to purely constitutive properties. Thus:

(*a*) The *refractive index*, when corrected for the density of the medium and for its molecular weight, is in the main an additive property, since it is possible to calculate the molecular refraction of a compound with the help of a table of atomic refractions (Table 26, p. 85) in just the same way as the molecular volume can be calculated from the atomic volumes of the constituent elements. The growing influence of the arrangement, as contrasted with the mere number of the constituent atoms, is, however, shown by the existence of the anomaly known as "optical exaltation" (see below, p. 86), in compounds which exhibit no anomaly at all either in the molecular volume or in the parachor.

(*b*) The *magnetic rotatory power* (p. 88) shows a regular increment in homologous series, and must therefore be in part an additive property, but it is so strongly influenced by molecular structure that it is no longer possible to use a simple addition formula in order to calculate the magnetic rotatory power of a compound.

(*c*) Finally, the *optical rotatory power* depends entirely on structure, and is therefore a purely constitutive property, although indications of an additive effect have been detected in rare instances.

Refraction.—When a ray of light enters a liquid it is bent as shown in Fig. 21. The *refractive index* is defined as

$$n = \frac{\sin i}{\sin r},$$

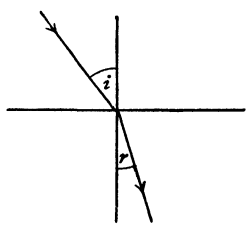


FIG. 21.—Refraction of light.

where i is the angle of incidence and r the angle of refraction. The refractive index n is the ratio of the velocity of light in air to its velocity in the medium. The refractive index of a liquid can be measured with a high degree of accuracy when only a small quantity of the substance is available; it is, therefore, a very suitable property to use in the investigation of organic compounds. One method of measuring the refractive index of a liquid is described in Expt. 7, i. For an account of other methods of measuring refractive indices a text-book of physics must be consulted.

Molecular refraction.—The refractive index of a liquid varies both with temperature and with the wave-length of the light used. The latter factor is eliminated by using a standard wave-length for all measurements. Two standards are in use, the *D* line of sodium and the red, H_α, line of hydrogen. Monochromatic light of the wave-length of the *D* line is readily obtained by feeding a Bunsen flame with common salt; the red H_α light is obtained by passing an electric discharge through a vacuum tube containing hydrogen at low pressure. The wave-length of light used is indicated by a suffix; thus $n_D = 1{\cdot}3333$ refers to the refractive index for the *D* line of sodium.

Many formulae have been suggested to eliminate the effect of temperature on refractive index. Thus Gladstone and Dale used the simple function

$$R = (n - 1)\frac{M}{D}$$

to represent the molecular refraction of a compound, where M is the molecular weight of the compound, D is its density as liquid or vapour, and $n - 1$ is the excess of the refractive index of the liquid or vapour above that of a vacuum. The relation which has the greatest theoretical significance, however, is due to Lorentz and Lorenz, who deduced from the electromagnetic theory of light that the quantity

$$R = \frac{n^2 - 1}{n^2 + 2}\frac{M}{D}$$

should not vary with temperature. Here M is again the molecular weight, and D the density of the liquid, and the quantity R is termed the **molecular refraction.** This function of the refractive index is the same for the liquid state at all temperatures, and in some cases it has been found to have the same value for the vapour state also. Thus Landolt found that $R_a = 3{\cdot}726$ for liquid water at 10°, and that $R_a = 3{\cdot}714$ for water-vapour at 100°.

Atomic refractions.—The molecular refractions of the members of a homologous series differ by a nearly constant quantity, corresponding to the value of a CH_2 group. This is illustrated by the data in Table 25. The mean value of the CH_2 group, calculated from a large number of series, is 4·598. The **atomic refractions** for carbon and hydrogen can be deduced from this increment together with the data for the hydrocarbons. Thus, subtracting $n$$CH_2$ from the molecular refraction of the hydrocarbon C_nH_{2n+2}, we get the value for 2H, as shown in the last column of the table. The best value for the atomic refraction of hydrogen is H = 1·092. Combining this with the value for CH_2, it follows that the atomic refraction of carbon is C = 2·413. Similarly, the refractivity of the oxygen atom in aldehydes can be found by subtracting $n$$CH_2$ from the refractivity of the aldehyde $C_nH_{2n}O$, as shown in the lower part of the table.

TABLE 25. MOLECULAR REFRACTIONS OF HOMOLOGOUS COMPOUNDS.

Substance.	Formula.	R_α	Diff.	nCH$_2$.	$R_\alpha - n$CH$_2$.	
Pentane - -	C_5H_{12}	25·27		22·99	2·28	
			4·47			
Hexane - -	C_6H_{14}	29·74		27·59	2·15	2H
			2 × 4·68			
Octane - -	C_8H_{18}	38·99		36·78	2·21	
			2 × 4·65			
Decane - -	$C_{10}H_{22}$	48·28		45·98	2 30	
Acetaldehyde -	C_2H_4O	11·51		9·20	2·31	
			4·44			
Propionaldehyde	C_3H_6O	15·95		13·79	2·16	O″
			4·59			
n-Butyraldehyde	C_4H_8O	20·54		18·39	2·15	
			4·79			
Valeraldehyde	$C_5H_{10}O$	25·33		22·99	2·34	

In this way the atomic refractions of a number of elements have been worked out, and can be used to predict the molecular refractions of compounds. The more important constants are collected in Table 26.

TABLE 26. ATOMIC REFRACTIONS FOR H_α.

C - -	2·413	Cl - -	5·933
H - -	1·092	Br - -	8·803
O (in OH)	1·522	I - - -	13·757
O (in ethers)	1·639	Double bond -	1·686
O″ (in >CO)	2·189	Triple bond -	2·328

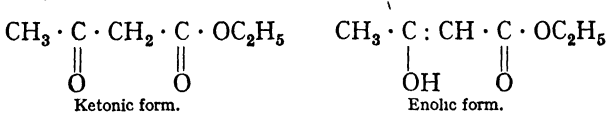
It can be seen from this table that molecular refractivity is not strictly an additive property, but is influenced by the arrangement of the atoms in the molecule. A definite increment has to be added for each double and triple bond present in the molecule ; and the value for oxygen is seen to vary considerably with the manner in which it is linked in the molecule.

Prediction of molecular refractions.—The use of these constants to predict molecular refractions may be illustrated by two examples :

(*a*) *Methyl ethyl ketone* C_4H_8O:

4C	= 9·65
8H	= 8·74
O″	= 2·19
M_α (calc.)	= 20·58
M_α (obs.)	= 20·56

(*b*) *Acetoacetic ester*, $C_6H_{10}O_3$, may exist in two isomeric forms, as follows:



Ketonic form. Enolic form.

The molecular refractions calculated for these two forms are set out below.

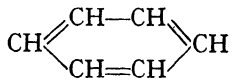
Ketone.		Enol.	
6C	= 14·48	6C	= 14·48
10H	= 10·92	10H	= 10·92
2O″	= 4·38	O″	= 2·19
1O′	= 1·64	O in OH	= 1·52
	31·42	O in ether	= 1·64
		Double bond	= 1·69
			32·44

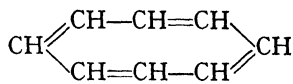
Thus M_α(calc.) is 31·42 for the ketonic form and 32·44 for the enolic form, the difference being due to the fact that a double bond between carbon and carbon increases the molecular refraction by 1·69 units, whereas a double bond between carbon and oxygen in a ketone or aldehyde only gives an increment of 0·67 or 0·55, as compared with a single bond between these atoms in an alcohol or ether. The observed value, 31·91, is intermediate between these two numbers, and indicates (in agreement with other evidence) that the substance is a mixture of the two forms.

Optical exaltation.—A characteristic property of refractivity is the mutual effect of two double bonds when separated from each other by one single bond. Thus two isomeric hydrocarbons of the formula C_6H_{10} have the following structure and refractivities:

		M_α (obs.)	M_α (calc.)
Diallyl	$CH_2=CH-CH_2-CH_2-CH=CH_2$	28·77	28·89
iso-Diallyl	$CH_3-CH=CH-CH=CH-CH_3$	29·87	28·89

The refractivity of diallyl is seen to be very close to the calculated value, whilst *iso*-diallyl gives a figure nearly a unit too high. The latter substance contains a chain of alternate single and double bonds in the grouping $-CH=CH-CH=CH-$. Substances which contain these chains are found to behave abnormally in their chemical reactions, and are said to contain a **conjugated system** of unsaturated linkages. Conjugated chains with open ends give a much higher molecular refractivity than would be predicted from their formulae, and are said to exhibit **optical anomaly** or **optical exaltation**; but this anomaly is not given by conjugated ring-compounds, such as

benzene 

or octatetrene 

where the conjugated system is continuous right round a closed ring. The presence or absence of optical exaltation has been used in order to determine the position of double bonds in the molecules of complex organic compounds.

Refraction, dispersion and absorption of light.—The refractive index of a liquid varies with the wave-length of the light, and in general increases as the colour of the light changes from red to blue. This effect is known as **dispersion**. The refraction and dispersion of a medium are related in a very intimate way to its **absorptive power** for light of various wave-lengths. Thus, if a medium is transparent, not only to visible light but also to light of shorter wave-length in the "ultra-violet" region of the spectrum, it generally has a small refractive index and small dispersion; but, if it has a strong **selective absorption** in the ultra-violet, the refractive index is found to increase very rapidly as the wave-length of maximum absorption is approached.

The refraction and dispersion therefore both become very high in the neighbourhood of a strong "band" of selective absorption. Since **absorption bands** are most commonly developed in *unsaturated* organic compounds, we can understand why there is an increment of refractive power for each double bond in the

system ; and since *conjugated double bonds* give rise either to a marked increase of absorptive power, or to a selective absorption at longer wave-lengths, we can understand why compounds of this group so often give rise to optical exaltation, as compared with compounds which do not contain a conjugated system of double bonds.

Magnetic rotatory power.—Faraday discovered in 1845 that the plane of polarisation of light was rotated when it travelled through a piece of glass in the direction of the lines of force of a strong magnetic field. This property of **magnetic rotatory power** is possessed by all transparent media, and shows many analogies to the refractive index. Sir William Perkin, who investigated this phenomenon during a period of twenty-five years from 1882 to 1907, used the **molecular magnetic rotation** as a measure of this property. This was defined as the *ratio* of the function $\omega M/D$ for the substance to the corresponding value for *water*, where ω is the rotation produced by a column of given length in a magnetic field of given strength, M is the molecular weight, and D the density of the substance. Perkin found that, if n is the number of atoms of carbon in the compound, the value of the molecular magnetic rotation $[\Omega]$ was given by the formula $[\Omega] = h + 1{\cdot}023n$, where h is a " series constant " for a given homologous series, *e.g.*

for the *normal* alcohols	$[\Omega] = 0{\cdot}699 + 1{\cdot}023n$,
for the *iso* and *sec.* alcohols	$[\Omega] = 0{\cdot}844 + 1{\cdot}023n$,
for the *normal* acids	$[\Omega] = 0{\cdot}303 + 1{\cdot}023n$,
for the *iso* acids	$[\Omega] = 0{\cdot}509 + 1{\cdot}023n$.

The property is *additive* in that there is a constant increment for each CH_2, which is the same for the various series ; but it is constitutive in that the series-constant is different for *normal* and for *iso* alcohols and acids.

Perkin calculated for the *ketonic* form of ethyl acetoacetate $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot OC_2H_5$, the value

$$[\Omega] = 0{\cdot}372 + 6 \times 1{\cdot}023 = 6{\cdot}510$$

where 0·372 is the series constant for a diketone and for the *enolic* form, $CH_3 \cdot C(OH) : CH \cdot CO \cdot OC_2H_5$

$$[\Omega] = 5{\cdot}714 + 1{\cdot}023 + 1{\cdot}112 = 7{\cdot}849,$$

where 5·714 was the value observed for ethyl lactate,

$$CH_3 \cdot CHOH \cdot CO \cdot OC_2H_5,$$

1·023 was the increment required to give the value for the next homologue, ethyl hydroxybutyrate,

$$CH_3 \cdot CHOH \cdot CH_2 \cdot CO \cdot OC_2H_5$$

and 1·112 was an increment for the conversion of a saturated into an unsaturated ester by removing two atoms of hydrogen and introducing a double bond. Since the observed value for the ester was 6·501, Perkin concluded that it was a saturated ketonic compound. Later experiments have shown, however, that the ester contains an appreciable proportion of the enolic isomeride.

Optical rotatory power.—Compounds which possess the property of **molecular dissymmetry** (*i.e.* compounds whose molecules are sufficiently unsymmetrical to give a " non-superposable " image when viewed in a mirror), rotate the plane of polarisation of light, apart from the influence of an external magnetic field. In the case of a homogeneous liquid, the **specific rotatory power** $[\alpha]$ of the compound is defined by the formula $[\alpha]=\frac{\alpha}{lD}$, where α is the observed rotation, l the length of the column in *decimetres*, and D the density. The corresponding formula for solutions is $[\alpha]=\frac{\alpha}{lc}$, where c is the concentration of the solution in grams per 100 c.c. The **molecular rotation** is given by the formula $[M]=\frac{M[\alpha]}{100}$. It will be noticed that in neither formula are the usual conventions followed, since the unit of length is the decimetre and not the centimetre, and the molecular weight is divided by 100. If the C.G.S. system were followed the values of the molecular rotatory power would be 10 times larger.

Since the optical rotatory power depends on molecular dissymmetry it is a wholly constitutive property. Additive relations have, therefore, only been observed when two dissymmetric groups of atoms are united into one molecule, when the **optical superposition** of the two independent rotations is sometimes found to obey an approximate additive law.

QUESTIONS ON CHAPTER III.

1. Describe a method of measuring the vapour-pressure of a volatile liquid. What explanation can you give for the rapid increase of vapour-pressure as the temperature rises ?

2. What methods are available for the determination of vapour densities ? Describe carefully how you would determine the density of a substance like ether by the aid of one of them. Of what value or importance is a knowledge of the vapour density of such a substance ? (Inter. Sci., Sheffield.)

3. What is meant by (*a*) surface tension, (*b*) interfacial tension. Describe two methods by which surface tension can be measured. (B.Sc. Hons.)

4. Describe carefully the methods you would employ to determine the molecular weight of a substance in the liquid state. (B.Sc. Hons., Sheffield.)

5. Discuss the relations which have been found between some one physical property and chemical constitution. (B.Sc., Manchester.)

6. The following figures were obtained for the surface tension and density of $POCl_3$: at 15°, $D = 1{\cdot}690$, $\gamma = 32\ 77$ dynes per cm. at 65°, $D = 1{\cdot}596$, $\gamma = 26{\cdot}57$. Calculate the molecular weight in the liquid state from these data.

7. From the data in Question 6, calculate the parachor of $POCl_3$, and by the aid of the constants in Table 23. discuss the nature of the linkage between phosphorus and oxygen.

8. What is meant by colligative, additive, and constitutive properties. Give examples of each.

9. Acetone has at 20° a refractive index of 1·3641 and a density of 0·8005. Calculate the molecular refractivity and compare it with the value predicted from the atomic constants.

CHAPTER IV.

THE SOLID STATE.

8. Properties of Solids.

i. **Determination of the melting-point. Capillary-tube method.**—Draw out a test-tube in the blow-pipe flame so as to make a thin-walled tube about 1-2 mm. in diameter. Break off a length of about 10 cm., seal up one end, and (when cold) shake down a few crystals of *p*-nitrotoluene or naphthalene to the closed end. Attach the capillary tube to a thermometer by means of a small rubber band, so that the part containing the substance is near the middle of the bulb. Support the thermometer vertically in a beaker of water containing a stirrer and raise the temperature slowly. Note the temperature (51·5° or 80° C.), at which the crystals suddenly melt.

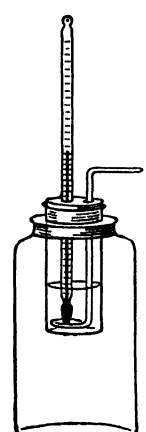


Fig. 22.—Apparatus for determination of freezing-points.

ii. **Determination of the freezing-point. Method of cooling.**—Fit a specimen-tube with a cork carrying a thermometer (0° to 100°) and a small stirrer made of thin glass rod. Mount the tube in a larger cork which closes the neck of a wide-mouthed bottle as shown in Fig. 22. This arrangement protects the tube from draughts and produces regular cooling. Place 10 grams of *p*-nitrotoluene in the tube. Insert the thermometer and stirrer and heat in a bath of hot water until all the substance is melted. Wipe the outside of the tube and insert in the neck of the bottle. Stir slowly and regularly and read the thermometer every half minute. The temperature will fall at first, but when crystals begin to form it will rise a little, and then remain steady for some time. (Why?) This steady temperature is the freezing-point

of the liquid and should be identical with the melting-point of the solid.

iii. **Behaviour of amorphous solids.**—(*a*) Procure a lump of soft pitch and break it into small pieces by blows from a hammer. Note the characteristic conchoidal fracture. Fill a glass funnel with the smaller pieces and leave in the laboratory for some weeks in order to observe the slow coalescence and flow through the funnel.

(*b*) Attempt to determine the melting-point by the capillary-tube method (using a rather wider tube), and note that there is no sharp transition from solid to liquid.

Characteristics of solids.—Both liquids and solids possess a dennite volume which is only altered to a small extent by changes of pressure or temperature. A solid has therefore a definite **compressibility**, which can be measured (like that of a liquid), by the ratio of the change of volume to the pressure or tension producing it. Liquids and solids differ, however, in that a solid object possesses and retains a characteristic shape, whilst a liquid assumes the shape of any vessel in which it is placed. This is due to the characteristic property of **rigidity**, which all solids possess to a greater or less extent.

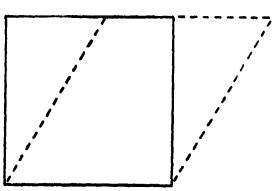


FIG. 23.—Shearing of a solid.

In general, when a solid is strained, both the shape and the volume are altered. Thus when a wire is stretched (in order to determine " Young's modulus "), its length is increased and its diameter is diminished; but these two effects do not balance one another, and the *volume* as well as the *length* of the wire is increased by stretching it. The rigidity of a solid can, however, be determined by applying to it a shearing-force, *i.e.* a force which tends to make one plane slide relatively to a parallel plane as in Fig. 23. In practice the rigidity can be measured most easily by measuring the force required to twist a wire or cylinder of a solid through a definite angle per unit of length, or indirectly by measuring the time of oscillation of a weight attached rigidly to the end of the wire when the wire is twisted and released.

In general, if we attempt to deform a solid by applying a force to it, the solid will " give " slightly under the load ; but when the force is removed, it will return to its original shape. If, however, the solid has been strained too much, it will not return to its original shape, but will be permanently deformed. All solids are permanently deformed if a force is used which is greater than a limiting value which is described as the **elastic limit** of the solid. This elastic limit (which can be measured in tons per square inch for a stretched rod of metal) varies enormously in different substances ; thus a much smaller force is required to bend or stretch permanently a bar of lead than one of the same dimensions made of steel.

FIG. 24. Cleavage-fragments of (*a*) rock-salt, (*b*) calcite, (*c*) barytes.

Crystalline and amorphous solids.—Solids can be divided into two distinct classes, namely, **crystalline solids** and **amorphous solids.**

(*a*) **Crystalline solids.**—Many substances, such as rock salt, alum and ice, separate in the form of **crystals** when deposited in the solid state from a solution, or from a homogeneous melt. The chief characteristics of this class of solids are :

(i) *They have a characteristic geometrical form.*—Crystals are usually bounded by plane faces which intersect one another at definite angles. These angles, as well as the angles between the edges, are fixed within very narrow limits, and often have simple integral values, *e.g.* 45°, 60° or 90°.

(ii) *They often have a plane fracture.*—If broken by a sudden blow, crystals often break most easily along certain planes which are parallel to important crystal faces. The planes along which a crystal breaks most easily are called cleavage planes (Fig. 24).

Thus mica, which has *one* very marked cleavage-plane, splits

up easily into thin sheets; whilst rock-salt, which has *three* cleavage planes at right angles to one another, breaks up easily into cubic or rectangular fragments. Many crystals, however, have no plane of easy cleavage, and break into irregular fragments. Rock-crystal is a familiar example of this kind.

(iii) *They have a definite melting-point.*—This varies with the nature of the liquid with which the melting solid is bathed. Thus ice floating in sea water melts at $-2{\cdot}4°$, and when bathed

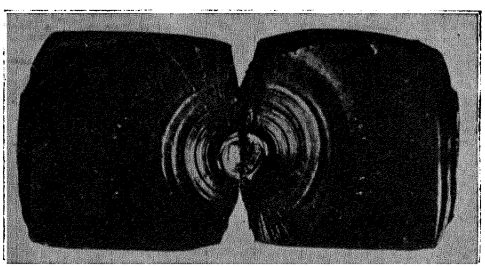


FIG. 25.—Conchoidal fracture of pitch.

with a saturated solution of common salt it may melt as low as $-22°$ C., as in a "freezing-mixture." If, however, the solid is pure (and melts to a pure liquid), the melting-point is remarkably constant, as in the case of melting ice, the temperature of which is used to fix the zero of a Centigrade thermometer.

(*b*) **Amorphous solids.**—Pitch and glass may be taken as examples of amorphous solids. This class of substances has the following properties.

(i) Amorphous solids, as their name implies, have no definite crystalline form.

(ii) When broken by a sharp blow they do not cleave along any particular plane, but fracture with equal ease in any direction. The broken surfaces often exhibit convexities or concavities shaped like a shell. Hence this type of fracture is often termed a **conchoidal fracture** (Fig. 25).

(iii) When heated, amorphous solids do not melt sharply at a definite temperature, but pass through an intermediate soft and pasty stage, which persists over a considerable range of temperature.

Amorphous solids can be regarded as supercooled liquids, *i.e.* liquids cooled to such a temperature that they have a very high viscosity and hence crystallise very slowly. Although they have many of the properties of solids, it is possible to show in certain cases that they will flow like a liquid. Thus, if a lump of pitch is struck smartly with a hammer, it will fly to pieces like any other solid; and the broken surfaces may exhibit a characteristic conchoidal fracture. If, however, some of the fragments are placed in a funnel, and allowed to stand for some months, they will gradually coalesce and flow through the funnel just as water does. Both water and pitch are liquids, but pitch has such a high viscosity that it takes months to flow through a funnel, whilst water only requires a few seconds. The properties of supercooled liquids and the conditions under which they are formed are discussed again in Chapter V. (p. 113).

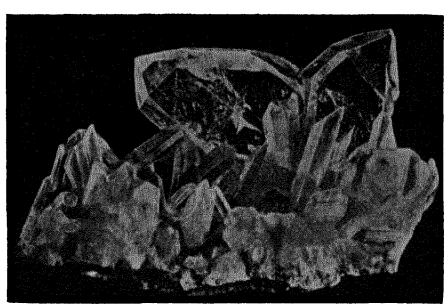


FIG. 26.—Crystals of quartz.

Structure of crystals.—The most obvious property of crystals is their characteristic geometrical form; thus, salt crystallises in cubes, and alum in octahedra. Silica, as rock crystal or quartz, is found in the form of six-sided prisms, capped by six-faced pyramids. Since, however, the different faces of a crystal may not all be developed equally, the shape of the crystals of a given substance is variable. Thus crystals of quartz, Fig. 26, are not bounded entirely by regular hexagonal prisms and pyramids, but are irregular in shape, some of the faces being much larger than others, although the angles at

which the faces meet are the same in all crystals of this substance. Again, when a solution of alum is allowed to cool, the crystals which are formed are not perfect octahedra, since accidental circumstances cause different faces to grow at different rates.

These facts suggest that the internal structure of crystals is more important than their external form or "habit," and that the constancy of the angles at which the faces of a crystal meet is due to a regular arrangement of the molecules composing the crystal. When a crystal grows, each new layer of molecules is laid down in such a way as to keep the growing face parallel to its original direction. This is well seen when a crystal of chrome alum is allowed to grow in a solution of potash alum. The colourless potash alum then forms layers parallel to the faces of the coloured chrome alum, so that it seems beyond doubt that its molecules have continued to reproduce the regular arrangement of the original crystal. We therefore think of the molecules as being arranged in a regular and orderly fashion within a crystal, whereas in an amorphous solid or glass they have the same chaotic distribution as in a liquid.

If we could see the individual molecules, the face of a crystal would probably look like a field planted with cabbages all arranged in regular rows, since the molecules could be joined up by a series of imaginary straight lines, all equidistant and parallel to one another. We should find, however, that the molecules were also spaced at regular intervals in each row, like the trees in a plantation, so that a second series of parallel lines could be drawn through them, intersecting the first series at some definite angle. All the molecules would then be located at points of intersection of a net-work or lattice of intersecting series of parallel straight lines.

This orderly arrangement of the molecules, however, is not merely in *two* dimensions, but in *three*. If, therefore, we joined up the corners of this lattice to the corresponding corners of the lattice on an adjacent sheet of molecules immediately below the surface, we should obtain a **space-lattice** composed of many series of parallel lines, each line passing through similarly-placed molecules (or atoms) in the crystal. Each crystalline substance has its own characteristic arrangement of molecules,

corresponding to a particular space-lattice, and this pattern is repeated throughout the crystal whatever its size or external form. This pattern or space-lattice determines all the properties of the crystal; in particular, it fixes the angles at which the plane faces meet, and the planes along which cleavage takes place most easily.

Analysis of crystals by X-rays.—This conception of the nature of crystals has been verified by the investigation of the effect of crystals upon X-rays. It has long been known that a ray of light is broken up into a spectrum when it is passed through a glass plate on which a series of parallel lines is ruled at intervals not many times greater than the wave-length of the light; if the spacing is not too small, a whole series of these spectra may be seen. The wave-length of ordinary light (say 4000 to 8000 Å.U.) is enormously greater than the distance between the atoms or molecules in a crystal, which amounts to only a few Å.U.; but X-rays have a wave-length which is perhaps 10,000 times smaller than that of visible light, and is actually less than the dimensions of the cells of the crystal-lattice. It is therefore found that, when a pencil of X-rays is passed through a crystal, a pattern of diffracted spots is produced, just as would be expected if the crystal were composed of a regular assemblage of molecules.

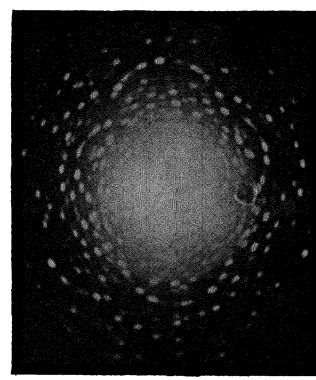


FIG. 27.—Laue pattern (potash alum).

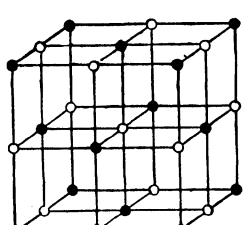


FIG. 28.—Space-lattice of rock-salt.

Fig. 27 shows the type of pattern produced in this manner. From a study of such photographs, and a closer investigation of the action of crystals on X-rays, the arrangement of the atoms in many crystals can be determined. Fig. 28 shows the space-lattice of common salt.

The black circles represent the centres of sodium atoms, and the white ones the centres of chlorine atoms (or conversely). The distance between neighbouring atoms of sodium and chlorine is $2{\cdot}81 \times 10^{-8}$ cm. This is very little larger than the diameter of the atoms as deduced by other methods, and we must suppose that in a crystal of common salt the atoms are very closely packed together.

Equilibrium between the solid and liquid states.—When a crystalline solid is heated it is converted into a liquid (if it does not first decompose) as soon as the temperature exceeds a definite value, which is termed the **melting-point** of the solid. If the temperature is then allowed to fall, the liquid may often be cooled below the melting-point, provided that no crystals are present; but, when a crystal is introduced, new crystals begin to form at once, and the temperature rises to the melting-point and remains there until all the liquid has solidified.

If the temperature of a pure substance is maintained a little above the melting-point, then all the solid will melt; if it is kept a little below the melting-point, then all the liquid will solidify. At the melting-point, but at no other temperature, liquid and solid can coexist in stable equilibrium with one another for an indefinite time. It follows therefore that, in the case of a pure substance, the melting-point of the solid and the freezing-point of the liquid are identical.

Latent heat of fusion.—The melting-point of a substance, at which *liquid* and *solid* are in equilibrium, is closely analogous to the boiling-point, at which *vapour* and *liquid* are in equilibrium. We have seen already that, when a vapour condenses to a liquid, heat is evolved, which is termed the latent heat of vaporization (Chap. III, p. 53). In the same way, heat is evolved when a liquid solidifies, and this amount of heat is termed the **latent heat of fusion.** Table 28 gives the melting-points and latent heats of fusion of some common substances. The figure in the last column is the number of calories of heat evolved when 1 gram of the liquid is converted into solid at the melting-point.

TABLE 28. MELTING-POINT AND LATENT HEAT OF FUSION.

Substance.	Melting-point.	Latent Heat.
Water - - -	0° C.	80 calories
Sulphuric acid - -	10°	24 ,,
Benzene - - -	5·4°	30 ,,
Naphthalene - -	80°	35 ,,
Sulphur - - -	115°	9 ,,
Potassium nitrate -	339°	47 ,,

Influence of pressure on the melting-point.—Just as the boiling-point is changed by alterations of pressure, so the melting-point changes when the pressure is increased. By thermodynamical reasoning the effect of pressure on the melting-point can be predicted. It is expressed by a formula exactly similar to that used for the effect of pressure on the boiling-point (p. 56), namely, Clapeyron's equation :

$$dT = \frac{dp(v_2 - v_1)T}{l}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Here dT is the increment of melting-point caused by a small increment of pressure dp. v_2 is the volume of 1 gram of liquid, v_1 the volume of 1 gram of solid, T the melting-point on the absolute scale, and l the latent heat of fusion per gram.

Most substances contract on solidification, *i.e.* v_2 is greater than v_1; dT is therefore *positive*. Thus, whenever the solid is denser than the liquid, the melting-point is *raised* by increased pressure, since pressure helps to keep the substance in a denser solid state. To calculate the extent to which the melting-point is raised, we must express the quantities in formula (1) in absolute units. For example, the effect of an increase of pressure of 100 atmospheres on the melting-point of lead can be calculated as follows : The metal melts at 327° at atmospheric pressure, *i.e.* $T = 327 + 273 = 600$; $dp = 100$ atm. $= 10^8$ dyn./cm.^{2}, since 1 atm.* $= 10^6$ dyn./cm.^{2}; $v_2 - v_1$ is found to be 0·00308 c.c. per gram, and $l = 5{\cdot}37$ cal. per gram $= 5{\cdot}37 \times 4{\cdot}2 \times 10^7$ ergs per gram, since 1 cal. $= 4{\cdot}2 \times 10^7$ ergs.

* The unit used here is not an atmosphere of 760 mm. of mercury, but a " megadyne " which is a slightly smaller unit.

Hence the rise in melting-point is

$$dT = \frac{10^8 \times 0{\cdot}00308 \times 600}{5{\cdot}37 \times 4{\cdot}2 \times 10^7} = 0{\cdot}82°.$$

The value actualiy found by experiment is 0·80°.

Water, bismuth, and a few other substances expand on freezing, so that v_2, the volume of one gram of liquid at the melting-point, is less than v_1, the volume of 1 gram of solid, and $v_2 - v_1$ is therefore negative. As the formula predicts, the melting-point of such substances is *lowered* by an increase in pressure, since pressure tends to keep the substance in the denser liquid state. Thus, for water the alteration in melting-point for an increase in pressure of 100 atmospheres is calculated as follows:

$$dp = 10^8 \text{ dyn./cm. as before.} \quad T = 273.$$

$$v_2 = 1{\cdot}00, \; v_1 = 1{\cdot}091 \; ; \quad \therefore \; v_2 - v_1 = -0{\cdot}091,$$

$$l = 80 \text{ cal.} = 80 \times 4{\cdot}2 \times 10^7 \text{ ergs.}$$

Hence $$dT = -\frac{10^8 \times 0{\cdot}091 \times 273}{80 \times 4{\cdot}2 \times 10^7} = -0{\cdot}74°.$$

This is in good agreement with the number observed experimentally, namely, −0·72° C.

It will be seen from these figures that the effect of pressure on the melting-point of lead and of ice and indeed of most substances is very small, since an increase of a hundred atmospheres changes the melting-point by less than one degree.

9. Specific Heats of Solids.

1. Determination of the specific heat and atomic heat of a metal.—(*a*) *Construction of a calorimeter.*—Procure a brightly-polished tinned vessel of about 1000 c.c. capacity. Support it by means of pointed corks in an outer vessel large enough to leave an air-gap of about half an inch between the two vessels. Fit a stirrer of copper wire to the inner vessel of the calorimeter. A thermometer graduated in $\frac{1}{5}°$ from 0° to 100° is then mounted centrally in the inner vessel. A second similar thermometer is required in order to give the temperature of the materials added to the calorimeter.

(*b*) *Determination of the water-equivalent of the calorimeter.*—When a hot body is immersed in the water of a calorimeter, the

temperature of the vessel, thermometer and stirrer are raised as well as that of the water. It is therefore necessary to determine the heat-capacity of the apparatus, and to allow for it as if it were so many additional grams of water. The **water-equivalent** of the calorimeter is determined as follows. Measure 500 c.c. of water from a graduated flask into the central vessel of the calorimeter. After allowing it to stand for some time, in order to attain the temperature of the laboratory, read off the initial temperature of the water, t_1, on the thermometer of the calorimeter. Meanwhile heat 200 c.c. of water to about 90° in a flask in a water bath, taking its temperature with the other thermometer. When its temperature, t_2, is steady, pour it rapidly but without splashing into the calorimeter; stir and take readings of the temperature every half minute for about five minutes. Let the maximum reading be t_3. Then the heat given out by the hot water is $200(t_2 - t_3)$ calories. This is absorbed in raising $(500 + W)$ grams of water through $t_3 - t_1$ degrees, where W is the water-equivalent of the calorimeter. Then

$$500 + W = \frac{200\,(t_2 - t_3)}{t_3 - t_1}.$$

The value of W should be determined three or four times and the mean value recorded.

(*c*) *Measurement of the specific heat of a metal.*—Heat about 100 grams of granulated zinc in a dry flask in a bath of boiling water for half an hour. Take the temperature, t_2, of the zinc by means of the second thermometer. Meanwhile place 600 grams of water in the calorimeter and take its temperature, t_1. When the zinc has been heated for half an hour, pour it into the water in the calorimeter, and after stirring read the maximum temperature, t_3. Then the heat given out by the zinc is

$$100s(t_2 - t_3),$$

where s is the specific heat of zinc. This must equal the heat taken up by the water and by the calorimeter, *i.e.*

$$(600 + W)(t_3 - t_1).$$

Hence

$$s = \frac{(600 + W)(t_3 - t_1)}{100\,(t_2 - t_3)}.$$

(*d*) *Calculation of atomic heats.*—Repeat the experiment with one or two other metals, *e.g.* copper and silver. Then multiply the specific heat of each metal by its atomic weight, in order to give its atomic heat.

ii. Determination of the specific heats and latent heat of fusion of *p*-nitrotoluene.—Carry out three experiments with 50 grams of *p*-nitrotoluene in the same manner as for zinc, but varying the temperature of the initial reading.

(*a*) *Heat to* 45°.—Since the substance melts at 51·5°, it remains solid throughout the experiment, and liberates $50s(45-t_3)$ calories in cooling from 45° to t_3°. At the same time the calorimeter and the water in it gain $(600+W)(t_3-t_1)$. The specific heat s_1 of the solid is therefore given by

$$s_1=\frac{(600+W)(t_3-t_1)}{50(45-t_3)}.$$

(*b*) *Heat to* 55°.—The substance is now liquid. Let the latent heat of fusion per gram be l and let s_2 be the specific heat of the liquid. Then the heat evolved by the substance is

$$50\{s_2(55-51\cdot5)+l+s_1(51\cdot5-t_3)\}.$$

As before, this equals $(600+W)(t_3-t_1)$. Hence

$$3\cdot5s_2+l=\frac{(600+W)(t_3-t_1)}{50}-s_1(51\cdot5-t_3). \quad \text{.....(i)}$$

In this equation, s_1 is known from the first experiment, but s_2 is still unknown.

(*c*) *Heat to* 90°.—The substance is again liquid, but is so hot that a considerable amount of heat is given out by the liquid in cooling to the melting-point. As in experiment (*b*), we have

$$38\cdot5s_2+l=\frac{(600+W)(t_3-t_1)}{50}-s_1(51\cdot5-t_3). \quad \text{.....(ii)}$$

Subtracting equation (i) from equation (ii), we can calculate s_2, and then, by substituting this value in equation (i) or (ii), get the value of l.

Kinetic theory of the solid state.—We have seen that the properties of crystals lead us to conclude that their constituent molecules or atoms occupy fixed positions in a space-lattice. The forces of attraction between the molecules are sufficient to hold each one in its place in the orderly array that constitutes the crystal. Although, therefore, the molecules can still oscillate about a mean position, they have not the same freedom of movement as in the liquid and gaseous states, where the molecules have freedom of " translation " as well as of oscillation.

Whilst the greater number of the molecules in a crystal are

thus fixed, it is readily conceivable that from time to time a particular molecule may, by collision with its neighbours, attain a velocity great enough to tear it from its moorings and to transplant it to another position. Its place will be taken by another molecule, with the result that a slow migration will set in, as molecules are occasionally ejected from one place in the lattice and fit themselves into similar vacant spaces in a neighbouring part of the lattice.

This behaviour gives rise to a very slow **diffusion in the solid state**, which has been detected by experiment in some cases. Thus, if a cylinder of gold is placed on the top of a cylinder of lead, and left for some weeks, the gold slowly diffuses into the lead and the lead into the gold. By cutting slices from the lead cylinder, and analysing them, the very small amounts of gold which have diffused into the lead can be estimated and the rate of diffusion calculated. Some of the results obtained in this way are given in Table 29. It will be seen that the rate of diffusion in the solid is much less than in the liquid, and falls off very rapidly as the temperature decreases. At temperatures below the melting-point, therefore, only a very small percentage of the molecules are changing places in the crystal lattice.

TABLE 29. DIFFUSION COEFFICIENTS OF GOLD INTO LEAD.

Temperature.	Diffusion coefficient.
100°	0·00002
165°	0·005
200°	0·008
251°	0·027
500°	3·18 Lead molten.

Specific heat of solids.—The molecules or atoms in the crystal-lattice of a metal * are not at rest, but must be assumed to be oscillating about their fixed positions. We have seen in Chapter I, that the mean kinetic energy of one gram-molecule of a gas at a temperature T is $\frac{3}{2}RT = 3T$ calories,

* The molecules of a metal are generally monatomic. Each node of the space-lattice is therefore occupied by a single atom.

since $R = 2$ cal. nearly. It is plausible to assume that the average kinetic energy of the atoms in a solid monatomic element will be the same as that of the molecules of a gas. The oscillating atoms, however, because of the attraction of the neighbouring atoms, also possess potential energy; and from the laws of mechanics it can be deduced that the average potential energy will be equal to the average kinetic energy. The total energy possessed by one gram atom of a solid element should therefore be $6T$ calories at $T°$, and $6(T+1)$ calories at $(T+1)°$. That is, the heat required to raise one gram-atom of a solid element through one degree should be 6 calories. This quantity, which is obtained by multiplying the specific heat by the atomic weight of an element, is known as its **atomic heat.** The experimental relation discovered by Dulong and Petit, that *the atomic heat is a constant for many solid elements*, and is equal to 6·3 calories, is therefore a verification of the theoretical value deduced above.

TABLE 30. ATOMIC HEATS OF SOLID ELEMENTS.

Element.	Atomic Weight.	Specific Heat. 20° to 100°.	Atomic Heat.	
			20° to 100°.	−230° to 195°.
Boron	11·0	0·2616	2·9	0·24
Carbon	12·00	0·1990	2·4	0·03
Magnesium	24·32	0·2492	6·1	1·74
Aluminium	27·1	0·2173	5·9	1·12
Phosphorus	31·04	0·1981	6·2	1·34
Sulphur	32·07	0·1780	5·7	1·75
Chromium	52·0	0·1210	6·3	0·70
Iron	55·84	0·1146	6·4	0·98
Copper	63·57	0·0936	6·0	1·56
Zinc	65·37	0·0931	6·1	2·52
Silver	107·88	0·0566	6·1	2·62
Tin	119·0	0·0556	6·6	3·41
Gold	197·2	0 0316	6·2	3·16
Lead	207·1	0·031	6·4	4·96

Table 30 shows that the atomic heat over the range from 20° to 100° C. is approximately 6 calories for most elements. Carbon and boron give very much lower values, but this behaviour is not really exceptional, for the atomic heats of other elements, as recorded in the last column of the table, also fall much below

6 calories when measured at very low temperatures, namely, over the range between the boiling-points of liquid hydrogen and liquid nitrogen. Conversely, the atomic heat of carbon increases rapidly towards a normal value at higher temperatures. Thus it is 3·25 at 200°; at 600° it is 5·28; and at 1000°, when the value rises to 5·51, it approaches closely to the normal value of 6·3.

In general it has been found that the variation of atomic heat with temperature follows a curve of the type shown in Fig. 29.

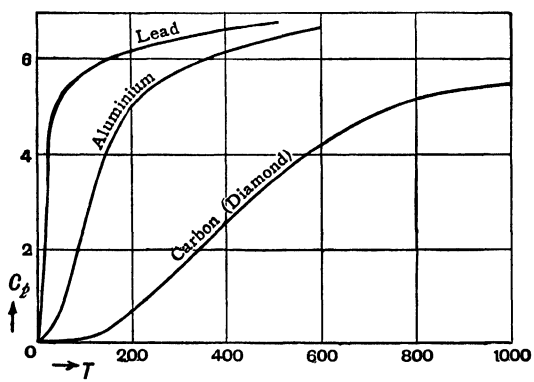


FIG. 29.—Atomic heats of solid elements.

For most solid elements, the atomic heat has nearly reached the limiting value of 6 calories at the ordinary temperature, as shown in the curve for lead; but in the cases of carbon and aluminium the atomic heat at 273° on the absolute scale is still low, and only rises towards the maximum value when the temperature is raised substantially. Conversely, the atomic heats of all other elements at low temperatures are much lower than 6 calories, and these values become very small indeed as the absolute zero is approached.

Molecular heats of compounds.—The **molecular heat** of a compound is the heat-capacity of one gram-molecule. It is obtained by multiplying the specific heat of the compound by its molecular weight. It has been found that in general the molecular heat of a compound is equal to the sum of the atomic

heats of the component atoms. Since the atomic heat of most elements is about 6·3, the molecular heat is about $6{\cdot}3n$, where n is the number of atoms in the molecule. For example, calcium chloride, $CaCl_2$, has a specific heat of 0·174, and a molecular weight of 111. The molecular heat is therefore $111 \times 0{\cdot}174 = 19{\cdot}3$ which is nearly equal to $3 \times 6{\cdot}3$. Special values must be used for carbon (2·4), hydrogen (2·3), and oxygen (4·0), since these elements have low atomic heats in compounds as well as in the free state. The fact that the characteristic atomic heat of an element persists in its compounds is sometimes useful in determining the approximate atomic weight of an element whose specific heat cannot easily be measured in the free state.

QUESTIONS ON CHAPTER IV.

1. What is a crystal? Give a short account of the properties characteristic of the crystalline state, mentioning any observations about crystalline form that have been of theoretical importance in chemistry.

Why is crystallisation a good method of purifying many substances?

(Oxford and Cambridge Schools Examination Board.)

2. What evidence is there for the occurrence of diffusion in solids? In terms of the kinetic theory describe how diffusion may occur in (*a*) gases, (*b*) liquids, (*c*) solids.

3. Describe the law of Dulong and Petit and point out its value for the determination of atomic weights. Discuss the deviations from this law observed (*a*) at ordinary temperatures, (*b*) at low temperatures.

4. Naphthalene melts at 80° at one atmosphere pressure The density of the solid is 1·14 and that of the liquid 1·07 at this temperature. The latent heat of fusion is 35 calories per gram. Calculate the melting-point of naphthalene at 100 atmospheres pressure.

5. Calculate the specific heat of calcium carbonate, given the following atomic heats. Ca = 6·3, C = 2·4, O = 4·0.

6. Discuss the effect of pressure on the melting-point of a solid. Illustrate your answer by reference to the melting-point of ice.

The latent heat of fusion of paraffin wax at 52·7° and 1 atmosphere pressure is 35·35 calories per gram. The increase in volume on melting is 0·135 c.c. per gram. What will be the melting-point of paraffin wax under a pressure of 10 atmospheres?

(B.Sc. Hons., Sheffield.)

CHAPTER V.

THE PHASE RULE: SYSTEMS OF ONE COMPONENT.

10. Changes of State in Pure Substances.

(Experiments illustrating this section have been described in §§ 3 and 8.)

Equilibrium between ice, water and steam.—(*a*) *Vapour-pressure curve.*—It has been stated in Chapter III (p. 52) that the vapour-pressure of a liquid increases rapidly as the

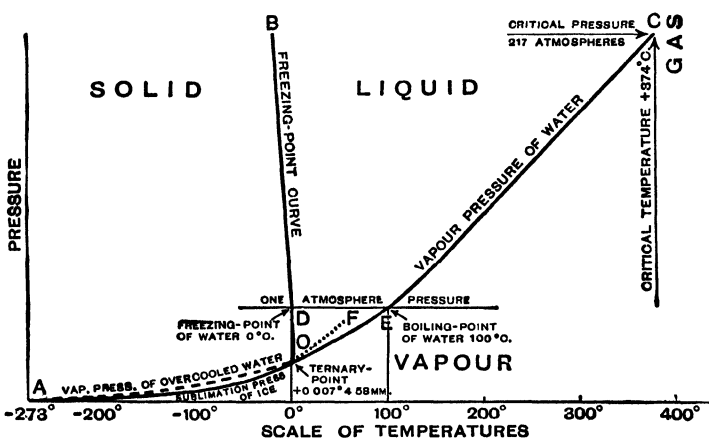


Fig. 30.—Equilibrium-diagram for water (not drawn to scale).

temperature rises. Thus, if we plot the vapour-pressure of water against temperature, we obtain the curve which is represented diagrammatically by the line *OC* in Fig. 30. (The pressures are not drawn to scale in this diagram.) The curve

shows a series of pressures and temperatures at which water and its vapour can co-exist, *e.g.* in a vessel from which all the air has been removed. At higher pressures, corresponding with points *above* the line *OC*, the vapour would condense to a liquid; on the other hand, if the pressure were reduced, corresponding to points *below* the line *OC*, the whole of the liquid would boil and pass into vapour. At the upper limit of temperature, the curve terminates at the critical-point *C*, since above this temperature liquid and vapour are indistinguishable, and the term vapour-pressure has then no meaning. At the lower limit, the curve would normally terminate at the point *O*, at which water freezes to ice; but, if the water could be prevented from freezing, the vapour-pressure curve could be continued below the freezing-point, as is indicated by the broken line *OA*, which is labelled "Vapour-pressure of overcooled Water."

(*b*) *The sublimation-pressure curve.*—Even after freezing, however, ice has a small vapour-pressure, as is proved by the fact that snow can disappear in frosty weather, when the temperature is never high enough to melt it. This vapour-pressure is described as the **sublimation-pressure** of the solid. Although small, it can be measured. It is then found that the curve representing the vapour-pressure of ice at different temperature is not a continuation of the curve *OC*, which represents the vapour-pressure of water, but falls off more steeply as shown by the full line *OA*. This line cuts the curve *OC* at *O*. The point *O* therefore shows the freezing-point of water, not at atmospheric pressure, but under the vapour-pressure of melting ice. This pressure is about 4·58 mm.; and since the freezing-point of ice is lowered to the extent of about 1° for each additional 140 atmospheres (p. 100), it will be raised slightly when the pressure is reduced from 760 to 4·58 mm. The point *O* therefore represents a temperature about +0·007° C. higher than the freezing-point under atmospheric pressure.

(*c*) *The freezing-point curve.*—Starting from *O*, we can draw a third curve *OB* on the diagram, to represent the effect of pressure on the freezing-point. This curve, although very different in direction from the two vapour-pressure curves, is in some ways very similar to them, since it shows the

temperature at which *ice and water* are in equilibrium at different pressures, just as the other curves show the conditions under which *water and steam*, or *ice and steam* can co-exist. Since the effect of pressure is small, the curve *OB* is nearly parallel to the vertical axis of pressure. Moreover, since the freezing-point of water is *lowered* by pressure (p. 100), the curve slopes towards the left; but in the case of most other substances the freezing-point is *raised* by increasing the pressure, and the curve slopes towards the right.

Equilibrium-diagrams.—An **equilibrium-diagram** of the same general type as Fig. 30, can be drawn for any pure substance. These diagrams contain a number of *areas*, *lines*, and *points of intersection*, of which the significance may now be discussed.

(*a*) *Areas.*—The water-diagram of Fig. 30 is divided by the curves *OA*, *OB*, *OC*, into three areas, which we can label *solid*, *liquid* and *vapour*. If we bring the substance to the pressure and temperature represented by any point in the area bounded by *AOB*, it will pass completely into the *solid* state. No liquid can remain since the temperature is lower than the freezing-point represented by the line *OB*; and any vapour initially present will be condensed, since the pressure is higher than the sublimation-pressure of the solid as represented by the line *OA*. Similarly it will be seen that, at pressures and temperatures represented by points in the area *BOC*, we can have only *liquid*, and in the area below *AOC* only *vapour*.

Note that in each case we can vary both the pressure and the temperature over a considerable range without trespassing into a different area. Thus it is possible for the solid state to persist alone over a wide range of temperatures and pressures, provided that the temperature is not raised above the limit imposed by the line *OB*, or the pressure lowered below the limit imposed by the line *OA*. In the same way, the liquid persists alone throughout its own area, until we reach the boundary *OB* of the " solid " area or *OC* of the " vapour " area.

(*b*) *Boundary lines.*—The curve *OC* represents a series of temperatures and pressures at which liquid and vapour are in equilibrium. If, at a point *E* on this curve, we keep the temperature constant and slightly *increase the pressure*, the vapour

will all be condensed to liquid. If, on the other hand, we slightly *decrease the pressure* the liquid will all evaporate or boil away to vapour. Again, if we keep the pressure constant and slightly *raise the temperature*, the liquid (being above its boiling-point) will all evaporate; but, if, on the other hand, we *lower the temperature* slightly, the vapour will all condense. Hence, if we wish to have a system containing both liquid and vapour we cannot vary both pressure and temperature, because if we choose one of these quantities, the other is fixed by the position of the corresponding point on the curve *OC*. Similarly the curve *OA* indicates that at each temperature there is only one pressure at which solid and vapour are in equilibrium with each other, whilst the line *OB* imposes a similar limitation in reference to the co-existence of liquid and solid.

(*c*) *The central point.*—The point *O* has a special significance. It represents the only temperature and pressure at which *solid*, *liquid* and *vapour* can co-exist. If we vary either the temperature or the pressure from the rigidly determined values for this unique point, one of the three states of aggregation will disappear. Thus, if the temperature be raised without altering the pressure, we shall pass into the vapour area and the solid and liquid will both change into steam. Conversely, if the temperature be lowered, the vapour will condense to ice and all the water will freeze, since we shall have passed into the area which belongs exclusively to the solid. It is possible, however, by varying temperature and pressure together, to move along one of the lines *OA*, *OB*, *OC* of the figure, and so to preserve *two* of the three states of aggregation.

The Phase Rule.—The conclusions arrived at from a consideration of Fig. 30 are set out on p. 111 in a tabular form.

The number of conditions (in this case pressure or temperature) which can be varied independently of one another without changing the type of system is shown in the third column. It will be seen that the number of independent variables decreases as the system becomes more complex. This is one example of a very general rule, formulated in 1874 by Willard Gibbs, which is usually termed the **Phase Rule**. It applies to any system which is in equilibrium, and defines the number of variables

which can be chosen independently without altering the system.

The Phase Rule is written algebraically thus:

$$F = C - P + 2.$$

In this equation (i) P represents the number of **phases**. A phase is *a part of a system which is marked off from other parts by a boundary at which there is an abrupt change of physical properties.* Thus, in the system represented by Fig. 30, ice, water, and steam are separate phases.

System.	Conditions for Equilibrium.	Number of Independent Variables.	Method of Representation on Pressure-Temperature Diagram.
Solid Liquid Vapour	Pressure and temperature can be varied independently	2	Area
Solid-liquid Liquid-vapour Solid-vapour	Pressure and temperature can be varied, but not independently	1	Line
Solid-liquid-vapour	Neither the pressure nor the temperature can be varied	0	Point

(ii) C is the number of **components**. This is defined as *the least number of substances in terms of which the composition of each of the phases may be defined.* In the system considered there is only one component, represented by the chemical formula, H_2O, since all three phases can be produced from water only. It would be wrong to regard hydrogen and oxygen as two components since the amount of either present determines exactly the amount of the other. If, however, we were working at very high temperatures, at which water dissociates, and we put an excess of hydrogen or oxygen into the gas phase, then it would be necessary to write the number of components as two (namely hydrogen and oxygen) when applying the phase rule.

(iii) F is the number of **degrees of freedom** of the system, that is, *the number of factors which can be varied independently without*

altering the number of phases. For a one-component system, only the pressure and temperature can be varied; hence the maximum number of degrees of freedom is 2. If there are two components, we can also vary the relative proportions of each, and hence a new degree of freedom, namely concentration, appears. In more complex systems each new component introduces another concentration which can be varied and hence gives another possible degree of freedom.

Systems of one component.*—If we apply the phase rule to the system ice-water-steam, we can confirm the results tabulated on p. 111.

(i) *Bivariant systems.*—Systems which possess two degrees of freedom are known as **bivariant systems.** When there is only one component, so that $C=1$, such systems are only possible when the number of phases is reduced to one, for

$$F=C-P+2,$$
$$2=1-P+2,$$
$$\therefore\ P=1$$

and $F=C-P+2=1-1+2=2$. This agrees with the fact, already noticed, that when the system consists entirely of ice, or of water, or of vapour, both pressure and temperature can be varied independently.

(ii) *Univariant systems.*—Systems with only one degree of freedom are described as **univariant systems.** When only one component is present, univariant systems are produced whenever two phases are formed, since in this case

$$F=C-P+2=1-2+2=1.$$

Three different univariant systems are represented in Fig. 30 by the lines *OA*, *OB* and *OC*.

(iii) *Non-variant systems.*—Systems with no degrees of freedom are described as **non-variant systems.** In systems containing only one component they are formed whenever three phases appear simultaneously, since in this case

$$F=C-P+2=1-3+2=0.$$

* The systems considered here are those in which only one solid phase is formed. Cases in which more than one type of solid appears are discussed in § 11 below.

The point *O*, which represents the unique temperature and the unique pressure at which solid, liquid and gas are in equilibrium, is also termed a **triple point** or **ternary point**, since three phases are there in equilibrium.

Stable, metastable and unstable equilibrium.—The three *areas AOB*, *BOC*, *COA*, the three *lines OA*, *OB*, *OC* and the *point O*, represent all the systems which are in **stable equilibrium**. If, however, water is carefully cooled below the normal freezing-point, *e.g.* in the form of drops suspended in an oil of equal density, it does not solidify immediately, but may remain for a long time in the condition of a supercooled liquid. Such water has a vapour-pressure represented by the broken line *OA*, which is a continuation of the curve *CO*. If, however, a crystal of ice is brought into contact with the water, it freezes immediately, and, as a result, the vapour pressure falls from a point on the broken line *OA* to a point on the full curve *OA* below it. The supercooled water is said to be in a **metastable state**, by which we mean that it can persist for an indefinite period of time, but is always in danger of passing over (often on very slight provocation) into some more stable condition. On the other hand, if we attempt to heat ice above its normal melting-point, it melts immediately, and no " over-heating " of the ice occurs.

Ice above the melting-point is therefore in a completely **unstable state**, and the dotted curve *OF* of Fig. 30, which is a continuation of the full curve *AO*, has never been realised experimentally. On the other hand, a solid like quartz, which melts to an extremely viscous liquid, can be heated for a considerable time above its true melting-point, without losing its crystalline form. Indeed, the fusion of the solid at this temperature can only be detected by the slow " sintering " of the powder, and a much higher temperature is required to produce even a gradual " flow " of the fused material.

II. Transition-temperatures.

i. **Determination of the transition-point of cuprous mercuric iodide.**—(*a*) Dissolve 6·8 grams of mercuric chloride in about 300 c.c. of water and add 8·3 grams of potassium iodide dissolved

in 50 c.c. of water. Allow the precipitate of mercuric iodide to settle, pour off the clear liquid, and wash once by decantation. Dissolve the washed precipitate in a solution of 8·3 grams of potassium iodide in 50 c.c. of water and add a filtered solution of 12 grams of copper sulphate in 150 c.c. of water. Pass sulphur dioxide through the liquid until no more is absorbed. Filter and wash the precipitate of cuprous mercuric iodide, Cu_2HgI_4, and dry it in the steam oven.

(*b*) Place a little of the red powder in a wide melting-point tube, attach it to a thermometer, and heat slowly in a beaker of water provided with a stirrer. Note the temperature at which a change of colour takes place on heating and on cooling. (It will usually be found that the change from red to black on heating to about 71° takes place more sharply than the reverse change on cooling.)

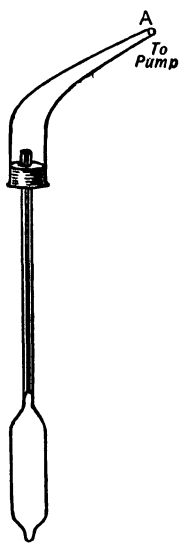


FIG. 31.—Dilatometer and adapter.

ii. **Determination of the lower transition-point of ammonium nitrate at 32°.**—(*a*) *Preparation of a dilatometer.*—Cut off the bulb of a 50 c.c. pipette, leaving about 3 cm. of tube at each end. To one end seal 20 cm. of glass tube of about 3 mm. internal diameter. Fill the bulb with small crystals of ammonium nitrate through the other end and seal off. Attach an adapter to the open end of the long tube as shown in Fig. 31. Half-fill the adapter with methylated spirit tinted with magenta, and connect the end A to the water pump. When the apparatus has been partially evacuated, disconnect it from the pump; spirit will then enter the bulb. By repeating the process two or three times, the bulb and stem can be filled completely with the coloured methylated spirit.

Attach a paper millimetre scale to the tube and support the dilatometer vertically in a large beaker of water containing a stirrer and a thermometer. By means of a fine capillary tube, adjust the amount of spirit so that the meniscus is near the bottom of the scale when the temperature of the dilatometer is about 26°.

(*b*) *Preliminary experiment.*—The transition-point is first found approximately as follows. Raise the temperature of the bath about 1° per minute, and take readings of the temperature

and volume every minute. Continue the heating to 40° or beyond, until a sudden expansion is observed which is much greater than the normal thermal expansion. This gives an upper limit for the temperature at which the nitrate changes from a denser to a lighter form. Allow the transition to proceed for about ten minutes, and then cool slowly to 25° or below, taking readings of volume and temperature as before. Notice the temperature at which a large contraction in volume occurs. This temperature gives a lower limit for the point at which the lighter form of the nitrate reverts to the denser form.

(*c*) *Measurements of rate of change.*—In order to fix the transition-temperature more precisely, it is necessary to observe the rate of change on either side of the transition-point. Strictly, one should measure the rate of change with about 50 per cent. of either form present, but the following procedure is simpler and gives very fair results.

Take a dilatometer containing the low-temperature form of the nitrate, and heat it in a beaker of water maintained at 40°. Take readings of the volume every minute for 15 minutes. When the thermal expansion is over at the end of about 5 minutes, a steady increase in volume should occur as the result of a slow transition to the lighter high-temperature form. (If this does not happen, raise the temperature by increments of about a degree until the transition starts.) Take readings for a further ten minutes until the expansion amounts to 3·5 cm. on the scale, and calculate the rate of expansion in divisions per minute. Cool the bath to 39° and take readings for ten minutes or so in order to determine the steady rate of change at this temperature. Repeat at 38°, and so on at lower temperatures, until the rate is too slow to be followed. (Unless several hours are spent over this experiment it is usually necessary to stop at 36°.)

Immerse the dilatometer for 15 minutes in a bath of water at about 70° in order to convert most of the ammonium nitrate into the high-temperature form. Then transfer to a beaker of water maintained at 26° and take readings every minute. A steady contraction should be found as the result of a gradual transition to the denser low-temperature form. Allow this to proceed for ten minutes, then raise the temperature of the bath to 27°, and measure the rate of change at this temperature. Repeat at 28° and if possible at 29°.

Plot the rates of change against the temperature. Two curves will be obtained as in Fig. 32. Join together pairs of points on the two curves which give the same rate of change

and bisect these lines. A line drawn through these bisections will cut the axis of temperature at the transition-point.

iii. **Determination of the higher transition-points of ammonium nitrate.**—Make up a thick paste of powdered ammonium nitrate and nitrobenzene (or better, of fused 1 : 2 : 4 chlorodinitrobenzene) in a wide test tube provided with a stirrer and a thermometer. Mount the test tube in a wider tube, so as to provide an air-jacket around it, and heat it in an oil-bath. Stir the sludge and plot curves showing (*a*) the course of the heating from 75° to 130°, (*b*) the course of the cooling from 130° to 75°. The " arrests " on the heating and cooling curves give the transition-temperatures of the salt.

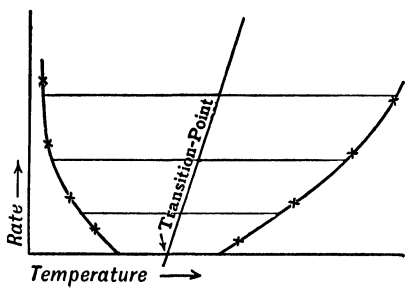


FIG 32.—Diagram to illustrate the determination of the transition-temperature of ammonium nitrate.

Polymorphism.—Many substances exist in more than one crystalline form, so that two or more solid " phases " are possible. Such substances are said to be **dimorphic, trimorphic** or **polymorphic,** according as there are 2, 3 or many solid phases. Thus, " soluble " sulphur crystallises in *four* polymorphic forms, the most familiar of which are known as **rhombic sulphur** and **monoclinic sulphur.** In the same way ammonium nitrate is known in not less than *five* polymorphic forms, which can be distinguished by their crystalline structure, density, etc.; and ice under varying pressures appears in *six* different solid forms. In the case of *elements* this phenomenon is generally described as **allotropy,** although this term is also used to include many cases of isomerism and polymerism, in which the nature of the molecules (as well as their arrangement in the crystal-lattice) is different in the different forms.

Polymorphism of sulphur.—In general the various solid forms of a substance appear as separate solid phases. The simple diagram (Fig. 30) which shows the equilibrium of solid, liquid and vapour, will therefore no longer represent all the possible

conditions of equilibrium and a more complex diagram is necessary. In the case of sulphur, two of the four crystalline forms, namely **nacreous sulphur** and **tabular sulphur** are only known in a metastable state, and need not therefore be considered at the present stage. We must, however, allow for the possible existence of all or any of the following four phases, (i) rhombic sulphur (solid), (ii) monoclinic sulphur (solid), (iii) liquid sulphur, and (iv) sulphur vapour. The phase rule then enables us to lay down certain limiting conditions, and to predict what types of system may exist; but it is still necessary to make experiments in order to fix the positions and intersections of the lines on the equilibrium-diagram.

(*a*) First of all let us see if a system of four phases can exist. Putting $P=4$, $C=1$, we find from the Phase Rule $F=-1$. Since this is an impossible value (a negative degree of freedom has no meaning), we conclude that there is no temperature and pressure at which all the four phases can be in equilibrium.

(*b*) Secondly, we can choose four systems of three phases, namely:

1.	2.	3.	4.
Rhombic	Rhombic	Rhombic	Monoclinic
Monoclinic	Monoclinic	Liquid	Liquid
Liquid	Vapour	Vapour	Vapour

For each of these systems the Phase Rule gives $F=0$, that is, they will be represented by a point. The equilibrium-diagram should therefore show four triple-points.

(*c*) Similarly, there are six possible systems of two phases, namely:

1. Rhombic Monoclinic	2. Rhombic Liquid	3. Monoclinic Liquid
4. Rhombic Vapour	5. Monoclinic Vapour	6. Liquid Vapour

For each of these the Phase Rule gives $F=1$. These six univariant systems may, therefore, be represented by six lines on the diagram, since they are bivariant systems for which $F=2$.

Equilibrium-diagram for sulphur.—It should be noted that although these systems may all exist, the schemes set out above represent the maximum number of possible systems, and all

of them may not be found to exist when a particular substance is studied. In the case of sulphur, however, they can all be realised experimentally, and are shown on the equilibrium diagram in Fig. 33. The area marked S_α gives the range of pressures and temperatures within which **rhombic sulphur** can exist, the area S_β indicates the range of existence of **monoclinic sulphur**, and the remaining areas show the range of existence of liquid and vapour. The line *OP* shows the rise of the vapour-pressure of rhombic sulphur with temperature. *PQ* shows the vapour-pressure of monoclinic sulphur at different temperatures. These two curves intersect at 96°. This is, therefore, the only temperature at which the two solid forms of sulphur have the same vapour-pressure and can exist in stable equilibrium with one another. It can be described as the **triple point** for the rhombic, monoclinic and vapour phases; but it is also known as the **transition-temperature** for the two solid phases. Thus, if rhombic sulphur is kept a little above 96°, it is converted slowly but completely into monoclinic sulphur, whilst at temperatures a little below 96° monoclinic sulphur changes completely to rhombic sulphur. Above 96°, therefore, rhombic sulphur is metastable and below 96° monoclinic sulphur is metastable. From the form of the curves it will be seen that the metastable form always has a greater vapour-pressure than the stable form.

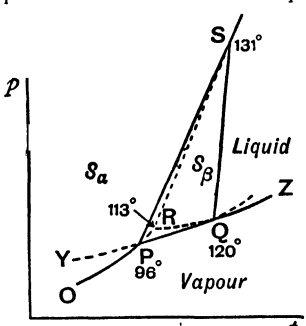


FIG. 33.—Equilibrium-diagram for sulphur. The diagram is not drawn to scale, and the vapour-pressures do not represent values experimentally determined

The change from rhombic to monoclinic sulphur takes place very slowly even above 96°. It is therefore possible, by heating rapidly, to realise the metastable part *PR* of the vapour-pressure curve of rhombic sulphur up to the melting-point of rhombic sulphur at *R* (113°). This is a second triple point, for the three phases *rhombic sulphur*, *liquid*, and *vapour*; but since rhombic sulphur is always liable to change into monoclinic sulphur at this temperature, it is a metastable triple point, which can only

be realised precariously, when the conditions happen to be favourable. The vapour-pressure curve of monoclinic sulphur ends at its melting-point Q (120°); this is the third triple point, and shows the conditions under which *monoclinic sulphur, liquid* and *vapour*, are in stable equilibrium with one another.

The curve PS shows the change of the transition-temperature with pressure, and the curve QS the change in the melting-point of monoclinic sulphur with pressure. These curves intersect at S (131°) which is a fourth triple point, since it shows the conditions under which *rhombic, monoclinic*, and *liquid* sulphur are in stable equilibrium with one another, without any vapour-phase.

Enantiotropic and monotropic substances.—In the case of sulphur, the rhombic and the monoclinic form of the element have each an area of complete stability in the pressure-temperature diagram. By changing the conditions, so as to move from one area to another, it is therefore possible to change one form into the other and back again as often as may be desired. Dimorphous compounds, in which two solid forms can be converted reversibly into one another by changing the temperature or pressure, are called **enantiotropic**, in order to indicate that the change can be effected *in either direction*. Other cases are known, however, in which one of the forms is metastable under all conditions, and these compounds are distinguished as **monotropic**, in order to indicate that the change of state can be effected *in one direction only*. Nacreous and tabular sulphur are polymorphic forms of this type, since neither form has an area of stable equilibrium in the pressure-temperature diagram; they can therefore only appear precariously as trespassers on an area belonging to a different phase, into which they will change on very slight provocation.

White phosphorus is also a monotropic solid, since it passes progressively into red or violet and ultimately into "metallic" phosphorus when exposed to light or heated with iodine, etc.; these products can, however, be changed back by distillation, when white phosphorus condenses from the vapour. It may be suspected that the molecules of white phosphorus are tetratomic, like those of the vapour, and that the other forms of phosphorus are formed by the polymerisation of these molecules.

Polymorphism of benzophenone.—The behaviour of a monotropic substance can be inferred from a consideration of the form of the hypothetical vapour-pressure curves of benzophenone. The diagram (Fig. 34) shows that the vapour-pressure curve of the metastable form ST approaches that of the stable form OP; but before these two curves meet they are intersected by the vapour-pressure curve TPQ of the liquid and the substance melts. The transition-temperature is therefore above the melting-point and cannot be realised experimentally.

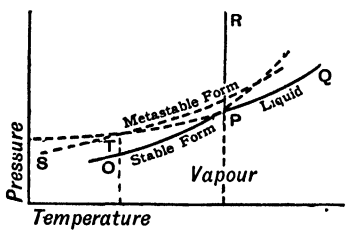


FIG. 34.—Equilibrium-diagram for a monotropic substance.

In general, the stable form melts at P and the metastable form at T; but, since the metastable form may revert at any moment to the stable form, it is not always possible to observe experimentally the metastable melting-point T. It should also be noticed that, since the melting-point of the metastable form at T is always *below* that of the stable form at P, it is possible for the stable form to crystallise out from the liquid which is obtained by melting the metastable form. The metastable form of the substance may therefore be observed to melt twice, first at T, and then (after resolidification) for the second time at P.

This phenomenon has actually been observed in the case of benzophenone, the metastable form of which melts at 26·5° C., then goes solid and remelts at 48·5° C. On the other hand, since a solid above its melting-point is, in general, *unstable* (as in the case of ice, which cannot be heated above 0° C. without melting) rather than *metastable*, the transition-point of a monotropic substance represents an unstable condition, which, unlike the metastable melting-point, cannot be realised experimentally.

From the diagrams it will be seen that the metastable form of a monotropic substance has a higher vapour-pressure and a lower melting-point than the stable form. In the same way it is found that a metastable modification is always more soluble in a given solvent than the stable form.

Experimental determination of transition-points.—(*a*) *From measurements of vapour-pressure.*—If the vapour-pressures of two solid forms of a substance can be measured directly, it is possible to determine the transition-temperature by plotting the vapour-pressure curves and noticing the point at which they intersect. This method, however, is rarely used, because the vapour-pressure of a solid is generally small and difficult to measure.

(*b*) *By observations of colour.*—The two forms of a polymorphic substance sometimes differ in colour. The transformation can then be followed visually as in Expt. 11, i. Thus mercuric

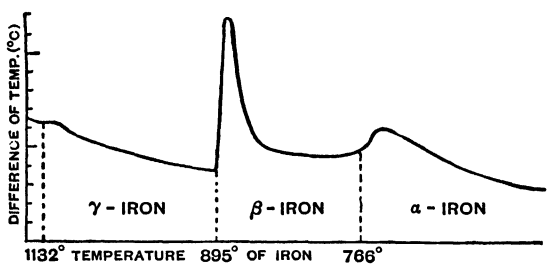


FIG. 35 —Liberation of heat by iron when cooling through its transition-temperatures

iodide changes from red to yellow when heated through the transition-temperature at 126° C., and cuprous mercuric iodide changes in the same way from red to black at 71° C.

(*c*) *Thermal method.*—There is usually an evolution of heat when a solid form which is stable at higher temperatures is converted into a form which is stable at lower temperatures. This **latent heat of transformation** can be used in some cases to determine the transition-point, just as the latent heat of fusion is used to determine the melting-point (Chap. IV. Expt. 8, ii). When the substance is cooled slowly, the heat liberated by the transition may then suffice to keep the whole mass at the transition-temperature until the transformation is complete. This method is used very generally in the case of metals, where the heat is conducted very quickly from one part of the mass to another. Thus the two peaks in Fig. 35 (which shows the difference of temperature between pieces of iron and platinum cooling in the

same furnace), are a measure of the heat liberated when iron changes from the γ to the β and from the β to the α-form on cooling through 895° and 766° C. In other cases, however, it is not always possible to record an arrest, since the heat is not conveyed quickly enough to the thermometer; but, by stirring a sludge of ammonium nitrate with a liquid in which it will remain suspended, it is possible to determine accurately by this method the transition-temperatures at 125·2° and 84·1° C. The use of the heat of transformation in order to determine the transition-temperature of a two-component system is illustrated in Expt. 14, iii., Chapter VI.

(*d*) *Dilatometric method.*—The two forms of a polymorphic solid often differ in density. This property is used in order to follow the transformation by means of a dilatometer. This instrument resembles a large thermometer, of which the bulb is filled in part by the solid under investigation. The substance in the bulb is immersed in a suitable liquid, which fills the bulb completely and extends into a narrow graduated stem. As the instrument is heated, the meniscus moves slowly as a result of the thermal expansion of the solid and liquid in the bulb; but, when a transition takes place, a large change of volume is recorded within a narrow range of temperatures in the neighbourhood of the transition-point. An example of the use of the dilatometer in fixing transition-points is given in Expt. 11, ii.

The transition from one form of a solid to the other generally takes place only slowly, and, if crystals of the new phase are not already present, it may not start until the substance is cooled considerably below the transition-point. The dilatometric method, therefore, works best when about equal parts of the two solid forms are present. By measuring the rate of contraction or expansion at temperatures a little above and below the transition-point, two temperatures can then be found close to one another, at one of which there is a slow expansion and at the other a slow contraction. The mean of these two temperatures is taken as the transition-point.

(*e*) *Solubility method.*—Determinations of the solubility of the two forms in a suitable solvent have often been used to determine transition-temperatures. At any given temperature the

form which is metastable always has the greater solubility; but at the transition-point the solubilities of the two forms become identical. (Curves *AA*, *BB*, Fig. 36.) If, therefore, the solubilities of the two forms of an enantiotropic substance are plotted against the temperature, the intersection of the two curves gives the transition-point *E* of the substance. This method is also useful in the study of monotropic substances. The solubility curve *DD* (Fig. 36) of the metastable form can often be determined; but it is now found to be entirely above the solubility curve *CC* for the stable form, showing there is no transition-point within the limits of temperature covered by the observations.

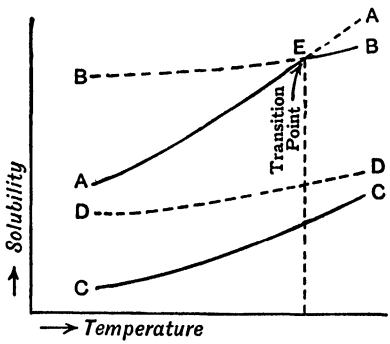


FIG. 36.—Solubility curves for enantiotropic and monotropic solids.

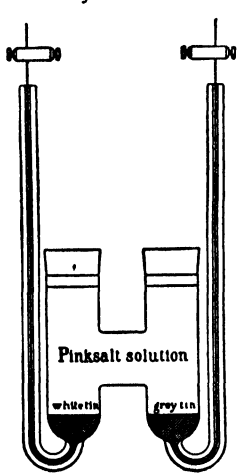


FIG. 37.—Apparatus for determining the transition-temperature of white and grey tin.

(*f*) *Electrometric method.*—A special method, applicable only to metals, has been used in the case of tin. This metal exists normally in the form of **white tin**; but when exposed to extreme cold, or by prolonged exposure to a temperature below 18°, it is converted into **grey tin**. Since this is much lighter than white tin, the metal swells up and crumbles when changing into grey tin. This change has, therefore, been described as **tin-plague**.

In order to determine the transition-temperatures, a voltaic cell was made up, in which the electrodes consisted of the two forms of tin surrounding two platinum wires, whilst the electrolyte was a solution of ammonium stannic chloride, $(NH_4)_2SnCl_6$ (Fig. 37). By joining the poles

through a delicate galvanometer it was found that, at temperatures above 18°, a current flowed through the solution from the "grey tin" electrode to the "white tin" electrode, so that grey tin was dissolved and white tin deposited, whilst below 18° the current flowed in the reverse direction. At 18° no current flowed. The two forms were therefore in equilibrium at this temperature and had the same potential relatively to the electrolyte.

In this way, then, the transition-point was fixed at 18°, in spite of the fact that the change at this temperature is too slow to be detected by any of the other methods described above. The conversion of grey tin into white tin at higher temperatures is, however, sufficiently rapid to be shown as a lecture experiment, in which the contraction produced by plunging grey tin into hot water can be exhibited by means of a dilatometer.

QUESTIONS ON CHAPTER V.

1. State clearly what you understand by the terms "phase," "component," "degree of freedom," "equilibrium." Illustrate your answer by reference to the system ice-water-steam.

2. Describe as fully as you can the conditions which are found to determine the mutual transformations of allotropic forms of (*a*) rhombic and monoclinic sulphur, (*b*) white and red phosphorus.
(Natural Science Schols., Oxford.)

3. Give three examples of substances which show a transition-point. In each case state how this transition-point may be determined.

4. Show that of two allotropic forms of a substance (*a*) the one which has the lower vapour-pressure is the more stable, (*b*) the one which has the smaller solubility in a given solvent is the more stable.

5. Describe the behaviour of sulphur on heating to its boiling-point. Under what conditions can the two chief crystalline forms of sulphur be obtained.
(Joint Matriculation Board, Higher School Certificate.)

6. Write short notes on the following, (*a*) triple-point (*b*) enantiotropic substances, (*c*) monotropic substances. Give an example of each. How many triple-points could be obtained with the liquid as one of the three phases in the case of a substance which exists in three enantiotropic solid forms?

CHAPTER VI.

THE PHASE RULE: SYSTEMS OF TWO COMPONENTS.

Systems of two components.—When a system contains two components it may have as many as three degrees of freedom, for we can vary (i) temperature, (ii) pressure, and (iii) the relative proportions of the two components. This last degree of freedom is usually expressed as the concentration of one or other of the two components. A full diagrammatic representation of such a system would therefore need a solid model, in which pressure, temperature and concentration would be plotted along three axes at right angles to one another. For most purposes, however, we can use a series of plane diagrams, in which temperature and concentration are plotted against one another for a series of constant pressures, or pressure and concentration are plotted against one another for a series of fixed temperatures.

These plane diagrams are sections of the solid model; and the solid model can be built up quite readily from a series of such plane diagrams. When only solid and liquid phases are present, small changes of pressure have very little effect on the system, and a single temperature-concentration diagram can be used to express the results of all measurements, except those made under greatly increased pressures.

The Phase Rule enables us to predict the existence of the following types of two-component system. Examples of each type are discussed in the present chapter.

SYSTEMS OF TWO COMPONENTS.

	Number of Phases.	Degrees of Freedom.	Examples.
Case I.	1	3	(*a*) Mixture of gases.
,, I.			(*b*) Mixture of liquids.
,, I.			(*c*) Solid solutions.
,, II.	2	2	(*a*) Gas + saturated solution.
,, III.			(*b*) Liquid + saturated solution.
,, III.			(*c*) Solid + saturated solution.
,, IV.	3	1	(*a*) Gas + solution + solid.
,, IV.			(*b*) Two liquids + solid.
,, IV.			(*c*) Liquid + two solids.
,, IV.			(*d*) Vapour + two solids.
	4	0	(*a*) Vapour + two liquids + solid.
			(*b*) Vapour + solution + solid + ice.

CASE I.—TWO COMPONENTS: ONE PHASE.

12. SOLID, LIQUID AND GASEOUS SOLUTIONS.

1. Preparation of solid solutions of copper sulphate and ferrous sulphate.—(*a*) Dissolve 80 grams of hydrated copper sulphate, $CuSO_4$, $5H_2O$, and 20 grams of hydrated ferrous sulphate, $FeSO_4$, $7H_2O$, in about 120 c.c. of water at the boiling-point; filter the solution and allow it to cool. Drain the crystals which separate, and allow them to dry in the air. Estimate the percentage of copper in the dry crystals by means of potassium iodide and thiosulphate, and the percentage of ferrous iron by titration with potassium permanganate.

Calculate the percentage of $CuSO_4$, $5H_2O$ from the percentage of copper in the crystals; then calculate the percentage of ferrous sulphate on the assumption that this salt also contains only five molecules of water of crystallisation. Note whether the two percentages add up to 100.

(*b*) Measure the densities of the "mixed crystals" of

$$[CuFe]SO_4, 5H_2O,$$

and compare them with those of copper sulphate and of ferrous sulphate.

Solutions: gaseous, liquid, and solid.—(*a*) *Gases.*—Since all gases will mix in all proportions, a mixture of two gases is an example of a system of two components with only a single phase.

Such a system has three degrees of freedom, since the pressure, temperature and concentration can be varied independently over a wide range. The limits of this variation are set by the temperature and pressure at which one or other of the gases liquefies or solidifies. These limits are therefore found on the side of *low temperatures* and *high pressures*. In general, therefore, the temperature can be increased or the pressure decreased indefinitely without any risk of a new phase appearing in the system.

(*b*) *Liquids*.—In the same way, a mixture of two liquids, such as alcohol and water, which are miscible in all proportions, has three degrees of freedom, since we can vary (i) the pressure, (ii) the temperature, and (iii) the concentration, within wide limits, without causing the appearance of a new phase. These limits are imposed by the possibility that a solid or vapour phase may be produced from the liquid mixture. Thus the pressure must not be decreased below the vapour pressure of the mixture, otherwise a vapour-phase will appear; but provided that this lower limit is not passed, the system will remain homogeneous over a wide range of pressures. Similarly, the temperature must be kept above that at which ice (or perhaps solid alcohol) can crystallise out from the solution; but there is a wide range of temperatures above this limit within which the system will remain all liquid.

Since alcohol and water are miscible in all proportions, there is no limit to the range of concentrations within which a homogeneous liquid can be prepared in this particular case. In other cases, however, we find that, when the concentration of one component is increased, a limit is reached at which two liquid layers are formed. Thus, when ether is added to water, only one liquid phase is formed so long as there is less than 7 per cent. of ether; the unsaturated solution of ether in water which is thus produced has three degrees of freedom, since temperature, pressure and concentration can all be varied. When, however, more than 7 per cent. of ether is added, two liquid layers are formed. The upper layer is now a *saturated solution of water in ether*, which has a definite composition for a given temperature and pressure, and in practice contains 2·7 per cent. of water at

20° ; the lower layer is a *saturated solution of ether in water*, and contains a definite proportion of ether, namely, 7 per cent. at 20°.

In the ether-water system, therefore, the concentration can be varied only within certain limits, namely up to 7 per cent. of ether, or up to 2·7 per cent. of water, if the system is to consist of one phase only. Between these two limits the mixture always separates into two phases, as a result of the limited miscibility of the two compounds.

(*c*) *Solids.*—Systems of two components containing only one solid phase are described as **solid solutions.** Whereas all gases, and many liquids, will mix in all proportions, it is quite exceptional for two components to unite to form a single solid crystalline phase ; but some **isomorphous crystals**, *i.e.* crystals of identical symmetry and similar crystalline form, possess the additional property of forming **isomorphous mixtures**, *i.e.* homogeneous crystals in which the molecules of both components are distributed throughout the mass with the same uniformity as in a liquid mixture or solution. Thus, if we allow a mixture of potash alum and chrome alum to crystallise from water, we do not get separate white and purple crystals, but only a single type of crystals, intermediate in colour and in composition between the white potash alum and the purple chrome alum. Thus, by varying the composition of the solution a complete series of crystals can be prepared, ranging in tint and in composition from pure potash alum to pure chrome alum. These **mixed crystals** are represented by the formula

$$K[Al, Cr](SO_4)_2, 12H_2O,$$

where it is understood that those elements of which the symbols are enclosed in square brackets can replace one another to any extent *in equivalent proportions.*

Many examples of isomorphous mixed crystals are known in mineralogy, where the phenomenon is described as **vicarious replacement.** In metallurgy also solid solutions are frequently formed and their presence can often be detected by studying the form of the cooling-curves of a series of binary alloys (§ 14, p. 147). Since we can vary the composition of the crystals as well as the temperature and pressure under which they exist,

these isomorphous mixtures or solid solutions provide another example of a tervariant system.

CASE II.—TWO COMPONENTS: TWO PHASES (ONE PHASE A VAPOUR).

13. Saturated Solutions of Gases.

i. Separation and analysis of air dissolved in water.—By means of a water-jet pump, draw air through about 2 litres of distilled water for half an hour, in order to saturate the water with oxygen and nitrogen. Fill a round-bottomed 1500 c.c. flask with this water. Fit the flask with a rubber stopper and delivery tube, leading to a graduated eudiometer, filled with mercury and standing in a suitable trough. The delivery tube must also be filled with water. Heat the flask slowly at first, and then bring the water to the boil. Collect the expelled gases in the eudiometer, and transfer the eudiometer to a deep jar of water. Measure the volume of gas when the level of water is the same inside and outside the tube. (Any mercury left in the eudiometer will fall to the bottom of the jar.) The temperature of the water and the height of the barometer should be read at the same time.

Push up into the gas a wire carrying a pellet of phosphorus, and leave it for 24 hours; then remove the phosphorus and read the volume of the nitrogen which remains, noting the temperature and barometric height as before. Calculate from these measurements the percentages by volume of oxygen in the dissolved gas, and compare your results with the values calculated from the absorption-coefficients (p. 131).

ii. Steam-distillation.—Place 100 c.c. of chlorobenzene and 150 c.c. of water in a 500 c.c. distilling flask, fitted with a thermometer and a condenser. Distil the mixture, collecting the distillate 50 c.c. at a time in graduated cylinders. Read the temperature at which each fraction distils. After a few minutes read the volumes of the chlorobenzene (lower layer) and water in each fraction. Taking the density of chlorobenzene as 1·110, calculate the ratio by weight of chlorobenzene to water. Compare this with the value predicted from the vapour-pressures at the temperature of distillation, as recorded in Table 8 (p. 52).

Saturated solutions.—The one-phase systems described in the preceding section were all **unsaturated solutions**, since if brought up to the point of saturation a new phase would begin to separate. **Saturated solutions** are therefore generally prepared

as two-phase systems, in which a condition of saturation is maintained by the presence of one component in sufficient quantity to give rise to a second phase. This second phase may be gaseous, liquid or solid, since a liquid may be saturated with a gas, with another liquid, or a solid. When the second phase is solid, it generally (but not always) contains only one component; but if it is gaseous or liquid, it will be saturated with the other component also.

Solutions of gases in liquids.—When a gas is in contact with a liquid which it has saturated, the system has two components and two phases; it therefore has two degrees of freedom. Hence, if the pressure and temperature are fixed, the concentration must have a definite value. In order to study this type of system, we fix one variable, say, temperature; then for each pressure there will be only one concentration at which the system is in equilibrium. This is a statement in other words of the well-known fact that the solubility of a gas at a given temperature is determined by the pressure. The Phase Rule does not tell us quantitatively how the solubility will change with pressure, but merely that, when the temperature is fixed, the solubility cannot change unless the pressure is also changed, and conversely. In order to determine the law of variation of solubility with pressure, an experimental study of the system is necessary. In this case the law, which is known after the name of its discoverer as **Henry's Law**, is very simple. It can be stated as follows:

The solubility of a gas in a liquid at constant temperature is proportional to the pressure.

The solubility may be defined as the weight of gas dissolved by 1 c.c. of a liquid, or more conveniently as the volume of gas which is dissolved by unit volume of the liquid. This latter definition gives the **absorption-coefficient** of the gas in the given liquid. If Henry's Law is true, the absorption-coefficient of a gas should be independent of the pressure under which the solubility is measured, since if the pressure is doubled the weight of gas dissolved would be doubled, but the volume of gas dissolved would be the same as before. Some absorption coefficients are given in Table 31; it will be seen that gases vary enormously in their solubility in water.

TABLE 31. ABSORPTION-COEFFICIENTS OF GASES IN WATER AT 0° AND 100°, UNDER 760 MM. PRESSURE.

Substance.	Absorption-coefficient at 0°.	Absorption-coefficient at 100°.
Hydrogen - - -	0·0215	0·0160
Nitrogen - - - -	0·0239	0·0100
Oxygen - - -	0·0489	0·0170
Argon - - - -	0·053	—
Carbon dioxide - -	1·713	0·359 (60°)
Sulphur dioxide - -	79·8	18·8 (40°)
Ammonia - - -	1305·0	195·0

Deviations from Henry's Law.—Henry's Law is very nearly true for sparingly soluble gases. For carbon dioxide, Henry's Law holds at small pressures, but appreciable deviations are found at higher pressures (Table 32). A very soluble gas such as ammonia does not obey Henry's Law even at low pressures, since the quotient s/p decreases rapidly as the pressure increases, even at pressures which are only a small fraction of an atmosphere; but at 100°, when ammonia is much less soluble, Henry's Law is nearly true.

TABLE 32. SOLUBILITY OF GASES IN WATER.

	Pressure—p.	Solubility—s.	s/p.
(*a*) Carbon dioxide at 0°	1 atm.	1·80 c.c./c.c.	1·80
	5	8·65	1·73
	10	16·03	1·60
	20	26·65	1·33
	30	33·74	1·12
(*b*) Ammonia at 0°	20 mm.	82 gm./L.	4·10
	40	148	3·70
	80	240	3·00
	200	421	2·11
	500	770	1·54
	1000	1126	1·13
(*c*) Ammonia at 100°	750	74 gm./L.	0·099
	1000	96	0·096
	1200	115	0·096
	1400	135	0·096

Dalton's Law of partial pressures.—This law may be stated as follows :

In a mixture of gases, the solubility of each gas varies proportionally with its partial pressure.

The pressure exerted by a mixture of gases may be regarded as made up of the sum of the partial pressures of its constituents. From Boyle's Law it follows that the partial pressure of any particular constituent is proportional to the fraction by volume in which it is present in the mixture. Thus air contains by volume 78 per cent. of nitrogen, 21 per cent. of oxygen, and 1 per cent. of argon ; the partial pressures of these gases in air at one atmosphere pressure are therefore :

$$p_{N_2}=0{\cdot}78 \text{ atm.}, \quad p_{O_2}=0{\cdot}21 \text{ atm.}, \quad p_A=0{\cdot}01 \text{ atm.},$$

whilst in air at half an atmosphere pressure the partial pressures of the constituents are half these numbers.

When air is dissolved in water, the nitrogen, oxygen and argon dissolve in amounts proportional to their absorption-coefficients and to their partial pressures. Thus, one litre of water dissolves from air at 0° and 760 mm. pressure.

Nitrogen	$1000 \times 0{\cdot}0239 \times 0{\cdot}78 = 18{\cdot}65$ c.c.	$= 63{\cdot}3\%$.
Oxygen	$1000 \times 0{\cdot}0489 \times 0{\cdot}21 = 10{\cdot}27$ c.c.	$= 34{\cdot}9\%$.
Argon	$1000 \times 0{\cdot}053 \times 0{\cdot}01 = 0{\cdot}53$ c.c.	$= 1{\cdot}8\%$.
	29·45 c.c.	

By boiling the water the dissolved gases can be expelled and collected. The mixture thus obtained agrees in composition with that calculated from the absorption-coefficients, namely, 63·3 per cent. of nitrogen, 34·9 per cent. of oxygen and 1·8 per cent. of argon by volume. It is richer in oxygen and in argon than the original air, since these two gases have higher absorption-coefficients than nitrogen.

Influence of temperature on solubility of gases.—From the figures in Table 31 it will be seen that the solubility of carbon dioxide and of ammonia in water is diminished by increasing the temperature. In most cases dissolved gases can be expelled completely from a liquid by boiling. This is not because the

solubility is zero at the boiling-point, but because the partial pressure of the gas in the bubbles of vapour is small, so that the gas gradually passes into the vapour and is swept away.

The same effect can be produced at ordinary temperatures by bubbling a sparingly soluble gas through the liquid. Thus ammonia can be removed completely from water by drawing a current of air through the solution. There are, however, some exceptions to this rule. Thus, solutions of hydrochloric acid in water give a mixture of constant composition when boiled, and the gas cannot be removed from solution by a current of air. The behaviour of this type of mixture is discussed in the next section.

Vapour-pressure of mixtures.—Mixtures of liquids can be divided into three groups according as the liquids are (*a*) miscible in all proportions, (*b*) soluble in one another to a limited extent, or (*c*) insoluble in one another. An example of the first group is given by alcohol and water. The number of components is $C=2$; and since there can only be one liquid phase in such a system, the number of phases is $P=2$ (liquid and vapour). The Phase Rule then tells us that

$$F=C-P+2=2-2+2=2,$$

i.e. the system is bivariant. If, therefore, we fix the temperature, it follows that the pressure and composition must vary together, *i.e.* each mixture will have a definite vapour-pressure; or, if we fix the composition, then the pressure and temperature must vary together, *i.e.* the vapour-pressure of a given mixture is determined by the temperature. In practice, the vapour-pressure curves of binary mixtures of completely miscible liquids are found to fall into three classes, (i), (ii) and (iii), which are shown diagrammatically in Fig. 38.

(i) In the first type of curve, the vapour-pressure of the mixture varies progressively from that of one liquid to that of the other liquid. Mixtures of benzene and toluene, or of ether and aniline, give curves of this kind. The diagram, Fig. 38 (*a*), represents the behaviour of an ideal mixture of liquids in which (in accordance with Raoult's Law of Vapour Pressures, p. 181), the partial vapour-pressure of each component is proportional

to its molecular concentration in the mixture. The partial vapour-pressure of the component A is therefore represented by a straight line PS, falling from the vapour-pressure of A at P to a zero value at S. In the same way, the partial vapour-pressure of the component B is represented by a straight line QR. The total vapour-pressure of the mixture, which is equal to the sum of these two partial pressures, is therefore represented by the straight line PR.

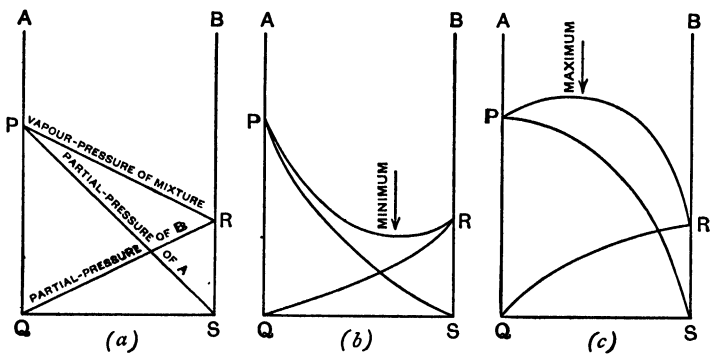


FIG. 38.—Vapour-pressure of mixtures.

The molecular composition of the vapour from such a mixture is proportional to the partial pressures of the two components. In the particular case shown in Fig. 38 (*a*), these are proportional to the vapour pressures of the pure components multiplied by their concentrations in the mixture. The vapour is therefore richer than the liquid in the component of higher vapour-pressure ; and the mixture can be separated by distillation into fractions which are richer and poorer in this component than the original liquid mixture. By repeated distillation (or by distillation through a stillhead) both components of such a mixture can be isolated in a pure state. Precisely similar results follow if the lines PS, QR, and PR are not straight but curved, provided that the line PR, which represents the total vapour-pressure of the mixture, neither rises to a maximum nor falls to a minimum between P and R.

(ii) The second group of liquid mixtures is that in which the

vapour-pressure composition curve exhibits a minimum as in Fig. 38 (*b*). If a mixture of this kind is rich in component *A*, a vapour rich in *A* is first obtained on distillation; and the composition of the residue in the distilling flask changes (towards the right in the diagram), until the composition corresponding to the minimum vapour-pressure is reached. This mixture then distils unchanged. Similarly, if a mixture rich in *B* is distilled, it loses *B* more rapidly than *A* and finally the same mixture of minimum vapour-pressure distils. Since the vapour-pressure of this mixture is lower than that of its constituents, its boiling-point is *higher* than that of either of the liquids of which it is composed. Examples of such pairs of liquids giving **mixtures of maximum boiling-point** and minimum vapour-pressure are set out in Table 33.

TABLE 33. MIXTURES OF MAXIMUM BOILING-POINT.

	Composition.	Boiling-point.
Sulphuric acid + water -	98·7% H_2SO_4	338°
Nitric acid + water -	68% HNO_3	120·5°
Hydrofluoric acid + water -	37% HF	120°
Hydrochloric acid + water -	20·24% HCl	110°
Hydrobromic acid + water -	48% HBr	125°
Hydriodic acid + water -	58% HI	127°

It is noteworthy that these pairs of liquids all liberate heat when mixed. Their molecules have, therefore, considerable affinity for one another, and for this reason give rise to mixtures of high boiling-point and low vapour-pressure.

(iii) The third group of liquid mixtures gives rise to vapour-pressure curves which exhibit a maximum, Fig. 38 (*c*). A mixture of this composition therefore boils at a *lower* temperature than any other mixtures of the series. On distillation, this mixture of minimum boiling-point distils first at constant temperature and without any variation of composition, leaving behind any excess of one or other of the two components of the mixture. By repeated fractional distillation the mixture of maximum vapour-pressure and one of the components can be isolated. Examples of constant-boiling **mixtures of minimum**

boiling-point and maximum vapour-pressure are set out in Table 34.

TABLE 34. MIXTURES OF MINIMUM BOILING-POINT.

	Composition.	Boiling-point.
Pyridine + water - -	59% C_5H_5N	92°
Alcohol + water - -	95·59% C_2H_5OH	78·13°

Vapour-pressure of partially miscible liquids.—A system consisting of two liquids which are soluble in one another only to a limited extent, as in the case of ether and water at 20°, gives a different type of diagram (Fig. 39). As ether is added to water, the vapour pressure increases, as indicated by the line *OP*, until the water is saturated with ether (about 7 per cent.). An upper layer of ether saturated with water then appears as an additional phase. It then follows from the Phase Rule that the system has now only one degree of freedom. Hence, the vapour-pressure at a given temperature is constant over a range of compositions, as represented by the line *PQ*. Over this range, the addition of more ether alters the relative amounts of the two phases, but it does not alter the vapour-pressure until the point *Q* is reached. At this point, enough ether has been added to dissolve all the water, giving rise to an unsaturated solution of water in ether. The vapour-pressure curve then rises from the value for a saturated solution of ether in water (or of water in ether) to the vapour-pressure of pure ether at *R*.

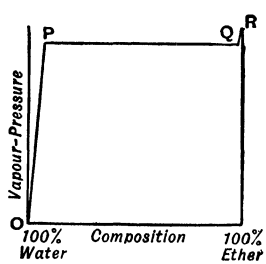


FIG. 39.—Vapour-pressure of partially-miscible liquids.

Two mutually saturated solutions which are in equilibrium with one another are termed **conjugate solutions**. The composition of these conjugate solutions is given by the points *P* and *Q*. Since they are in equilibrium with one another, their vapour-pressures must be equal, and this condition applies also to the partial vapour-pressures of the two components. The

vapour-pressure of two conjugate solutions is always *less* than the sum of the vapour-pressures of the pure components; and in the case of ether and water (though not in all other cases) it is less than the vapour-pressure of the more volatile constituent, namely, the ether.

Vapour-pressure of immiscible liquids. Steam-distillation.—If two liquids, A and B, are completely insoluble in one another, the line PQ of Fig. 39 extends across the whole of the diagram. The constant vapour-pressure represented by this horizontal line is then equal to the sum of the vapour-pressures of the components, since, when two liquids do not dissolve at all in one another, their partial vapour-pressures must remain unaltered.

This property is utilised in the operation of **steam-distillation** (Expt. 13, ii.). Let us suppose that two immiscible liquids have vapour-pressures p_1 and p_2 at the boiling-point of the mixture. The volumes of vapour produced will then be proportional to these vapour-pressures. Since the densities of the vapours are proportional to their molecular weights, it follows that the ratio by weight in which the two liquids distil is given by $\frac{M_1 p_1}{M_2 p_2}$, where M_1 and M_2 are the molecular weights of the liquids. As an example, let us consider the system bromobenzene and water. The vapour-pressures of the pure liquids are set out in Table 35, and their sum is given in the last column.

TABLE 35. VAPOUR-PRESSURES OF WATER AND BROMOBENZENE.

Temperature.	Vapour-Pressure of		Mixture.
	Water.	Bromobenzene.	
80°	$p_1 = 356$ mm.	$p_2 = 66$ mm.	$p_1 + p_2 = 422$
85	434	79	513
90	526	98	624
95	634	117	751
100	760	141	901

By graphical interpolation it is found that the sum of the vapour-pressure rises to 760 mm. at 95·2°; the mixture therefore boils

at 95·2° C. under atmospheric pressure. At this temperature $p_1 = 641$ and $p_2 = 119$ mm. The molecular weights of the liquids are 18 and 157 respectively. The ratio by weight in the distillate of bromobenzene to water is therefore

$$\frac{157 \times 119}{18 \times 641} = 1{\cdot}62.$$

Although, therefore, the vapour-pressure of bromobenzene is much lower than that of water, its greater molecular weight has the effect of increasing the relative weight of this compound in the vapour to such an extent that the distillate actually contains considerably more bromobenzene than water. If the distillation were carried out at 450 mm., the boiling-point of the mixture would be 81·7°, $p_1 = 381$ and $p_2 = 69$ mm. The ratio of bromobenzene to water would then be $\frac{69 \times 157}{381 \times 18} = 1{\cdot}58$, and at lower pressures still less. In general, the rate at which the less volatile substance distils in steam increases with increase of pressure, and in certain technical processes distillation is carried out under pressure with superheated steam, in order to take advantage of this behaviour.

CASE III.—TWO COMPONENTS: TWO PHASES (NEITHER PHASE A VAPOUR).

14. Systems Containing no Gaseous Phase.

i. **Critical solution temperature of phenol and water.**—Weigh a clean dry test-tube, place in it about 1 gram of pure phenol and weigh again. Draw out the upper part of the tube to a neck about 4 mm. wide and when cold add about 4 c.c. of water. Seal off at the neck, and weigh the tube again with the portion removed in sealing. In this way a sealed tube containing a known amount of phenol and water is readily prepared. Six tubes, containing approximately the following amounts of phenol and water, should be made and marked with a diamond.

	Phenol.	Water.
I. - -	0·6 grams	4·4 grams
II. - -	1	4
III. - -	1½	3½
IV. - -	2	3
V. - -	2½	2½
VI		

Grip one of the tubes in a wooden test-tube holder, so that it can be shaken vigorously, and immerse in a large beaker of water containing a thermometer. Raise the temperature; shake the tube from time to time, and note the temperature at which the milky liquid suddenly becomes clear. Allow the temperature to fall until the liquid in the tube becomes turbid again. Repeat the heating and cooling and note carefully the temperatures at which the turbidity appears and disappears; these should not differ by more than 1°. The mean of these figures is the temperature at which phenol and water are soluble in one another in the proportion in which they are present in the tube. Similar observations should be made with the remaining tubes.

Plot the temperatures at which solution occurs against the percentage of phenol in the mixtures, and draw a smooth curve through the points obtained. The maximum of this curve gives the **critical solution temperature** (see Fig. 40, p. 142).

ii. **Solubility-curve for Glauber's salt.**—Place 100 c.c. of distilled water and about 60 grams of Glauber's salt in a small wide-mouthed bottle fitted with a rubber stopper. Close the bottle, and place it in a water-bath maintained at 20°, shaking vigorously every five minutes for half an hour. A small teat-pipette (*e.g.* a fountain-pen filler) should be kept in a dry test-tube in the bath, in order to bring it to the same temperature as the solution. After half an hour, allow the crystals to settle, and with the teat-pipette transfer 1½ to 2 c.c. of the clear saturated solution to a weighed dish. Weigh rapidly, then place the dish in the steam-oven, and dry to constant weight. From the weights of solution and of anhydrous sodium sulphate calculate the solubility in grams of Na_2SO_4 per 100 grams of solution.

Measure the solubility of the salt also at 25°, 30°, 35° and 40° C. Plot the solubility against the temperature and note the break in the curve at the transition-point.

iii. **Determination of the transition temperature of Glauber's salt by a thermal method.**—Fit a specimen-tube with a cork carrying a thermometer and a stirrer of stout copper wire. Mount the tube by means of a cork in the neck of a wide-mouthed bottle, in order to protect it from draughts, (compare Fig. 22, p. 91). Place in the tube 10 grams of clear (uneffloresced) fragments of Glauber's salt, and about ½ gram of anhydrous sodium sulphate. Heat the tube in a water-bath to about 36-40°, when the crystals will melt to a thin mush of anhydrous sodium sulphate and water. Insert the thermometer

and stirrer in this mixture, dry the outside of the tube and mount it in the neck of the bottle. Stir steadily, and read the temperature every minute. A fall will first be observed, and finally the temperature will remain steady at the transition point for several minutes. If the temperature falls below 31° without a halt, introduce a small crystal of Glauber's salt to start crystallisation.

iv. **Freezing-point diagram for a binary mixture.**—(*a*) Using the apparatus described in Expt. 14, iii., follow the rate of cooling of naphthalene and of *p*-nitrotoluene over a range of temperatures covering the freezing-points of the substances. Plot cooling-curves, with temperatures as ordinates and time as abscissae. Notice the length of time during which the temperature remains constant, and whether there is any "overcooling" of the melt below this temperature before crystallisation begins.

Then weigh out mixtures of the two substances as follows:

	Nitrotoluene.	Naphthalene.
I. - -	2	8
II. - -	4	6
III. - -	6	4
IV. - -	8	2

In each case place the mixture in the tube, melt in a water bath, insert the thermometer and stirrer, wipe the outside of the tube and mount it in the bottle. Stir steadily and read the temperature every minute.

Notice the temperature at which crystals begin to separate in mixture No. I., and mark on the cooling-curve the point at which a change of slope occurs. The cooling of mixtures II., III. and IV. should be continued until a further prolonged arrest of temperature occurs. This arrest marks the eutectic temperature at which the two constituents of the mixture crystallise together from a liquid which is saturated simultaneously with both components.

Plot the initial freezing-points and the eutectic temperatures against the composition of the mixture, and complete the thermal diagram. What conclusions can be drawn from the data as regards (*a*) the formation of compounds, (*b*) the existence of solid solutions in this system?

Condensed systems.—Since liquids and solids have only a small compressibility, the effect of pressure on the equilibrium of systems containing only liquids and solids is very small.

Thus, as long as the pressure is maintained higher than the vapour-pressure of the system, so that no gaseous phase exists, small variations of pressure will not alter appreciably the form of the curves which represent the relationships between the other two variables, namely, the temperature and the composition. Such a system is termed a **condensed system.** For condensed systems we may write a " reduced " phase rule,

$$F' = C - P + 1.$$

This will give the remaining degrees of freedom which the system can possess, in addition to the pressure, which, as we have seen, is always capable of independent variation as long as it is higher than the vapour pressure. It is convenient to use this rule in the discussion of the solubilities of liquids and solids.

Examples of condensed systems may also be found in the eutectic mixtures discussed in the following section, where two solids and their saturated solution in one another are in equilibrium at one fixed temperature and one fixed composition. It must be remembered, however, that, although small changes of pressure have only a negligible influence on a condensed system, yet the effect of pressure is a real one, and the conditions of equilibrium are altered appreciably under high pressures, just as the melting-point of a solid is altered under these conditions (p. 99). The " reduced " phase rule, whilst very convenient, is therefore only an approximate guide to the behaviour of condensed systems and can only be used when no large changes in pressure occur.

Mutual solubility of liquids. Critical solution temperature.— If two liquids are only partially soluble in one another and form two liquid phases, then from the reduced phase rule

$$F' = C - P + 1 = 2 - 2 + 1 = 1.$$

Such a system is therefore univariant, and the composition of each of the phases is fixed as soon as the temperature has been determined.

An example of such a system is given by phenol and water (Expt. 14, i.). The solubility of liquid phenol in water increases as the temperature rises, as shown by the curves AB

(Fig. 40). The solubility of water in phenol also increases with rise of temperature, as in curve *CB*. The two curves meet at *B*. The point *B* shows the highest temperature at which two layers can be formed, and also the limiting composition of the two layers just before they vanish. For phenol and water the **critical solution temperature** is 68·3°, and the critical solution contains 33 per cent. of phenol.

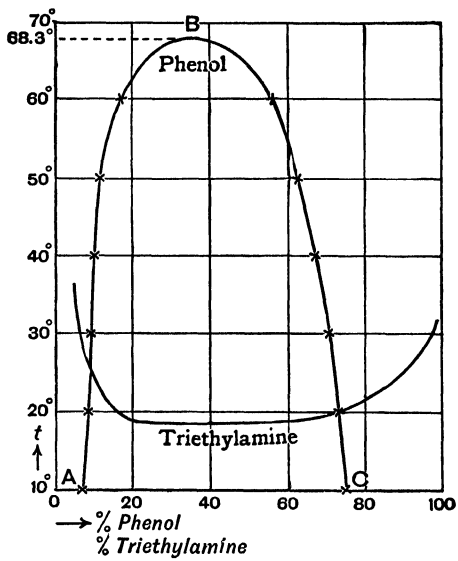


FIG. 40.—Critical solution temperatures of phenol and triethylamine in water.

The critical solution temperature is very similar to the critical temperature of a liquid or gas. Thus when the temperature is raised, the composition and densities of the two liquid phases approach one another, just as do the densities of a liquid and of its saturated vapour. The interfacial tension between the two layers also decreases as the temperature rises. Finally, at the critical solution temperature, the composition and density of the two layers become equal, the interfacial tension vanishes and it is no longer possible to form two distinct layers.

Triethylamine, $(C_2H_5)_3N$, and water give a similar system, but

in this case the solubility of the liquids in one another decreases as the temperature rises, and the curve representing the solubilities is concave, as shown in Fig. 40. The critical solution temperature is at 19° C. The two liquids are therefore miscible in all proportions *below* this temperature, whilst above it two liquid layers can be formed.

In a few cases the solubility curve forms a complete loop, so that there is both a maximum and a minimum critical solution temperature. Nicotine and water give a curve of this type.

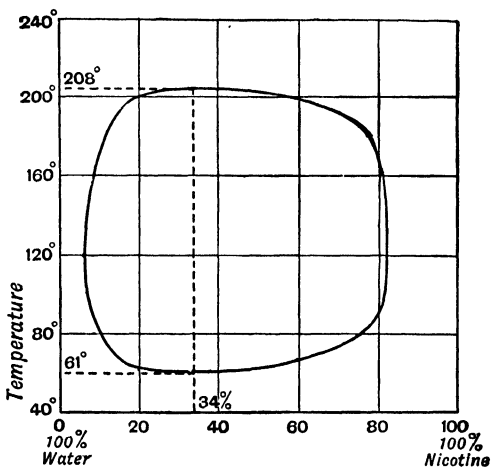


FIG. 41.—Critical solution temperatures of nicotine in water.

The upper critical solution temperature is at 208° and 34 per cent. nicotine + 66 per cent. water. Above this temperature (under a pressure great enough to prevent the escape of vapour) the two liquids are miscible in all proportions. Below 208° two liquid layers form; and the composition of these diverges, as the mutual solubility of the liquids decreases with falling temperature, until at 120° the two layers have the compositions:

(i) 6·5 per cent. nicotine + 93·5 per cent. water,
(ii) 83 per cent. nicotine + 17 per cent. water.

As the temperature falls below this point the mutual solubility

begins to increase again, until the lower critical solution temperature is reached at 61° and a composition 34 per cent. nicotine 66 per cent. water.

Solutions of solids in liquids.—When a liquid mixture is cooled to a sufficiently low temperature, it generally begins to deposit crystals. Since the crystals form a new phase, one degree of freedom is lost. In other words, whilst an unsaturated solution can exist over a range of concentrations and temperatures, a saturated solution must have a definite concentration when the temperature is fixed, and conversely.

In studying such systems we use temperature-concentration diagrams, on which bivariant systems are represented by areas, univariant systems by lines, and invariant systems by points. From the reduced phase rule the possible types of system are :

Bivariant.	One phase.	Unsaturated solutions (solid or liquid).
Univariant.	Two phases.	Saturated solution and one solid phase.
Invariant.	Three phases.	Saturated solutions and two solid phases.

The curves representing the univariant systems may be regarded as **freezing-point curves**, *i.e.* as showing the temperature at which crystals are frozen out from a mixture of a given composition ; or they may be regarded as **solubility curves**, showing the composition of the saturated solution of one component in the other at a series of temperatures. The form of the curves can be determined experimentally either from a study of the cooling-curves of mixtures of known composition (Expt. 14, iv.), or from determinations of solubility (Expt. 14, ii.).

Solutions of solids in solids.—A system in which the components will mix in any proportion both in the solid and in the liquid state, giving rise to a complete series of isomorphous crystals or solid solutions (p. 128), is always univariant, since for any given mixture only one liquid and one solid phase is possible. The curves showing the relation between the composition and freezing-point are therefore continuous and exhibit no breaks. Moreover, when solid solutions are formed, there is no segregation of the components in crystals of different forms and only

one kind of crystal can be detected even under the highest magnification. Examples of such systems are given in Fig. 42.

A complete freezing-point diagram always includes two curves which are distinguished as the "liquidus" and the "solidus" respectively. The **liquidus** shows the temperature at which a *liquid* of given composition begins to deposit crystals whilst the **solidus** shows the composition of the *solid* which is deposited at a given temperature. Thus, if a horizontal line is drawn to represent a given temperature, its intersection with the liquidus will show the composition of the liquid which is just ready to begin to deposit crystals at that temperature, and

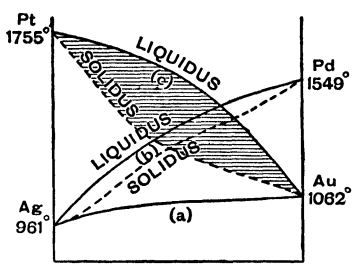


FIG. 42.—Freezing-point diagram for isomorphous metals.

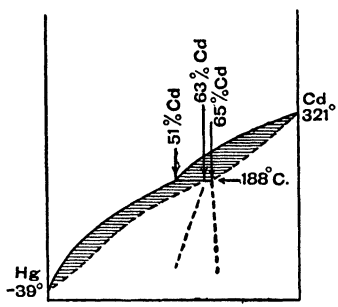


FIG. 43.—Equilibrium-diagram for mercury and cadmium.

its intersection with the solidus will show the composition of the crystals which begin to separate. The two intersections therefore represent the compositions of the liquid and solid solutions which are in equilibrium with one another at a given temperature. A number of these horizontal lines are shown in Fig. 42. In (*a*) the liquidus and solidus for silver and gold are too close together to be drawn separately, showing that the solid has almost exactly the same composition as the liquid from which it separates. In (*c*), on the other hand, the liquidus and solidus for gold and platinum are widely separated, and the diagram shows clearly that the crystals are always richer in platinum than the liquid from which they separate.

Isodimorphism.—Solid solutions are sometimes formed by substances of which the crystals are not normally isomorphous.

Thus, although cadmium and mercury crystallise in different crystalline systems, it is possible to obtain crystals of mercury containing up to 63 per cent. of cadmium, and crystals of cadmium containing up to 35 per cent. of mercury (Fig. 43). In cases such as these it is probable that both components are dimorphic (p. 116); the two solid solutions then contain one component in its normal form, and the other in a form which is not stable when the substance is allowed to crystallise alone. This phenomenon is known as **isodimorphism.**

It is also possible for a hydrate to separate with a different number of molecules of water of crystallisation when forming a solid solution with another salt. Thus, when ferrous sulphate, $FeSO_4, 7H_2O$, forms mixed crystals with copper sulphate, $CuSO_4, 5H_2O$, as in Expt. 12, i., the whole of the material crystallises with five molecules of water of crystallisation, as an isomorphous mixture of the composition $[CuFe]SO_4, 5H_2O$, where the two elements shown inside the square brackets can replace one another in equivalent proportions.

The equilibrium-diagram for mercury and cadmium is shown in Fig. 43. The liquidus (shown as a full line) exhibits a break at 51 per cent. of cadmium and 188° C. Above this temperature, the crystals which separate are isomorphous with cadmium, whilst below it they are isomorphous with mercury. The solidus (shown by dotted lines) is discontinuous, since the crystals (having the form of cadmium) which separate just above this temperature contain 65 per cent. of cadmium, whilst the crystals (having the form of mercury) which separate just below it contain only 63 per cent. of cadmium. The series of crystals which are isomorphous with mercury therefore extends from 0 – 63 per cent. of cadmium, whilst the series which are isomorphous with cadmium extends from 65–100 per cent. cadmium. No solid solutions are formed with 63–65 per cent. of cadmium; a solid of this composition must, therefore, form a mixture of two kinds of crystals, just like a mixture of ether and water containing between 7 and 97·3 per cent. of ether.

Eutectic mixtures.—Since the formation of solid solutions is the exception and not the rule, the first crop of crystals from a liquid mixture generally contains one component only. Thus,

when solutions of salt are frozen, they begin by depositing pure ice, which is free from salt. When this separation occurs, the solution always freezes at a lower temperature than the pure substance. In the same way, the freezing-point of the second component of the mixture is lowered by the addition of a small amount of the first. The freezing-point diagram therefore consists of two intersecting branches, giving rise to a V-shaped curve, as in Fig. 44. The minimum, at which the freezing-point curves for the two components intersect, is described as the **eutectic point**, and shows the composition of a mixture from which both components crystallise simultaneously. The **eutectic mixture**, as it is called, has a definite composition, and freezes like a pure substance at a definite temperature ; this is described as the **eutectic temperature**, and is the lowest freezing-point of the whole series.

On account of their constancy of composition and of melting point, it was at one time supposed that eutectic mixtures were definite chemical compounds. Thus eutectic mixtures formed by freezing solutions of various salts in water were named ' cryohydrates." That these products are not compounds but mixtures is shown by the following facts :

(i) Although the composition of the eutectic is fixed by the intersection of the two branches of the freezing-point curve, it does not usually correspond with the calculated composition of a simple chemical compound.

(ii) In spite of the fact that the segregation of the two components in the eutectic mixture is often very slight, so that the product may appear to be homogeneous when viewed under a low magnification, it is always possible, by using a sufficiently high magnification, to detect the separate crystals of the two components.

Study of eutectic systems.—The method used in studying mixtures which form eutectics has been illustrated in Expt. 14, iv., where cooling-curves were plotted for a series of mixtures of *p*-nitrotoluene and naphthalene. This method is widely employed in metallurgy, as in the case of the alloys of tin and lead, which is illustrated in Fig. 44. These two metals give

an eutectic-point at 181° C. and 36 per cent. of lead, which is approximately the composition of soft solder. The tin separates in a state of almost complete purity; but the lead forms solid solutions containing a small percentage of tin, and gives a sloping

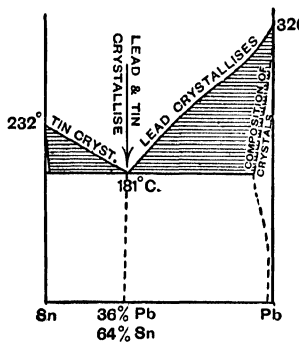


FIG. 44.—Equilibrium-diagram for lead and tin.

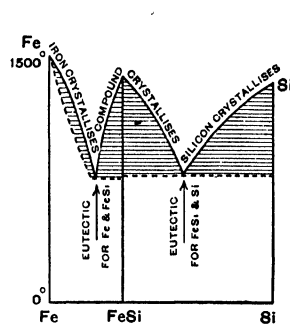


FIG. 46.—Equilibrium-diagram for iron and silicon.

solidus, as shown by the dotted line marked "composition of crystals" in Fig. 44. Alloys containing less than 16 per cent. of tin can, therefore, form homogeneous crystals, but all others contain separate crystals of both metals. The appearance of the eutectic alloy is shown in Fig. 45.

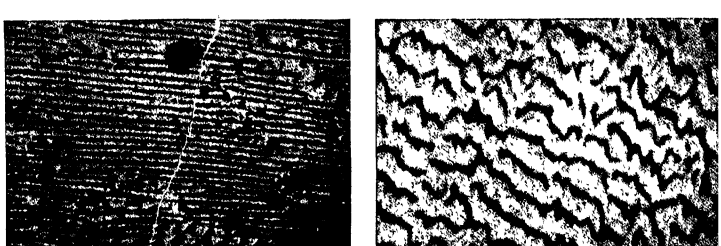


FIG 45.—Eutectic alloys of lead and tin (× 600)

Formation of compounds.—In many cases the two components of a mixture unite to form a chemical compound. Since the melting-point of this compound is usually depressed by the addition of an excess of either of its components, a

W-shaped freezing-point curve is obtained, as in Fig. 46, where the central maximum represents the composition of the compound.

If the compound is not completely stable, but begins to dissociate into its components when it melts, its freezing-point will be lowered by the products of dissociation, even when neither component is present in excess. The maximum in the

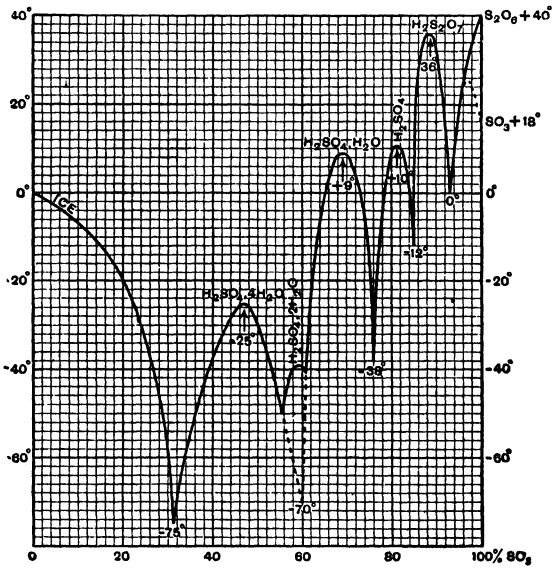


FIG. 47.—Equilibrium-diagram for sulphuric anhydride and water.

curve then becomes rounded instead of sharp, so that the sharpness of the maximum gives a rough indication of the stability of the compound.

In some cases more than one compound may be formed. An example of this is given by sulphur trioxide and water, which unite to form the compounds $H_2S_2O_7$, H_2SO_4, $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$, $H_2SO_4 \cdot 4H_2O$. Each of these compounds gives a separate maximum in the freezing point curve (Fig. 47).

Finally the compound may only exist over a narrow range of concentrations, and a maximum may not occur; the formation

of a compound is then indicated by a break in the freezing-point or solubility-curve. The special characteristics of this case are (i) that the compound is decomposed before its melting-point is reached, (ii) that this decomposition takes place at a definite transition-temperature, just as in the case of a dimorphic solid, (iii) that a liquid having the exact composition of the compound deposits crystals of the decomposition-product

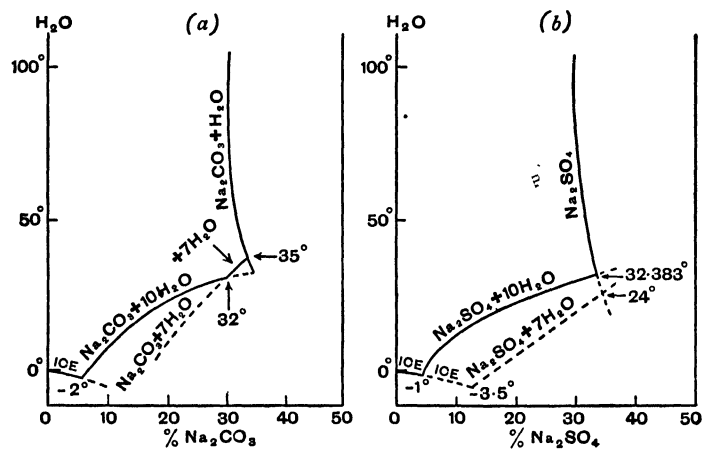


FIG. 48.—Equilibrium-diagrams for
(*a*) Sodium carbonate and water; (*b*) Sodium sulphate and water.

instead of the compound itself. Fig. 48 gives the solubility-curves for sodium carbonate and sodium sulphate. The dotted lines represent metastable systems which can only be realised in the absence of crystals of the stable phase. It will be seen that all these hydrates decompose before the maximum is reached, and have therefore no true melting-point, and that, whilst the heptahydrate of sodium carbonate, $Na_2CO_3 \cdot 7H_2O$, has a short range of stability, the heptahydrate of sodium sulphate, $Na_2SO_4 \cdot 7H_2O$, is metastable at all temperatures.

CASE IV. TWO COMPONENTS: THREE PHASES.

15. Vapour-pressure of Hydrates and of Saturated Solutions.

1. Determination of vapour-pressure by Cumming's dew-point method.—(*a*) A wide-mouthed bottle is fitted with a rubber stopper carrying a glass tube bent at right angles and bearing a stopcock, and a bright silver test-tube (Fig. 49). Before use, the end of this silver tube is dipped obliquely into distilled water heated to the boiling-point, producing a boundary-line which becomes visible only when dew begins to form on the tube, thus rendering it easier to detect the first deposit of dew. The silver tube contains a few cubic centimetres of ether, and is closed by a cork through which pass (i) a thermometer, (ii) a long tube dipping into the ether, and (iii) an exit tube. A layer of about 10 grams "Glauber's salt," Na_2SO_4, $10H_2O$, is placed in the bottle, the stopper is inserted and the bottle is partially evacuated through the stopcock by means of a water-pump. This evacuation causes equilibrium to be attained more rapidly between the hydrate and the vapour, but it does not alter the partial pressure of water-vapour.

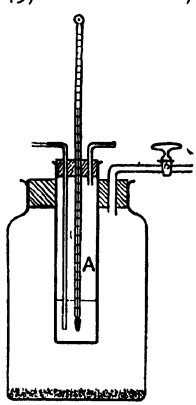


Fig. 49. — Apparatus for determination of dew-point

Support the bottle in a large beaker of water at 20° C., in a position in which there is a good light. By means of a rubber tube blow air slowly through the ether, and note the temperature at which mist appears on the polished surface of the silver tube. Allow the apparatus to stand, and note the temperature at which the mist vanishes. Make two or three determinations of these temperatures. The average of these readings is the dew-point. Read off from Table 44 (p. 180) the vapour-pressure of water at the dew-point. This is equal to the dissociation-pressure of the hydrate at 20°.

(*b*) Determine in the same way the dissociation-pressure of the blue crystals of hydrated copper sulphate at various temperatures.

ii. Preparation of lower hydrates of copper sulphate.—(*a*) *Monohydrate.*—Roughly powder about 15 grams of crystalline copper sulphate, $CuSO_4$, $5H_2O$, and weigh accurately about 10 grams in a weighed porcelain dish. Place the dish in an air-oven

and heat to 200°-220° for an hour. Remove the dish, cool in a desiccator and weigh again. Repeat for another half hour and weigh again. Repeat till the weight is nearly constant. The loss in weight will then correspond to a loss of 4 molecules of water. The pale greyish-blue residue is the *monohydrate*, which has only a small dissociation-pressure at 200°, and is therefore stable at this temperature, whilst the trihydrate and pentahydrate, which have large vapour-pressures, rapidly lose water.

(*b*) *Trihydrate.*—Select a wide-mouthed glass bottle, and fit it with a rubber stopper carrying a tube with a stopcock. Place in the bottle about 50 grams of roughly powdered crystals of copper sulphate pentahydrate and cover it with a layer of glass-wool. Weigh a specimen tube, place in it about 2 grams of the monohydrate and weigh again. Place the tube in the bottle, insert the cork and evacuate with a water-jet pump. Close the stopcock and leave the bottle in the steam oven for 3 or 4 hours. Open the stopcock carefully, remove the tube and weigh again. Replace it in the bottle, evacuate and heat again. The weight will increase at first and finally become constant when two molecules of water have been absorbed. The trihydrate is thus obtained as a blue powder, intermediate in colour between the pentahydrate and the monohydrate.

Since the pentahydrate has a greater vapour-pressure than the monohydrate or the trihydrate, water will distil on to the monohydrate in the tube so long as any remains which has not been converted into trihydrate. The distillation stops at this point because, as soon as a minute amount of pentahydrate is formed from the trihydrate in the tube, the vapour-pressure of the mixture in the tube becomes the same as that of the partially-dehydrated pentahydrate in the bottle.

Vapour-pressure of hydrated salts.—According to the Phase Rule, a two-component system in which three phases are present has one degree of freedom

$$F = C - P + 2 = 2 - 3 + 2 = 1.$$

Since we have already considered in the preceding section the limiting cases in which a liquid is in equilibrium simultaneously with two solids at an eutectic point or at a transition-temperature, the most important of the systems which remain to be discussed under Case IV is that in which the phases are two solids and a vapour. Since the system is univariant, it follows at once that the vapour-pressure of such a system is

fixed when the temperature is fixed, and (within limits) is independent of the composition of the system.

An interesting example of this type of system is given by the hydrates of copper sulphate. Table 36 gives the vapour-pressures at 78° C. of a number of mixtures of copper sulphate and water arranged in order of decreasing water-content. The first two mixtures consist of solid pentahydrate in contact with the saturated solution, and it will be seen that, even when water is removed from the system, the vapour-pressure remains constant at 290 mm. until only solid pentahydrate is left.

TABLE 36. VAPOUR-PRESSURES OF MIXTURES OF COPPER SULPHATE AND WATER AT 78° C.

Mols. of Water per mol. of $CuSO_4$.	Vapour-Pressure mm. Hg.	Phases.
6·05 5·13	289 291	Saturated solution $+CuSO_4 \cdot 5H_2O$
4·13 3·71 3·41	234 238 232	$CuSO_4 \cdot 5H_2O$ $+CuSO_4 \cdot 3H_2O$
2·61 2·10 1·75	142 145 148	$CuSO_4 \cdot 3H_2O$ $+CuSO_4 \cdot H_2O$

As soon as a little more water is removed, a new system is established in which the phases are $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 3H_2O$. This has its own vapour-pressure of about 235 mm., which is unaltered by further removal of water until the composition $CuSO_4 \cdot 3H_2O$ is reached. Here again the removal of water only alters the relative amounts of the two phases; but as the trihydrate and pentahydrate are always present the vapour-pressure remains constant. When the water-content of the mixture falls below that of $CuSO_4 \cdot 3H_2O$, a new system is produced with a vapour-pressure of about 145 mm.; this is the equilibrium-pressure of the system $CuSO_4 \cdot 3H_2O$, $CuSO_4 \cdot H_2O$, vapour. Finally, we have at the end of the series the system $CuSO_4 \cdot H_2O$, $CuSO_4$, vapour, which has only a small vapour-pressure at 78°.

When the figures in Table 36 are plotted, a stepped curve is

obtained, in which a sudden decrease in vapour-pressure n shown at the composition of each new hydrate. Hence a stuc ir of the vapour-pressures of hydrated salts during dehydratior makes it possible to detect intermediate hydrates and to determine their composition.

Deliquescence and efflorescence.—It is evident that the stability of a hydrate depends upon the pressure of water-vapour in the atmosphere with which it is in contact. Thus, if we keep copper sulphate at 78° in air with a partial pressure of water-vapour greater than 290 mm., water will condense to form the saturated solution, and the crystals will become wet and **deliquesce.** Conversely, if the partial pressure of water-vapour is less than 235 mm., and greater than 142 mm., then the pentahydrate will lose water continually at 78° until it reaches the composition of the trihydrate. This change will break up the large crystals of the pentahydrate to a fine powder, and the salt is said to **effloresce.**

It is evident from this example that the conditions which determine whether a salt will deliquesce or effloresce or remain unchanged in air include two factors, (i) the pressure of water-vapour in the air, and (ii) the vapour-pressures of the hydrate and of its saturated solution. The partial pressure of water-vapour in the air may be taken as about 14 mm. on an average day; but on dry days, *e.g.* when it is frosty out of doors, it is lower; and on "muggy" days, when the weather is warm and wet, it is higher than this value. The vapour-pressures of a few common salts and of their saturated solutions are shown in Table 37.

TABLE 37. VAPOUR-PRESSURES OF HYDRATES AND OF SATURATED SOLUTIONS AT 20°.

	Hydrate.	Saturated solution.
$CaCl_2 \cdot 6H_2O$ - - -	2·5 mm.	7·5 mm.
NH_4NO_3 - - -	—	10·5 mm.
$CuSO_4 \cdot 5H_2O$ - - -	5·1 mm.	16·0 mm.
$Na_2SO_4 \cdot 10H_2O$ - -	16·3 mm.	16·6 mm.

(*a*) *Calcium chloride.*—Table 37 shows that, under ordinary conditions, the hexahydrate of calcium chloride, which has a

vapour-pressure less than 14 mm., will absorb moisture from the air. The hydrates with $4H_2O$, $2H_2O$ and $1H_2O$, which have an even smaller vapour-pressure, will also absorb moisture from the air. Moreover, since the vapour-pressure (7·5 mm.) of a saturated solution of calcium chloride is also less than the partial pressure of water-vapour in the air, the absorption of water will not stop when a minute amount of the saturated solution is formed, but will continue until all the solid calcium chloride has dissolved, and the solution has become so diluted that its vapour-pressure is at last raised to that of the water-vapour in the atmosphere. It is for this reason that calcium chloride deliquesces in the air.

(*b*) *Ammonium nitrate* behaves similarly, except when the amount of water-vapour in the air is less than 10 mm. In practice, therefore, this salt is deliquescent in the summer, when the air is generally wet, but not in the winter, when the proportion of moisture in the air of the laboratory is limited by the coldness of the air outside.

(*c*) *Copper sulphate* neither deliquesces nor effloresces, and is therefore quite stable in air. Thus, deliquescence cannot take place, because an atmospheric vapour-pressure of 14 mm. is less than that of a saturated solution of this salt at 20° C.; on the other hand, the crystals do not effloresce, since the normal pressure of water-vapour in the air is greater than that of the water-vapour emitted by the pentahydrate. The trihydrate and monohydrate, which have much lower vapour-pressures than the pentahydrate, will absorb water from the air, and form the pentahydrate, but the product will remain dry and solid, because the vapour-pressure is not sufficient to convert the pentahydrate into a saturated solution.

(*d*) *Sodium sulphate.*—The decahydrate, $Na_2SO_4 \cdot 10H_2O$, which has long been known as "Glauber's Salt," effloresces in air, losing water to form anhydrous sodium sulphate, since its vapour-pressure is greater than the usual partial pressure of water-vapour in the air.

It is obvious from these considerations that the humidity of the atmosphere as well as the specific properties of the salt must be taken into account. All soluble salts will deliquesce in the

presence of saturated water-vapour; on the other hand, in the dry conditions of a very severe winter, when nearly all the water-vapour has been frozen out of the air, calcium chloride does not deliquesce, and the hydrated crystals may actually become efflorescent.

Dissociation-pressures.—Many systems are known in which the gaseous-phase is formed by substances other than water. An important example of this type is the system $CaCO_3$, CaO, and CO_2. This system is made up of two components, and not of three as might be thought at first sight, since the composition of any phase can be expressed in terms of two components, *e g* CaO and CO_2. The Phase Rule predicts that the system is in equilibrium at a definite pressure of carbon dioxide at each given temperature. If this amount of carbon dioxide is not present, some of the calcium carbonate will dissociate; if it is exceeded some of the carbon dioxide will combine with the lime to form chalk. It is important to note that the pressure is independent of the *amount* of the solids, and is therefore the same for chalk with a trace of lime as for lime with a trace of chalk. Further, the system is not defined rigidly unless both solid phases are present. It is customary to speak loosely of the pressure of the system as the dissociation-pressure of calcium carbonate; but the presence of lime as a second solid phase is always assumed.

TABLE 38. DISSOCIATION-PRESSURES.

Reaction.	Temperature.	Dissociation-pressure.
$CaCO_3 \rightleftharpoons CaO + CO_2$	525°	18 mm. Hg.
	750	100 ,,
	840	342 ,,
	910	755 ,,
	926	1022 ,,
$AgCl \cdot 3NH_3 \rightleftharpoons AgCl + 3NH_3$	0	29·3 ,,
	24	93·7 ,,
	48	241·4 ,,
	57	488·0 ,,
$2BaO_2 \rightleftharpoons 2BaO + O_2$	525	20 ,,
	650	65 ,,
	750	340 ,,
	790	670 ,,

Table 38, which gives some examples of systems of this type, shows that the dissociation-pressures of such systems, like the vapour-pressure of a pure liquid, increase very rapidly with rise of temperature.

QUESTIONS ON CHAPTER VI.

1. Henry's Law says that " the solubility of a gas is proportional to the pressure." It also states that " the volume of a gas dissolved is independent of the pressure." Explain this paradox. (Inter. Sci., Bombay.)

2. How would you determine as accurately as possible the amount of carbon dioxide that dissolves when a current of the gas is bubbled through water at room temperature. Give full experimental details.

What grounds have we for thinking that combination takes place between carbon dioxide and water ?

(Oxford Higher School Certificate.)

3. The transition-point between anhydrous sodium sulphate and sodium sulphate decahydrate is at 32° C. Describe three experimental methods of determining this transition temperature, explaining the principle involved in each. (B.Sc., Sheffield.)

4. Discuss the vapour-pressure curves of the following systems, (*a*) toluene and water, (*b*) propyl alcohol and water, (*c*) hydrogen chloride and water. How would these systems behave in distillation. (B.Sc., Manchester.)

5. Propyl alcohol and water are miscible in all proportions. The vapour-pressure curve of mixtures of these substances passes through a maximum corresponding to a mixture containing 80 per cent. by weight of propyl alcohol. The corresponding curve for formic acid-water mixtures passes through a minimum at the mixture containing 73 per cent. of formic acid. Compare the behaviour on distillation of aqueous solutions containing 50 per cent. of formic acid and propyl alcohol respectively. (B.Sc., Sheffield.)

6. Discuss carefully the methods you would adopt in order to decide whether a given homogeneous material (*e.g.* a distillate of constant boiling-point or an alloy of maximum or minimum freezing-point) should be regarded as a mixture or as a definite chemical compound. (B.Sc. Hons., Sheffield.)

7. Describe the methods by which the vapour-pressures of salt hydrates have been determined and discuss the results obtained. (B.Sc. Hons., Sheffield).

8. Show that (*a*) of two allotropic forms of a substance the one which has the lower vapour-pressure is the more stable, (*b*) two

liquid phases in equilibrium with each other have the same vapour-pressure, (*c*) the vapour-pressure of a solution of a non-volatile substance cannot be greater than that of the pure solvent.

(Natural Science School, Oxford, 1923.)

9. Describe how you would determine the solubility of $MgSO_4$, $7H_2O$ in water at 40°.

100 parts of water dissolve

4 parts of A at	0°	44 parts of B at	27·5°
10 ,, ,,	10°	44·2 ,, ,,	30°
15·5 ,, ,,	15°	45·4 ,, ,,	32·5°
22 ,, ,,	20°	47 ,, ,,	35°
29·5 ,, ,,	25°	54·8 ,, ,,	40°
39 ,, ,,	30°	66 ,, ,,	45°
50·2 ,, ,,	35°		
58·5 ,, ,,	37·5°		

Plot the solubility curves of A and B on as large a scale as possible on the squared paper provided and indicate clearly the portions of the curves which represent the metastable condition. Deduce the transition-temperature of A $\rightleftharpoons$ B.

Describe in detail one other method for the determination of transition-temperatures. (B.Sc., Manchester.)

10. Sulphuric acid is said to form solid hydrates of definite composition. How would you proceed to test this statement and to ascertain the composition of the hydrates ?

(London Higher School Certificate.)

11. Explain the principles on which the phase rule depends. Discuss with the aid of a temperature-concentration diagram extending over the whole range of compositions the equilibrium between water and a gas such as sulphur dioxide which is easily liquefiable and forms a crystalline hydrate.

(Trinity College Senior Schol.)

12. Discuss the equilibrium between chlorine, water, and chlorine hydrate with the aid of the phase rule. Is it possible for chlorine hydrate to exist in the presence of liquid chlorine ? Discuss briefly any other interactions which are possible between chlorine and water. (Trinity College Senior Schol.)

13. Ammonia is absorbed by anhydrous ammonium nitrate with the formation of a liquid. The following table gives the relationship between the molecular percentage (p) of ammonium nitrate in the liquid and the temperature (t) at which the liquid begins to deposit a solid phase.

p	100	53·8	32·3	30·0	25·0	13·9	6·25	0
t	168°	68·8°	−30·0°	−40·0°	−38·0°	−44·5°	−60·0°	−80·0°

Plot these results on squared paper and discuss their interpretation.

(Trinity College Senior Schol.)

14. Under what conditions may a maximum appear in the freezing-point curve of a series of binary mixtures ? Give

examples of cases of this type amongst (i) metallic alloys, (ii) aqueous solutions.

Maass and Wright have shown that when a series of mixtures of ethylene and hydrogen bromide is frozen, a rounded maximum appears in the freezing-point curve at a composition corresponding with one molecular proportion of each constituent. What conclusions can you draw from this observation ?

(B.Sc. Hons., Sheffield.)

15. Discuss the conditions which prevail during the distillation, and during the crystallisation of a pair of isomers which do not combine with one another and do not form isomorphous crystals or mixtures of constant boiling-point. How are these conditions modified by the addition to the mixture of a catalyst which renders the isomers interconvertible, (*a*) slowly, (*b*) rapidly ? Apply these considerations to the problem of separating two isomers from ethyl acetoacetate. (B.Sc. Hons.)

16. Write a concise account of the system sodium chloride, water, in terms of the Phase Rule. (B.Sc. Punjab.)

17. Describe the behaviour of two non-miscible liquids on distillation. A mixture of ethylene dibromide and water boils at ordinary pressure at 91°, the vapour-pressure of water at this temperature being 545 mm. What will be the percentage composition of the distillate ? (Cambridge Schols.)

18. State the phase rule and explain the terms involved. Apply the rule to explain the fact that the dissociation of calcium carbonate depends upon the temperature only. (B.A., Bombay.)

19. How would you distinguish between (*a*) a pure liquid and a constant boiling mixture, (*b*) a pure and an impure specimen of a crystalline solid ? Illustrate your answer by examples.

(Cambridge Higher School Certificate.)

CHAPTER VII.

OSMOTIC PRESSURE.

16. Osmosis and Osmotic Pressure.

i. Osmosis through parchment paper.—Fit a diffusion-thimble of parchment-paper (Sleicher and Schull's No. 579 is suitable), with a rubber stopper carrying a narrow glass tube, which at the inner end is level with the cork. Fill the thimble with a strong solution of cane-sugar, insert the stopper, so that no air-bubble is present, and immerse the thimble in water. Attach a paper scale, *e.g.* a strip of squared paper, to the tube, and read the level of the liquid in the tube. In the course of half an hour it should rise by one or two centimetres, showing that water is passing inward through the membrane to the sugar solution.

ii. Preparation of a semipermeable membrane of copper ferrocyanide.—(*a*) Prepare solutions of 6·25 grams of copper sulphate in 250 c.c. of water, and of 5·5 grams of potassium ferrocyanide in 250 c.c. Mix a few cubic centimetres of the two solutions in a test-tube, and note the chocolate-brown precipitate of copper ferrocyanide, $Cu_2Fe(CN)_6$.

(*b*) Half-fill a boiling-tube with the ferrocyanide solution. Draw out the end of a tap funnel to a fine point and fill the funnel and stem completely with the copper sulphate solution. Lower the stem of the funnel to the bottom of the boiling-tube, allow the liquid to rest for a few minutes in order to become completely quiescent, then open the tap and allow the copper sulphate to flow in slowly, so as to form a distinct layer at the bottom of the tube. Close the tap and observe the interface. The boundary will be seen to be covered with a thin membrane of copper ferrocyanide, which does not grow thicker since neither of the two salts can pass through it. On standing, the membrance will gradually bulge downwards, since the ferrocyanide solution has the greater osmotic pressure and will therefore abstract water from the copper sulphate solution below it.

(*c*) Half-fill another tube with the copper sulphate solution. Dissolve 10 grams of sugar in 50 c.c. of the ferrocyanide solution, and allow a few drops of this solution to fall from a pipette to the bottom of the copper sulphate solution. The drops will be seen to grow by absorption of water. As they do so, the membrane bursts and heals itself by fresh deposits of copper ferrocyanide. When the drops have absorbed enough water to make them less dense than the copper sulphate solution, they will rise, still surrounded by the membrane, and float to the surface.

iii. Measurement of osmotic pressure.—Procure a glass filter with a fused-in glass mat as shown in Fig. 50. Moisten the mat thoroughly by sucking water through it. Invert the cup and fill the tube with the copper sulphate solution used in the previous experiment; then close the end *A* with a rubber stopper, taking care not to enclose an air bubble. Fill *B* with the potassium ferrocyanide solution used in Exp. 16, ii. Allow three days for the membrane to form and then wash the apparatus thoroughly with water. Fill the lower part with a 1 per cent. solution of cane-sugar, and insert the stopper *A* carrying the bent capillary tube *C*, on which a paper scale should be mounted. The sugar-solution should then fill completely the space below the mat and the capillary up to the scale.

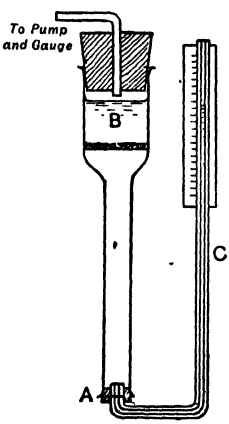


FIG. 50.—Apparatus for measurement of osmotic pressure.

Fill the cup *B* with water and close the top with a rubber stopper carrying a tube connected to an empty bottle, gauge and water-jet pump. Maintain a difference of pressure of about 700 mm. between *B* and the open end of *C*, and read the level of the solution in *C* every five minutes for twenty minutes. A steady rate of flow of water from *C* to *B* should be recorded. Repeat the observations with a difference of pressure of 600, 500 and 400 mm. The direction of flow should reverse between 600 and 500 mm. Plot the rate of flow against the pressure, and read off the point of zero flow. The pressure at which this occurs is the osmotic pressure of the sugar-solution. The experiment is, however, a difficult one to carry out, and should not be attempted unless ample time is available.

iv. Preparation of a liquid semipermeable membrane.—Prepare two mutually saturated solutions by shaking phenol and water together in a separating funnel, and running off the lower layer of phenol, after allowing time for the two layers to separate. Saturate a concentrated solution of calcium nitrate (50 grams in 100 c.c.) with phenol in a similar manner. Half-fill a boiling tube with the phenol-saturated solution of calcium nitrate. Pour on to this a layer, about 3 mm. thick, of phenol saturated with water. By means of a tap-funnel with a capillary tip, place above this a layer, 3-4 cm. thick, of water saturated with phenol. Place a scale behind the tube and read the position of the layer of phenol. After a few hours the layer of phenol will be displaced upwards.

In this experiment, since calcium nitrate is insoluble in phenol, whilst water is soluble in it, the layer of phenol acts as a semi-permeable membrane. Osmosis therefore occurs, water passing through the phenol from the upper layer of water in order to dilute the lower layer of calcium chloride solution.

Osmosis.—It has long been known that the cells of living plants and animals are usually surrounded by a membrane through which water can pass readily. Thus, when red blood cells are placed in water they rapidly swell and burst, owing to the passage of water through their outer membrane into the cell. On the other hand, if the red corpuscles are placed in a strong solution of salt, water passes out of the cells into the solution, with the result that the corpuscles lose their characteristic disc-like shape and shrivel up. In the same way, if a solution of sugar is placed in a bag of parchment paper, and the bag is immersed in water as in Expt. 16, i, water passes spontaneously through the parchment to the sugar solution inside the bag. This spontaneous flow of liquids through a membrane is termed **osmosis**, and is obviously of great importance in the study of living cells.

A close study of the phenomenon of osmosis has resulted in the discovery of a number of rules. These are important, because they have led to a great advance in our knowledge of the nature of solutions.

(i) In the first place, osmosis is observed only when the membrane is more permeable to the solvent (usually water) than to the dissolved substance. Thus, if the membrane is equally

permeable to both constituents of a solution, mixing may occur through the membrane, but osmosis will be reduced because a flow of liquid will take place in both directions. When a bag of parchment paper containing a sugar solution is immersed in water, very little sugar escapes from the bag, although water passes into it freely; there is therefore a very marked osmosis. A membrane which allows the solvent but not the solute to pass is termed a **semipermeable membrane.** Parchment paper is not a perfect semipermeable membrane for sugar and water, since it allows a little sugar to escape; a number of more efficient membranes were, however, discovered by Traube, including copper ferrocyanide, $Cu_2FeC_6N_6$, which inhibits completely the passage of sugar and has therefore been very largely used in the investigations of the osmotic properties of solutions. (Expt. 16, ii.).

(ii) Secondly, it has been found that the direction in which water flows through the membrane is determined by the concentrations of the solutions on either side of it. Thus, if a solution is placed on one side of the membrane, and pure water on the other side, then water always passes into the solution so as to make it more dilute. This behaviour is closely related to the diffusion of a substance in solution. Thus if a layer of a strong solution of a coloured salt, *e.g.* potassium permanganate, is carefully placed at the bottom of a column of water, it will be seen after some hours that the boundary of the solution is no longer sharp but has become indefinite, and shades off through a series of intermediate tints to the colourless layer of water.

This diffusion of substances in solution was studied by Graham who found that, although different substances diffused at very different rates, yet the direction of the diffusion was always from regions of high concentration to regions of lower concentration, so that *the concentrations throughout the solution tended to become equal.* This is precisely what is found in the phenomenon of osmosis. The salt cannot diffuse, since it is restrained by the semipermeable membrane; but dilution is effected by the transit of water through the membrane to the stronger solution.

In agreement with this conception of osmosis it is found that,

when a membrane separates two solutions of the same substance, an osmotic flow of water takes place from the weaker solution to the stronger solution, but that this osmotic flow ceases *when the solutions have the same concentration.* When two solutions containing different substances are used, the concentrations at which osmosis ceases will not be identical, but can be determined by experiment. A pair of solutions which produce no flow through a semipermeable membrane are said to be "isotonic" and are described as **isotonic solutions.** It is also found that *solutions which are isotonic with a given solution are isotonic with one another.* This is sometimes called the **law of isotonic solutions,** and provides a very convenient method for comparing the osmotic pressures of a series of different substances since the concentrations of solutions which are isotonic with certain cells can readily be determined. Thus red blood corpuscles placed in 0·85 per cent. sodium chloride solution and observed under the microscope do not change in appearance. If they are placed in weaker solutions they swell and burst, whilst in stronger solutions they shrivel up. This concentration of salt is therefore isotonic with the contents of the red cells; it is known in medicine and surgery as a "normal saline solution." By making similar experiments with other substances, we can determine the concentrations at which they are isotonic with the cell contents, and therefore with 0·85 per cent. sodium chloride solution or with each other.

Osmotic pressure.—A membrane of copper ferrocyanide is so fragile that it can support only a very minute pressure; but by precipitating copper ferrocyanide in the pores of a vessel of porous earthenware, Pfeffer obtained a membrane which could support considerable pressures. In this way, for example, he was able to show that the osmotic flow could be stopped by applying a pressure to the solution. When a small pressure is applied to the solution, the flow slackens, but does not cease; but when a high pressure is applied, the direction of flow can actually be reversed. With a given solution there is one pressure which just causes osmosis to cease and this is termed the **osmotic pressure** of the solution.

The measurement of osmotic pressure.—(*a*) *Pfeffer.*—The

osmotic pressure of a solution can be determined by applying a measured pressure to the solution by mechanical means, and observing the direction of osmosis. This was the method adopted by some of the later workers, but Pfeffer (1877) used the simpler arrangement of allowing water to pass into a closed cell, and thus to raise the pressure spontaneously until the equilibrium pressure was reached.

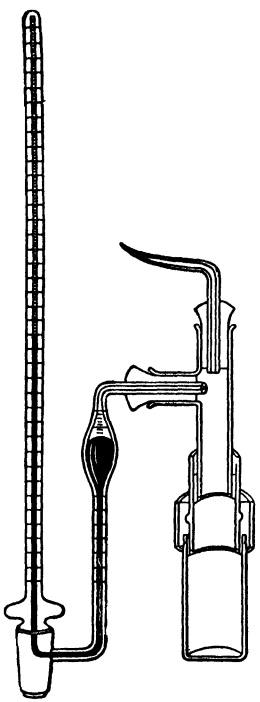


FIG. 51.—Pfeffer's apparatus for the measurement of osmotic pressure.

Pfeffer's apparatus is shown in Fig. 51. The solution is placed in a cylindrical porous pot, which carries the membrane and is tightly clamped to a headpiece communicating with a mercury-gauge filled with nitrogen. The whole of the space between the pot and the mercury in the gauge is filled with solution, any excess being expelled through the bent glass tube at the top of the headpiece, which is finally sealed off. When the pot is immersed in water, the pressure inside it rises slowly, and (if the membrane is satisfactory) a constant pressure is finally reached, which is the osmotic pressure of the solution. The magnitude of this pressure can be deduced from the volume of the nitrogen in the left-hand limb.

(*b*) *Morse and Frazer.*—The preparation of a good membrane is a matter of considerable difficulty, and many failures are experienced. Morse and Frazer, who made a very thorough study of the measurement of osmotic pressures by this method in the years from 1905 to 1913, found it necessary to manufacture special pots from suitable clays, in order to secure fine and even pores, which would give the membrane suitable support and enable it to withstand the large pressures (up to 300 atmospheres), to which it was afterwards subjected. The

pots finally prepared had the open end glazed, in order to make a gas-tight connection with the gauge.

After removing the air by soaking the pots in water and evacuating, the semipermeable membrane was deposited in the pores. This was done by placing a tenth-molecular solution of copper sulphate in the cell, and immersing it in a vessel containing a tenth-molecular solution of potassium ferrocyanide. An electric current was passed from a platinum plate dipping into the cell to a platinum cylinder surrounding it, in order to facilitate the diffusion of the two salts into the pores, where they met and formed the membrane. The electrical resistance of the cell rose as the membrane was formed, and finally reached a maximum. At this stage the current was stopped, the cell was placed in distilled water for some time, and then tested with a solution of cane-sugar. The treatment was then repeated several times until a constant osmotic pressure was found, showing that the membrane was free from holes. Sometimes more than six months of repeated electrolysis and washing were necessary to bring a cell into good condition.

TABLE 39. OSMOTIC PRESSURES OF CANE SUGAR SOLUTIONS. (Morse and Frazer.)

Concentration. Gram-mols per 1000 grams of water.	Osmotic Pressure in Atmospheres.			
	0° C.	10° C.	20° C.	25° C.
0·1	2·462	2·498	2·590	2·634
0·2	4·722	4·893	5·064	5·148
0·3	7·085	7·334	7·605	7·729
0·4	9·442	9·790	10·137	10·296
0·5	11·895	12·297	12·748	12·943
0·6	14·381	14·855	15·388	15·624
0·8	19·476	20·161	20·905	21·252
1·0	24·825	25·693	26·638	27·053

Morse and Frazer measured the pressures with a gauge similar to that used by Pfeffer. For the higher pressures they used an interferometer in which the change of refractive index with compression was used to determine the osmotic pressure of the solution. Table 39 contains some of their data for aqueous

solutions of cane-sugar. It will be seen that the osmotic pressure increases with concentration and with rising temperature, and that the osmotic pressures of the solutions are large. Thus, a solution containing 1 gram-molecule ($C_{12}H_{22}O_{11} = 342$), of cane-sugar in 1000 grams of water has an osmotic pressure at the ordinary temperature of more than 25 atmospheres.

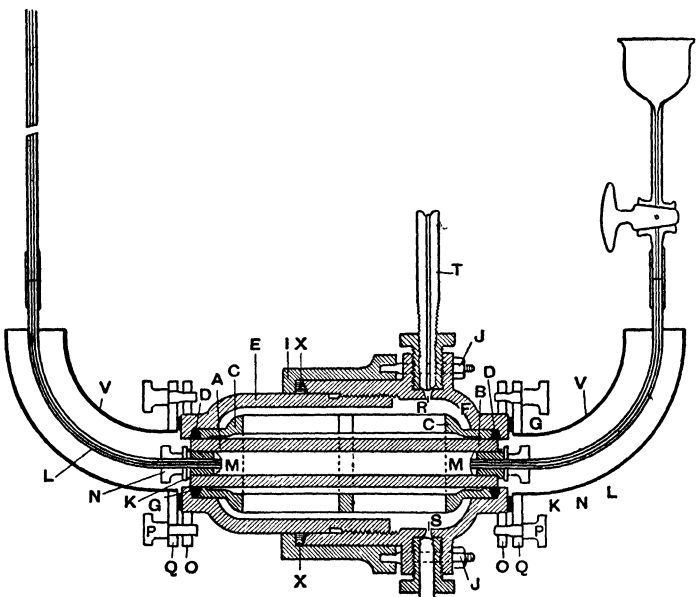


FIG. 52.—Berkeley and Hartley's apparatus for the measurement of osmotic pressure.

(*c*) *Berkeley and Hartley.*—An extended study of the osmotic pressure of solutions of various sugars, and other substances which do not pass through a membrane of copper ferrocyanide, was made by the Earl of Berkeley and Mr. E. G. Hartley. These workers used the method of applying to the solution a pressure which was just sufficient to stop osmosis. Their apparatus is shown in diagrammatic form in Fig. 52. The solution was contained in an annular space *RS* around the porous cylinder *A* on which the membrane of copper ferrocyanide was deposited.

Hydraulic pressure was applied to the solution through the tube *T* and measured by a gauge.

The inside of the porous vessel, *MM*, contained water, and the occurrence of osmosis to or from the solution could be detected by the movement of the water-level in the capillary tube shown on the left-hand side of the figure. Two pressures, separated by a small interval, were found by experiment, of which the lower just allowed a slow flow of water into the solution, whilst the higher caused a slow flow of water from the solution. The mean of these two pressures was taken as the osmotic pressure of the solution.

Table 40 contains some of the results of Berkeley and Hartley for stronger solutions of cane-sugar, together with the values deduced from the work of Frazer and Myrick (using Morse's method) for the same solutions. It will be seen that the two methods of measurement give results which are in good accord; the osmotic pressures of these solutions are therefore known with considerable accuracy.

TABLE 40. OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS.

Concentration (Grams of Sugar in 1 litre of Solution).	Osmotic Pressure in Atmospheres at 0°.	
	B. and H.	F. and M.
180·1	15·48	15·59
300·2	29·72	29·78
420·3	48·81	47·88
540·4	74·94	73·06
660·5	111·87	109·10
750·6	148·46	148·80

The laws of osmotic pressure.—Shortly after Pfeffer had measured the osmotic pressures of aqueous solutions of cane sugar, van't Hoff showed that these pressures exhibited close analogies with the pressure of a gas. This parallelism can be illustrated better, however, by using the later and more accurate measurements of Berkeley and Hartley.

(*a*) *Influence of concentration.*—The osmotic pressure of a dilute solution is directly proportional to the concentration of

the solution, and therefore varies inversely as the volume of the solution in which a given weight of sugar is dissolved. In Table 41, the first column gives the number of grams per litre of cane-sugar, $C_{12}H_{22}O_{11}$, and the second column gives the osmotic pressure P in atmospheres of the solution at 0° C.; the third column gives the volume V in litres in which 1 gram-molecule (342 grams) is contained, and is calculated by dividing the numbers in the first column into 342. The last column gives the value of the product PV. It will be seen that this product is very nearly constant for these dilute solutions. Boyle's Law, $PV = \text{const.}$, can therefore be extended to solutions by using the symbol P to represent the osmotic pressure of a solution and V to represent the volume of solution containing one gram-molecule of the dissolved substance.

TABLE 41. OSMOTIC PRESSURE OF CANE-SUGAR SOLUTIONS AT 0°. (Berkeley and Hartley.)

Concentration.	Osmotic Pressure, *P*.	Volume, *V*.	Product, *PV*.
2·02 gm./litre	0·134 atm.	169·3 litres	22·7
10·0	0·66	34·2	22·6
20·0	1·32	17·1	22·6
45·0	2·97	7·60	22·6
93·75	6·18	3·65	22·5

(*b*) *Influence of temperatures.*—Van't Hoff showed further that the osmotic pressure of a solution varies with temperature in precisely the same way as the pressure of a gas of constant volume. This can be expressed most readily by saying that in both cases the pressure is directly proportional to the absolute temperature. This is shown by the numbers in Table 42, which are taken from the work of Morse and Frazer.

TABLE 42. VARIATION OF OSMOTIC PRESSURE WITH TEMPERATURE. (Morse and Frazer.)

t° C.	0°	10°	20°	25°
T° abs.	273	283	293	298
P	7·085	7·334	7·605	7·729
P/T	0·02594	0·02591	0·02595	0·02594

The osmotic pressures are given, for a series of temperatures,

of a solution containing 0·3 gram-molecules of sugar per 1000 grams of water; the last line gives the ratio P/T. From the constancy of this ratio it is seen that osmotic pressure is accurately proportional to the absolute temperature.

(*c*) *Value of the constant* PV/T. Since the osmotic pressure is proportional to the concentration of the solution and to the temperature, its magnitude can be expressed by an equation, precisely similar to that used for gases, namely,

$$PV = R'T,$$

where P and V have the meanings given above and R' is a constant. Van't Hoff showed that the constant R' of this osmotic equation has the same value as the R of the gas equation, which for ideal gases is equal to 0·0821 (p. 10) in litre-atmospheres. We can calculate R' for the osmotic equation from the data in Table 41. The mean value of PV is 22·6; dividing this by $T = 273$, we find $R' = 0·0828$ in good agreement with the value found for gases.

These relations may all be summed up in the following law:

The osmotic pressure of a dilute solution is equal to the pressure which the dissolved substance would exert if it were a gas at the same temperature, and occupying the same volume as the solution.

This law is generally true of non-electrolytes, but electrolytes have been shown (generally by indirect methods) to give higher osmotic pressures than those calculated from the preceding law. This result has been explained by the dissociation of the electrolyte into ions (see Chap. XIII.).

Molecular weights of dissolved substances.—The identity of the osmotic constant of cane-sugar with the gas constant suggests at once that we are dealing with a "molecular" property, which depends on the number of molecules of the solute and not on their nature. In other words, we should expect that the osmotic pressures of solutions of equal molecular concentrations would be equal, *i.e.* that Avogadro's hypothesis could be applied to solutions as well as to gases. In general, this is found to be true for dilute solutions, provided that they are not electrolytes. Thus Morse and Frazer's data for dilute

solutions of glucose give for the osmotic constant the normal value $R' = 0{\cdot}081$, just as in the case of cane-sugar. It can also be shown by indirect methods that the osmotic pressure is independent of the nature of the solvent, as indeed it must be in order to be identical with the gas constant.

This discovery is of great practical importance, since it enables us to determine the molecular weight *in solution* of many substances, such as the sugars, which decompose on heating, and cannot therefore be converted into vapour for the purpose of determining their molecular weights by measurements of vapour-density. For such substances the measurement of osmotic pressure gives us an independent method of finding the molecular weight.

As an example of the calculation of a molecular weight from direct measurements of osmotic pressure we may take an observation of Morse and Frazer on glucose. A solution containing 18 grams per litre had an osmotic pressure of 2·39 atmospheres at 23°. If M is the molecular weight of glucose, $V = \frac{M}{18}$, $P = 2{\cdot}39$ and $T = 296$. Since $R = \frac{PV}{T}$, we have

$$0{\cdot}0821 = \frac{2{\cdot}39 \times M}{18 \times 296},$$

or

$$M = \frac{0{\cdot}0821 \times 18 \times 296}{2{\cdot}39} = 183.$$

The formula $C_6H_{12}O_6$ gives $M = 180$.

Osmotic pressure of concentrated solutions.—The equality of osmotic pressures and gas pressures is true only for dilute solutions. As the solutions become more concentrated, the osmotic pressure increases more rapidly than the ideal gas pressure, and the product PV increases, just as it does in the case of gases at high pressures (Chap. I.). Table 43, taken from the work of Frazer and Lotz, illustrates this behaviour. The volume V containing one gram-molecule is calculated as before, by dividing the concentration in grams per litre into the molecular weight. The theoretical value of $PV (= RT)$ at 30° is $0{\cdot}821 \times 303 = 24{\cdot}9$. It will be seen that all the solutions give much larger values, and that PV increases rapidly as the osmotic pressure rises.

TABLE 43. OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS OF CANE-SUGAR AT 30°.

Concentration.		Osmotic Pressure.				
Grams per 1000 c.c.	Grams per 1000 grams of Water.	*P.*	*V.*	*PV.*	*V'.*	*PV'.*
478·3	680	57·5	0·715	41·1	0·503	28·9
605·4	980	90·4	0 565	51·1	0·349	31·6
700·2	1260	129·5	0·488	63·3	0·271	35·1
781·4	1549	169·1	0·438	74·0	0·221	37·3
839·8	1796	206·1	0·407	83·9	0·190	39·2

Some workers have thought that concentrations should be expressed in grams per 1000 grams of *water*. These concentrations are given in the table and the volume of *water* in the solution is given in the column V'. It will be seen that PV', whilst nearer to the theoretical value than PV, is still too large, and increases rapidly with increasing concentration of sugar. It has also been suggested that the sugar combines with some of the water, which is therefore not available to act as a solvent, and that the increase in PV can be accounted for in this way. Some evidence has indeed been obtained from other experiments for the existence of a hydrate $C_{12}H_{22}O_{11}$, $5H_2O$. Since, however, we are still ignorant as to the processes by which osmotic pressure is produced, it is difficult to decide exactly what part these influences play in affecting the value of PV. It should be noted, however, that (by analogy with gas pressures), we should expect PV to be larger than normal in solutions in which the osmotic pressure is 50 to 150 atmospheres.

Method of action of semipermeable membranes.—Some of the earlier investigators thought that the semipermeable membrane acted like a sieve, *i.e.* that it had pores which were small enough to let the water molecules pass but retained the larger molecules of sugar. This view was supported by the fact that an osmotic pressure can be produced by immersing a mixture of propyl alcohol and water either in propyl alcohol or in water. It was suggested that the solution contained hydrated molecules of propyl alcohol, which were unable to pass through a membrane

which was permeable to the simple molecules both of water and of propyl alcohol.

Another view is that water can dissolve in the membrane and pass through it by diffusion in either direction, whilst the solute is insoluble in the membrane and cannot therefore pass through it. This view is supported by an experiment suggested by Ramsay, in which platinum was used as a semipermeable membrane for a mixture of hydrogen and nitrogen. In this experiment, a quantity of nitrogen at one atmosphere pressure was confined in a platinum bulb and immersed in a vessel filled with hydrogen at atmospheric pressure (Fig. 53). The pressure inside the bulb was found to increase, *e.g.* from *A* to *B*, until an increase of one atmosphere was recorded on the gauge. This increase of pressure depends on the fact that hydrogen dissolves in platinum and diffuses through it, but nitrogen does not. The diffusion is controlled entirely by the partial pressure of the hydrogen, and is not affected by the presence or absence of nitrogen. It therefore continues until the partial pressure of hydrogen inside the bulb is equal to the partial pressure of one atmosphere of hydrogen outside the bulb. Since, however, the partial pressure of nitrogen remains constant at one atmosphere inside the bulb, but zero outside it, a difference of pressure of one atmosphere is set up between the inside and the outside of the bulb. This difference of pressure is recorded by the gauge. 'It may be described as the "osmotic pressure" of nitrogen, since we may compare the nitrogen with the solute, whilst the hydrogen, which diffuses through the membrane, may be compared with the solvent in a sugar-solution.

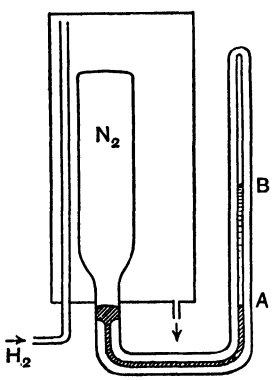


FIG. 53.—Ramsay's apparatus for osmotic pressure in gases.

A similar experiment with liquids is described in Expt. 16, iv. Here a layer of phenol, which dissolves water but not calcium nitrate, acts as a semipermeable membrane, since only the water is able to diffuse through it.

QUESTIONS ON CHAPTER VII.

1. Write a short essay on the mechanism and measurement of osmotic pressure. (B.Sc., Sheffield.)

2. Write a brief account of the principal phenomena of osmotic pressure. Calculate the osmotic pressure of a 5 per cent. solution of cane-sugar at 15° C. (H = 1, C = 12, O = 16).
(Downing College, Minor Schol.)

3. In what ways is the behaviour of a substance in the dissolved state similar to its behaviour in the gaseous state ?
Calculate the osmotic pressure at 25° C. of a solution containing 5 grams of urea in a litre of solution. The molecular weight of urea is 60. (B.A., Madras.)

4. Write a brief account of some of the phenomena of osmotic pressure. Calculate the osmotic pressure of a ten per cent. solution of cane-sugar $C_{12}H_{22}O_{11}$ at 15° C. (H = 1, C = 12, O = 16).
(Cambridge Higher School Cert.)

5. Give an account of the phenomena associated with semi-permeable membranes in connection with (*a*) gases, (*b*) solutions.
(B.Sc., Manchester.)

6. What do you understand by the osmotic pressure of a solution ?
A certain weight of a substance when in the gaseous state occupied a volume of 10 litres at 97° C. and 740 mm. pressure. The same weight of the substance when dissolved in 4·5 litres of water at 24° C. gave an osmotic pressure of 770 mm. of mercury. What explanation can you give of these facts ?
(Oxford Higher School Cert.)

7. What do you understand by the term " isotonic solutions." State the methods (direct and indirect) for comparing the osmotic pressure of solutions and describe in detail any one method.
(B.Sc., Manchester.)

CHAPTER VIII.

MOLECULAR WEIGHTS IN SOLUTION.

17. Lowering of Vapour-pressure.

1. Determination of lowering of vapour-pressure by Menzies' method.—The apparatus is shown in Fig. 54. The outer bulb *E* contains the solvent. The inner tube *C* contains the solution and is graduated in cubic centimetres. The lowering of the vapour-pressure Δp is measured by the depression of the level of the liquid in the inner tube *D* which is etched with a millimetre scale.

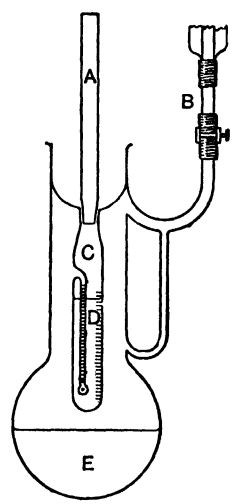


Fig. 54.—Menzies' apparatus for measuring the lowering of vapour-pressure.

Connect to a condenser *B*, half-fill the outer bulb *E* with pure acetone, and boil vigorously for a few minutes to remove dissolved gases. Fill the inner vessel *C* about two thirds full of this boiled-out liquid and then determine the zero reading in the following manner. With the liquid in the bulb boiling steadily, remove the stopper *A*, and partly close the screw-clip leading to *B*. Vapour will then blow through the solvent in the inner vessel. After a minute or two, place *A* loosely in position until it is warmed up, then insert *A* and open *B* at once to its full extent. Keep the liquid boiling steadily in the outer bulb and read the level on the graduated tube, shaking the apparatus occasionally. In 5 to 10 minutes the level of liquid in the inner tube should be steady, and a little higher than the surrounding liquid owing to capillary rise.

Repeat these operations until a constant value is found. Add a weighed pellet of *p*-nitrotoluene (about 0·3 gram) to *C*, and repeat the blowing-through as described above. Since the solution has a lower vapour-pressure than the solvent, the meniscus will come to rest below the level of the liquid in the inner tube. The difference between the reading for the solution and for the pure solvent gives the lowering of the vapour-pressure in millimetres of the solution. Read also the final volume of the solution.

Since the density of acetone at its boiling-point is 0·7518, and the density of mercury is 13·6, $\Delta p = \frac{x \times 0{\cdot}7518}{13{\cdot}6}$ mm. Hg, where x is the lowering observed in millimetres of acetone.

If m grams of pure nitrotoluene are dissolved in V c.c. of acetone, then $n = \frac{m}{M}$, where M is the molecular weight to be found. Also $N = \frac{V \times 0{\cdot}7518}{58}$. But $\frac{\Delta p}{p} = \frac{n}{N}$ and $p = 760$, so that

$$\frac{x \times 0{\cdot}7518}{13{\cdot}6 \times 760} = \frac{m \times 58}{M \times V \times 0{\cdot}7518}$$

or
$$M = \frac{m \times 58 \times 13{\cdot}6 \times 760}{xV \times (0{\cdot}7518)^2} = 1{,}061{,}000\frac{m}{xV}.$$

ii. Determination of molecular weights by lowering of vapour-pressure.—Dynamical method.—For this experiment the following apparatus is required:

2 gas wash-bottles.
2 Liebig potash-bulbs.
3 calcium chloride U-tubes.

The wash-bottles are filled with a 5 per cent. solution of cane-sugar; the Liebig bulbs are filled with water and weighed accurately, and the weight of two of the calcium chloride tubes is also determined; the third is merely a guard tube. The apparatus is connected together in the following order, using tightly-fitting pressure-tubing:

Wash-bottles.
Liebig potash bulbs.
Weighed calcium chloride tubes.
Guard tube.
Aspirator.

The whole apparatus is immersed in a tank of water in order to maintain a constant temperature, and the inlet of the first wash

bottle is connected to a length of composition tubing, immersed in the same bath, so that the air drawn through the system by the aspirator is brought to the temperature of the bath.

The aspirator is started at a speed which draws 1 or 2 bubbles per second through the bulbs, and is allowed to run for 1½ to 2 hours. The Liebig bulbs and calcium chloride tubes are then removed, dried carefully and weighed. If the air is passed slowly enough, it becomes saturated at the vapour-pressure of the solution in the wash-bottles, and takes up more moisture in the bulbs when it comes in contact with pure water. The whole of this is absorbed in the calcium chloride tubes. Hence

$$\frac{\text{Lowering of vapour-pressure}}{\text{Vapour-pressure of pure solvent}} = \frac{\Delta p}{p}$$

$$= \frac{\text{Loss in weight of Liebig bulbs}}{\text{Gain in weight of } CaCl_2 \text{ tubes}}.$$

From the loss and gain in weight, and the composition of the solution, calculate the molecular weight of cane-sugar.

iii. Determination of molecular weights by lowering of vapour-pressure. Cumming's dew-point method.—The apparatus required is shown in Fig. 49 and has been described earlier (Expt. 15, i, p. 151). A thermometer graduated to 0·1° should be used for the following experiments.

Place a 5 per cent. solution of sugar in the bottle, evacuate with a water-jet pump and close the tap. Support the bottle in a large beaker of water at the temperature of the air, and allow it to stand for half an hour. Half-fill the silver tube with ether, and blow air gently through it by a rubber tube attached to the long glass tube. Note the temperature at which dew first appears on the outside of the silver tube. Stop the current of air and allow the apparatus to warm up. Read the temperature at which the dew vanishes. Repeat these observations carefully. The mean of the temperatures of appearance and disappearance of dew (which should not differ by more than 0·2°), is the dew-point, t'. With the same thermometer determine the temperature of the water-bath $t°$. At the dew-point, liquid water is in equilibrium with the vapour from the solution, so that the vapour-pressure of water at the dew-point is equal to the vapour-pressure of the solution at the temperature of experiment.

From your results calculate the molecular weight of cane-sugar. The vapour-pressures of water can be taken from Table 44.

TABLE 44. VAPOUR-PRESSURE OF WATER.

t'.	p.	t'.	p.
0	4·579	10	9·210
1	4·926	11	9·845
2	5·294	12	10·519
3	5·685	13	11·233
4	6·101	14	11·989
5	6·543	15	12·790
6	7·014	16	13·637
7	7·514	17	14·533
8	8·046	18	15·480
9	8·610	19	16·481
		20	17·539

Lowering of vapour-pressure.—It has been shown in the previous chapter that the molecular weight of a dissolved substance can be calculated from the osmotic pressure of its solutions. Unfortunately, the measurement of osmotic pressures is a difficult operation, which cannot be carried out as an ordinary laboratory process, with the result that accurate results have been obtained only for a few substances, and for these only in aqueous solutions. This method is therefore of little value for the determination of molecular weights. There are, however, a number of other properties of a solution which are related to its osmotic pressure and which can be determined with moderate ease. Thus, when a non-volatile solute is added to a volatile liquid, the vapour-pressure is lowered to an extent which depends on the osmotic pressure that is developed; the boiling-point of the solution is therefore higher than that of the pure solvent, whilst its freezing-point is usually lower. All these properties can be used under certain conditions in order to determine the molecular weights of dissolved substances.

The earliest experiments on the vapour-pressure of solutions were made by the " barometer " method (Expt. 3, i.), although more accurate and convenient methods have since been discovered. Suppose the pure liquid has a vapour-pressure p, and that a solution of known concentration has a vapour-pressure $p - \Delta p$, where Δp is the lowering of vapour-pressure. It was

shown as early as 1848 by von Babo that, although the value of p increases rapidly with the temperature, the ratio $\Delta p/p$ is the same at all temperatures for a given dilute solution. This ratio is termed the **relative lowering of the vapour-pressure.**

Raoult's Law.—In 1887 Raoult showed that the relative lowering of the vapour-pressure obeyed certain definite and very simple laws. In the first place, the relative lowering of the vapour-pressure for a given solvent at a fixed temperature was found to be proportional to the concentration of added substance, provided that the solutions were dilute. Further, when a number of substances were studied in one solvent, at a uniform concentration of 1 gram of solute in 100 grams of ether (Table 45), it was found that the product of the molecular weight of the dissolved substance into the relative lowering of the vapour-pressure was constant. This law can be expressed by the formula

$$\frac{\Delta p}{p}\frac{M}{c}=K, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where c is the concentration in grams of solute per 100 grams of solvent, M is the molecular weight of the dissolved substance, and K is a constant.

TABLE 45. LOWERING OF VAPOUR-PRESSURE OF ONE PER CENT. SOLUTIONS IN ETHER. (Raoult.)

Substance.	$\Delta p/p$.	M.	$K=\Delta p/p \times M$.
Methyl salicylate -	0·00467	152	0·71
Benzoic acid - -	0·00582	122	0·71
Benzaldehyde - -	0·00680	106	0·72
Aniline - - -	0·00764	93	0·71
Antimony trichloride	0·00293	228·5	0·67

When the experiments were extended to other solvents, Raoult found that each liquid gave a characteristic value of K, but that these values were proportional to the molecular weight of the solvent. He was therefore able to deduce a very general relation for any non-volatile solute dissolved in any volatile solvent. Raoult's Law states that *the relative lowering of the*

vapour-pressure of a solution is equal to the ratio of the number of molecules of solute and of solvent in the solution, or

$$\frac{\Delta p}{p} = \frac{n}{N}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where n = number of gram-molecules of dissolved substance,

N = number of molecules of solvent.

Table 46 gives some of Raoult's results for the relative lowering of vapour-pressure of solutions containing 1 gram-molecule of the solute in 100 gram-molecules of solvent, *i.e.* $n/N = 0{\cdot}01$. It will be seen that the relative lowering of the vapour-pressure $\Delta p/p$ varies from 0·0096 to 0·0108 and in every case is nearly equal to n/N.

TABLE 46. LOWERING OF VAPOUR-PRESSURE OF DIFFERENT SOLVENTS. (Raoult.)

Solvent.	$\Delta p/p$.	Solvent.	$\Delta p/p$.
Water - - - -	0·0102	Chloroform -	0·0105
Phosphorus trichloride -	0·0108	Benzene -	0·0106
Carbon disulphide -	0·0105	Ether - -	0·0096
Carbon tetrachloride -	0·0105	Acetone -	0·0101

Relation between vapour-pressure and osmotic pressure.—The great theoretical importance of Raoult's Law was demonstrated in 1887 by van't Hoff, who showed that the lowering of the vapour-pressure of a solution was related directly to its osmotic pressure. A simple method for deducing the relation between osmotic pressure and the lowering of vapour-pressure is to consider the conditions under which equilibrium may be attained when the solution is enclosed in a vessel provided with a semi-permeable membrane A, and immersed at constant temperature in a bath of the pure solvent as in Fig. 55, where the large outer vessel is supposed to be evacuated.

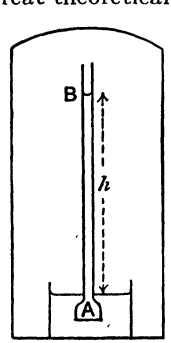


FIG. 55.—Apparatus to illustrate the relation between vapour-pressure and osmotic pressure.

Let us consider what the vapour-pressures must be in different parts of the system when osmotic equilibrium has been reached, *i.e.* when the pressure of the column of solution

in the tube attached to A is equal to the osmotic pressure. First of all, the vapour-pressure p' of the solution at B must be equal to the pressure of water-vapour in the surrounding space at B. Thus, if p' were less than the pressure of water-vapour at B, water would condense at B; this would dilute the solution, so that water would pass out through the semipermeable membrane at A, with the result that there would be a continuous flow of water from B to A, and consequently the system would not be in equilibrium.

Conversely, if p' were greater than the pressure of water-vapour at B, water would evaporate from the surface of the solution at B; this would increase the concentration of the solution, so that water would be drawn in through the semipermeable membrane, and there would be a continuous flow up the tube from A to B. Only when the vapour-pressure of the solution is equal to the pressure of water-vapour at B is there no flow of water through the tube, and only then is the system in equilibrium.

The pressure of water-vapour at B is not equal, however, to the vapour-pressure of pure water p, at the surface of the bath at A; for, just as the pressure of the atmosphere diminishes as a mountain is ascended, so the pressure of water-vapour in the vessel falls off slightly at higher levels. The difference in the pressures of water-vapour at A and B must be equal to the hydrostatic pressure of a column of vapour of height h equal to the height of the column of liquid within the tube which measures the osmotic pressure. That is

$$p - p' = \Delta p = hd,$$

where d is the density of the vapour.

Let M be the molecular weight of the solvent; then the volume occupied by M grams of vapour at a pressure p and at the absolute temperature T is $V = \frac{RT}{p}$. The density of the vapour is therefore

$$d = \frac{M}{V} = \frac{Mp}{RT}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Since the density of a dilute solution can be taken as equal to

that of the pure solvent s, the osmotic pressure P of the solution is given by the equation

$$P = hs \quad \text{or} \quad h = \frac{P}{s}. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Now we have seen that $\Delta p = hd$, so that, putting in the values of h and d given by (3) and (4),

$$\Delta p = \frac{P}{s}\frac{Mp}{RT} \quad \text{or} \quad \frac{\Delta p}{p} = \frac{MP}{sRT}. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

This equation gives the relation between the osmotic pressure of the solution and the relative depression of the vapour-pressure.

To calculate the osmotic pressure we have from the gas laws

$$P = n\frac{RT}{V'},$$

where V' is the volume of the solvent which contains 1 gram-molecule of the solute; or, since $V' = \frac{NM}{s}$, $P = \frac{nsRT}{NM}$.

Putting this in (5), we have

$$\frac{\Delta p}{p} = \frac{M}{sRT}\frac{nsRT}{NM} = \frac{n}{N}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

which is identical with Raoult's equation (2).

Ideal solutions.—In deducing Raoult's Law from van't Hoff's theory of osmotic pressure, we have assumed (i) that the *density* of the vapour varies only to a negligible extent throughout the column, although the variations of *pressure* are of fundamental importance, and (ii) that the density of the solution is equal to that of the pure solvent, (iii) that the osmotic pressure obeys the gas laws. These assumptions are nearly true for dilute solutions when Δp is small compared with p, but they are no longer valid for stronger solutions. This method of deduction is therefore very limited in its scope. On the other hand, Raoult's Law, unlike van't Hoff's application of the gas laws to osmotic pressures, can be applied just as readily to strong as to weak solutions, and therefore provides a very valuable criterion for detecting the existence of ideal solutions, and for measuring the extent to which the properties of other solutions deviate from the ideal. An ideal solution can in fact be defined as a solution

which obeys Raoult's Law over the whole range of concentrations from 0 *to* 100 *per cent., and* (it is generally added) *over a considerable range of temperatures.*

Static and dynamic methods for measuring vapour-pressures.—The experimental methods used in measuring vapour-pressures may be divided into two groups, which are termed " static " and " dynamic " methods. In the " static " methods, the vapour-pressure of the solvent or solution is balanced against a column of liquid, whilst in the " dynamic " methods a stream of gas is passed through the liquid, and its vapour-pressure is deduced from the rate of evaporation.

(*a*) *Static method.*—The barometer method (Chap. III) is a typical static method but cannot usually be applied for the determination of molecular weights, since the depressions of vapour-pressure are too small to be measured with accuracy. A number of methods have been devised in which the *difference* in vapour-pressure between the pure solvent and the solution is balanced against a column of the solvent and so can be measured with fair accuracy. The method of Menzies (Expt. 17, i.), is of this type.

(*b*) *Dynamic methods.*—In the " dynamic " method a stream of air is bubbled successively through (i) the solution, (ii) the pure solvent, and (iii) an absorbing agent which retains the vapour of the solvent. The air, and all the vessels, must be kept at the same temperature ; and the rate of bubbling must be slow enough to ensure that the gas is saturated with vapour in each vessel. It can then be assumed that the vapour-pressure of the solution is proportional to the loss in weight of (i) whilst the vapour-pressure of the pure solvent is proportional to the gain in weight of (iii). The depression of the vapour-pressure is proportional to the loss in weight in (ii), so that

$$\frac{\Delta p}{p} = \frac{\text{loss in weight of (ii)}}{\text{gain in weight of (iii)}},$$

the change in the weight of (i) being used only as a check. The experimental details for the application of this method to aqueous solutions are described in Expt. 17, ii.

18. Elevation of the Boiling-Point.

1. Measurement of elevation of the boiling-point by a simplified form of Cottrell's method.—The apparatus required is shown in Fig. 56. The essential feature is an inner funnel-tube, which collects the bubbles rising from a few fragments of porous pot (or better, from a platinum wire sealed through the bottom of *A*) and pumps a stream of liquid and vapour over the bulb of a thermometer supported one or two centimetres above the surface of the liquid. The vessel *A* is calibrated in cubic centimetres with the funnel in position.

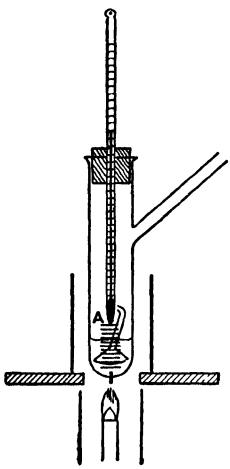


Fig. 56.—Cottrell's apparatus for measuring the elevation of the boiling-point.

Fit a thermometer, reading to 0·1° or 0·05° over the range from 50° to 100°, in the cork closing *A*. Place 12–15 c.c. of pure acetone in *A* and boil, using screens (as indicated in the figure), to shield the tube and burner from draughts. It will be found that above a certain rate of boiling the thermometer attains a steady temperature. Stop the flame and, as soon as bubbling ceases, read the volume. This gives the volume of solvent in the tube, and ignores that present in the condenser attached to the side arm. Remove the cork and drop in rapidly about 0·5 gram of the substance to be examined. Boil the solution and read the thermometer at intervals until it is again steady. In this way determine the molecular weight of (*a*) *p*-nitrotoluene, (*b*) acetanilide. The molecular elevation of the boiling-point is 2·22° for 1 gram-molecule in 1000 c.c. of acetone.

Elevation of the boiling-point.—Since the boiling-point is the temperature at which the vapour-pressure is equal to atmospheric pressure, it is obvious that a solution, of which the vapour-pressure has been lowered by the addition of a non-volatile solute, must boil at a higher temperature than the solvent. This elevation of the boiling-point was studied by Raoult, and later by Beckmann, who improved the experimental

methods and obtained results of considerable accuracy. The apparatus developed by Beckmann is shown in Fig. 57.

The "Beckmann thermometer," which passes through the neck of the vessel *A*, is designed for measuring small differences of temperature at various points of the thermometric scale. It has a scale of 6°, which is graduated to 0·01°; but the quantity of mercury in the bulb can be adjusted for use with solvents of widely different boiling-points by causing it to overflow into an auxiliary bulb or reservoir at the top of the thermometer. This device was introduced by Pickering with the view of making calorimetric measurements at different temperatures with the same thermometer. The mercury in the reservoir can be recovered by heating the thermometer until the thread reaches up and touches the surplus mercury, which can then be drawn back into the bulb as the thread retreats.

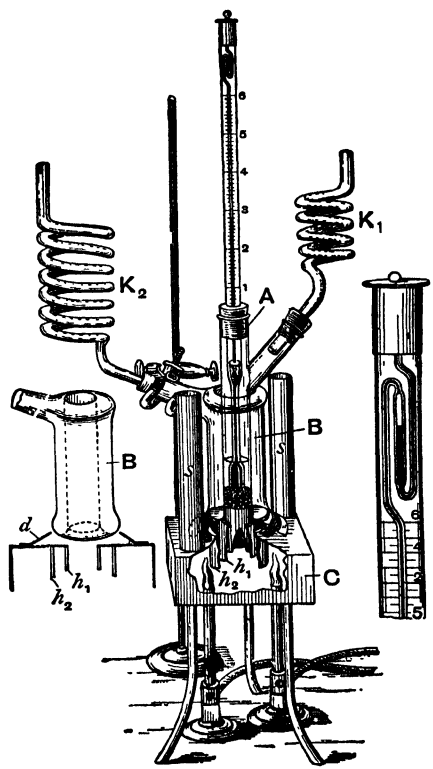


FIG. 57.—Beckmann's boiling-point apparatus.

The principal difficulty in determining the boiling-point with accuracy is to eliminate superheating of the liquid, by getting a steady and quiet evolution of bubbles. For this purpose the boiling-tube *A* of Beckmann's apparatus, which carries the Beckmann thermometer and an air-condenser K_1, is surrounded by a vapour-jacket *B*, with an air-condenser K_2,

in which the pure solvent is boiled and condensed. A platinum peg passes through the bottom of the tube *A* to conduct heat to the liquid; and the bubbles which rise from it are broken up by a layer of glass or agate beads in order to produce good stirring and steady boiling. Even with these precautions considerable skill and experience are required to get good results with this apparatus.

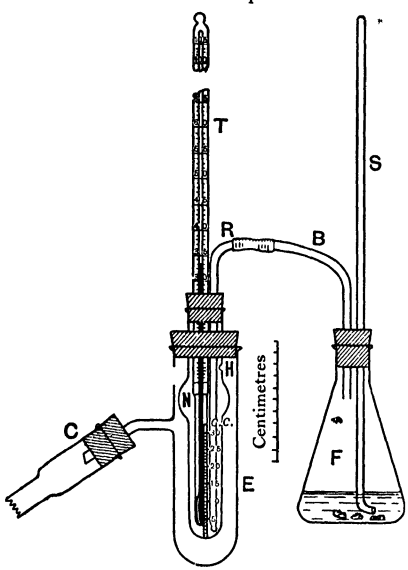


Fig. 58.—Landsberger's boiling-point apparatus.

A more effective method of preventing superheating is to raise the solution to the boiling-point by blowing into it a stream of vapour of the solvent. This method is used in Landsberger's apparatus, which is shown in Fig. 58. In this apparatus, vapour from the flask *F* passes into the solution in the vessel *N*, and condenses there, its latent heat of evaporation raising the solution to the boiling-point. This vessel is graduated so that as soon as a steady boiling-point has been read off the volume of the solution (which increases continuously) can be determined. Excess of vapour escapes through the orifice *H* and is condensed by the condenser *C*. A still better method has been devised by Cottrell in which the bulb of the thermometer is raised above the surface of the solution and is continually bathed by a stream of the solution forced up a bent tube by bubbles of vapour. A simple form of Cottrell's apparatus is described in Expt. 18, i.

Laws of elevation of boiling-point.—A study of the boiling-points of solutions by the methods described has shown that

(*a*) the rise of boiling-point ΔT is proportional to the concentration, provided that the solutions are dilute;

(*b*) for a given solvent, the same rise of boiling-point is produced by dissolving 1 gram-molecule of any substance in a fixed quantity of solvent.

These relations may be expressed by the formula

$$\frac{M\Delta T}{c}=K,$$

where M is the molecular weight of the dissolved substance, ΔT the rise in boiling-point, and c the weight of substance dissolved in 1000 grams of solvent. The constant K is termed the **molecular elevation of the boiling-point** or the **ebulioscopic constant** of the solvent. It represents the rise of boiling-point which would be produced by dissolving 1 gram-molecule of a solute in 1000 grams of the solvent if the ratio observed in dilute solutions were maintained. It is sometimes more convenient to measure the *volume* of the solvent (as in Landsberger's method), than its weight. The concentration is then expressed in grams per 1000 c.c., and the molecular elevation of the boiling-point is indicated by the symbol K'. Obviously $K'=K/d$, where d is the density of the solvent at its boiling-point. Table 47 gives the values of K and K' found experimentally for a number of common solvents.

TABLE 47. MOLECULAR ELEVATION OF THE BOILING-POINT.*

K = rise in B.P. for 1 gram-molecule per 1000 grams of solvent.
K' = " " " " " c.c. " "

Solvent.	K.	$\frac{0{\cdot}002T^2}{l}$	K'.
Water - - -	0·52°	0·515°	0·54°
Ether - - -	2·11	2·09	3·03
Chloroform - -	3·88	3·80	2·77
Ethyl alcohol - -	1·15	1·19	1·56
Acetone - - -	1·72	1·72	2·22
Benzene - - -	2·57	2·61	3·15

Relationship between molecular elevation and latent heat of vaporisation.—Van't Hoff showed by thermodynamical arguments that the elevation of the boiling-point depends on the

* See footnote on p. 192.

osmotic pressure of the solution, and that the constant K can be predicted from the physical properties of the solvent by the formula

$$K = \frac{0{\cdot}002\,T^2}{l}$$

Here T is the boiling-point on the absolute scale and l the latent heat of evaporation per gram of solvent. The third column in Table 47 gives the values of K calculated from measurements of the latent heat. It will be seen that they are in good agreement with the values found experimentally.

19. Depression of the Freezing-Point.

1. Determination of molecular weights from freezing-points.—(*a*) Fit a stout boiling-tube with a cork carrying a thermometer (50° to 100° in 0·1° or 0·05°) and a stirrer of thin glass rod. Mount the tube by means of a cork in the neck of a wide-mouthed bottle, which thus forms an air-jacket round the tube. Weigh out 10 grams of naphthalene, and place it in the tube. Remove the latter from its jacket, and then heat in a bath of boiling water.

Fix the thermometer and stirrer in position, and, when all the naphthalene is melted, remove from the bath, dry the outside of the tube rapidly and insert in the bottle. Stir steadily and watch the thermometer. It will fall at first a little below the freezing-point, but will rise as crystals begin to separate and finally reach a maximum. The maximum reading is taken as the freezing-point of the pure solvent. Make two determinations in this way, reading the temperature to the nearest 0·01°.

(*b*) Add a weighed pellet of *p*-nitrotoluene (about 0·7 gram) and repeat the determination of the freezing-point. A second determination should be made on the same mixture, stirring when the temperature falls 0·1° below the value first found, in order to avoid excessive supercooling. If desired, a second weighed pellet can be added and the determination repeated.

(*c*) Starting with fresh solvent for each substance, make similar observations with camphor, monochloracetic acid, and β-naphthol.

(*d*) The m.p. of naphthalene is 80°, and its latent heat of fusion is 35·6 cal. per gram. Use these figures in order to calculate the molecular depression of the freezing-point, and compare it with the value found experimentally in (*b*).

ii. **Determination of molecular weights. Rast's method.**—Weigh accurately 0·05 gram of the substance and 0·5 gram of camphor; place them in a small tube, seal off and melt. Allow the melt to solidify, break the tube (removing adhering fragments of glass) and crush the mixture on a clean watch glass or in an agate mortar. Place some of the melt in a moderately wide melting-point tube attached to a thermometer, and heat in a bath of sulphuric acid in the usual melting-point apparatus. When the mixture is completely molten, allow it to cool until a skeleton of camphor crystals has formed; then heat slowly and note to 0·5° the temperature at which the last crystal of camphor disappears. This is the freezing-point of the solution. Determine the freezing-point of pure camphor with the same thermometer and under the same conditions.

The molecular depression of the freezing-point for camphor is 40° for 1 gram-molecule in 1000 grams of camphor. By this method determine the molecular weight of (*a*) *p*-nitrotoluene, (*b*) naphthalene.

Depression of the freezing-point.—The freezing-point of a substance is generally lowered by the presence of a foreign substance. This effect was studied quantitatively by Raoult, who found that the laws for the depression of the freezing-point were the same as for the elevation of the boiling-point. Thus, the lowering of the freezing-point is proportional to the concentration of the dissolved substance, and the depression is the same for one gram-molecule of a large number of solutes dissolved in 1000 grams of a given solvent. Thus

$$K = \frac{M\Delta t}{c},$$

where K is described as the **molecular depression of the freezing-point** or the **cryoscopic constant** of the solvent, M is the molecular weight of the solute, and Δt the depression of the freezing-point brought about by a concentration of c grams of solute in 1000 grams of solvent. Table 48 gives the values found experimentally for this constant, together with values calculated (in the same manner as in the case of the boiling-point constant) from the latent heat of fusion of the solvent, by means of the formula

$$K = \frac{0{\cdot}002\,T^2}{L},$$

where T is the freezing-point on the absolute scale, and L is the *latent heat of fusion* of 1 gram of the solvent. The table shows that this formula gives results in good agreement with those found by direct measurement.

TABLE 48. MOLECULAR DEPRESSION OF THE FREEZING-POINT.*

Solvent.	F. P.	K.	$\frac{0{\cdot}002\,T^2}{L}$.
Water - - -	0°	1·85°	1·86°
Benzene - - -	5·5	5·12	5·07
Acetic acid - -	17	3·9	3·82
Phenol - - -	39	5·3	5·05
Naphthalene - -	80	6·9	6·95
Camphor - - -	175	40·0	—

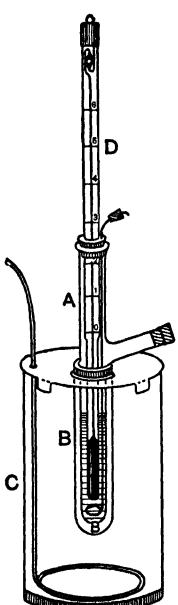


FIG. 59.—Beckmann's freezing-point apparatus.

Experimental methods.—Beckmann's apparatus for use with solvents of low melting-point is shown in Fig. 59. The pure solvent in known amount is placed in the inner tube A, which is separated by a narrow air-jacket B from the cooling bath C. The solvent is allowed to supercool a little below its freezing-point and is then stirred vigorously to start crystallisation. As crystals separate, the temperature rises and remains steady at the freezing-point. A weighed pellet of solute is then added by the side tube, dissolved by removing A and warming in a suitable bath, and the freezing-point is redetermined. Care must be taken to allow only a small degree of supercooling, since otherwise a considerable amount of solvent crystallises out, and the concentration of the solution becomes greater than that calculated from the weights of solvent and solute.

* Raoult's constant K was defined using c as the concentration per 100 gm. of solvent. The values of K recorded in the literature are therefore 10 times the numbers given in Tables 47 and 48.

The freezing-bath used in *C* varies with the solvent employed. For water as solvent, ice and salt would be placed in *C*; for acetic acid or benzene, ice and water; for phenol, cold water, etc. When a solvent with a small molecular depression is used, a Beckmann thermometer is required to give accurate readings; with naphthalene, however, quite good results can be obtained with a thermometer divided in 0·1°; and in Rast's method with camphor an ordinary whole-degree thermometer suffices.

Limitations of the methods for determining molecular weights in solution.—The methods described in this chapter allow of the determination of the molecular weights of a large number of substances which cannot be vaporised without decomposition, but which can be dissolved in suitable solvents. These methods are therefore used constantly in organic chemistry, in order to determine the molecular formula of a compound after its empirical formula has been found by analysis. For this purpose a rough value of the molecular weight is sufficient. Most of the methods described will give numbers within 5 per cent. or less of the true value, and, when special apparatus is used, some of them can give results of much higher accuracy.

The experimental conditions which must be observed in order to ensure accurate results have already been indicated, *e.g.* the use of sufficiently sensitive thermometers, the avoidance of superheating in the boiling-point method, or of too great a supercooling in the freezing-point method, etc. There are, however, a number of theoretical conditions which are equally important. Thus a thermodynamical investigation shows that the simple formulae only hold accurately for very dilute solutions. More complex formulae can be developed to deal with more concentrated solutions, but, if errors up to 5 per cent. may be tolerated, the simple formulae may be used for solutions containing up to half a gram-molecule of solute per 1000 grams of solvent.

A second condition is that the solute must remain entirely in the solution, and not escape from it into the vapour or solid phase, since this would give rise to just the same sort of errors as the use of a leaky membrane in the measurement of osmotic pressure. When using the boiling-point and vapour-pressure

methods this means that the solute must be non-volatile, or in practice that the boiling-point of the solute should be at least 100° higher than that of the solvent.

In the freezing-point method this condition means that the solvent and solute must not form solid solutions, but that the crystals which separate must consist of pure solvent only. In some cases, where solid solutions are formed, there is a *rise* in freezing-point on adding the solute instead of a depression. An example of this, in the system naphthalene, β-naphthol, is given in Expt. 19, i. Fortunately, in organic chemistry, it is usually only compounds of similar constitution which form solid solutions, so that by choosing a suitable solvent, or by using several solvents of different chemical character, this source of error can be avoided.

Abnormal molecular weights.—(*a*) *Association.*—Many substances are found to give molecular weights in solution greater than those corresponding to the usual formula. Thus acetic acid in benzene has a molecular weight of nearly 120 instead of 60, which is the value to be expected from the formula

$$CH_3 \cdot CO \cdot OH.$$

Chloracetic acid in naphthalene behaves similarly (Expt. 19, i.). In these cases the molecular weight often varies with the solvent, and with the concentration of the solution. Thus, observations of the freezing-point of solutions of acetic acid in water give a normal molecular weight of 60 for the acid. In general, we may suppose that there is an equilibrium between complex and simple molecules of the acid, *e.g.*

$$(CH_3 \cdot CO \cdot OH)_2 \rightleftharpoons 2CH_3 \cdot CO \cdot OH.$$

This view is confirmed by the fact that the vapour-density of acetic acid in the neighbourhood of the boiling-point is much greater than the normal value, so that even the vapour must contain a considerable proportion of double molecules.

Substances which behave in this manner are said to be "associated" in solution. In general, acids, hydroxy-compounds and amines exhibit this phenomenon. These are precisely the substances which have anomalous physical properties in the liquid state (See Chap. III.).

(*b*) *Dissociation.*—In contrast to the associated compounds described above, most salts in aqueous solution give values for the molecular weight which are lower than those deduced from the formulae of the salts. This is accounted for by their dissociation into ions, *e.g.*

$$KCl \rightleftharpoons K^{\cdot} + Cl'.$$

Thus, at extreme dilutions, when dissociation is complete, the apparent molecular weight of potassium chloride is only half of that calculated from the formula KCl. The theory of electrolytic dissociation which is used to explain these results is discussed more fully in Chapter XIII.

It is interesting to note that precisely similar abnormalities are found amongst vapour-densities. Thus, the vapour of ammonium chloride has only half the density expected for the formula NH_4Cl, since it is completely broken up into $NH_3 + HCl$; but H. B. Baker has shown that, when dried for a long time over phosphoric oxide, ammonium chloride does not dissociate on heating, since the vapour-density has a normal value.

QUESTIONS ON CHAPTER VIII.

1. Show how the lowering of the vapour-pressure caused by dissolving a non-volatile solute in a solvent is related to the osmotic pressure of the solution. (B.Sc., Sheffield.)

2. Dry air was drawn in succession through a series of bulbs containing 4·257 gm. of a substance *X* in 52·68 gm. of ethyl alcohol and then through a similar series of bulbs containing pure alcohol. The indrawn air and the two sets of bulbs were at the same constant temperature. The loss of weight in the first series of bulbs was 1·292 gm. and in the second series 0·0313 gm. Calculate the molecular weight of *X*.
(Pembroke College, Entrance Schol.)

3. How may the molecular weight of a substance in solution be determined by the elevation of the boiling-point?
The boiling-point constant for water is 5·2.* A normal solution of a monobasic acid was found to give an elevation of 0·910°. Calculate the degree of dissociation of the acid. What would be its degree of dissociation in a hundredth normal solution?
(Cambridge Entrance Schols.)

* For 100 grams of solvent.

4. How may the molecular weight of a substance be determined by the method of elevation of the boiling-point ?

The boiling-point of pure acetone is 56·38° at normal barometric pressure. A solution of 0·707 gm. of a compound in 10 gm. of acetone boiled at 56·88°. What is the molecular weight of the compound ? (The molecular elevation constant for acetone is 16·7.*) (Trinity Coll., Camb.)

5. Explain how the molecular weight of a substance may be determined from observations of the depression of the freezing-point. If one gram of a substance is dissolved in 15 grams of water the freezing-point is lowered 0·37° C. What is the molecular weight of the dissolved substance ? The " constant " for water is 19.* (Cambridge Higher School Cert.)

6. When 0·5 gm. of sodium chloride was dissolved in 50 gm. of water the freezing-point of the water was depressed 0·615° C. The molecular depression for water is 18·5°.* Calculate the apparent molecular weight of the dissolved salt and explain the result obtained.

What other solvents are usually employed in determining molecular weights by this method ?

(London Higher School Cert.)

7. Describe the freezing-point method for determining molecular weights. A solution of 34·2 gm. of cane-sugar in 100 gm. of water froze at −1·9°; a solution of 7·5 gm. of potassium chloride in 100 gm. of water froze at −3·36° and a solution of 9·8 gm. of an unknown substance in 100 gm. of water froze at −3·82°. The constant for water is 18·9°.*

What conclusions do you draw from these data concerning the molecular condition of the first two substances in aqueous solution, and what is the molecular weight of the unknown substance.

(B.A., Bombay.)

8. 2·167 and 2·833 gm. of a substance were dissolved in 100 gm. of benzene. The depressions of freezing-point were 0·348° and 0·452° respectively. What was the molecular weight of the substance ? The molecular lowering of the freezing-point of benzene is 50°.* (B.Sc., Punjab.)

9. What methods are available for the determination of the molecular weight of (*a*) a gas, (*b*) a pure liquid in the liquid state, (*c*) a non-volatile non-electrolyte ? Describe in detail one method for a substance belonging to the third (*c*) class.

(Inter. Sci., Sheffield.)

10. A solution containing 0·7269 gm. of camphor (molecular weight 152) in 32·08 gm. of acetone (boiling at 56·30° C.), boiled at 56·55° C. What is the molecular elevation of boiling-point, and the latent heat of vaporisation of acetone ? (B.Sc., Sheffield.)

* For 100 grams of solvent.

11. The following freezing-point data are given :

(*a*) Weight of formamide 18·59 gm. Solute urea.
Weight of solute 0·2250, 0·5268, 0·9128 gm.
F.P. depression 1·035°, 2·446°, 4·227°.

(*b*) Weight of formamide 24·16 gm. Solute ethyl tartrate.
Weight of solute, 0·3190, 2·8145, 3·8825 gm.
F.P. depression, 0·333°, 2·924°, 4·042°.

(*c*) Cryoscopic constant of benzene 5·12° for 1 gm. mol. per 100 gms. benzene.

(*d*) Weight of benzene 18·16 gm. Solute ethyl tartrate.
Weight of solute, 0·2241, 0·4125, 0·6274, 1·9243, 3·5463 gm.
F.P. depression, 0·322°, 0·527°, 0·694, 1·965°, 2·845°.

Assuming the molecular weight of urea to be known, calculate the cryoscopic constant of formamide. What conclusions can be drawn as to the molecular weight of ethyl tartrate in formamide and in benzene ? (B.Sc. Hons.)

12. Write a brief essay on the properties of dilute solutions. (Cambridge Entrance Schols.)

CHAPTER IX.

THERMOCHEMISTRY AND THERMODYNAMICS.

20. Heat of Reaction.

i. Heat of precipitation of copper by zinc.—Make a calorimeter by supporting a tall glass beaker of about 600 c.c. capacity on three corks inside a larger beaker. The inner beaker is fitted with a stirrer of light glass rod, and a thermometer graduated to 0·1° is clamped in the centre. Place in the inner beaker 250 c.c. of a solution containing 40 grams of $CuSO_4$, $5H_2O$ per litre. Weigh out 20 grams of zinc dust and place in a dry test-tube dipping into the copper sulphate solution. (A large excess of zinc is used in order to make sure that the action shall be completed rapidly.)

Allow the apparatus to stand for 20 minutes, then stir steadily and read the temperature, to the nearest 0·01°, every minute for 5 minutes. Remove the test-tube and empty the zinc into the solution of copper sulphate. Continue to stir and to read the temperature. This will rise at first and then fall slowly; observations should be continued until the rate of fall has been steady for at least five minutes. The method of correcting for heat losses by radiation, etc., is shown by the example on p. 200. Inspection of the last seven results shows that the temperature was falling at a steady rate of 0·03° per minute. The loss by radiation, etc., is proportional to the difference between the temperature of the liquid and that of the air. Except during the first minute after adding the zinc this is nearly constant, so allowing half-value for this first minute,

$$\text{correction for heat losses} = (n - \tfrac{1}{2}) \times 0{\cdot}03,$$

where n is the time in minutes since the zinc was added. The column headed t (corr.) gives the recorded temperature plus these corrections, and the final constant value of 18·07° gives the

temperature which would have been attained if no heat had been lost to the surroundings. Hence,

$$\text{rise in temperature} = 18{\cdot}07 - 10{\cdot}12 = 7{\cdot}95^{\circ}$$

and $$\text{heat evolved} = 7{\cdot}95\,(250 + w + 20s),$$

where w is the water-equivalent of the calorimeter and s the specific heat of zinc.

Before adding zinc.		Zinc added.		
z	t	z	t	t (corr.)
0	10·02	6	15·40	15·41
1	10·04	7	16·45	16·49
2	10·06	8	16·90	16·97
3	10·08	9	17·30	17·40
4	10·10	10	17·60	17·73
5	10·12	11	17·81	17·97
		12	17·88	18·07
			0·03	
		13	17·85	18·07
			0·03	
		14	17·82	18·07
			0·03	
		15	17·79	18·07
			0·03	
		16	17·76	18·07
			0·03	
		17	17·73	18·07
			0·03	
		18	17·70	18·07

The water-equivalent can be determined as described in Expt. 9, i. For the calorimeter used in the above experiment $w = 9{\cdot}5$ gm., whilst $s = 0{\cdot}09$, so that

$$\text{heat evolved} = 7{\cdot}95\,(250 + 9{\cdot}5 + 20 \times 0{\cdot}09)$$
$$= \mathbf{2065}\ \text{cal.}$$

(It is here assumed that the specific heat of the solution is the same as that of water.) This is the heat developed by the precipitation of 10 grams of copper sulphate, according to the equation

$$CuSO_4,\ aq + Zn \rightarrow ZnSO_4,\ aq + Cu.$$

For one gram-molecule ($CuSO_4$, $5H_2O = 250$)

$$Q = 2065 \times 25 = 51{,}625 \text{ cal.}$$

ii. Heat of solution of sodium chloride.—Carry out the measurements in exactly the same way as in Expt. 20, i., but with 250 c.c. of water in the calorimeter, and 20 grams of finely powdered common salt in the test-tube. Break the test-tube, stir until all the salt has dissolved, and read the temperature as before. Calculate the number of calories liberated or absorbed during the dissolution of one gram-molecule of salt.

iii. Heat of neutralisation of hydrochloric acid by sodium hydroxide.—(*a*) Place 200 c.c. of N/2 NaOH in the calorimeter and 200 c.c. of N/2 HCl in a small flask dipping into the calorimeter. After allowing half an hour for the temperatures to become steady, mix and note the rise in temperature and the radiation correction as before. Then calculate the heat of neutralisation per gram-molecule of acid and alkali.

(*b*) Instead of the calorimeter described above, a vacuum flask may be used. When this is done, no correction for cooling need be made. The water equivalent of the calorimeter may be determined by adding, say, 100 c.c. of water to it at a known temperature, and noting the fall of temperature.

In the vacuum flask place 100 c.c. of normal caustic soda solution. This may be done as follows:

(1) Wash out a 100 c.c. measuring flask with the solution, and fill up to mark.

(2) Pour the solution as completely as possible into the vacuum vessel.

(3) Wash out the graduated flask with 10 c.c. of distilled water and add to the vacuum flask.

Next fill the measuring flask with 100 c.c. of normal hydrochloric acid. Measure accurately the temperature of the acid and alkali. Prepare a little distilled water of the same temperature as the acid. Then add the acid to the vacuum flask, and wash out with 10 c.c. of distilled water, stir well and note the highest temperature attained.

Let w be the water equivalent of the vessel.

t_1 ,, final temperature of the mixture.

t_2 ,, temperature of the NaOH before mixing.

t_3 ,, ,, ,, ,, HCl ,, ,,

Then the rise of temperature is taken as

$$\left(t_1 - \frac{t_2 + t_3}{2}\right).$$

Taking the specific heats of the solutions as unity, the heat evolved is

$$(220 + w)\left(t_1 - \frac{t_2 + t_3}{2}\right).$$

From your results calculate the heat evolved when one gram-molecule of hydrochloric acid is neutralised by one gram-molecule of caustic soda.

Thermochemistry.—Many chemical changes are accompanied by a considerable evolution of heat, and it was at one time supposed that the heat given out when two substances interact could be used as a measure of their chemical affinity for one another. This supposition is only roughly correct; but a study of the heat changes which accompany chemical change is nevertheless of great interest, on account of the important link which it provides between the sciences of physics and chemistry. This branch of physical chemistry is usually called **thermochemistry**.

The amount of heat which is given out (or absorbed) in a chemical change is expressed in calories. The **calorie** is usually defined as *the amount of heat required to raise one gram of water through* 1° *C.* Since, however, the specific heat of water varies rapidly with the temperature, it is necessary to specify the temperature of the water as well as the range of the heating. For accurate work the calorie is therefore defined as *the heat required to raise one gram of water from* 15° *to* 16° *C.* This is known as the **15° calorie.**

Intrinsic energy of chemical compounds.—It follows from the law of conservation of energy (see below, p. 214) that, when a process is accompanied by the evolution of heat, an equivalent amount of some other form of energy must have been transformed into heat. Thus, in the reaction:

$$\begin{array}{cccc} Cu + S_\alpha & \rightarrow & CuS & + 11{,}600 \text{ calories} \\ 0 & & 0 & -11{,}600 \end{array}$$

11,600 calories of heat are evolved. In order to explain this effect, we may suppose that the uncombined copper and sulphur and the copper sulphide produced from them exist on two different energy levels, and that the liberation of heat in the action formulated above is due to the fact that the copper and sulphur are on a lower energy level when in combination than when in a free state. Alternatively, we may attribute to *each*

substance a definite **intrinsic energy**, and suppose that, since no energy is lost in the transformation, these intrinsic energies, when a proper allowance is made for the heat liberated or absorbed in the process, must balance on either side of the equation. It then follows that

Intrinsic energy of copper + intrinsic energy of sulphur = intrinsic energy of copper sulphide + 11,600 calories.

At the present time we have no means of knowing how much energy is contained in the complex system which constitutes an atom; nor can we tell what share of energy is associated with each atom in a chemical compound; but, since all chemical changes depend on the *difference* of the intrinsic energies of reactants and resultants, it is convenient to regard the intrinsic energy of the free elements in their normal state as *zero*. It then follows that, since the intrinsic energies of the elements on the left-hand side of the preceding equation are zero, the sum of the energies on the right-hand side of the equation must also be zero. The *intrinsic energy* of copper sulphide must therefore be equivalent to −11,600 calories. The intrinsic energies of the various substances are shown under their formulae in the chemical equation at the beginning of the paragraph.

Heat of formation of chemical compounds.—The heat evolved during the combination of 63·4 grams of copper with 32 grams of sulphur is 11,600 calories. This is described as the **heat of formation** of copper sulphide, and is obviously equal to the intrinsic energy of the compound, but with the sign reversed. In general, *the heat of formation of a compound is measured by the number of calories of heat that are set free when the elements in their normal state unite to produce one gram-molecule of the compound.*

TABLE 49. HEATS OF FORMATION.

Chemical reaction.	Calories.
$\frac{1}{2}H_2 + \frac{1}{2}F_2 \rightarrow HF$	+38,500
$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$	+22,000
$\frac{1}{2}H_2 + \frac{1}{2}Br_2 \rightarrow HBr$	+ 8,440
$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightarrow HI$	− 6,040
$C + O_2 \rightarrow CO_2$	+97,000
$C + 2S \rightarrow CS_2$	−25,400
$P + 1\frac{1}{2}Cl_2 \rightarrow PCl_3$	+76,600

The heats of formation of a few common compounds are given in Table 49. In order that the heat of formation of a compound may be defined accurately, however, it is important to state the exact condition both of the elements and of the compound. Thus, when monoclinic sulphur, S_β, is converted into rhombic sulphur, S_α, 80 calories are liberated, that is

$$S_\beta \rightarrow S_\alpha + 80 \text{ cal.}$$

The intrinsic energy of S_β is therefore +80 cal. if S_α is taken as zero; and the heat of formation of copper sulphide from copper and monoclinic sulphur would be greater by 80 calories.

$$\begin{array}{rrrr} Cu + S_\beta = & CuS & +11{,}680 \text{ cal.} \\ 0 \quad 80 & & -11{,}600. \end{array}$$

In the preceding table all the elements are taken in their normal condition at atmospheric temperature, *e.g.* gaseous chlorine, liquid bromine and solid iodine; the sulphur is in the rhombic form, the carbon is in the form of charcoal and the phosphorus is white phosphorus. A similar statement applies also to the products.

Endothermic and exothermic compounds.—It will be seen from Table 49 that heat may be either liberated or absorbed in the formation of a chemical compound from its elements. Chemical compounds are therefore divided into two classes: those which are formed from their elements with evolution of heat are known as **exothermic compounds,** whilst those which are formed from their elements with absorption of heat are known as **endothermic compounds.** Carbon dioxide is an example of an exothermic compound, and carbon disulphide of an endothermic compound.

Endothermic compounds contain more energy than their constituent elements, and are very reactive, very easily decomposed, and are only formed from their elements at high temperatures. On the other hand, exothermic compounds can usually be produced from their elements at low or moderate temperatures, and are much less reactive and less easily decomposed than endothermic compounds.

Hess's law.—In a very large number of cases it is impossible to prepare a chemical compound by the direct combination of

its elements in a calorimeter, under conditions which will allow of the accurate measurement of its heat of formation. In all these cases, the heat of formation of the compound must be deduced by an indirect method from a study of the heat changes which occur in other actions in which the compound is formed or decomposed. This can be done with the help of the **law of thermoneutrality**, which was put forward by Hess in 1840. Hess's law states that

The heat evolved in any chemical change is independent of the manner in which it is carried out, whether in one or in many steps.

Thus, the oxidation of carbon to carbon monoxide

$$C + \tfrac{1}{2}O_2 \rightarrow CO + U \text{ cal.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (a)$$

cannot readily be carried out under conditions which permit of the measurement of the heat of the reaction. On the other hand, it is easy to burn either carbon or carbon monoxide to carbon dioxide; and this can be done in such a way as to measure the heats of combustion at constant pressure. These are set out in the following equations:

$$C + O_2 \rightarrow CO_2 + 97{,}000 \text{ cal.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (b)$$
$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 + 68{,}000 \text{ ,,} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (c)$$

The heat change U can then be calculated readily by means of Hess's law. Thus, by adding together the quantities of heat which are liberated when the combustion of carbon to carbon dioxide takes place in the two stages (a) and (c), and equating the sum to the heat given out in the direct combustion (b), we get

$$U + 68{,}000 = 97{,}000 \text{ cal.}$$

or

$$U = \mathbf{29{,}000} \text{ cal.}$$

This quantity is the heat of formation of carbon monoxide from its elements.

Heats of solution and of dilution.—The process of solution is usually accompanied by absorption or liberation of heat, although it is not always easy to say whether this should be attributed to physical or to chemical causes. Most salts on solution in water give rise to an absorption of heat, which may be compared with the " latent heat of fusion " which is absorbed when a substance

passes from the solid to the liquid state (p. 98). On the other hand, many deliquescent solids liberate heat, perhaps as a result of chemical combination with the solvent. Table 50 gives the **heat of solution** of sodium chloride in different amounts of water.

TABLE 50. HEATS OF SOLUTION OF SODIUM CHLORIDE.

Composition of solution.	Heat of solution.
NaCl + 9·2 mols. H_2O	− 410 calories.
,, + 14·3 ,, ,,	− 560 ,,
,, + 33·3 ,, ,,	− 840 ,,
,, + 100 ,, ,,	− 1030 ,,
,, + 325 ,, ,,	− 1010 ,,

By applying Hess's law to the heats of solution of sodium chloride at different concentrations, it can be deduced that the strong solutions absorb a further quantity of heat on dilution. This heat change is described as the **heat of dilution**. Thus, when a solution of the composition NaCl, $9{\cdot}2H_2O$ is diluted with water until it has the composition NaCl, $325H_2O$, there is a further liberation of $-(1010-410) = -600$ calories, *i.e.* another 600 calories are *absorbed*; the heat of dilution of the solution is therefore **− 600 calories**. This heat of dilution diminishes rapidly, however, so that for solutions containing more than $100H_2O$ it is so small that it can usually be neglected.

The numbers cited in the table also show that, when a sufficiently large quantity of water is used, the heat of solution of the solid salt is no longer dependent on the dilution. Since many reactions are carried out in aqueous solutions, it is convenient to write the symbol *aq.* after a formula, in order to indicate that the substance is "in dilute solution," *i.e.* in a solution which is so dilute that no further heat changes are produced by further dilution. Thus we may write:

$$NaCl + aq. \rightarrow NaCl, aq. - 1010 \text{ cal.}$$

This equation means that the heat of solution of sodium chloride in a large amount of water to form a very dilute solution is − 1010 calories.

Heat of neutralisation.—Another very important type of chemical change, which can be carried out in aqueous solution, is the neutralisation of an acid by a base. The amount of heat

liberated in the neutralisation of a number of common acids and bases is shown in Table 51.

TABLE 51. HEATS OF NEUTRALISATION.

Base.	Acid.	Calories.
KOH, aq.	+HCl, aq.	+13,695
NaOH, aq.	+HCl, aq.	+13,700
KOH, aq.	+HNO_3, aq.	+13,705
NaOH, aq.	+HNO_3, aq.	+13,685
$\frac{1}{2}Ca(OH)_2$, aq.	+HNO_3, aq.	+13,950
$\frac{1}{2}Ba(OH)_2$, aq.	+HNO_3, aq.	+13,900
NaOH, aq.	+HF, aq.	+16,400
KOH, aq.	+HCN, aq.	+27,700
NH_4OH, aq.	+HCl, aq.	+12,270
NH_4OH, aq.	+HCN, aq.	+ 1,300

The most striking characteristic of these numbers is the constancy of the values obtained for the heat of neutralisation of a "strong" acid by a "strong" base. This important regularity will be referred to again later (Chap. XIII.). When "weak" acids or "weak" bases are concerned, as in the last four lines of the table, the heat of neutralisation varies markedly.

Heat of combustion.—Most organic reactions proceed too slowly to allow of a direct measurement of the heat change involved. The heats of formation of organic compounds, either from their elements or from one another, are therefore usually deduced with the help of Hess's Law from the **heats of combustion** of the compounds, *i.e.* from the heat which is liberated when the compound is burned completely to carbon dioxide and water.

(*a*) *Heat of polymerisation of acetylene to benzene.*—Suppose we wish to find the heat evolved when acetylene polymerises to benzene,

$$3C_2H_2 \rightarrow C_6H_6.$$

The heats of combustion of the two hydrocarbons are as follows:

C_2H_2 gas $+2\frac{1}{2}O_2 \rightarrow 2CO_2 + H_2O$ liq. +312,700 cal. .....(i)

C_6H_6 liq. $+7\frac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O$ liq. +782,000 cal. .....(ii)

Multiplying (i) by 3, we get the equation

$3C_2H_2 + 7\frac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O$ +938,100 cal. .....(iii)

By subtracting (ii) from (iii) and rearranging the equation we get

$$3C_2H_2 \text{ gas} \rightarrow C_6H_6 \text{ liq.} + \mathbf{156{,}100} \text{ cal.}$$

This gives us the required heat of polymerisation of gaseous acetylene to liquid benzene at constant pressure.

(*b*) *Heat of formation of acetylene and of benzene.*—In order to calculate the heats of formation of the two hydrocarbons, we require to know also the heats of formation of carbon dioxide and water. These are given by the thermochemical equations (iv) and (v):

$$C + O_2 \rightarrow CO_2 \quad + 97{,}000 \text{ cal.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(iv)}$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \text{ (liq.)} + 68{,}150 \text{ cal.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(v)}$$

The intrinsic energies of water and carbon dioxide are therefore $-68{,}150$ cal. and $-97{,}000$ cal. per gram-molecule. Put x for the intrinsic energy of acetylene

$$C_2H_2 + 2\tfrac{1}{2}O_2 \rightarrow 2CO_2 \quad + H_2O \quad + 312{,}700 \text{ cal.}$$

$$x \quad + 0 \quad = -194{,}000 - 68{,}150 + 312{,}700 \text{ cal.}$$

$$\therefore\ x = +\mathbf{50{,}550} \text{ calories.}$$

Acetylene is therefore a highly endothermic compound since its intrinsic energy is 50,550 calories greater than that of its elements, and its heat of formation is $-\mathbf{50{,}550}$ calories. For benzene

$$C_6H_6 + 7\tfrac{1}{2}O_2 \rightarrow 6CO_2 \quad + 3H_2O \quad + 782{,}000 \text{ cal.}$$

$$x + 0 \quad = -6 \times 97{,}000 - 3 \times 68{,}150 + 782{,}000 \text{ cal.}$$

$$\therefore\ x = -582{,}000 - 204{,}450 + 782{,}000 = -\mathbf{4{,}450} \text{ calories.}$$

Benzene is therefore an exothermic compound, with an intrinsic energy of $-4{,}450$ cal., and a heat of formation of $+\mathbf{4{,}450}$ cal. Many stable organic compounds of carbon and hydrogen have only small heats of formation, so that their heats of combustion are nearly equal to that of the carbon and hydrogen which they contain.

Chemical affinity.—When Mayow, in 1674, noticed that potash would displace ammonia from its salts, he explained this result by supposing that "the acid is capable of entering into closer union" with the fixed alkali (potash) than with the volatile alkali (ammonia). This explanation, which is commonly expressed by the term **chemical affinity**, assumes that the

elements unite or refuse to unite according to their "inherent love or hatred" for one another; but it gives no explanation of the affinity of an acid for a base, of copper for sulphur, or of a combustible substance for air, nor does it indicate any way in which the affinity of two substances for one another can be determined quantitatively. "Tables of affinity" in which the relative affinities of a series of bases for an acid or of a series of acids for a base were deduced from their mutual displacement were, however, drawn up by Geoffroy in 1718, and by Stahl in 1720. Finally, in *A Dissertation on Elective Attractions*, Bergman in 1775 compiled a series of charts showing the relative affinities of various acids and bases according to the order of mutual displacement, when two acids competed for a base, or conversely, (i) *in the dry way, i.e.* by ignition together, (ii) *in the moist way, i.e.* by mutual interaction in solution. In the former case, the more volatile component was generally expelled, as in the preparation of hydrochloric or nitric acid by the action of sulphuric acid on salt or on saltpetre, whilst in the latter case the action was influenced both by the volatility and the insolubility of the various components.

The influence of the physical conditions on the mutual displacement of acids and bases may be illustrated by contrasting Mayow's observation in 1674 of the easy expulsion of nitric acid from nitre by distillation with sulphuric acid, with Baumé's converse observation in 1760 of the separation of crystals of nitre from a mixture of potassium sulphate and nitric acid as illustrated by the reversed arrow in the equation.

Mayow (1674), $2KNO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_3$.
Baumé (1760), $2KNO_3 + H_2SO_4 \leftarrow K_2SO_4 + 2HNO_3$.

Berthollet in his *Researches into the Laws of Chemical Affinity* (1801) cited a large number of similar cases, in which the displacement of one substance by another was incomplete and reversible, in order to prove that Bergmann was wrong in supposing that "elective affinity is an invariable force, and of such a nature that a body which expels another from its combination cannot possibly be separated from the same by the body which it eliminated." He showed that the direction in

which a chemical change takes place is often determined by the proportions in which the various substances (raw materials and products) are present, and that the addition of a large excess of one of the products of a reaction will often serve to drive the action backwards. In this way, he established the general principle of **balanced actions** and laid the foundation for the quantitative theory of "mass-action," which is described in Chapter X. The way in which this quantitative theory can be used in order to calculate the chemical affinity of a balanced action is discussed in a later paragraph (p. 234).

Heat and work as measures of chemical affinity.—A new method, by which chemical affinity can be studied quantitatively, was introduced by Thomsen in 1856 and by Berthelot in 1858. Since chemical changes in which a large amount of heat is evolved are usually rapid and vigorous, whilst those in which less heat is evolved proceed only slowly or incompletely, these authors suggested that the heat of a chemical change could be used as a measure of the chemical affinity or driving force which causes the reaction to proceed. Whilst this conception provides a useful method of classifying chemical changes, by distinguishing exothermic from endothermic actions, it is found on closer examination to be unsound. Thus it implies that *chemical changes will only proceed in the direction in which heat is evolved*,* whereas in reality physical and chemical changes which proceed with absorption of heat are quite common, *e.g.* the formation of acetylene from carbon and hydrogen at high temperatures, the solution of salts in water, and the spontaneous evaporation of liquids. Further, the existence of chemical equilibrium is contrary to the Thomsen-Berthelot hypothesis, which would require that all chemical changes should proceed to completion in the direction in which heat is evolved.

A true measure of chemical affinity has been found, however, in the **maximum external work** which a reaction can be made to do, although, as we shall see in §§ 20A and B, this definition is only complete when we specify that the reaction must also be

* Absorption of heat was therefore usually attributed to some secondary "physical" change.

carried out "reversibly" (p. 221) and "isothermally" *i.e.* at constant temperature. Thus the chemical change which takes place during the precipitation of copper by zinc, which was carried out in a calorimeter in Expt. 20, i., is identical with the chemical change which provides the electrical energy of a Daniell cell. When this action takes place in a calorimeter, it is accompanied by a liberation of 25,065 calories per equivalent:

$$Zn + CuSO_4 = Cu + ZnSO_4 + 2 \times 25065 \text{ cal.}$$

When carried out in a Daniell cell, each equivalent of zinc and copper sulphate produces, under ideal conditions, a "total current" or *quantity* of electricity amounting to 96,540 coulombs under a pressure of 1·09 volts, giving rise to $96,540 \times 1{\cdot}09 = 105,000$ joules of electrical energy, or $105,000 \times 10^7$ ergs of work. It is this maximum amount of electrical energy derived from the battery, or the corresponding amount of external work which it can do, that is a true measure of the chemical affinity of the two reagents; and it is a mere coincidence if this agrees even approximately with the amount of heat that is set free when the reagents interact directly with one another in a calorimeter.

This later method of measuring chemical affinity has the advantage that, whilst many chemical changes take place with absorption of heat, it is obviously impossible for the chemical change in a battery to take place spontaneously in any other direction but the one which produces a positive electromotive force, *i.e.* in the direction which produces a positive amount of electrical energy and therefore of *external work*. The anomaly of endothermic action has therefore no counterpart when the maximum work, and not the heat of the reaction, is used as a measure of the chemical affinity of the reagents. The relation between these two quantities is discussed below (p. 227).

20A. The First Law of Thermodynamics.

Transformations of energy.— The evolution of heat during a chemical change is only one example of a large number of transformations of energy. Thus in industry the heat of combustion of coal is used to produce the mechanical energy of the steam engine. This mechanical energy may be used in turn to produce

the electrical energy of a dynamo, and the electrical energy can then be transformed into chemical energy by electrolysing a suitable solution, or into heat or light by passing the electrical current through a wire or filament of high resistance. The electrical energy may also be transformed into radiant energy by generating electrical waves in a wireless transmitter, whilst at a receiving station this radiant energy is again transformed into the mechanical energy of vibration of the telephone diaphragm, and then into another kind of radiant energy, namely, sound. Very many different forms of energy can therefore be recognised, and the laws which govern the transformation of energy from one form to another are of great importance in both chemistry and physics. The study of these laws forms the essential feature of the science of **thermodynamics.**

Transformation of work into heat.—The transformation of work into heat was studied by Joule and by many later workers. This transformation can be brought about in many ways.

(*a*) Joule caused falling weights to drive a series of paddles and thus to stir vigorously the water in a calorimeter. He found that the water became warmer, since the mechanical energy of the falling weights was converted by friction into heat. There was, moreover, a direct proportionality between the work done by the falling weights and the heat set free in the calorimeter. Thus one calorie of heat was produced for every $4{\cdot}2 \times 10^7$ ergs of work which disappeared.

(*b*) In another experiment a copper disc was spun between the poles of an electromagnet. Here electrical "eddy currents" were induced in the disc, which tended to stop its rotation in the magnetic field, so that work had to be done to keep the disc spinning. The energy of these eddy currents was used up in overcoming the electrical resistance of the metal, so that the plate became warmer. By measuring the rise in temperature of the copper disc, and the work required to spin it for a given time, the ratio of work done to heat evolved was again found to be approxinately 1 calorie of heat for every $4{\cdot}2 \times 10^7$ ergs of work.

(*c*) A third method of converting work into heat is to compress

a gas. The work done in compression, and the rise of temperature of the gas, can both be determined, and again it is found that each calorie of heat corresponds to the disappearance of $4{\cdot}2 \times 10^7$ ergs of work.

In these three different ways, and in many others, work can be converted into heat; but, although the methods used to effect the transformation may be very different, the same ratio of heat to work is always found. Maxwell stated this conclusion in the following words:

When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.

The important ratio known as **mechanical equivalent of heat,** when determined by methods such as those described above, is found to have the value

$$1 \text{ calorie} = 4{\cdot}182 \times 10^7 \text{ ergs.}$$

This ratio is also known as **Joule's equivalent,** and is indicated by the symbol J.

The various ways in which the mechanical equivalent of heat can be expressed are set out below. It should be noticed that the practical units of electricity have been arranged so that 1 coulomb flowing under an electromotive force of 1 volt (or through a resistance of 1 ohm) does 1 joule or 10^7 ergs of work.

TABLE 52. THE MECHANICAL EQUIVALENT OF HEAT.

1 calorie $= 4{\cdot}182 \times 10^7$ ergs
$= 4{\cdot}182$ joules
$= 0{\cdot}04127$ litre-atmospheres.
1 litre-atmosphere $= 14{\cdot}23$ cal.
1 joule $= 1$ volt-coulomb $= 10^7$ ergs
$= 0{\cdot}2391$ cal.

The first law of thermodynamics.—The fact that, when various forms of energy are converted into heat, there is always a constant ratio between the amount of energy that disappears and the amount of heat that is produced, suggests at once that in all these processes energy is not created or destroyed, but is merely *transformed* from one type to another. This statement

is generally described as the **Law of Conservation of Energy.** It is a partial expression of the **First Law of Thermodynamics,** which was defined more accurately by Helmholtz in 1847 in the following words :

In all processes occurring in an isolated system the energy of the system remains constant.

In this definition, a **system** means any collection of apparatus or materials which we require for a particular experiment or problem. It may consist of a few cubic centimetres of gas in a suitable container, or it may be a complicated engine ; in astrophysics it may even include a whole stellar system.

An **isolated system** is one which neither receives energy nor gives energy to surrounding bodies ; changes taking place in an isolated system are said to be **adiabatic** since no energy passes through the boundaries. In practice an isolated system cannot be realised experimentally, for it is impossible to ensure that energy is not conveyed to or from a system by radiation or conduction, etc. ; and if an isolated system existed, there would be no possible method of observing it or even of proving its existence. In many cases, however, we can make sure that the amount of energy transferred to or from the system is very small compared with the changes of energy taking place within it and thus study what is very nearly an isolated system.

Since we cannot obtain an isolated system, it is impossible to give by direct experiment a rigid proof of the first law of thermodynamics ; but the validity of the law is indicated by the fact that, the more nearly we succeed in isolating a given system (*e.g.* by careful heat-insulation, as in the experiments of Joule referred to above), the more accurately do we find that the disappearance of one form of energy is accompanied by the appearance of a definite amount of another form.

Again, the first law of thermodynamics claims to apply to "all processes" chemical, mechanical, electrical, etc. This statement also cannot be tested directly in every case, but strong evidence for the general truth of the law is found in the fact that when other physical processes are intermediaries in

the transformation of work into heat (*e.g.* the electrical currents in method (*b*) above), the same value is found for Joule's constant.

The validity of the first law of thermodynamics is also shown by the fact that no one has yet succeeded in devising a mechanism which produces energy continuously without at the same time and at a definite rate causing the disappearance of another form of energy. Thus, a steam engine produces mechanical energy, but it uses up the heat energy developed under the boiler. An electric lamp evolves radiant energy, but only so long as it is supplied with electrical energy. The evidence for the truth of this law is indeed so convincing that, whenever a process is found to liberate energy spontaneously, as in the case of a radioactive element, it is at once assumed that some other form of energy is being used up. Thus, at the present time, it is believed that an enormous store of energy is locked up in the atoms themselves ; but this view is merely a hypothesis to explain the fact that, when certain atoms disintegrate, a large amount of energy is evolved.

Deduction of Hess's law from the first law of thermodynamics. —Hess's *Law of Thermoneutrality* (p. 205), is obviously a particular case of the first law of thermodynamics, and can be deduced from it immediately as follows. Let the initial substances be called A, and the final products of the reaction Z. Then the direct action will be

$$A \rightarrow Z + Q_1, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (a)$$

where Q_1 is the heat evolved. Now suppose the reaction can go through one or more intermediate stages

$$A \rightarrow B + q_1 \rightarrow C + q_2 \rightarrow Z + q_3. \quad \ldots\ldots\ldots\ldots\ldots\ldots (b)$$

Let the total heat evolution be

$$Q_2 = q_1 + q_2 + q_3.$$

Now Q_1 must equal Q_2. For, if not, let Q_2 be the greater. Then by transforming a quantity of material from condition A to Z by the method (*b*) and retransforming directly back to A by method (*a*), there would be a net gain of heat equal to $Q_2 - Q_1$. Since this cycle can be repeated any number of times an unlimited amount of heat might therefore be developed by an

isolated system containing A. This is contrary to the law of conservation of energy, so that, if the latter be true, $Q_1 = Q_2$. This argument obviously holds for any type of change in a system, whether physical or chemical.

Total energy of a chemical system.—The arguments set out in the preceding paragraphs lead at once to the conclusion that a system in a state A must contain a definite amount of energy U_A, which is fixed by its physical conditions and cannot be increased or diminished unless energy is taken from or given to the system. When the system is in a different state, B, its energy is changed to another fixed value, U_B.

These quantities of energy are termed the **internal energy**, or sometimes the **total energy**, of the system in its different states. Their absolute values are unknown; but, since we are concerned only with the *change of internal energy* which accompanies a particular chemical or physical change (*e.g.* from condition A to condition B), this limitation is usually of no importance. The symbol U is employed therefore to represent the *decrease of internal energy* during the change, *i.e.* $U = U_A - U_B$. Thus, in the reaction

$$Cu + S \rightarrow CuS + 11{,}600 \text{ cal. (p. 202)},$$

it is clear that

$$U = U_{(Cu+S)} - U_{CuS} = 11{,}600 \text{ cal.}$$

In this case, we do not know the total energy content of the copper, sulphur, or copper sulphide; but we do know from calorimetric measurements that there is a decrease of 11,600 cal. in the total energy of the system copper + sulphur, when two equivalents of copper and sulphur are converted into one gram-molecule of copper sulphide. The *internal energy of the system* can, of course, be made up by adding together the *intrinsic energies* of all its components.

Conversion of chemical energy into heat and work.—Since all forms of energy can be converted quantitatively into heat, the *total energy change*, U, which accompanies a given chemical reaction can be measured merely by allowing the energy to be frittered away and converted into heat in a calorimeter; it is therefore identical with the heat balance shown in an ordinary thermochemical equation. If, however, the action is allowed

to do external work equivalent to A calories, the amount of heat set free in the action will be less by this amount. Thus if Q units of heat are *absorbed*,* and A units of external work are done, it follows from the First Law of Thermodynamics that

$$U = A - Q. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

If no external work is done, *e.g.* if the action takes place at constant volume or in a vacuum, then $A = 0$ and $U = -Q$, in agreement with the previous statement as to the method of determining U.

This condition is satisfied in the interaction between copper and sulphur to form copper and sulphide, where only solid substances are concerned and the changes of volume are insignificant. When, however, gases take part in a reaction, it is necessary to consider the difference in the energy changes according as the action takes place at constant volume or at constant pressure. Thus, the heat change resulting from the dissociation of calcium carbonate (as deduced from the heats of formation of the components of the system) is given by the thermochemical equation

$$CaCO_3 \rightarrow CaO + CO_2 \text{ (gas)} - 42{,}900 \text{ cal.}$$

The value of Q is therefore $+42{,}900$ at constant pressure, *i.e.* $Q_p = 42{,}900$ cal.

It is obvious, however, that the evolution of gaseous carbon dioxide from solid calcium carbonate will use up energy, if the gas is allowed to do work by driving back the constant pressure under which the change is supposed to take place. The amount of energy thus used can be calculated readily. Let us suppose that the action is carried out in a long cylinder of unit cross-section closed by a piston maintained at the constant pressure p. As the action proceeds, the piston will be pushed back by the gas evolved, and the distance which it travels will be equal to v, the volume of gas evolved. Hence the work done by the gas = force × distance = pv, and for one gram-molecule of gas

* In *thermochemistry* the calorific value U of a process is measured by the heat *liberated*; but in *thermodynamics* we have to consider the heat Q which is *absorbed* in order to give out useful work A. Q is therefore opposite in sign to U, and appears with a negative sign in the equation.

evolved $pV = RT$. Then, since $R = 1{\cdot}985$ cal., the external work done when n molecules of gas are evolved is $nRT = 1{\cdot}985nT$. In this particular case, the external work

$$A = 1{\cdot}985 \times 293 = 582 \text{ cal.}$$

Hence $$U = A - Q = 582 - 42{,}900 = -42{,}318 \text{ cal.}$$

Thus, if the action were carried out at constant volume, the heat absorbed would be $Q_v = 42{,}318$ calories.

Heating and cooling in a system doing external work.—A full description of the energy changes in a system must include a complete study of the relations between U, A, and Q. Equation (1) (p. 217), which follows immediately from the first law of thermodynamics, gives one relation between these quantities; another and more important relation is given by the second law which is discussed below (p. 220). Meanwhile, it should be noticed that the work done by a system on surrounding bodies may vary very widely.

(*a*) The external work may be zero, as in a chemical change which takes place at constant volume or under zero pressure, or more generally in a chemical change in which the whole of the energy is dissipated in the form of heat. Thus, when the action

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu + 2 \times 25{,}065 \text{ cal.}$$

is carried out by adding zinc dust to a solution of copper sulphate in a calorimeter, all the chemical energy is converted into heat and $U = -Q = 25{,}065$ calories per gram-equivalent.

(*b*) If, however, zinc and copper plates are dipped into solutions of zinc and copper sulphate, and connected by a wire to form a Daniell cell, nearly all the chemical energy is converted into electrical energy, and the current produced may be used to drive a motor and so converted into mechanical energy. The maximum value of the external work A which can be obtained in this way has already been given (p. 211) as

$$96{,}540 \times 1{\cdot}09 = 105{,}000 \text{ joules.}$$

Since 1 calorie $= 4{\cdot}182 \times 10^7$ ergs, this is equivalent to a liberation of $105{,}000 \div 4{\cdot}182 = 25{,}100$ calories.

It will be seen that, in this very exceptional case, there is a close approximation to equality in the amounts of heat which are liberated when copper is precipitated by zinc (i) in a

calorimeter, and (ii) in a battery, of which the electric energy is dissipated in a use of high-resistance wire. Since $U=A$ approximately, it follows at once that $Q=0$; the equality between U and A therefore implies that, when the battery is doing the largest possible amount of external work, no marked absorption or liberation of heat takes place in the battery itself.

(*c*) Finally, some systems are known in which the maximum work A is greater than the calorific value U. It then follows that Q must be positive and that the system must absorb heat, and actually become cooler, when doing a maximum amount of external work. A striking case of this kind is the adiabatic expansion of a perfect gas, where $U=0$, so that $A=Q$; the whole of the energy used up by the gas in doing external work is therefore derived from the cooling of the gas.

Kirchoff's equation.—The First Law of Thermodynamics enables us to deduce an important relation between the rate of change with temperature of the calorific value of a process, and the specific heats of the materials before and after the change has taken place.

Let the change, *e.g.* the fusion of a solid, take place at a temperature T, and let the decrease in total energy be U. Now heat the substance to $T+\mathrm{d}T$, the heat absorbed will be $c_2\mathrm{d}T$, where c_2 is the specific heat of the substance after the change. Now reverse the change and let the decrease in total energy be $-(U+\mathrm{d}U)$. Finally, cool the system back again to T. This will evolve heat equal to $c_1\mathrm{d}T$ where c_1 is the specific heat of the substance in its original condition. Since the substance is now in its original state, the algebraic sum of the energy changes must be zero.

$$\therefore\ -U+c_2\,\mathrm{d}T+U+\mathrm{d}U-c_1\,\mathrm{d}T=0$$

$$\text{or}\quad \frac{\mathrm{d}U}{\mathrm{d}T}=c_1-c_2.$$

In general, if Σc_1 is the total heat capacity of the materials used, and Σc_2 is the total heat capacity of the products, in a process which has a calorific value U at a temperature T, we may write

$$\frac{\mathrm{d}U}{\mathrm{d}T}=\Sigma c_1-\Sigma c_2.$$

20B. The Second Law of Thermodynamics.

Transformation of heat into work.—The first law of thermodynamics states that it is impossible to obtain a continuous development of energy from an isolated system; but it allows of a quantitative conversion of any one form of energy into any other. Moreover, it is found in practice that any other form of energy can be converted quantitatively into *heat*. It might be thought, therefore, that a quantitative conversion could also be effected in the opposite direction. Thus, we might imagine the existence of a machine which would pump water from the sea, take heat from it, and return cooler water to the sea, using the energy thus abstracted to drive a vessel. This process does not contradict the First Law of Thermodynamics, since no creation of energy is postulated, but it has proved to be impossible in practice to construct a machine which will continuously develop energy at the expense of the heat of surrounding bodies of the same temperature.

The **Second Law of Thermodynamics**, which expresses this limitation in a more precise form, was stated by Clausius as follows:

> *It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a low to one at a higher temperature*, or, *Heat cannot of itself (i.e. without the performance of work by some external agency) pass from a cold to a warmer body.*

This law limits in a very rigid way the extent to which heat can be converted into other forms of energy. Thus, since electrical energy and mechanical work are interconvertible, it is possible to construct an electric motor or a dynamo with an efficiency of perhaps 90 per cent., allowing only 10 per cent. for loss of energy by friction, etc., but, even under ideal conditions, the efficiency of a steam-engine is limited by the second law of thermodynamics (in accordance with a formula set out below, p. 225), to a maximum of, say, 40 per cent. of the theoretical value deduced from the first law of thermodynamics. Thus, of 100 units of heat supplied to the boiler, not more than 40

can be turned into useful work, and not less than 60 units are inevitably " wasted " or " lost " in heating the cooling-water in the condenser.

Reversibility a condition for maximum work.—In the preceding paragraph it has been stated that a heat engine can only convert into work a limited fraction of the heat supplied to it. It is obviously important to be able to deduce a numerical value for the *maximum* yield of useful work which can be obtained from a given expenditure of heat. The first step in this deduction is contained in the statement that :

The maximum external work which can be done by a physical or chemical change is only obtained when the change takes place reversibly.

Thus, if we have a reservoir of compressed air, such as is used to drive a torpedo, it is easy to waste the whole of the energy by blowing off into an empty space, so that no work at all is done by the compressed air. In order to do a large amount of useful work, therefore, it is clear that the gas must be made to drive a piston (or some similar mechanism) which is loaded to such a point that there is only a very small margin of pressure available. In order that the *maximum* amount of work may be obtained, the load on the piston must be such that it is practically *equal* to the pressure exerted by the gas at every stage of its expansion, so that if the load were increased very slightly the piston would be driven backwards. This is, however, exactly what is meant by **reversibility**, since this term is used to describe an ideal condition in which the system can be restored to its original condition by an expenditure of work which is no greater than that which has just been derived from it.

The significance of reversibility in *chemical* changes can be illustrated by considering the interaction of lime and carbon dioxide to form chalk. Suppose we have calcium carbonate, lime, and carbon dioxide in a vessel maintained at constant temperature and closed by a piston. If the pressure on the piston is exactly equal to the dissociation pressure of carbon dioxide, the system is in equilibrium and no chemical change

occurs. If the load on the piston is increased very slightly, combination will take place; if it is decreased a little, some calcium carbonate will dissociate. Thus the direction of the change can be reversed by a very slight change in pressure. Such a change is said to be *reversible*, since it can be made to proceed in either direction by using a pressure a little higher or a little lower than the equilibrium-pressure.

Again, in a Daniell cell, the chemical change represented by the equation

$$Zn + CuSO_4 \text{ aq.} \rightarrow Cu + ZnSO_4 \text{ aq.}$$

produces an electromotive force of 1·09 volts, giving rise to 105,000 joules of electrical energy for each equivalent of zinc that is consumed (p. 211); and if the internal resistance of the cell is negligible compared to the external resistance, almost the whole of this can be converted into external work. If, however, we apply to the cell an electromotive force which is slightly greater than 1·09 volts a current will flow in the opposite direction, so that zinc is deposited and copper dissolved. The direction of the chemical change is therefore reversed by a slight change in the magnitude of the applied electromotive force. The Daniell cell is only reversible, however, when very small changes in electromotive force are used, since, if a large current is driven backwards through the cell, hydrogen is set free instead of zinc, and the electromotive force of the cell is altered. The Daniell cell cannot therefore be used as an accumulator for the storage of electrical energy.

In practice, it is impossible to construct a reversible system of any kind, since some energy is always dissipated, *e.g.* in friction in the moving parts of a steam engine, or of an electric motor. In some cases, however, we can make a very close approach to reversible conditions, and thus obtain an accurate measure of the maximum external work. Thus, when the electromotive force of a cell is measured by the balance method in a potentiometer, the current passing through the cell can be reduced to a few millionths of an ampere when the final readings are made. A very close approach to the reversible electromotive force is then obtained.

Work done by an expanding gas.—A convenient illustration

of a reversible change, in which the maximum external work can be calculated, is afforded by the expansion of a perfect gas.

Consider a system in which one gram-molecule of gas is confined in a cylindrical vessel by a frictionless piston. Let the pressure p on the piston be lowered by an infinitesimal amount to $p - \mathrm{d}p$. The volume of the gas then increases, also by an infinitesimal amount, from V to $V + \mathrm{d}V$. The work done by the gas in expanding is given by the product of pressure into change of volume, *i.e.*

$$A = p\,\mathrm{d}V = \frac{RT}{V}\mathrm{d}V, \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

since it makes no difference whether we assign to the pressure its initial value p or the final value $p - \mathrm{d}p$.

To calculate the maximum work done by a *finite* expansion of a gas, it is necessary to suppose that the expansion takes place in a series of reversible steps, in each of which the pressure is lowered by an infinitesimal amount $\mathrm{d}p$, so that there is at no point any appreciable difference between the pressure exerted by the gas and the resistance offered by the piston. The maximum work done by the gas is then no longer given by the formula $A = p\,\Delta V$ (where ΔV is a *finite* change of volume), but must be deduced by a process of integration. In the case of a perfect gas, where $pV = RT$, the work done by one gram-molecule in expanding from V_1 to V_2 is given by

$$A = \int_{V_1}^{V_2} p\,\mathrm{d}V = \int_{V_1}^{V_2} \frac{RT}{V}\mathrm{d}V = RT \log_e \frac{V_2}{V_1}. \quad \ldots\ldots\ldots(2)$$

where the ratio $\mathrm{d}V/V$ in (1) is replaced by the difference $\log V_2 - \log V_1$.

Also, since $p_1V_1 = p_2V_2$, $A = RT \log_e \dfrac{p_1}{p_2}$. $\ldots\ldots\ldots\ldots\ldots(3)$

A reversible cycle.—A **cycle** consists of a series of processes, such as those which make up one complete "stroke" of a steam engine, of such a character that the system is restored to its original state when the cycle has been completed. The **reversible cycle** described below* consists of a series of reversible operations,

* This differs from Carnot's cycle in that adiabatic changes (p. 214) are not used, but it involves the assumption that the internal energy of a perfect gas is independent of the pressure (p. 45).

four in number, carried out on a perfect gas, whereby the system is restored to its original condition, after the gas has done a definite amount of work by taking heat from a high temperature "source" and giving it out to a low temperature "sink."

Operation 1. Take 1 gram-molecule of a perfect gas, confined by a frictionless piston at a temperature T. Let the gas expand reversibly and at constant temperature from V_1 to V_2. The work done by the system is $A = RT \log \frac{V_2}{V_1}$; at the same time a quantity of heat Q_1 will be absorbed from the high temperature source which is used to maintain the temperature of the gas. Since the gas is perfect, its internal energy at constant temperature is independent of its pressure or volume so that

$$Q_1 = A = RT \log \frac{V_2}{V_1}. \quad \text{.....(3)}$$

Operation 2. Cool the gas at constant volume from T to $T - dT$. No work is done and the heat *absorbed* by the system is $-C_v\,dT$, where C_v is the molecular heat of the gas at constant volume.

Operation 3. Compress the gas from V_2 to V_1 at this lower temperature $T - dT$. The work done on the system is

$$A - dA = R(T - dT) \log \frac{V_2}{V_1},$$

and the work done by the system is

$$-(A - dA) = -R(T - dT) \log \frac{V_2}{V_1}.$$

At the same time a quantity of heat Q_2 is evolved, or $-Q_2$ is absorbed.

Operation 4. Heat the gas from $T - dT$ to T. The heat absorbed is equal to $C_v\,dT$.

Since the system is now in its original condition, it follows from the first law of thermodynamics that the sum of all the energy given up by the system or added to it must be zero. The net work done by the system must therefore be equal to the net absorption of heat, *i.e.*

$$dA = R\,dT \log \frac{V_2}{V_1} = Q_1 - Q_2, \quad \text{.....(4)}$$

since the two quantities $-C_v\,dT$ and $+C_v\,dT$ cancel out.

We can now eliminate $\log \frac{V_2}{V_1}$ by dividing equation (4) by equation (3). We thus reach the equation

$$\frac{dA}{Q} = \frac{dT}{T}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

In this equation we have omitted the subscript and replaced Q_1 by the symbol Q, since, by the first law of thermodynamics, Q_2 is obviously equal to $Q - dA$.

If the temperature of the source and sink are T_1 and T_2 the total work A done by this heat engine for a consumption of Q units of heat is given by the equation

$$\frac{A}{Q} = \frac{T_1 - T_2}{T_1}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The ratio of A to Q is termed the **efficiency** of the heat engine. It represents the greatest fraction of the heat absorbed at the higher temperature which can be converted into work.

Carnot's theorem. Reversible heat engines in general.—In the previous paragraph we have calculated the efficiency of a reversible heat engine, using as working substance a perfect gas. By applying the second law of thermodynamics it can be shown that equation (6) can be applied to *any* reversible heat engine, no matter what substance is used in the machine, *e.g.* steam, water, mercury, etc. This statement is known as **Carnot's Theorem,** and can be set out as follows:

All reversible heat engines possess the same efficiency when absorbing and rejecting heat at the same two temperatures.

To prove it, let us suppose that two heat engines can be made so that I is more efficient that II, *e.g.* that, by taking Q units of heat from a boiler at a temperature T_1, and handing on its surplus heat to a condenser at a temperature T_2, the first produces A_I units of work; and the second produces A_{II} where $A_I > A_{II}$. Now let them be coupled so that I drives II backwards. At each cycle an amount of work $A_I - A_{II}$ will be available in excess of that required to reverse II. This work is done at the expense of heat taken, not from the *boiler*, but from

the *condenser*, since the boiler receives back from II the whole of the heat Q taken from it by I; but the heat $Q - A_I$ given to the condenser by I is less than the heat $Q - A_{II}$ taken from it by II, the difference being

$$(Q - A_{II}) - (Q - A_I) = A_I - A_{II}.$$

There will therefore be a continuous drain of heat at the lower temperature, and the system of two engines is one which continuously supplies energy by cooling surrounding bodies. This is contrary to the Second Law of Thermodynamics. Hence A_I must be equal to A_{II}.

The thermodynamic scale of temperature.—In the preceding paragraphs we have calculated the maximum work done by any reversible heat engine which absorbs heat from a source at a temperature T_1 and gives out the excess of heat to a sink at a temperature T_2. The efficiency of such an engine is given by

$$\frac{A}{Q} = \frac{T_1 - T_2}{T_1}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

This equation shows that the efficiency of a reversible heat engine depends only on the temperatures T_1 and T_2 of the source and sink (or of the boiler and condenser), and is independent of all other conditions, including the nature of the medium by which the work is done, and the type of machinery in which the medium is used. Lord Kelvin therefore proposed to use the efficiency of a reversible heat engine as the basis of an **absolute scale of temperature,** which should be entirely independent of the choice of a particular material, *e.g.* mercury, alcohol, air, nitrogen, hydrogen or helium or even a "perfect gas" for use in the thermometer. Thus, if we make the interval between the freezing-point T_2 and boiling-point T_1 of water equal ·100° on our new scale, the maximum efficiency of an engine working between the boiling-point and freezing-point is

$$\frac{A}{Q} = \frac{100}{T_1}.$$

The value of T_1 must then be adjusted to give to the ratio A/Q a value (about 0·268) which agrees with the most trustworthy values for the thermodynamic efficiency of a reversible engine working between these two temperatures. In practice, this leads

to the values $T_1 = 373°$, and $T_2 = 273°$, exactly as in the thermometric scale based upon the expansion of a perfect gas at constant pressure, or upon its increase of pressure at constant volume.

The Gibbs-Helmholtz equation.—From the First Law of Thermodynamics it follows that, when a chemical change with a calorific value U does A units of external work with the absorption of Q units of heat, $U = A - Q$ or $Q = A - U$.

If the chemical change gives work A and absorbs heat Q when carried out reversibly at a temperature T, and gives work $A - \mathrm{d}A$ at $T - \mathrm{d}T$ then, from the Second Law, the work done in a reversible cycle between these temperatures is $\mathrm{d}A = Q\frac{\mathrm{d}T}{T}$ or $Q = \frac{T\,\mathrm{d}A}{\mathrm{d}T}$

These two equations can now be combined so as to eliminate Q, and we thus obtain

$$A - U = T\frac{\mathrm{d}A}{\mathrm{d}T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

This is known as the **Gibbs-Helmholtz equation.**

Many instructive deductions may be made from this equation: (*a*) The difference between the changes of total energy U and of free energy A diminishes steadily as T becomes smaller, until at the absolute zero (where $T = 0$ and the expression $T\frac{\mathrm{d}A}{\mathrm{d}T}$ is also zero), the change of free energy A is exactly equal to the change of total energy U. At the absolute zero, therefore, all reactions which can do external work (A positive), and which can therefore proceed spontaneously, must also be exothermic (U positive) as Thomsen and Berthelot supposed, since U and A are equal and identical in sign.

(*b*) Again, if $\mathrm{d}A/\mathrm{d}T = 0$, *i.e.* if the free energy or maximum work of a process is independent of the temperature, it follows at once that $A = U$, so that the heat and work are again equivalent to one another. Thus, from the fact that the temperature coefficient of E.M.F. in a Daniell cell is almost zero, we can predict that A and U will be practically equal, as we have already found them to be (p. 218). In all cases such as this, where the energy of the action is independent of the temperature, the Thomsen-Berthelot hypothesis is valid, since U and A are again equal and identical in sign.

(*c*) On the other hand, since U and A can vary independently, it is quite possible for a positive value of A to be accompanied by a negative value of U, *i.e.* for a spontaneous chemical change to proceed with *absorption* of heat. An absorption of heat is only possible, however, when A is so small and $T\frac{dA}{dT}$ is so large that the difference $A - T\frac{dA}{dT}$ is negative. Whilst, therefore, endothermic changes are not impossible, as Thomsen and Berthelot supposed them to be, the Gibbs-Helmholtz equation restricts them to those cases in which the change of free energy A is small and the temperature coefficient dA/dT is positive and large; moreover, even when it is positive in sign, the magnitude of the product $T dA/dT$ is not likely to exceed A, except when T is also large. It is therefore only at high temperatures that endothermic changes are common enough to become of great practical importance. At atmospheric temperatures, which are not very far removed from the absolute zero, the majority of chemical changes are exothermic, since $T\frac{dA}{dT}$ is relatively small, even when it is positive in sign.

Evaporation of a liquid. Equation of Clausius.—Suppose that one gram of liquid is confined by a frictionless piston at a pressure p equal to the vapour-pressure of the liquid. If the liquid evaporates at a constant temperature T, the piston will move and the external work done will be given by

$$A = p(V - V')$$

where V is the volume of the vapour and V' that of the liquid. The decrease in total energy U is given by

$$U = p(V - V') - l$$

where l is the latent heat of evaporation of one gram, which is absorbed from surrounding bodies by the evaporating liquid. Putting these values in the Gibbs-Helmholtz equation we have

$$A - U = T\frac{dA}{dT}; \quad \therefore\ l = T\frac{dp}{dT}(V - V').$$

This is the equation of Clausius which has been used in Chap. III. (p. 56).

The volume of the liquid is usually very small compared with the volume of the vapour and can generally be neglected. Further, if the vapour behaves as a perfect gas, $V=\frac{RT}{Mp}$ where M is the molecular weight. Hence

$$L=Ml=\frac{RT^2}{p}\frac{\mathrm{d}p}{\mathrm{d}T}=RT^2\frac{\mathrm{d}\log_e p}{\mathrm{d}T} \quad \text{or} \quad \frac{\mathrm{d}\log_e p}{\mathrm{d}T}=\frac{L}{RT^2},$$

where L is the latent heat for 1 gram-molecule.

This equation enables us to calculate the latent heat from the change of vapour-pressure with temperature; or conversely to calculate the change of vapour-pressure when the latent heat is known. If it is assumed that L does not change with temperature (which is true for small intervals of temperature) then on integration we have:

$$\log_e\frac{p_2}{p_1}=\frac{L}{R}\left\{\frac{1}{T_1}-\frac{1}{T_2}\right\}$$

where p_1 and p_2 are the vapour-pressures at temperatures T_1 and T_2. An example of the use of this formula is given on p. 57.

Elevation of the boiling-point.—The equation of Clausius was used by van't Hoff to calculate the molecular elevation of the boiling-point from the latent heat of evaporation of the solvent.

The molecular elevation K is defined by the equation (p. 189),

$$K=\frac{M\Delta T}{c},$$

where ΔT is the rise in boiling-point for a solution containing c grams of solute in 1000 grams of solvent, and M is the molecular weight of the solute. Let the boiling-point of the pure solvent be T and that of the solution $T+\Delta T$ under the atmospheric pressure p_1. We can then write

p_1 = vapour pressure of the solution at $T+\Delta T°$
= ,, ,, ,, ,, solvent at $T°$
p_2 = ,, ,, ,, ,, ,, at $T+\Delta T°$

The vapour-pressure p_2 of the pure solvent at $T+\Delta T°$ can, however, be calculated from the equation of Clausius, which gives

$$\log_e\frac{p_2}{p_1}=\frac{L}{R}\left\{\frac{1}{T}-\frac{1}{T+\Delta T}\right\}=\frac{L}{R}\frac{\Delta T}{T(T+\Delta T)}$$
$$=\frac{L\Delta T}{RT^2} \text{ when } \Delta T \text{ is small.}$$

We can now get rid of the logarithm by remembering that $\log_e (1+x) = x$ when x is small. For this purpose we rewrite the preceding equation as follows:

$$\log_e \frac{p_2}{p_1} = \log_e \left(1 + \frac{p_2 - p_1}{p_1}\right) = \frac{p_2 - p_1}{p_1} \quad \text{or} \quad \frac{p_2 - p_1}{p_2}$$

when $p_2 - p_1$ is small compared with p_2 and p_1.

But Raoult's law (p. 182) tells us that $\frac{p_2 - p_1}{p_2} = \frac{n}{N}$ where n and N are the number of molecules of solute and solvent respectively. Also $n = \frac{c}{M}$ and $N = \frac{1000}{M'}$ where M' is the molecular weight of the solvent, so that

$$\frac{p_2 - p_1}{p_2} = \frac{cM'}{1000\,M} = \frac{L\Delta T}{RT^2}$$

or

$$\Delta T = \frac{cM'RT^2}{1000ML}.$$

Putting this in the formula for K we have

$$K = \frac{M\Delta T}{c} = \frac{McM'RT^2}{1000MLc} = \frac{RT^2}{1000L/M'},$$

and since $R = 2$ cal. approximately, and $l = L/M' =$ the latent heat of evaporation for one gram

$$K = \frac{0{\cdot}002\,T^2}{l}.$$

The agreement between the values of K predicted by this formula and those obtained by experiment is shown on p. 189.

Depression of the freezing-point. In this case it is necessary first to determine the relation between the lowering of the vapour-pressure of a solution and its change in freezing-point. The equation $L = RT^2 \frac{\mathrm{d} \log_e p}{\mathrm{d}T}$ gives the relation between the latent *heat of evaporation* L and the vapour-pressure p of the liquid. If T is lower than the freezing-point, p is the vapour-pressure of the supercooled liquid.

An equation for the *heat of sublimation* of the solid can, however, be established in exactly the same way, namely

$$S = RT^2 \frac{\mathrm{d} \log q}{\mathrm{d}T}$$

where S is the heat of sublimation of one gram-molecule of ice, and q is the vapour-pressure of ice. Integrating these equations we have:

$$\log p = -\frac{L}{RT} + C$$

$$\log q = -\frac{S}{RT} + C',$$

where C and C' are integration constants. By subtraction

$$\log \frac{p}{q} = \frac{(S-L)}{RT} - (C' - C).$$

At the freezing-point, T_0, however, the liquid and solid have the same vapour-pressures, which we can call p_0, so that when $T = T_0$, $p = q = p_0$, and therefore $\log \frac{p}{q} = 0$. The integration-constant $C' - C$ is therefore given by the equation

$$C' - C = \frac{S-L}{RT_0}.$$

Hence, at any other temperature,

$$\log \frac{p}{q} = \frac{S-L}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right].$$

Now the vapour-pressure p_1 of the solution at its freezing-point, $T = T_0 - \Delta T$ is equal to the sublimation-pressure q of the solid at the same temperature, since they are in equilibrium. We can therefore write

p_1 = vapour-pressure of the solution at $T_0 - \Delta T$
= sublimation-pressure q of the solid at $T_0 - \Delta T$
p_2 = vapour-pressure of supercooled liquid at $T_0 - \Delta T$.

Then $$\log \frac{p}{q} = \log \frac{p_2}{p_1} = \frac{S-L}{R}\left\{\frac{1}{T_0 - \Delta T} - \frac{1}{T_0}\right\} = \frac{S-L}{R}\,\frac{\Delta T}{T_0(T_0 - \Delta T)},$$

$$= \frac{S-L}{RT_0^2}\Delta T \text{ when } \Delta T \text{ is small.}$$

But if $p_2 - p_1$ is small compared with p_2 and p_1 we can get rid of the logarithm as before by writing

$$\frac{p_2 - p_1}{p_1} \text{ or } \frac{p_2 - p_1}{p_2} \text{ for } \log \frac{p_2}{p_1} \text{ so that}$$

$$\frac{p_2 - p_1}{p_2} = \frac{S-L}{RT^2}\Delta T$$

and from Raoult's Law

$$\frac{p_2 - p_1}{p_2} = \frac{n}{N} = \frac{cM'}{1000M}.$$

Hence

$$\Delta T = \frac{cM'RT_0^2}{1000M(S-L)}.$$

But $S - L$ is the difference between the latent heats of sublimation and evaporation, and is therefore equal to the latent heat of fusion for one gram-molecule. Hence if l_f is the latent heat of fusion for 1 gram $l_f = (S - L)/M'$

and

$$\Delta T = \frac{cRT_0^2}{1000Ml_f}.$$

Putting this in the formula (p. 191) for the molecular depression of the freezing-point, we have

$$K = \frac{M\Delta T}{c} = \frac{McRT_0^2}{1000Ml_fc} = \frac{0{\cdot}002T_0^2}{l_f}.$$

The experimental verification of this expression is discussed on p. 192.

The measurement of chemical affinity.—Three principal methods are available for determining the affinity or "free energy" of a chemical change. The first requires that the action shall take place in a battery the E.M.F. of which can be determined. The second depends on a knowledge of vapour-pressures or of solubilities, whilst in the third the chemical affinity is deduced from the equilibrium constant (p. 250) of a reversible reaction.

(1) *E.M.F. method.*—The reaction in the Daniell cell:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

has already been cited (p. 211), as an example of the first method. In general, the affinity of an electrochemical change is proportional to the electromotive force and to the current developed. Thus, for one equivalent $A = FE$, where F is the output of current per gram-equivalent; and for μ equivalents $A = \mu FE$. According to Faraday's second law of electrolysis (p. 322) the output of current per gram-equivalent is the same for all

electrolytic cells, and has the fixed value $F = 96,540$ coulombs. The affinity of the Daniell cell is therefore :

$$A = 1{\cdot}09 \times 96,540 = 105,250 \text{ joules per equivalent,}$$

or, in heat units,

$$A = 105,250 \div 4{\cdot}189 = \mathbf{25,120} \text{ cal. per equivalent}$$

or **50,240** cal. per gram-molecule.

The Gibbs-Helmholtz equation, which may be written

$$A = U + T\frac{dA}{dT},$$

enables us, however, to check this value by equating the chemical affinity A of the cell to the sum of U (the total energy change as measured by carrying out the reaction in a calorimeter), and $T\frac{dA}{dT}$ (which depends on the variation of the electromotive force of the cell with temperature). Alternatively, this check can be regarded as an experimental test of the validity of the Gibbs-Helmholtz equation. The data for three particular cells are set out in Table 53.

TABLE 53. FREE AFFINITY AND ELECTROMOTIVE FORCE OF ELECTRIC CELLS.

				A	U	$A-U$	$T\frac{dA}{dT}$
(i) Cu	$CuSO_4$ 100 H_2O	$ZnSO_4$ 100 H_2O	Zn	50,530	50,110	420	430
(ii) Ag	AgCl	$ZnCl_2$ 50 H_2O	Zn	46,900	49,080	− 2190	− 2640
(iii) Hg	Hg_2Cl_2	KOH Hg_2O	Hg	7,570	− 3,280	10,950	11,280

These present some important points of contrast, thus :

(i) In the Daniell cell, the values of A and U are nearly equal ; the E.M.F. of the cell therefore changes very little with temperature and $T\,dA/dT$ is less than 1 per cent. of A.

(ii) For the second cell, A is less than U and $A - U$ is negative. The temperature coefficient $\frac{dA}{dT}$ is therefore also negative and the E.M.F. of the cell diminishes as the temperature rises.

(iii) The third cell is specially interesting, since the calorific value U of the process is *negative*, and yet the cell develops a substantial *positive* quantity A of free energy. Although this is directly opposed to the hypothesis of Berthelot and Thomsen, there is still a satisfactory agreement between the figures in the

last two columns, and the Gibbs-Helmholtz equation is again valid. It will also be seen that the exceptional behaviour of this cell is associated with a positive temperature coefficient which is 30 times greater than that of the Daniell cell.

(2) *Vapour pressures.*—The affinity of water for sulphuric acid or for anhydrous copper sulphate can be deduced quite readily from the vapour pressures. Thus if p_0 is the pressure of aqueous vapour over pure water, and p_1 is the vapour pressure over concentrated sulphuric acid, the expansion of one gram-molecule of water vapour by an isothermal and reversible process from one pressure to the other will give rise to a definite amount of work, which is a measure of the chemical affinity of the acid for the water. Thus, since the attenuated vapour can be treated as a perfect gas, we have

$$A = \int_{p_1}^{p_0} V\,dp = RT \log \frac{p_0}{p_1}.$$

A similar expression can be used to calculate the maximum work of a chemical or physical change from the solubilities in a given solvent of the initial material and of the product. Thus, if the solubilities in water of the hydrates Na_2SO_4, $7H_2O$ and Na_2SO_4, $10H_2O$, are S_0 and S_1 corresponding to osmotic pressures p_0 and p_1, the maximum work obtained per water molecule in this reaction is

$$A = RT \log \frac{p_0}{p_1} = RT \log \frac{S_0}{S_1}.$$

(3) *van't Hoff's "equilibrium box."*—The third method of calculating the affinity of a chemical change, which is due to van't Hoff, depends on a knowledge of the equilibrium constant of a balanced action. When the substances taking part in such an action have reached a condition of equilibrium, the free energy is obviously at a minimum, and may be taken as zero. If, however, any of the reactants are present in proportions differing from the equilibrium concentrations, chemical change will proceed in the directions in which energy is liberated. The affinity of the system therefore depends upon (i) the equilibrium constant, (ii) the concentrations of the reacting substances and of the products.

In order to calculate the maximum external work, the chemical change must proceed by a series of reversible operations. For the sake of simplicity, consider a gaseous reaction

$$A + B \rightleftarrows C + D.$$

Let $A_i B_i$ be the initial pressures of A and B, and $C_f D_f$ be the final pressures of C and D, when A and B have interacted quantitatively to form C and D. The equilibrium concentrations are represented by A_e, B_e, C_e, D_e.

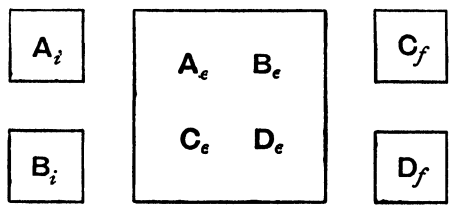


FIG. 60.—The equilibrium box.

van't Hoff then postulates the existence of a series of independent boxes or vessels containing the four substances A, B, C, D at pressures A_i, B_i, C_f, D_f, together with an "equilibrium box," containing A, B, C and D in equilibrium at pressures A_e, B_e, C_e, D_e. This box is supposed to have one wall permeable to A only, one permeable to B, and others permeable to C and D only. The four essential operations are as follows:

(*a*) By means of a suitable vessel (i) Take out a small fraction dN of a gram molecule of A from the first box. (ii) Let this expand reversibly until it reaches a pressure A_e. (iii) Pass the expanded gas through the semipermeable membrane into the equilibrium box at a pressure of A_e. In the first stage of the operation, the gas does work represented by $A_i v_i$, where v_i is the volume of gas removed; but this is cancelled by the work $A_e v_e$ done on the gas in the third stage when it is forced into the equilibrium box, since the gas is assumed to obey Boyle's Law. The total work done in operation (*a*) is therefore that of second stage,

$$w_1 = dNRT \log \frac{A_i}{A_e}.$$

(*b*) By a similar series of operations transfer dN molecules of B to the equilibrium box. The work done is

$$w_2 = dNRT \log \frac{B_i}{B_e}.$$

Let these combine to give C and D within the box. No work will be done since the volume is unchanged.

(*c*) Now remove dN molecules of C from the equilibrium box, compress it reversibly to a pressure C_f, and transfer it to the box containing C at this pressure. The work done is

$$w_3 = \mathrm{d}NRT \log_e \frac{C_e}{C_f}.$$

(*d*) The transference of dN molecules of D in the same manner gives an amount of work

$$w_4 = \mathrm{d}N\ RT \log_e \frac{D_e}{D_f}.$$

The maximum free energy for the chemical change of dN molecules is given by

$$w_1 + w_2 + w_3 + w_4 = \mathrm{d}N\ RT\left(\log_e \frac{A_i}{A_e} + \log_e \frac{B_i}{B_e} + \log_e \frac{C_e}{C_f} + \log_e \frac{D_e}{D_f}\right),$$

or from one gram molecule,

$$A = RT\left(\log_e \frac{A_i}{A_e} + \log_e \frac{B_i}{B_e} + \log_e \frac{C_e}{C_f} + \log_e \frac{D_e}{D_f}\right).$$

Rearranging the logarithmic terms

$$A = RT \log_e \frac{C_e D_e}{A_e B_e} - RT \log_e \frac{C_f D_f}{A_i B_i}.$$

But, by definition, the ratio $\frac{C_e D_e}{A_e B_e}$ is equal to the "equilibrium-constant" K of the balanced action (p. 250).

$$\therefore\ A = RT \log_e K - RT \log_e \frac{C_f D_f}{A_i B_i}. \quad \ldots\ldots\ldots\ldots (8)$$

If one molecule each of A and B interact to form one molecule each of C and D, we can select the concentration so that $A_i = B_i = 1$ and $C_f = B_f = 1$. The second term,

$$RT \log \frac{C_f D_f}{A_i B_i} = RT \log 1,$$

then vanishes and the equation assumes the simple form

$$A = RT \log_e K.$$

Notice (i) that the equilibrium constant K always has the

equilibrium concentrations of the *products* in the numerator and of the *initial materials* or reactants in the denominator, and (ii) that the second term, when written with a negative sign, includes the logarithm of a quantity of the same form as the equilibrium constant, but with the *final* concentrations of the products in the numerator and with the *initial* concentrations of the reactants in the denominator.

The van't Hoff isotherm.—The formula deduced in the preceding paragraph can readily be extended to cover any reversible reaction, whether in the gaseous or in the liquid state. Thus the chemical equation for the balanced action may be written in the general form

$$n_1A_1 + n_2A_2 + \ldots \rightleftharpoons n_1'A_1' + n_2'A_2' + \ldots,$$

where n_1, n_2, etc., are the number of molecules of the initial materials or reactants A_1, A_2, etc., which take part in the interaction, and n_1', n_2', etc., are the number of molecules of the products or resultants A_1', A_2', etc., to which they give rise. The equation for the free energy of the action then assumes the general form

$$A = RT\log_e K - RT\log_e \frac{[A_1']^{n_1'}[A_2']^{n_2'}\ldots}{[A_1]^{n_1}[A_2]^{n_2}\ldots},$$

where the symbols in square brackets are the concentrations (*e.g.* in gram-molecules per litre) of the components in the two series of substances from which the equilibrium mixture can be derived. This equation, which is known as the **van't Hoff isotherm**, can be written

$$A = RT\log_e K - RT\Sigma n \log C, \quad \ldots\ldots\ldots\ldots\ldots\ldots(9)$$

where $\Sigma n \log C = n_1' \log A_1' + n_2' \log A_2' \ldots - n_1 \log A_1 - n_2 \log A_2$.

The second term of equation (9) can vary within wide limits if the reactants and products are at different pressures. Thus, if the *products* are at a low pressure, the concentrations in the numerator are small and the fraction

$$\frac{[A_1']^{n_1'}[A_2]^{n_2'}\ldots}{[A_1]^{n_1}[A_2]^{n_2}\ldots.}$$

tends to zero, whilst its logarithm (which defines the second

term) tends to $-\infty$. Conversely, if the *reactants* are at a very low pressure this fraction becomes infinitely large. It is therefore necessary to state the initial and final pressures in order to define the affinity of a chemical change. Since the gases which form the system are assumed to be perfect, we can measure their concentrations in terms of their pressures. We therefore choose an arbitrary unit of pressure (usually one atmosphere), and start with 1 gram-molecule of each reactant at unit pressure, and (with the help of the equilibrium box) end with 1 gram-molecule of each resultant at unit pressure. The second term then vanishes, and the equation is reduced to the simple form in which affinity constants are usually tabulated

$$A = RT \log K. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

The unit of pressure used in measuring the initial and final concentrations must be defined, and must be the same as that used in determining the equilibrium constant K. If, however, there is no change in the number of molecules during the reaction, the equilibrium constant K and the affinity A are independent of the pressure (provided that it remains constant), and of the units in which it is measured.

Calculation of chemical affinity from equilibrium constants.—An example to illustrate the application of van't Hoff's isotherm to calculate the affinity of a homogeneous chemical reaction is provided by Bodenstein's study of the balanced action

$$H_2 + I_2 \rightleftarrows 2HI.$$

Bodenstein found that at 300°, $K = 80$.

$$\therefore A = RT \log_e K = 2 \times 573 \times 2{\cdot}303 \log_{10} 80 = +5000 \text{ calories.}$$

Since the number of molecules on each side of the equation is the same, there is no change of volume or pressure when they interact, and the maximum work then is independent of the pressure of the reactants. The second term in van't Hoff's equation therefore vanishes, and the maximum work which could be done by the combination of one gram-molecule of hydrogen and iodine to give hydriodic acid at the same pressure is 5000 calories.

Similarly, the affinity of hydrogen for oxygen can be calculated

if the equilibrium-constant can be found. Nernst and von Wartenburg found that, when water vapour was heated to 1000° (abs.), the fraction dissociated was $3{\cdot}0 \times 10^{-7}$. In order to calculate the equilibrium-constant we write

$$p_{H_2O} = 1, \quad p_{H_2} = 3{\cdot}0 \times 10^{-7}, \quad p_{O_2} = 1{\cdot}5 \times 10^{-7};$$

$$\therefore K = \frac{p^2_{H_2O}}{p^2_{H_2} \times p_{O_2}} = \frac{1}{1{\cdot}35 \times 10^{-20}}$$

and
$$A = RT \log_e K - RT\Sigma n \log C$$
$$= 2 \times 1000 \times 2{\cdot}303 \log_{10} \frac{1}{1{\cdot}35 \times 10^{-20}} - 0$$
$$= 90{,}600 \text{ calories.}$$

This is the maximum work that can be obtained when one gram molecule of steam at 1 atmosphere pressure is produced from hydrogen at a pressure of one atmosphere and oxygen at a pressure of one atmosphere, at a temperature of 1000°. Since the pressures are all in atmospheres, the second term of the isotherm is zero. On the other hand, if the initial pressures of hydrogen and oxygen were reduced to the equilibrium pressures, the free energy would obviously be reduced to zero, because the negative term would then become equal to the positive term.

The van't Hoff isochore.—By combining the van't Hoff isotherm with the Gibbs-Helmholtz equation, we can obtain an important formula for deducing the variation of the equilibrium constant with temperature from the calorific value of a balanced action. Thus if we differentiate the equation (9)

$$A = RT \log_e K - RT\Sigma n \log_e C$$

with regard to *temperature*, keeping the *volume* constant, we get

$$\left(\frac{dA}{dT}\right)_v = R \log_e K + RT \frac{d}{dT}(\log_e K)$$
$$- R\Sigma n \log_e C - RT \frac{d}{dT}(\Sigma n \log_e C).$$

Since, however, n and C are constants, which do not vary with temperature, the last term is zero. Hence

$$T\left(\frac{dA}{dT}\right)_v = RT \log_e K + RT^2 \frac{d \log_e K}{dT} - RT\Sigma n \log_e C$$
$$= A + RT^2 \frac{d \log_e K}{dT}.$$

But by the Gibbs-Helmholtz equation,

$$A - U = T\frac{dA}{dT};$$

$$\therefore\ A - U = A + RT^2\frac{d\log_e K}{dT}$$

or

$$\frac{d\log_e K}{dT} = \frac{-U}{RT^2}. \qquad \text{.....(10)}$$

This equation is known as the **van't Hoff isochore.** Its application is discussed in Chapter X. below (p. 254).

Variation of affinity with temperature. Nernst's heat theorem. —The Gibbs-Helmholtz equation

$$A - U = T\frac{dA}{dT}$$

enables us to calculate the *calorific value* or change of *total* energy U of a process, if the *maximum work* or change of *free* energy A of the process and its temperature coefficient are known; but it does not enable us to perform the converse operation of calculating the maximum work from the calorific value, since we cannot then solve the Gibbs-Helmholtz equation unless we can determine or postulate certain additional constants. Thus, in order to integrate the equation:

$$T\frac{dA}{dT} - A = -U,$$

we divide throughout by T^2;

$$\therefore\ \frac{1}{T}\frac{dA}{dT} - \frac{A}{T^2} = -\frac{U}{T^2}.$$

This is the same as

$$\frac{d}{dT}\left(\frac{A}{T}\right) = -\frac{U}{T^2}.$$

On integration this gives

$$\frac{A}{T} = -\int\frac{U}{T^2}dT + I,$$

where I is a constant of integration; but we have no method at present for determining the value of the unknown constant I unless we already know the value of A.

The principal information that we have on this point is that at the absolute zero A and U are equal, *i.e.* $A_0 = U_0$. In order

to obtain a relationship between A and U at other temperatures, Nernst suggested the hypothesis that U and A are not only identical at the absolute zero, but that their temperature coefficients are also identical at a zero value, so that, if A and U are plotted against T, the curves coincide and are parallel to the axis of temperature for an appreciable distance from the absolute zero. This means that $\frac{dA}{dT}$ and $\frac{dU}{dT}$ are both zero when $T=0$.

Starting from its value at the absolute zero, the effect of temperature on U can obviously be expressed by an ascending series of terms of T, *i.e.*

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \dots .$$

The equation $\frac{A}{T} = I - \int \frac{U}{T^2}\, dT$ then becomes

$$\frac{A}{T} = I - \int \left(\frac{U_0}{T^2} + \frac{\alpha}{T} + \beta + \text{etc.} \right) dT,$$

or on integration,

$$\frac{A}{T} = I + \frac{U_0}{T} - \alpha \log T - \beta T - \frac{\gamma T^2}{2} - \text{etc.},$$

or, multiplying both sides of the equation by T,

$$\therefore\ A = IT + U_0 + -\alpha T \log T - \beta T^2 - \frac{\gamma T^3}{2}, \text{ etc.},$$

whereas $U = U_0 + \alpha T + \beta T^2 + \gamma T^3$, etc.

We now have two parallel equations for the influence of temperature on A and U, to which we can apply Nernst's supplementary hypothesis that

$$\frac{dA}{dT} = 0 \quad \text{and} \quad \frac{dU}{dT} = 0 \text{ when } T = 0.$$

The first gives $\frac{dA}{dT} = I + \alpha - \alpha \log T - 2\beta T - \frac{3}{2}\gamma T^2$, etc.

The second gives $\frac{dU}{dT} = 0 + \alpha + 2\beta T + 3\gamma T^2$, etc.

The first expression can only become zero for $T=0$, if $\alpha = 0$ (since otherwise $-\alpha \log T$ would be infinite); and the integration constant I must also be equal to 0 in order to give a zero value

to the sum. The early terms of both expressions therefore disappear.

We can, moreover, write $\frac{dU}{dT} = c_1 - c_2$, when c_1 and c_2 are the specific heats of the reactants and the resultants which (by the First Law of Thermodynamics) must determine the temperature variations of the calorific value or total energy of the process (see Kirchoff's equation, p. 219). In this way we obtain the following relationships between affinity, temperature and heat change.

$$U = U_0 + \beta T^2 + \gamma T^3, \text{ etc., } \ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

$$A = U_0 - \beta T^2 + \frac{\gamma}{2} T^3, \text{ etc., } \ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

$$c_1 - c_2 = 2\beta T + 3\gamma T^2, \text{ etc. } \ldots\ldots\ldots\ldots\ldots\ldots\text{(iii)}$$

If, therefore, we treat γ as negligible, we can deduce the value of the constant β from the specific heats of the reactants and resultants at a given temperature T; we can then use the value of β to deduce U_0 from the measured value of U; and, finally, we can combine this value of U_0 with the known value of β to give the free-energy change A at the temperature T.

Deductions from Nernst's heat theorem.—Nernst's heat theorem is obviously based on assumptions that cannot be tested directly, since we cannot make experiments at the absolute zero of temperature, and it is not yet certain in what range of cases it can be applied. Thus, it has been suggested that, since over-cooled liquids need not give up all their energy when cooled to the absolute zero, the theorem in its simple form should only be applied to crystalline solids. The following examples are given to illustrate some possible applications of the theorem.

(*a*) Nernst's heat theorem implies that the quantity

$$\frac{dU}{dT} = c_1 - c_2 = 2\beta T$$

becomes zero at 0° K. If, therefore, the fusion of a solid is regarded as a transformation to which the theorem can be applied, it follows that *the difference in the specific heats of solid and liquid should vanish at the absolute zero.* This conclusion was verified in Nernst's laboratory in 1910 by experiments on the

specific heat of benzophenone and of betol in the crystalline and overcooled liquid states, where the *difference* of specific heats falls to a negligible value at low temperatures.

(*b*) In a similar manner the heat theorem, in the form

$$A = U - 2\beta T^2,$$

can be used to calculate the temperature T_0 at which $A = 0$, by making use of the measured values of U and the value of β deduced from the specific heats of the initial and final products. For example, the transition temperature for the transformation of monosymmetric into orthorhombic sulphur can be deduced from the specific heats of the two allotropic forms of the element and their latent heat of transformation. In this case the value selected for the difference of the specific heats gives $\beta = 1{\cdot}15 \times 10^{-5}$,

whence $$U = 1{\cdot}57 + 1{\cdot}15 \times 10^{-5} T^2$$

and $$A = 1{\cdot}57 - 1{\cdot}15 \times 10^{-5} T^2.$$

It will be seen that $A = 0$ when

$$T = \sqrt{\frac{1{\cdot}57}{1{\cdot}15 \times 10^{-5}}} = 370^\circ \text{ Abs.}$$

The observed value of the transition temperature is 96° C. or 369° K.

QUESTIONS ON CHAPTER IX.

1. What is meant by exothermic and endothermic reactions ? From the thermal data below, show that dry hydrogen sulphide and iodine will not react.

(1) $H_2 + S$ (gas) $= H_2S + 4600$ cal.

(2) $\frac{1}{2}H_2 + \frac{1}{2}I_2$ (gas) $= HI - 6200$ cal.

Under what conditions can the reaction be brought about ?

(B.A., Bombay.)

2. How would you determine approximately the heat of neutralisation of an acid ? The heats of neutralisation of one gram molecule of sodium hydroxide in aqueous solution by various acids are as follows : HF, 16,300 cal., HCl, 13,700 cal., HBr, 13,700 cal., HNO_3, 13,700 cal., CH_3COOH, 13,200 cal., HCN, 2,800 cal. Discuss and explain these results.

(Oxford and Cambridge Schools Exam. Board.)

3. How is the heat of formation of a compound usually determined ? Given that

$$K + aq. = KOHaq. + \tfrac{1}{2}H_2 + 481K,$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 684K,$$
$$KOH + aq. = KOH\ aq. + 133K.$$

Find the heat of formation of KOH from its elements.

(B.A., Bombay.)

4. State and explain the law of Hess. Indicate its use in determining the heat of formation of an organic compound.

The heat of formation of water is 68,360 cal. and of carbon dioxide is 96,960 cal., both at 17° and constant pressure. The heat of combustion of methane at 17° and constant pressure is 211,930 cal. Calculate the heat of formation of methane at 17° C. (*a*) at constant pressure, (*b*) at constant volume.

(B.A., Bombay.)

5. Define the terms endothermic and exothermic as applied to compounds. Illustrate your answer by reference to compounds of nitrogen.

The heat of combustion of hydrogen is 65,000 cal. per gm. mol., of carbon 97,000 cal. per gm. atom ; if the heat of combustion of ethylene is 340,000 cal. per gm. mol., what is its heat of formation ?

(Cambridge Entrance Schols.)

6. How can it be determined experimentally whether heat is given out or absorbed in the synthesis of (*a*) ammonia, (*b*) nitric oxide ? What is the technical importance of these results ?

(Cambridge Schols.)

7. Explain the importance of a knowledge of (*a*) heats of formation, (*b*) heats of combustion. Suggest and explain a method by which the heat of formation of sodium hydroxide could be determined. (Trinity College, Cambridge.)

8. From the following data, calculate the heat of formation of anhydrous aluminium chloride :

$$2Al + 6HCl\ aq. = Al_2Cl_6\ aq. + 3H_2 + 239{,}760\ cal.$$
$$H_2 + Cl_2 = 2HCl + 44{,}000\ cal.$$
$$HCl + Aq. = HCl\ aq. + 17{,}315\ cal.$$
$$Al_2Cl_6 + Aq. = Al_2Cl_6\ Aq. + 153{,}690\ cal.$$

(Inter. Sci. Sheffield.)

9. From the following thermochemical equations, all of which refer to a temperature of 17° C., calculate the heat evolved in the polymerisation of acetylene to benzene, (*a*) at constant volume, (*b*) at constant pressure.

$$C + O_2 = CO_2 + 96{,}960\ cal.$$
$$2H_2 + O_2 = 2H_2O\ (liquid) + 136{,}720\ cal.$$
$$2C_6H_6 + 15O_2 = 12CO_2 + 6H_2O\ (liquid) + 1{,}598{,}700\ cal.$$
$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O\ (liquid) + 620{,}100\ cal.$$

(B.Sc. Sheffield.)

10. From the heats of formation of carbon dioxide from carbon and from carbon monoxide :

$$C + O_2 = CO_2 + 97{,}650 \text{ cal.}$$
$$CO + \tfrac{1}{2}O_2 = CO_2 + 68{,}000 \text{ cal.}$$

calculate the heat of formation of carbon monoxide. Does the result accord with your expectation ? How do you account for it ? (Inter. Sci. Sheffield.)

11. What is meant by the heat of combustion and how is it determined ? 0·702 gram of benzoic acid, the heat of combustion of which is 6,234 cal. per gram when burnt in compressed oxygen in a calorimeter, raised the temperature 1·263°. 0·621 gram of fuel oil when similarly treated raised the temperature 1·682°. What is the heat of combustion of the latter substance ? (B.A., Madras.)

12. State Hess's law of thermochemistry. Calculate the heat of formation of formic acid from the following data :

Heat of combustion of carbon (C, O_2) = 96,960 cal.
,, ,, ,, ,, hydrogen (H_2, O) = 68,360 ,,
,, ,, ,, ,, formic acid (CH_2O_2, O) = 65,900 ,,
(B.Sc., Punjab.)

13. Give an account of the different methods which can be employed for the measurement of affinity. Calculate the affinity of sodium sulphate for water in the formation of $Na_2SO_4 . 10H_2O$ at 15° C. At this temperature the dissociation pressure of the hydrate is 9·7 mm. and the vapour-pressure of water 12·7 mm. of mercury. ($R = 2$ calories per 1° C. $\log_e 10 = 2{\cdot}3$).
(Trinity College Senior Schol.)

14. Define molecular heat of neutralisation. When a dilute solution of a strong acid is neutralised by a solution of a strong base, the heat of neutralisation is found to be as nearly as possible the same in all cases. How do you account for this ?
How would you proceed in the laboratory to measure the heat of neutralisation of an acid ? (B.A., Madras.)

15. From thermodynamical considerations deduce the formula connecting latent heat of vaporisation and the change of vapour-pressure with temperature. The gas constant R = 2 cal. (approximately) and $\log_e x = 2{\cdot}303 \log_{10} x$. The vapour-pressure of an organic liquid at 20° C. is 74·6 mm and at 40° C. is 181·8 mm. Calculate its latent heat of vaporisation. (B.Sc., Bombay.)

16. The vapour-pressure of BCl_3 is 562·9 mm. at 10° C. and 807·5 mm. at 20° C. What is the molecular heat of evaporation and the boiling point under atmospheric pressure ?
(B.Sc., Sheffield.)

17. Calculate the affinity of the reaction

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$

at 480° C. using oxygen at 0·4 atm. pressure and HCl at 3·4 atm., given that when a mixture containing 49 per cent. of HCl and

51 per cent. of oxygen is heated at a constant pressure of 723 mm. at 480° C., 76 per cent. of the HCl is transformed at equilibrium. (B.Sc., Sheffield.)

18. At 2000° C. the equilibrium constant for pressures in atmospheres for the reaction $CO+O_2=CO_2$ is $1{\cdot}07\times10^2$. What is the maximum work obtainable by the formation at 2000° C. of one gram-molecule of CO_2 at atmospheric pressure from one gram-molecule of CO and half a gram-molecule of oxygen, both at atmospheric pressure ? (B.Sc., Sheffield.)

19. Show how the van't Hoff isochore may be derived. Discuss its applications and limitations with regard to various types of chemical and physical equilibrium. (B.Sc. Hons., Sheffield.)

20. Discuss the limitations of the Gibbs-Helmholtz equation in correlating the heat and affinity of a reaction.

Show how by making certain assumptions, Nernst has been able to express the complete relationship of these quantities. (B.Sc. Hons., Sheffield.)

21. Discuss from the standpoint of (*a*) thermodynamics, (*b*) experiment, the effect of pressure on the melting of a solid. Illustrate your answer by reference to the melting point of ice.

The latent heat of paraffin wax at 52·7° and 1 atm. pressure is 35·35 calories per gram. The increase of volume on melting is 0·125 c.c. per gram. What will be the melting point of paraffin wax under a pressure of 10 atmospheres ? (B.Sc. Hons., Sheffield.)

22. Explain what you mean by the term " free energy." Discuss the importance of a knowledge of free energy values, giving illustrations of some of the methods by which these data may be obtained experimentally. (B.Sc. Hons., Sheffield.)

23. Deduce a relationship between the freezing point and latent heat of fusion of a solvent and the depression of the freezing point produced by adding 1 gram-molecule of a solute to 1000 grams of the solvent. (B.Sc. Hons.)

24. Explain precisely in what sense the equation

$$dA = Q\frac{dT}{T}$$

may be considered as a complete expression of the second law of thermodynamics. From this equation deduce an expression for the heat of dilution of a dilute solution from concentration c_1 to concentration c_2. (B.Sc. Hons., Manchester.)

CHAPTER X.

CHEMICAL EQUILIBRIUM.

21. Chemical Equilibrium.

1. Equilibrium in the interaction of alcohol and acetic acid.

Weigh into three drawn-out test-tubes:

(*a*) About 3 grams glacial acetic acid.
,, 1 gram absolute alcohol.
(*b*) About 2 grams glacial acetic acid.
,, 2 grams absolute alcohol.
(*c*) About 1 gram glacial acetic acid.
,, 3 grams absolute alcohol.

Seal off the tubes and heat in a bath of water at about 60° for five to six hours. Allow to cool, open the tubes, rinse out with cold water and titrate rapidly with normal NaOH (free from carbonate), using phenol phthalein as indicator. Also titrate a weighed amount of the glacial acetic acid used. From your results calculate the number of molecules of ester formed in each case. Set out the results in tabular form as follows:

Tube.	*Mols. acid.*	*Mols. alcohol.*	*Molecules ester.*	
			(*a*) Found.	(*b*) Calc.

The numbers in the last column can be calculated by the equation on p. 261.

Chemical equilibrium.—A large number of chemical changes are known in which the interacting substances are not used up completely to form the products of the action. Thus, if equivalent amounts of hydrogen and iodine are heated together in a sealed tube at 356°, only 80 per cent. of the theoretical amount of hydrogen iodide is formed, no matter how long the heating is continued. Conversely, if pure hydrogen iodide is heated in a sealed tube to the same temperature, it is partly decomposed;

but 80 per cent. of it remains unchanged, and no further decomposition takes place if the temperature is maintained at 356° for an indefinite period. At this temperature, hydrogen, iodine, and hydrogen iodide in the proportions set out above are said to be in **chemical equilibrium** with each other. The system then satisfies the test of a true equilibrium, since a mixture of the same composition is obtained whether one starts with pure hydrogen iodide or with a mixture of hydrogen and iodine in molecular proportions.

This experimental fact rules out the possibility that, when the equilibrium is reached, hydrogen and iodine cease to combine together and hydrogen iodide ceases to decompose. It must be supposed that these actions still go on, but with equal and opposite velocities, so that in each second just as much hydrogen iodide decomposes as is formed from hydrogen and iodine. Two opposite actions are therefore proceeding in the equilibrium-mixture, namely : $H_2 + I_2 \rightarrow 2HI$

and $H_2 + I_2 \leftarrow 2HI$;

or, as it is usually written,

$$H_2 + I_2 \rightleftharpoons 2HI.$$

According to this view, the composition of the equilibrium-mixture remains constant, not because chemical reactions are no longer taking place between the molecules, but because the speeds of the forward and back reactions have become the same.

Velocity of reaction.—Since chemical equilibrium depends on the balancing of two opposite reaction-velocities, it is essential to investigate the factors which determine the velocity of a chemical change. The principal factors are three in number, namely :

(i) Temperature.
(ii) Catalysis.
(iii) Concentration.

(i) *Influence of temperature.*—A rise of temperature usually increases the reaction-velocity very greatly. This effect is discussed in Chapter XI., but it need not be considered here, since the present chapter is limited to the consideration of chemical equilibrium, which depends on the *ratio* of two opposing

velocities at a given temperature. Thus, if the two reaction-velocities are increased *in the same ratio*, the final condition of equilibrium will be independent of the temperature.

(ii) *Influence of catalysts.*—The presence of catalysts has a very large effect upon the speed of a chemical change, and may increase a reaction-velocity a millionfold. It can be shown, however (p. 304), that the effect of catalysts upon the forward and back reactions must be exactly the same, since the final condition of equilibrium cannot be altered by the addition of a mere trace of a foreign substance. Whilst, therefore, the influence of catalysts is of great importance when we are concerned with the speed at which a chemical change occurs in one direction or other, or with the velocity with which a system attains equilibrium, we need not consider their action when we are discussing the final condition of equilibrium in a given system.

(iii) *Influence of concentration.*—The effect of concentration on the speed of a chemical change was discussed fully by Guldberg and Waage in 1867. Their **Law of Mass Action** states that:

The velocity of a chemical change is proportional to the product of the "active masses" of the interacting substances.

Since the *concentrations* of the various components have an opposite influence on the 'forward' and 'back' reactions, these concentrations are the principal factor in determining the conditions of equilibrium in a given system when the temperature of the system is kept constant.

Equilibrium in homogeneous systems.—In **homogeneous systems**, *i.e.* systems in which all the interacting molecules are present in one phase, the "active mass" is measured by the concentration of the reacting substances, *e.g.* in gram-molecules per litre. Thus, if we consider the reaction:

$$A + B \rightleftharpoons C + D,$$

the law of mass action then tells us that the speed of the reaction represented by the upper arrow is

$$v_1 = k_1 \times \textit{concentration of } A \times \textit{concentration of } B,$$

where k_1 depends upon temperature and catalysts, but is a constant under a given set of conditions. This relation is

expressed more concisely by using the symbol $[X]$ to represent the concentration of a given component X. We therefore write

$$v_1 = k_1[A][B].$$

Similarly, the velocity of the reverse reaction between C and D is given by

$$v_2 = k_2[C][D],$$

where k_2 is another constant. When the system is in equilibrium $v_1 = v_2$.

$$\therefore\ k_1[A][B] = k_2[C][D];$$

$$\therefore\ \frac{[C][D]}{[A][B]} = \frac{k_1}{k_2} = K. \quad \text{.....(1)}$$

The constant K is known as the **equilibrium-constant.** The law of mass action therefore leads to the conclusion that:

At the equilibrium-point the product of the concentrations of the substances on the right-hand side of the equation divided by the product of the concentrations of the substances on the left-hand side of the equation is a constant.

Thus by applying the law of mass action to the equilibrium of hydrogen iodide with hydrogen and iodine, we find that

$$HI + HI \rightleftharpoons H_2 + I_2,$$

$$K = \frac{[H_2][I_2]}{[HI]^2}. \quad \text{.....(2)}$$

By writing the left-hand side as HI + HI instead of 2HI, we see that the concentration of HI must be squared in the expression for the equilibrium-constant. In general, if n molecules of a substance take part in a reaction, the corresponding term in the equilibrium-constant is the concentration of this substance raised to the nth power.

Verification of the law of mass action.—In applying the law of mass action to a chemical equilibrium, there is no need for the reacting substances or the products to be present in equivalent amounts. Excess of any of them may be present and the relation should still be true. We can therefore test the law of mass action experimentally by analysing a number of equilibrium-mixtures, containing varying amounts of A, B, C, and D, in order to determine whether the concentrations of these

substances in the various mixtures give identical values of K. The determination of the composition of an equilibrium-mixture is, however, rendered very difficult by the mobile character of the materials to be analysed. Thus, if one of the components is removed by any of the ordinary analytical operations, *e.g.*, by titration or precipitation, the original condition of equilibrium will be destroyed, and a further quantity of the missing component will be formed, in the endeavour to restore the equilibrium of the system. Thus, it is well known that iodine combines with potassium iodide to form a tri-iodide, as expressed by the reversible equation

$$KI + I_2 \rightleftharpoons KI_3.$$

The amount of free iodine cannot, however, be determined by titration with sodium thiosulphate, since as soon as some free iodine is removed, the tri-iodide dissociates, and gives more iodine. In this case an end point is obtained only when *all* the iodine, both free and combined, has been used up. This behaviour is characteristic of all equilibria in which the forward and back reactions proceed with considerable speed. Special methods have, therefore, to be adopted in the investigation of systems of this type (see p. 270).

In other cases, a chemical change which proceeds to equilibrium rapidly at high temperatures is found to take place only slowly at ordinary temperatures. It is therefore possible by rapid cooling to fix the condition of equilibrium which prevails at the higher temperature, just as the high temperature form of steel can be fixed by "quenching" a piece of the hot metal in cold water. Thus Bodenstein investigated the equilibrium of hydrogen iodide with hydrogen and iodine by sealing up known amounts of the reacting substances in small glass bulbs, which were heated at a given temperature for a sufficient time to ensure that equilibrium was established; the bulbs were then cooled rapidly to air temperature, opened, and the contents analysed.

Consider the equation

$$2HI \rightleftharpoons H_2 + I_2.$$
$$2x \quad a-x \quad b-x.$$

If we start with a gram-molecules of hydrogen, and b gram-

molecules of iodine in a volume V and $2x$ gram-molecules of hydriodic acid are formed, then at equilibrium

$$[H_2] = \frac{a-x}{V}, \quad [I_2] = \frac{b-x}{V} \quad \text{and} \quad [HI] = \frac{2x}{V};$$

$$\therefore K = \frac{[H_2][I_2]}{[HI]^2} = \frac{(a-x)(b-x)}{4x^2}. \quad \ldots\ldots\ldots\ldots(3)$$

Note that in this case the term V cancels out from the numerator and denominator, and does not appear in the function which determines the value of K. This particular equilibrium is therefore not affected by changes in the volume occupied by the reacting gases, and is therefore *independent of the pressure.* Bodenstein verified this conclusion by filling bulbs at pressures above and below atmospheric pressure, when he found that the same equilibrium was reached in each case.

Equation 3 was then tested by sealing up different quantities of hydrogen and iodine and estimating the amount of hydrogen iodide produced after heating until equilibrium was attained. The results of these experiments are given in Table 54, where the quantities of each gas are given in cubic centimetres at N.T.P., and are therefore proportional to the number of gram-molecules present in a given quantity of the equilibrium mixture. The values of K in the last column are approximately constant.

TABLE 54. DECOMPOSITION OF HYDROGEN IODIDE AT 356°. (Bodenstein.)

Initial concentrations.		Equilibrium concentrations.				Equilibrium constant.
H_2 (a)	I_2 (b)	H_2 $(a-x)$	I_2 $(b-x)$	HI $(2x)$	HI (calc.) $(2x)$	K
6·63	2·59	4·12	0·08	5·02	4·98	0·013
6·22	5·71	1·42	0·90	9·60	9·55	0·014
6·41	10·40	0·57	4·56	11·68	11·88	0·019
6·51	22·29	0·17	15·95	12·68	12·71	0·017

Since in the first experiment only 0·08 c.c. of iodine remained, and in the last experiment only 0·17 c.c. of hydrogen, it is evident that a very small error in determining these quantities will have a large effect on the value of K. It is better, therefore, to test the law of mass action by predicting the concentration of

hydrogen iodide, using a value of K deduced from observations in the middle region. Bodenstein found that when $a=1$ and $b=1$ (*i.e.* with equivalent amounts of hydrogen and iodine at the start, or with pure hydrogen iodide as initial substance)

$$x=0{\cdot}8036 \text{ at } 356°.$$

Hence $$K=\frac{(1-0{\cdot}8036)^2}{4\times 0{\cdot}8036^2}=0{\cdot}01494.$$

Putting this value into equation (3), we have

$$\frac{(a-x)(b-x)}{4x^2}=0{\cdot}01494;$$

expanding, this becomes

$$0{\cdot}9402x^2-(a+b)x+ab=0,$$

from which $$2x=\frac{a+b-\sqrt{(a+b)^2-3{\cdot}761ab}}{0{\cdot}9402}. \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

(If a $+^{ve}$ sign is used before the square root, $2x$ is greater than $a+b$, so that this solution of the quadratic has no significance). The values calculated by means of equation (4) are given in the sixth column of Table 54. It will be seen that there is good agreement between the calculated figures and the amount of hydrogen iodide found by experiment.

Table 54 illustrates also the effect of adding an excess of one component to an equilibrium mixture. In the first experiment hydrogen is present in excess and nearly all the iodine is converted into hydriodic acid. Similarly, in the last experiment, where iodine is in excess, nearly all the hydrogen is used up.

Influence of pressure and temperature on chemical equilibrium.—The effect of changes of pressure and temperature can be predicted qualitatively by making use of **Le Chatelier's theorem.** This may be stated as follows:

> *If one of the conditions of a system in equilibrium be altered, the system will adjust itself in such a direction as partially to neutralise the change in condition.*

Thus if a solid *contracts* on fusion, as ice does when it melts to water, a relief of compression will result from fusion; the solid therefore melts more easily when compressed, and the melting point is *lowered* by increase of pressure; but if the solid *expands* on fusion, a relief from compression will result from the solidifica-

tion of the liquid, and the melting point will be raised by increase of pressure (compare Chap. IV., p. 99). The principal conditions which affect a chemical equilibrium and are usually discussed in this connection are temperature and pressure.

(*a*) *Influence of temperature.*—Suppose that U calories of heat are *evolved* in the balanced action

$$A + B \rightleftarrows C + D + U \text{ cal.},$$

when the change proceeds completely from left to right, and conversely that U calories are *absorbed* when the reverse action occurs. In a system in equilibrium at $T°$ there will be certain equilibrium-proportions of A, B, C and D. If the temperature is now raised to $T + 1°$, then, according to Le Chatelier's theorem, an adjustment of the system must occur which absorbs heat and tends to lower the temperature. This can only be brought about by a change of some C and D into A and B. That is, as the temperature is raised, the amount of C and D in the equilibrium-mixture diminishes, and that of A and B increases. Generally, the theorem predicts that *as the temperature rises there will be an increase in the equilibrium-concentration of the substances which are formed by an endothermic change.*

Le Chatelier's Theorem gives only a qualitative indication of the direction in which an equilibrium is displaced by rise in temperature. A quantitative relation between the heat of the reaction and the change in the equilibrium-constant has been obtained by van't Hoff (p. 240), and is expressed by the equation

$$\frac{d \log_e K}{dT} = -\frac{U}{RT^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where K is the equilibrium-constant, U the heat evolved when the reaction goes completely from left to right, and T the absolute temperature. This equation holds strictly only for small concentrations and over very small intervals of temperature. If, however, we assume that U does not change appreciably between two temperatures T_1 and T_2, which are not too widely separated, then this equation can be integrated to give the relation :

$$\log_e \frac{K_1}{K_2} = \frac{U}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right),$$

and since $\log_e x = 2{\cdot}303 \log_{10} x$ and $R = 1{\cdot}985$ cal., we have

$$\log_{10} \frac{K_1}{K_2} = \frac{U}{4{\cdot}57} \left(\frac{T_2 - T_1}{T_1 T_2} \right). \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Equation (6) may be used to calculate U from the values K_1 and K_2 found for the equilibrium-constant at temperatures T_1 and T_2.

As an example we may take some of the data obtained by Bodenstein for the decomposition of hydrogen iodide which are contained in Table 55.

TABLE 55. DISSOCIATION OF HYDROGEN IODIDE. CHANGE OF EQUILIBRIUM-CONSTANT WITH TEMPERATURE.

$t°$ C.	$T°$ abs.	K.	U
508	781	0·02515	
			−4053 cal.
443	716	0·01984	
			−3160 ,,
393	666	0·01679	
			−2619 ,,
356	629	0·01494	
			−2220 ,,
283	556	0·01183	

The calculation is carried out as follows. For the first pair of data :

$$\log_{10} \frac{K_1}{K_2} = \log_{10} \frac{0{\cdot}02515}{0{\cdot}01984} = 0{\cdot}1031.$$

Then from equation (6) the *heat of dissociation* is

$$U = \frac{4{\cdot}57 \times 0{\cdot}1031 \times 781 \times 716}{-65} = -4053 \text{ cal.}$$

This value for the heat-change U may be contrasted with the maximum work A at 508° C. for the same reaction which is given by the equation $A = RT \log_e K$,

$$= 1{\cdot}985 \times (508 + 273) \times 2{\cdot}303 \log_{10} 0{\cdot}02515$$

$$= 5710 \text{ calories, since } K = 0{\cdot}02515 \text{ at this temperature.}$$

The value of U decreases as the temperature falls, and undergoes a reversal of sign before reaching atmospheric temperatures, at which the dissociation is exothermic. The assumption which

was used in obtaining Equation 6, that the heat of the reaction is independent of temperature, is therefore not strictly true, and the values of U in Table 55 must be taken as average values between the two temperatures for which they are calculated.

(*b*) *Influence of pressure.*—The influence of pressure on a chemical equilibrium can also be predicted by Le Chatelier's theorem. Consider a reaction of the type

$$A + B \rightleftharpoons C.$$

Since the number of molecules on the right-hand side of the equation is less than the number on the left-hand side, a change of $A + B$ into C will produce a diminution in volume; or, if the system is kept at constant volume, it will cause a fall in pressure. Hence it follows from Le Chatelier's theorem that the equilibrium-mixture will contain a larger amount of C at higher pressures than at lower pressures.

A chemical change of this type, which is of great industrial importance, is the synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

Although neither the formation nor the decomposition of ammonia can be effected at atmospheric temperatures, it is possible to attain to a condition of equilibrium fairly rapidly by passing a mixture of nitrogen and hydrogen over a suitable catalyst at a temperature of 500°. Table 56 shows some values of the equilibrium percentage of ammonia as found by Haber.

TABLE 56. FORMATION AND DISSOCIATION OF AMMONIA.

Temperature.	Equilibrium percentage of NH_3 at		
	1 atm.	100 atm.	200 atm.
550° C.	0·0769	6·7	11·9
650	0·0321	3·02	5·71
750	0·0159	1·54	2·99
850	0·0089	0·874	1·68
950	0·0055	0·542	1·07

It will be seen that much larger amounts of ammonia are formed at higher pressures. Moreover, the rapid fall in the

equilibrium-concentration of ammonia as the temperature rises shows that a large amount of heat is evolved in its formation. The successful application of this reaction to the fixation of atmospheric nitrogen depends upon the use of high pressures, and of a catalyst which will bring a mixture of gases to the equilibrium-point in a reasonable time and at as low a temperature as possible.

The effect of pressure on an equilibrium in a gaseous system can also be predicted quantitatively. In the equation

$$\underset{1-x}{N_2} + \underset{3(1-x)}{3H_2} \rightleftarrows \underset{2x}{2NH_3},$$

if we start with one gram-molecule of nitrogen and three of hydrogen and $2x$ gram-molecules of ammonia are formed, then the amounts of nitrogen, hydrogen, and ammonia in the equilibrium-mixture will be $(1-x)$, $3(1-x)$, and $2x$ respectively. If the total pressure at equilibrium is P, then the partial pressure of a particular molecule is proportional to the ratio between the number of molecules of that kind and the total number of molecules. This total number is obviously

$$1-x+3-3x+2x=4-2x.$$

Hence

$$p_{N_2}=P\frac{1-x}{4-2x}$$

$$p_{H_2}=P\frac{3(1-x)}{4-2x}$$

$$p_{NH_3}=P\frac{2x}{4-2x}.$$

Since partial pressures are a measure of the concentration:

$$K=\frac{p^2_{NH_3}}{p_{N_2}p^3_{H_2}}=\frac{P^2\dfrac{4x^2}{(4-2x)^2}}{P\dfrac{1-x}{4-2x}\cdot P^3\dfrac{27(1-x)^3}{(4-2x)^3}}$$

$$K=\frac{4x^2(4-2x)^2}{P^2 27(1-x)^4}.$$

The equilibrium-constant therefore involves the *inverse square*

of the pressure. If x is small compared with unity, this equation can be simplified to

$$\frac{64x^2}{27} = KP^2,$$

so that x is proportional to P. It will be seen from Table 56 that the equilibrium-concentration of ammonia at 200 atmospheres is roughly double that at 100 atmospheres.

Dissociation of nitrogen peroxide.—Another example of a gaseous equilibrium to which the law of mass-action has been applied is the dissociation of nitrogen peroxide :

$$\underset{1-x}{N_2O_4} \rightleftharpoons \underset{2x}{2NO_2}.$$

This reaction can be followed by measurements of the vapour-density, which varies from 23 for pure NO_2 to 46 for pure N_2O_4, when the density of hydrogen is taken as unity.

If we start with one gram-molecule of N_2O_4, and by partial dissociation produce from it $2x$ gram-molecules of NO_2, then the one gram-molecule of N_2O_4 becomes

$$1 - x + 2x = 1 + x$$

gram-molecules of the equilibrium mixture. If, therefore, the pressure is kept constant at 1 atmosphere, the volume will increase in the ratio $1 : 1 + x$. Conversely, the vapour-density will be lowered, so that

$$d = \frac{46}{1+x},$$

whence

$$x = \frac{46 - d}{d}.$$

Table 57 gives the densities of nitrogen peroxide as found by Deville and Troost. It will be seen that at 26·7°, 20·1 per cent. of the compound has dissociated, and that as the temperature rises the dissociation increases rapidly.

TABLE 57. DISSOCIATION OF N_2O_4.
(Deville and Troost.)

t.	$d(H_2=1)$.	x.	K.	U.
26·7°	38·3	0·201	0·168	
60·2	30·65	0·501	1·34	−9960 cal.
100·1	25·7	0·790	6·64	

This rapid increase shows that the dissociation is accompanied by a large absorption of heat, which can be calculated as follows. At the working-pressure of one atmosphere

$$p_{N_2O_4} = \frac{1-x}{1+x} \quad \text{and} \quad p_{NO_2} = \frac{2x}{1+x};$$

$$\therefore \quad K = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{4x^2}{(1+x)(1-x)} = \frac{4x^2}{1-x^2}.$$

The values of K in the fourth column have been calculated by this formula and from them, by equation 6, the value of U in the last column. The first observation at 26·7° is not used, since it is so near the boiling-point of the liquid (22°) that the gas laws will not hold and the density is probably too high.

Dissociation of phosphorus pentachloride.—Another illustration of the application of the law of mass-action is found in the dissociation of phosphorus pentachloride. Observations of the vapour-density of this substance show that it is largely split up into an equilibrium-mixture of phosphorus trichloride and chlorine according to the equation :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

The application of Le Chatelier's theorem shows that a diminution in pressure must bring about a greater degree of dissociation.

The equation for this dissociation is

$$\begin{array}{ccccc} PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2. \\ 1-x & & x & & x \end{array}$$

If we start with one gram-molecule of PCl_5, and if a fraction x is dissociated, then the number of gram-molecules in the equilibrium-mixture is $(1-x)+x+x=1+x$. The predicted density for PCl_5 is 104·2($H_2=1$), hence the density of the equilibrium-mixture is given by

$$d = \frac{104{\cdot}2}{1+x},$$

whence

$$x = \frac{104{\cdot}2 - d}{d}.$$

Table 58 gives the vapour-densities found by Cahours for this substance together with the corresponding values of x, K and U.

These have been calculated in the manner described above for N_2O_4. The values of U are only rough approximations because the observations of density are not sufficiently accurate. They show, however, that the dissociation of PCl_5 is accompanied by an absorption of heat of about 15,000 calories.

TABLE 58. DISSOCIATION OF PHOSPHORUS PENTACHLORIDE. (Cahours.)

t.	$d(H_2=1)$.	x.	K	U cal.
182	73·5	0·417	0·21	
				− 9050
200	70·2	0·485	0·31	
				−16000
230	62·2	0·674	0·85	
				−19300
250	57·9	0·800	1·78	
				−14200
274	55·6	0·874	3·24	

The law of mass-action requires that a dissociation of this type shall be repressed by the presence of an excess of one of the products of dissociation. This has been verified by Wurtz, who used an apparatus of the Victor Meyer type and determined the vapour density of PCl_5 in an atmosphere of PCl_3. He obtained values ranging from 98 to 107 (theory gives 104·2, $H_2=1$), which proves that very little dissociation occurs under these conditions.

Conversely, since each molecule of phosphorus pentachloride produces two molecules when dissociated, Le Chatelier's theorem tells us that the degree of dissociation must *increase* as the pressure on the gas is diminished. The same effect may be produced by dilution with an inert gas, *e.g.* nitrogen, since it is the concentration or partial pressure of the reacting substances which determines the composition of the equilibrium mixture.

Homogeneous equilibrium in liquids.—The examples of chemical equilibrium discussed above have been confined to gaseous systems, but similar equilibria can also occur in liquids. An example of this type is given by the interaction between ethyl alcohol and acetic acid to form ethyl acetate and water (Expt. 21, p. 247).

$$\underset{a-x}{C_2H_5\cdot OH} + \underset{b-x}{CH_3\cdot CO\cdot OH} \rightleftarrows \underset{x}{CH_3\cdot CO\cdot OC_2H_5} + \underset{c+x}{H_2O}.$$

This equilibrium was investigated by Berthelot and St. Gilles in 1862. If we start with a molecules of alcohol, b of acid, and c of water in a volume V, then if x molecules of ester are formed at equilibrium :

$$[C_2H_5 \cdot OH] = \frac{a-x}{V}, \quad [CH_3 \cdot CO \cdot OH] = \frac{b-x}{V},$$

$$[CH_3 \cdot CO \cdot O \cdot C_2H_5] = \frac{x}{V}, \qquad [H_2O] = \frac{c+x}{V},$$

and $$K = \frac{[CH_3 \cdot CO \cdot O \cdot C_2H_5][H_2O]}{[CH_3 \cdot CO \cdot OH][C_2H_5 \cdot OH]} = \frac{x(c+x)}{(a-x)(b-x)}.$$

Starting with pure acid and alcohol (*i.e.* $a=1$, $b=1$, $c=0$), it was found that $x=0{\cdot}667$, from which

$$K = \frac{0{\cdot}667^2}{0{\cdot}333^2} = 4{\cdot}00.$$

Table 59 gives some of the data obtained by Berthelot and St. Gilles for the amount of ester formed when a gram-molecules of alcohol were allowed to react with 1 gram-molecule of acid. In this case $b=1$, $c=0$, so that

$$K = 4{\cdot}00 = \frac{x^2}{(a-x)(1-x)}$$

Multiplying out $$3x^2 - 4(a+1)x + 4a = 0$$

from which $$x = \tfrac{2}{3}(1 + a - \sqrt{1 - a + a^2}). \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

TABLE 59. FORMATION OF ETHYL ACETATE FROM ALCOHOL AND ACETIC ACID.

(Berthelot and St. Gilles.)

Mols. of acid.	Mols. of alcohol.	Mols. of ester.	
b.	a	x (obs.).	x (calc.).
1·00	0·08	0·078	0·078
1·00	0·28	0·226	0·232
1·00	0·33	0·293	0·311
1·00	0·50	0·414	0·423
1·00	0·67	0·519	0·528
1·00	1·00	0·665	0·667
1·00	1·50	0·819	0·785
1·00	2·00	0·858	0·845

In Table 59, the last column gives the values of x calculated by equation 7. It will be seen that the agreement between the

observed and calculated values is good. This is somewhat remarkable, since the system is very far from a dilute solution, and some deviation from the theoretical values might have been expected.

This reaction occurs without appreciable evolution or absorption of heat. By Le Chatelier's theorem it follows that the composition of the equilibrium mixture will not be altered by rise in temperature and this has been verified by experiment.

Equilibrium in heterogeneous systems.—The reactions so far considered all take place in homogeneous gaseous or liquid systems. An example of a heterogeneous reaction is found in the dissociation of calcium carbonate

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

which involves two solids and a gas. At first sight it is difficult to give a definite meaning to the " active mass " of the solid phases. We may, however, suppose that equilibrium is attained in the gaseous phase when

$$\frac{p_{CaO} \times p_{CO_2}}{p_{CaCO_3}} = K,$$

where p_{CaO} and p_{CaCO_3} represent the very small vapour-pressures of solid lime and calcium carbonate. But at constant temperature these vapour-pressures are independent of the amount of lime or calcium carbonate present, so that

$$p_{CO_2} = K \frac{p_{CaCO_3}}{p_{CaO}} = \text{constant.}$$

The system is therefore only in equilibrium at a fixed temperature when a definite pressure of carbon dioxide is present. This is exactly the result that was obtained previously by the application of the Phase Rule (p. 156).

This example illustrates a general rule which is used in applying the law of mass-action to heterogeneous equilibria, namely *the " active mass " of a solid is constant and independent of the amount present.*

From this example we see that the dissociation-pressure of the system is proportional to the equilibrium-constant. We may, therefore, apply the van't Hoff isochore (p. 239) to calculate the

heat of dissociation from the dissociation-pressures at two temperatures, thus,

$$\log_{10}\frac{p_1}{p_2}=\frac{U}{4{\cdot}57}\left\{\frac{1}{T_1}-\frac{1}{T_2}\right\},$$

where p_1 and p_2 are the dissociation-pressures at temperatures T_1 and T_2, *e.g.* 57 mm. at 740° and 136 mm. at 787°, as found by Johnston. Inserting these data in the preceding equation, we have $\log\frac{57}{136}=-\log_{10}\frac{136}{57}=-0{\cdot}3776$, $T_1=1013$, $T_2=1060$;

$$\therefore\ U=-\frac{4{\cdot}57\log_{10}\frac{p_1}{p_2}\,T_1T_2}{T_2-T_1}$$

$$=-\frac{4{\cdot}57\times0{\cdot}3776\times1013\times1060}{47}$$

$$=-39{,}400\text{ cal.}$$

Table 60 gives values found for the dissociation-pressure at other temperatures together with the heats of the reaction calculated from them. The mean value, 39,000, is in fair agreement with the value, **42,900** cal., found by Thomson for the action of carbon dioxide on lime in a calorimeter at atmospheric temperatures.

TABLE 60. DISSOCIATION-PRESSURE OF $CaCO_3$.
(Johnston.)

t.	*T.*	*p* (mm. Hg.).	$-U$.
740	1013	57	39,400 cal.
787	1060	136	37,500 ,,
841	1114	323	40,200 ,,
882	1155	616	
			Mean = 39,000 ,,

The dissociation of salt hydrates (see p. 152) and of compounds of ammonia with metallic chlorides, *e.g.* $AgCl\cdot3NH_3$, $CaCl_2\cdot8NH_3$ are other examples of actions of this type in which measurements of the equilibrium-pressure at different temperatures can be used to calculate the heat of the reaction.

It is possible also to regard the vapour-pressure of a pure liquid as a measure of the equilibrium-constant in the reaction

$$\text{liquid}\rightleftharpoons\text{vapour}$$

and to calculate the latent heat of evaporation from the vapour-pressure at two temperatures (cf. Chap. III, p. 56). Thus water at 99° has a vapour-pressure of 733·24 mm. and at 100° 760·00 mm. If we now write $p_1 = 733{\cdot}24$, $p_2 = 760{\cdot}00$ and $T_2 - T_1 = 1$, we find

$$\log_{10} \frac{p_1}{p_2} = -0{\cdot}0155\ ;$$

$$\therefore\ U = -\frac{4{\cdot}57 \times 0{\cdot}0155 \times 372 \times 373}{1}$$

$$= -9826 \text{ cal./gram mol.}$$

$$= -546 \text{ cal./gram}$$

in good agreement with the numerical value found directly for the latent heat of vaporisation, namely, 538 cal./gram.

Activity of dissolved substances.—We have seen that the simple laws of mass-action can be verified by precise measurements of the conditions of equilibrium in reversible gas-reactions, such as

$$H_2 + I_2 \rightleftharpoons 2HI \text{ or } PCl_3 + Cl_2 \rightleftharpoons PCl_5.$$

The conditions of equilibrium are modified profoundly when the action is studied in a liquid phase, *e.g.* in presence of a solvent, instead of in a gaseous phase; but it has been suggested by various writers that the same laws and the same constants should be applicable if, instead of recording the total concentrations of the various components in the solution, we could make use of their **activities**, *i.e.* of quantities which are directly proportional to the true "active mass" of each component. For example, if one component of an equilibrium-mixture forms a hydrate, and if it is only the unhydrated material that enters directly into the interaction, we ought obviously to use the concentration of the free molecules in our equations and not the aggregate concentration of free and combined molecules. This conception of "activity" is commonly expressed by means of equations such as

$$a = cf,$$

where a is the **activity**,

c is the total concentration,

and f is the **activity-coefficient**,

i.e. the fraction of the total number of molecules which is directly available for the reaction in question. Thus, if the conception of activity is valid, we should obtain a fixed value for the equilibrium-constant in an action, such as

$$A + B \rightleftharpoons C + D$$

by writing $K'a_1a_2 = a_3a_4$,

instead of $Kc_1c_2 = c_3c_4$,

where $c_1c_2c_3c_4$ are the concentrations, and $a_1a_2a_3a_4$ are the activities of the four components in any given solvent.

Activities deduced from vapour-pressures and from solubilities.—(*a*) The simplest method of deducing activities depends on using the *vapour-pressures* of the various components of a given system in place of their *concentrations* in the liquid phase. Thus, we may consider an action $A + B \rightleftharpoons C + D$ as taking place (i) in a vapour-phase and (ii) in a solvent. If, then, we know the equilibrium-constant for the vapour-reaction, we can calculate the equilibrium-constant in the liquid from the absorption-coefficients of the various vapours (p. 130). Thus, if c_1, c_2, c_3, c_4, and C_1, C_2, C_3, C_4, are the concentrations in the vapour and in the liquid respectively, and q_1, q_2, q_3, q_4, are the absorption-coefficients

$$K = \frac{C_3C_4}{C_1C_2} = \frac{c_3q_3c_4q_4}{c_1q_1c_2q_2} = \frac{c_3c_4}{c_1c_2} \times \frac{q_3q_4}{q_1q_2} = k\frac{q_3q_4}{q_1q_2},$$

where k and K are the equilibrium-constants for the vapour and liquid respectively.

Again, if we use the vapour-pressure of each component of the liquid as a measure of its effective concentration or "activity," the equilibrium-constant must have the same value (namely, its value in the gas phase), whatever the actual concentrations in the liquid phase may be. This follows at once from the fact that the partial vapour-pressures p_1, p_2, p_3, p_4, of the various components of the liquid are proportional to their concentrations c_1, c_2, c_3, c_4, in the vapour, so that

$$K \text{ (for the liquid)} = \frac{p_3p_4}{p_1p_2} = \frac{c_3c_4}{c_1c_2} = k \text{ (for the vapour)}.$$

Thus, when a chemical change which depends on the action of

water is carried out in a solution of a salt, we may correct for the influence of the salt by replacing the concentration of the water in gram-molecules per litre by a function depending on its vapour-pressure or "fugacity," which we may regard as a measure of its activity. Similarly, in a mixture of alcohol and water, the activity of the molecules of water may be expected to be proportional to their partial vapour-pressure. Only in ideal solutions, however, which obey Raoult's Law perfectly (p. 184), will the active masses remain proportional to the concentrations.

(*b*) A second method of deducing a numerical value for the activity of a dissolved substance depends on the fact that the active mass of a solid is constant. Van't Hoff postulated that the active mass of a solid must be identical with the active mass of the substance *in a saturated solution*, whatever may be the nature of the solvent. If, therefore, we measure the concentration of a given component, not in gram-molecules per litre, but as a fraction of its concentration of a saturated solution in the given solvent, this fraction may be taken as a measure of its activity, since it is a definite fraction of the fixed activity of the solid.

This relationship between solubility and activity can also be deduced in a qualitative way from the view that the increased solubility of a solid in a good solvent depends on a mutual attraction between solvent and solute, since this attraction must produce a proportional decrease in the activity of the latter. In the simple case of an isomeric change

$$A \rightleftharpoons B,$$

if l_A and l_B are the solubilities of the isomerides, c_A and c_B their concentrations in the liquid, p_A and p_B their partial vapour-pressures, and a_A and a_B their activities, the equilibrium in the vapour may be represented by $p_A = Kp_B$. Van't Hoff then supposes that

$$\frac{a_A}{a_B} = \frac{c_A/l_A}{c_B/l_B} = G.$$

The ratio G should be independent of the solvent. The data used by Dimroth to test this law are set out in Table 61.

TABLE 61. SOLUBILITY AND EQUILIBRIUM PROPORTIONS OF ISOMERIC FORMS OF BENZOYLCAMPHOR AT 0°.

Solvent.	Equilibrium ratio. C_A/C_B	Solubility ratio. l_A/l_B.	Ratio.
	Enol . Ketone.	Enol : Ketone.	G.
Ether - -	87·2 : 12·8 = 6·81	12·86 : 2·012 = 6·39	1·06
Ethyl acetate	66·5 : 33·5 = 1·98	12·79 : 7·05 = 1·81	1·09
Ethyl alcohol	62·6 : 37·4 = 1·67	2·06 : 1·31 = 1·57	1·06
Methyl alcohol	46·5 : 53·5 = 0·869	1·49 : 1·99 = 0·748	1·15
Acetone -	46·0 : 54·0 = 0·852	11·69 : 14·53 = 0·80	1·06

It will be seen that whilst c_A/c_B varies between 6·81 and 0·852, and l_A/l_B varies between 6·39 and 0·748, the ratio $G = \frac{c_A}{c_B} \div \frac{l_A}{l_B}$ varies only from 1·06 to 1·15.

(*c*) The two preceding methods of measuring activity have been applied together to the decomposition of N-chloro-acetanilide by hydrogen chloride.

$$C_6H_5 \cdot NCl \cdot CO \cdot CH_3 + HCl \rightleftharpoons C_6H_5 \cdot NH \cdot COCH_3 + Cl_2$$

in presence of an agent (such as phenol) which will absorb all the chlorine as fast as it is set free. This action has been shown to proceed with a velocity which depends on (i) the activity of the chloro-amide *as measured by its solubility*, and (ii) the activity of the hydrogen chloride, *as measured by its vapour-pressure*, although in neither case can the velocity be predicted correctly by applying the laws of mass-action to the uncorrected concentrations. Incidentally, these observations show that the chlorine is derived (to the extent of 50 per cent.) from the *molecules* and not from the *ions* of the acid ; in other cases, however, it is the ions and not the molecules that take part in chemical change.

In general, it is necessary to find out by experiment in each individual case the particular method of deducing the " activity" of a substance which fits in best with the law of mass-action, since the whole conception of activity rests upon the necessity of finding some function of the concentration by which apparent failures of the simple weight law of mass-action can be corrected and set right.

22. Partition-coefficients.

i. Partition-coefficient of iodine between benzene and water.—Place 100 c.c. of water and 25 c.c. of benzene in a stoppered bottle of about 600 c.c. capacity, add about 1·5 grams of iodine and shake vigorously until all is dissolved. Immerse the bottle in a large vessel of water at air-temperature to serve as a thermostat. Shake well occasionally, and after 15 minutes allow the liquids to separate. Pipette off into separate flasks 5 c.c. of the layer of benzene and 25 c.c. of the layer of water and estimate the amount of iodine in each by titration with sodium thiosulphate. After shaking for another ten minutes, repeat the determination by withdrawing further liquid from the bottle. If the two results agree, equilibrium has been reached.

Repeat the whole experiment using about 1·0 gm., and 0·5 gm. of iodine. From your results calculate the partition-coefficient of iodine between benzene and water.

ii. Dissociation of potassium tri-iodide. This experiment is carried out in exactly the same way as the previous one, but with a solution of potassium iodide of $\frac{N}{20}$ strength in place of water. This method of calculating the results is given on p. 270. The equilibrium-constant obtained varies with temperature a little; at 13·5° it should be about 0·0010 and at 25°, 0·0013.

Partition-coefficients.—When iodine is added to a mixture of benzene and water, some of it is dissolved in each solvent. After shaking, the system is found to reach an equilibrium in which iodine is divided in a definite manner between the two solvents. It will be found that when the amount of iodine is varied the ratio

$$\frac{C_2}{C_1} = \frac{\textit{concentration of iodine in benzene}}{\textit{concentration of iodine in water}}$$

remains constant.

This behaviour is closely parallel to that of a gas dissolving in water under pressure, where according to Henry's Law

$$\textit{concentration of gas in solution} = K \times \textit{pressure}.$$

But since the pressure is a measure of the concentration of the gas

$$\frac{\textit{concentration of gas in solution}}{\textit{concentration in gaseous phase}} = K,$$

which is exactly similar in form to

$$\frac{\textit{concentration in first liquid}}{\textit{concentration in second liquid}} = K.$$

The latter constant is termed the **partition-coefficient.** Expt. 22, i. gives details for the study of the system benzene-water-iodine, whilst Table 62 gives some figures for the partition of mercuric bromide between water and benzene.

TABLE 62. PARTITION OF MERCURIC BROMIDE BETWEEN WATER AND BENZENE

Concentration in water.	Concentration in benzene.	Partition-coefficient.
C_1	C_2	C_1/C_2
0·00320	0·00353	0·90
0·00634	0·00715	0·89
0·01147	0 01303	0·88
0·0170	0·0194	0·88

TABLE 63. PARTITION OF ACETIC ACID BETWEEN CARBON TETRACHLORIDE AND WATER AT 25°.

Concentration in CCl_4.	Concentration in water.	Partition-coefficient.	
C_1	C_2	C_1/C_2	$\sqrt{C_1}/C_2$
0·0096	0·684	0·0140	0·143
0·0187	1·021	0·0183	0·132
0·0460	1·691	0·0266	0·127

The partition-coefficient is only constant when the dissolved substance has the same molecular weight in both solvents. If this is not the case, then the partition-coefficient varies with the concentration of the solutions. Thus Table 63 shows that the ratio C_1/C_2 of the equilibrium concentrations of acetic acid in carbon tetrachloride and water is not constant, but increases rapidly as the concentration increases. It is known, however, from the elevation of the boiling-point of the solutions, that acetic acid has a normal molecular weight in water, but twice the normal molecular weight in carbon tetrachloride. In the latter solvent there will therefore be an equilibrium

$$(CH_3 \cdot COOH)_2 \rightleftarrows 2CH_3 \cdot COOH.$$
$$(1-\alpha)c \qquad\qquad 2\alpha c.$$

If a small fraction α of the double molecules is dissociated into single molecules, then by the law of mass-action

$$\frac{4\alpha^2c^2}{(1-\alpha)c}=K \quad \text{or} \quad \alpha^2=\frac{K(1-\alpha)}{4c}.$$

If α is small, $1-\alpha$ may be taken as 1 and α varies as $\frac{1}{\sqrt{c}}$. Hence the concentration of single molecules of acetic acid in the carbon tetrachloride is

$$\alpha c = \text{const.} \times c \times \frac{1}{\sqrt{c}}$$

$$= \text{constant} \times \sqrt{c}.$$

Thus, if the partition law holds for the *single* molecules in both liquids, we should expect $\sqrt{c_1}/c_2$ to be constant. The last column of Table 63 shows that this is nearly true.

The partition of iodine between carbon disulphide and aqueous solutions has been used in the same way to test the application of the law of mass-action to the equilibrium

$$KI_3 \rightleftarrows KI + I_2.$$

As stated before (p. 251), titration of a solution of iodine in potassium iodide with thiosulphate gives the *total* iodine both free as I_2 and combined as KI_3, since, as soon as some iodine is removed, the equilibrium is displaced towards the right, and a fresh amount of iodine is liberated from the tri-iodide. If, however, the solution is shaken with carbon disulphide (which dissolves iodine, but not potassium iodide or potassium tri-iodide), then the iodine dissolved in the disulphide is in equilibrium with the *free* iodine in the solution.

If then the concentration of iodine in the carbon disulphide is determined, and the partition-coefficient of iodine between water and carbon disulphide is known, the concentration of free iodine in the equilibrium mixture can be calculated. Thus, Dawson found that the partition-coefficient $\frac{c_{CS_2}}{c_{H_2O}}$ for iodine was 625. Carbon disulphide was then shaken with a solution containing 125 millimols. of potassium iodide and a quantity of iodine. When equilibrium was reached, portions of the aqueous and disulphide layers were titrated with sodium thiosulphate. The

aqueous solution contained 4·959 millimols. of iodine, both free and combined. The disulphide layer contained 26·19 millimols. of iodine per litre. Dividing this by the partition-coefficient 625, the *free* iodine in the aqueous layer must have had a concentration of 0·0419 millimols. per litre. Subtracting this from the *total* iodine we have, concentration of combined iodine, $[KI_3] = 4·917$ millimols. per litre. The free KI is then obtained by subtracting the concentration $[KI_3]$ from the original concentration, so that

$$[KI] = 125·0 - 4·9 = 120·1 \text{ millimols. per litre.}$$

Expressing all the concentrations in gram-molecules per litre, we find

$$K = \frac{[KI][I_2]}{[KI_3]} = \frac{0·1201 \times 0·0000419}{0·004917} = 0·00102.$$

Table 64 gives a series of results for different amounts of iodine and shows that the law of mass-action holds, since K is constant. It is interesting to note that in these experiments, where the potassium iodide was in large excess, the degree of dissociation of KI_3 was very small, only about 1 per cent. of the iodine being present in the free state.

TABLE 64. DISSOCIATION OF KI_3 AT 13·5°.
(Dawson.)

Concentrations in millimols. per litre.

Initial KI.	Total Iodine.	Iodine in CS_2.	$[I_2]$.	$[KI_3]$	[KI]	$K = \frac{[KI][I_2]}{[KI_3]}$.
125·0	4·959	26·19	0·04190	4·917	120·1	0·00102
,,	8·992	49·98	0·07998	8·912	116·1	0·00104
,,	17·44	100·85	0·1613	17·28	107·7	0·00101
,,	28·32	189·6	0·3033	28·02	97·0	0·00105

QUESTIONS ON CHAPTER X.

1. The equilibrium-constant for the reaction between acetic acid and alcohol, forming ethyl acetate and water, at 25° C. is 4. Explain precisely what is meant by this statement. If 5 gram-molecules of acetic acid react with 1 gram-molecule of alcohol at 25° C as completely as possible, what will be the composition of the equilibrium mixture ? (Natural Science Schols., Oxford.)

2. Give an outline of the effect of temperature on chemical equilibrium and describe the experimental investigation of some actual case. (Trinity Coll., Senior Schol.)

3. Distinguish between decomposition and dissociation, giving examples of each. The vapour-density of phosphorus pentachloride was determined at 250° and was found to be 57·92. Calculate its degree of dissociation (P = 31, Cl = 35·5).
(Cambridge Schol.)

4. State Le Chatelier's Law. Discuss this law with respect to *either* (*a*) the union of nitrogen and hydrogen, *or* (*b*) the union of nitrogen and oxygen. (Cambridge Schol.)

5. Discuss the variation of vapour-pressure with composition in mixtures of two liquids, and explain the principles which underlie the process of fractional distillation.
Show from the principle of Le Chatelier that a mixture of minimum vapour-pressure must distil unchanged.
(Trinity College, Senior Schol.)

6. Reversible reactions between gases may be divided into two types according as the number of molecules is unaltered by dissociation or increased. Taking the reaction $2HI \rightleftharpoons I_2 + H_2$ as an example of the former type and the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ as an example of the latter, point out how these two types differ as regards the effect of physical conditions on the equilibrium.
(Downing College, Minor Schol.)

7. In what respects does thermal dissociation (such as in the dissociation of iodine vapour $I_2 \rightleftharpoons 2I$) resemble and in what respects does it differ from the ionic dissociation of an electrolyte ?
One litre of iodine vapour at 1092° C. and 760 mm. was found to weigh 2·25 gm. Calculate the proportion of monatomic molecules (I = 127). (Oxford Higher School Certificate.)

8. Discuss the behaviour of nitrogen peroxide when heated from −20° to 650° C. The density of the gaseous peroxide at 80° is 25·6 ($H_2 = 1$) ; what inferences can you draw from this fact ?
(Oxford Higher School Certificate.)

9. State exactly what you understand by the expression

$$FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl.$$

What is the effect of adding to the system (*a*) ammonium thiocyanate, (*b*) ammonium chloride. Give your reasons.
(London Higher School Certificate.)

10. What do you understand by a reversible reaction ? Illustrate your answer by reference to (*a*) the production of quicklime, and (*b*) the cause and removal of temporary hardness in water.
(Joint Matric. Board, Higher School Certificate.)

11. In a series of six experiments with hydrogen iodide 0·96 gram of the latter in each experiment was entirely converted into

vapour at the given temperatures and constant pressure and then quickly cooled. The amount of iodine liberated in each experiment was determined by titration with 0·1N sodium thiosulphate, and the volumes of the latter for corresponding temperatures were as follows :

250°	290°	330°	360°	400°	420°
13·25 c.c.	12·4 c.c.	12·0 c.c.	12·9 c.c.	14·6 c.c.	15·7 c.c.

Calculate the percentage of hydrogen iodide dissociated at each temperature and express your results in form of a graph. What conclusions do you draw from the form of the curve.
(Joint Matric. Board, Higher School Certificate.)

12. Write a short essay on chemical equilibrium with special reference to (*a*) the meaning of the term, (*b*) the factors which determine the condition of equilibrium. Give examples.
(Joint Matric. Board, Higher School Certificate.)

13. Give an account of the factors which are of essential importance in the reversible changes represented by

(*a*) $CaCO_3 \rightleftarrows CaO + CO_2$,

(*b*) $SbCl_3 + H_2O \rightleftarrows SbOCl + 2HCl$.

(Joint Matric. Board, Higher School Certificate.)

14. Explain exactly what is meant by the following equation :

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2.$$

Describe with all experimental details how you would prepare (i) oxygen, (ii) chlorine, making use of the reactions indicated by the above equation. (Bristol, Higher School Certificate.)

15. Dumas found the following values for the vapour-density of phosphorus pentachloride (H = 1) :

182°, 146·6; 200°, 140·0; 250°, 115·2; 300°, 104·8.

(P = 31, Cl = 35·5.)
How did he account for the progressive fall in density ; how can his explanation be confirmed experimentally ; and how can the fall be diminished or prevented ? (Inter. Sci., Sheffield.)

16. What is the principle of Le Chatelier ? Show how it may be applied to forecast the result of the following changes :

(*a*) Increase of pressure on the system ;

$$N_2 + 3H_2 \rightleftarrows 2NH_3.$$

(*b*) Increase of temperature on the reaction ;

$$I_2 + H_2 \rightleftarrows 2HI + Q.$$

(*c*) Increase of pressure on the melting-point of wax, given the information that solid wax will sink in molten wax.
(Inter. Sci., Sheffield.)

17. State the law of mass action. What applications of this law are made use of in qualitative analysis ? Why is ammonium chloride added to the ammonia before the precipitation of the hydroxides of iron, aluminium and chromium.

(Cambridge Schol.)

18. A saturated solution of iodine in water at 25° C. contains 0·34 gm. per litre. The partition-coefficient of iodine between a given solvent and water is 85·5. What will be the weight of iodine per litre contained in the solvent when it is in equilibrium with the saturated aqueous solution ? (Inter. Sci., Sheffield.)

CHAPTER XI.

VELOCITY OF CHEMICAL CHANGE.

23. Reactions of Zero Order.

A reaction of zero order.—In Chapter X. we discussed the application of the law of mass-action to chemical systems which are in equilibrium and deduced a formula for the equilibrium-constant by postulating equal velocities of the forward and back reactions. The law of mass-action can also be used to predict the velocity with which chemical changes proceed in the limiting case in which a reaction which goes completely from left to right, *e.g.*

$$H_2 + Cl_2 \rightarrow 2HCl.$$

In the photometer of Bunsen and Roscoe, hydrogen and chlorine are confined over water at constant pressure and combination takes place on exposure to light. The water dissolves the hydrogen chloride as fast as it is formed, and the speed of the reaction can therefore be determined by measuring the rate at which the volume of gas decreases. Under these conditions the *concentrations* of hydrogen and chlorine do not change as the reaction proceeds. The rate of formation of hydrogen chloride should therefore be given, according to the law of mass-action, by the expression $k[H_2][Cl_2]$, where k is a constant. Since $[H_2]$ and $[Cl_2]$ are constant, a constant rate of contraction should then be observed. This can be verified by experiment, since the amount of hydrochloric acid formed under a constant illumination and at constant pressure is proportional to the time, although it is not strictly proportional to the concentrations of hydrogen and chlorine. Reactions in which the concentrations of the reacting substances do not change as the reaction proceeds are said to **be reactions of zero order.**

24. Reactions of the First Order.

i. Transformation of N-chloroacetanilide into *p*-chloroacetanilide.—Dissolve about 9 grams of N-chloroacetanilide, $C_6H_5 \cdot NCl \cdot CO \cdot CH_3$ in 50 c.c. of 20 per cent. acetic acid, and place in a small corked flask in the thermostat at 25°. In a similar flask place 50 c.c. of normal hydrochloric acid, together with 5 grams of phenol (see p. 278). After 20 minutes, when the liquids have attained the temperature of the thermostat, mix the two solutions by pouring rapidly from one flask to the other and back again. Withdraw 5 c.c. of the mixture, and add it to 15 c.c. of 5 per cent. KI in a small flask. Note the time of withdrawal, and titrate the liberated iodine with $N/10$ thiosulphate. Withdraw further portions of the mixture at 15, 30, 45, 60, 90 and 120 minutes, and analyse in the same way. From your results calculate the velocity-constant of the isomeric change by means of the formula

$$k = \frac{2{\cdot}303}{t} \log_{10} \frac{a}{a-x},$$

where a is the initial titration and $a - x$ is the titration at time t.

ii. Inversion of cane-sugar.—Prepare a 20 per cent. solution of cane-sugar and a normal solution of hydrochloric acid. Heat 50 c.c. of each solution to 25°, mix and fill into a polarimeter tube surrounded by a water jacket at 25°. Place the tube in the polarimeter, and read the rotation as quickly as is consistent with accuracy. Note the time at which this reading was taken. Read the rotation again after intervals of 15, 30, 60, 90, 120 minutes. Take a final reading after the tube has been allowed to stand for 48 hours. If α_0 is the initial reading, α_t the reading at time t, and α_∞ the final reading, then

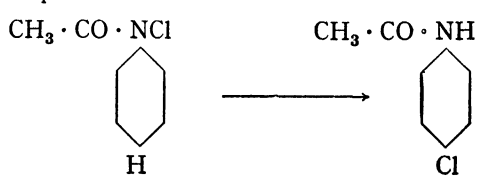
$$k = \frac{2{\cdot}303}{t} \log_{10} \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}.$$

Calculate k from your results. The mean value should be approximately 0·006.

iii. Mutarotation of glucose.—Weigh out into a 25 c.c. graduated flask 2·5 grams of *crystalline* glucose, either anhydrous or hydrated; fill the flask up to the mark with water previously heated to about 20°, shake vigorously to dissolve the glucose, and pour into a 2 dm. polarimeter tube with a water-jacket at 20°, filtering if necessary in order to obtain a clear solution. (Alternatively, a jacketed polarimeter tube may be attached to a water-tap, and fed with water at a nearly constant temperature

from the main supply.) The zero of the polarimeter should be read before and after completing the experiment. Determine the optical rotatory power of the sugar at intervals of 4, 8, 16, 32, 64, 128 and 256 minutes after preparing the solution, and take a final reading on the following day. Deduce a velocity-coefficient for the spontaneous " mutarotation " of the reducing sugar by means of the formula given above for the inversion of cane-sugar. For glucose at 20° the value should be about 0·0146.

Reactions of the first order.—The simplest type of reaction in which changes of concentration occur is that in which the changes are limited to a single component, and, moreover, are confined to molecules which appear only once in the equation. Changes of this type are known as **reactions of the first order,** or **unimolecular reactions.** An example of this group of changes is given by the transformation of N-chloroacetanilide into *p*-chloroacetanilide. This is an isomeric change, in which an atom of chlorine attached to nitrogen wanders to a carbon atom in the *para*-position of the benzene nucleus.



The isomeric change does not take place spontaneously, but proceeds readily under the influence of hydrochloric acid. The fundamental action is in fact a liberation of chlorine according to the equation (p. 267).

$$C_6H_5 \cdot NCl \cdot CO \cdot CH_3 + HCl \rightleftharpoons C_6H_5 \cdot NH \cdot CO \cdot CH_3 + Cl_2;$$

but the chlorine set free is used up in a further chlorination

$$C_6H_5 \cdot NH \cdot CO \cdot CH_3 + Cl_2 \rightarrow Cl \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3 + HCl$$

in which an equivalent amount of hydrogen chloride is again produced, so that its concentration remains constant. Of the two reactants concerned, therefore, only one undergoes a change of concentration and the chemical change follows the course of a unimolecular reaction (compare pp. 284-285).

The course of the action can be followed without difficulty, since the chlorine attached to nitrogen is very reactive and displaces iodine from potassium iodide, whilst the chlorine in *p*-chloroacetanilide is inactive and does not affect potassium iodide. Details for the study of this reaction are given in Expt. 24, i. Phenol is added in order to ensure that *all* the chlorine set free in the first stage of the action is rendered non-reactive to potassium iodide, and, in particular, to prevent the formation of dichloroacetanilide, $Cl \cdot C_6H_4 \cdot NCl \cdot CO \cdot CH_3$ (see p. 292). A typical series of results is given in Table 65.

TABLE 65. TRANSFORMATION OF N-CHLOROACETANILIDE.

Time.	Titration.	Average loss per minute.	Average concentration	Ratio.
0 min.	49·3	0·26	48·0	0·0054
10 ,,	46·7			
60 ,,	35·6	0·18	34·7	0·0052
70 ,,	33·8			
120 ,,	25·75	0·135	25·1	0·0054
130 ,,	24·4			
180 ,,	18·6	0·10	18·1	0·0055
190 ,,	17·6			
240 ,,	13·4	0·07	13·0	0·0054
250 ,,	12·7			

According to the law of mass-action, the rate of change should be proportional to the amount of N-chloroacetanilide present. Since, however, this amount decreases progressively as the action proceeds, the actual rate of change diminishes continually, and the rate of reaction can only be defined in terms of the concentration of the material which still remains unchanged.

The validity of the law of mass-action can be tested roughly by determining the amount of N-chloroacetanilide which is

changed during two similar intervals in the course of the action, and comparing these rates of change with the amounts of unchanged material still present at the middle of the two intervals. Thus, in Table 65, the loss of N-chloroacetanilide during the first 10 minutes is equivalent to 2·6 c.c. of thiosulphate solution, or an average rate of 0·26 c.c. per minute. The concentration of N-chloroacetanilide on the same scale was 49·3 at the beginning of this interval, and at the end of 10 minutes 46·7, so that the average concentration during this time was 48·0. Similar pairs of observations after 1, 2, 3, and 4 hours are contained in the table.

It will be seen that the rate of change decreases, but that it is always proportional to the concentration of the N-chloroacetanilide. This is shown by the constancy of the numbers in the last column, which were obtained by dividing the average rate in the first ten minutes of each hour by the average concentration of the unchanged material. A much neater and more accurate treatment of the problem can be given by using the methods of the differential and integral calculus.

Let the initial concentration of N-chloroacetanilide be a molecules per litre. After a time t let x molecules be transformed into *p*-chloroacetanilide. From the law of mass-action it follows that at the time t

$$\textit{rate of reaction} = k(a-x) \text{ where } k \text{ is a constant.}$$

The rate of change at the time t may be written $\frac{dx}{dt}$, where dx is a very small change in x during a very small interval of time dt. We can therefore write the equation as follows :

$$\frac{dx}{dt} = k(a-x). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Integration of this equation gives

$$x = a(1-e^{-kt}), \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where $e = 2{\cdot}718$ is the base of the natural system of logarithms. If the value of k is known, this equation may be used to calculate x, and the values thus found may be compared with those obtained experimentally ; but it is more convenient to change

the equation into a form by means of which k can be calculated. Thus:

$$x = a - ae^{-kt}, \quad \text{or} \quad a - x = ae^{-kt}$$

or

$$\frac{a}{a-x} = e^{kt}.$$

Taking logarithms

$$\log_e \frac{a}{a-x} = kt$$

or

$$k = \frac{1}{t} \log_e \frac{a}{a-x} \quad \ldots\ldots(3)$$

$$= \frac{2{\cdot}303}{t} \log_{10} \frac{a}{a-x} \quad \ldots\ldots(4)$$

(since $\log_e a = 2{\cdot}303 \log_{10} a$).

Equation (4) is the characteristic equation of a unimolecular reaction or reaction of the first order. We may use this equation to test the law of mass-action by putting in the values of t and $a-x$ and seeing if k is constant. Table 66 gives some data obtained by Blanksma for this reaction.

TABLE 66. TRANSFORMATION OF N-CHLOROACETANILIDE.

Time, min.	Titration $(a-x)$.	$k = \frac{2{\cdot}303}{t} \log_{10} \frac{a}{a-x}$.
0	49·3	—
60	35·6	0·00543
120	25·75	0·00542
180	18·5	0·00545
240	13·8	0·00531
360	7·3	0·00531
		Mean = 0·00538

Thus $a = 49{\cdot}3$ when $t = 0$, and $a - x = 18{\cdot}5$ when $t = 180$.

Therefore $k = \frac{2{\cdot}303}{180} \log_{10} \frac{49{\cdot}3}{18{\cdot}5} = \frac{2{\cdot}303}{180} \times 0{\cdot}4256 = 0{\cdot}00545$.

A difficulty sometimes arises from the fact that the early stages of a reaction are irregular, owing to the time taken to mix the solutions completely, development of heat or other disturbing factors. This difficulty can be avoided by putting equation (4)

into a form in which the initial stages of the action can be neglected, since the action is formulated as if it started at time t, and concentration $a-x_1$. The equation then becomes

$$k=\frac{2\cdot303}{t_2-t_1}\log_{10}\frac{a-x_1}{a-x_2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Thus, from the data in Table 64, we can choose

$$t_1=60, \quad a-x_1=35\cdot6;$$
$$t_2=120, \quad a-x_2=25\cdot75,$$

then $$k=\frac{2\cdot303}{120-60}\log_{10}\frac{35\cdot6}{25\cdot75}=0\cdot00540 \text{ as before.}$$

Significance of the velocity-coefficient.—The constant k is termed the **velocity-coefficient** of the reaction. It represents the fraction of the original substance which would undergo the change in unit time if the concentration were maintained at unity. Thus, putting $dt=1$, and $a-x=1$, the equation $\frac{dx}{dt}=k(a-x)$ becomes $k=dx$. Thus $k=0\cdot0054$ for the reaction discussed above means that 0·0054 of the N-chloroacetanilide present is transformed into *p*-chloroacetanilide every minute. The value of k obviously depends on the units of time chosen, and in order to express this fact one should write $k=0\cdot0054$ per minute.

For a reaction of the first order k does *not* change if the units in which a and $a-x$ are measured are altered. Thus, suppose we change to units of n times smaller than those used originally, then a becomes na, and $a-x$ becomes $n(a-x)$, so that

$$k=\frac{1}{t}\log_e\frac{na}{n(a-x)}=\frac{1}{t}\log_e\frac{a}{a-x} \text{ as before,}$$

since the n's cancel out. This is only true for unimolecular reactions; for reactions of a higher order the numerical value of k depends upon the units in which the concentrations of the reacting substances are measured. It is because the units used do not matter in a reaction of the first order that the titration figures were employed in calculating Table 66, instead of reducing them to concentrations expressed as gram-molecules per litre.

The inversion of cane-sugar.—The rate of hydrolysis of cane-sugar to glucose and fructose was measured by Wilhelmy in

1850, and has been studied subsequently by many other investigators. From the equation

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6},$$

it would be expected that the reaction would be of the *second* order, since the concentrations of cane-sugar and of water both change as the reaction proceeds. Except, however, in very concentrated solutions, the concentration of water remains nearly constant, since only a very small fraction of the total amount of water present is used up in the hydrolysis. The velocity of the change will therefore be given by

$$\frac{dx}{dt} = k[C_{12}H_{22}O_{11}][H_2O]$$

$$= k'[C_{12}H_{22}O_{11}],$$

where $k' = k[H_2O]$ and is constant.

This reaction can be followed readily by polarimetric measurements, since cane-sugar is dextro-rotatory whilst the mixture of glucose and fructose is laevorotatory. It is indeed for this reason that the hydrolysis is usually described as the **inversion of cane-sugar**. Experimental details for carrying out measurements on this reaction are given in Expt. 24, ii. Some figures from a recent study of this action by Lewis are given in Table 67.

TABLE 67. INVERSION OF CANE-SUGAR IN 0·9 N-HYDROCHLORIC ACID AT 25°.

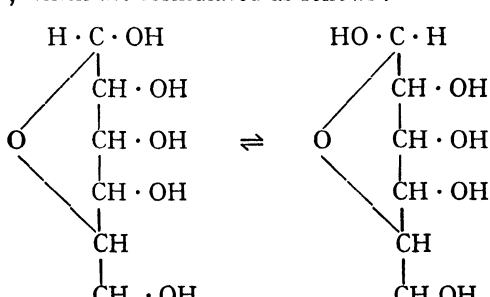
Time. t	Rotation. a_t	Change of rotation. $a_t - a_\infty$	Velocity-coefficient. k
0·0 min.	+24·09°	+34·83	0·01118
7·18 ,,	21·405	32·145	0·01119
18·00 ,,	17·735	28·475	0·01117
27·05 ,,	15·00	25·74	0·01111
36·80 ,,	12·40	23·14	0·01123
46·00 ,,	10·02	20·76	0·01124
56·07 ,,	7·80	18·54	0·01125
68·02 ,,	5·455	16·155	0·01124
101·70 ,,	0·30	11·04	0·01129
∞	−10·74		

The initial rotation was $+24{\cdot}09°$; the final rotation, when the reaction was practically complete was $-10{\cdot}74°$; the total change of rotation was therefore $34{\cdot}83°$. The amount of cane-sugar $(a-x)$ remaining at time t is proportional to $\alpha_t - \alpha_\infty$, where α_t is the rotation at time t. These differences, which are given in the third column, were used to calculate k.

The rate of inversion of cane-sugar in pure water is too slow to be measured. In order to secure suitable readings at convenient intervals of time, therefore, it is necessary to speed up the action by the addition of a catalyst (p. 302). In this case, mineral acids are found to be effective catalysts and the experiment quoted above was, therefore, carried out in the presence of 0·9N-hydrochloric acid. Since, however, the concentration of the acid, like that of the large excess of water, does not change appreciably during the inversion of the sugar, the action maintains its unimolecular character.

The mutarotation of glucose.—Dubrunfaut discovered in 1846 that freshly-prepared solutions of glucose have an abnormally high optical rotatory power, which diminishes in the course of a few hours to about half its original value, *e.g.* $[\alpha]_D$ 105° to 52·5°. He therefore described the phenomenon as " birotation " ; but since the *ratio* is quite different for other sugars which show similar changes of optical rotatory power, the phenomenon is now generally known as *mutarotation*.

The mutarotation of glucose is attributed to the reversible isomeric change of two sugars, α- and β-glucose, of rotatory power 105° and 22°, which are formulated as follows:



The reversible isomeric change represented by the scheme

$$\alpha\text{-glucose} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \beta\text{-glucose}$$

proceeds as a unimolecular action, the velocity-coefficient of the reversible reaction being given by the *sum*, $k_1 + k_2$, of the coefficients, k_1 and k_2, of the forward and backward reactions. Galactose, however, gives more complex mutarotation curves, which make it necessary to postulate the occurrence of *two consecutive isomeric changes* in a system of three isomeric sugars, *e.g.* $\alpha \rightleftharpoons \mu \rightleftharpoons \beta$, where μ is an intermediate form in the isomeric change of the α- and β-sugars.

Other unimolecular actions.—The three unimolecular actions which have been considered up to the present are all concerned with organic substances. It is noteworthy that most of the reactions met with in inorganic chemistry (*e.g.* the reactions between ions which are so important in qualitative analysis) take place with a velocity which is too high to be measured. There are, however, some inorganic reactions which proceed sufficiently slowly for measurements of velocity to be made. Thus the decomposition of pure hydrogen peroxide is extremely slow, but can be accelerated to any desired extent by the addition of a catalyst. The rate of decomposition can then be followed very easily, either by titrating the residue of hydrogen peroxide with potassium permanganate, or by measuring from time to time the volume of oxygen which has been evolved. This action is found to obey the unimolecular law, whatever the nature of the substance which is added in order to accelerate the decomposition (see Expt. 27).

Other actions which proceed according to the unimolecular law are (i) the hydrolysis of esters in presence of acids, (Expt. 26, i.), (ii) the decomposition of diazo-compounds, (iii) the mutarotation of glucose and other sugars, and (iv) the disintegration of the radioactive elements. In the last case the unimolecular change appears to take place independently in individual atoms of the radioactive element; but all the other actions cited in this paragraph can be shown to depend on the presence of some substance, not shown in the equation, of which the concentration

remains constant throughout the action, like the acid which was used in Expts. 24, i. and ii. to promote the transformation of N-chloroacetanilide into *p*-chloroacetanilide or the inversion of cane-sugar to a mixture of glucose and fructose.

25. Reactions of Higher Orders.

i. Saponification of ethyl acetate.—(*a*) *Preparation of caustic soda free from carbonate.*—Dissolve 22 grams of stick caustic soda, from a freshly-opened bottle, in about 900 c.c. of water. Add to this 5 grams of freshly-slaked lime, suspended in 100 c.c. of water, and allow to stand in a stoppered bottle. The clear solution is syphoned off from the precipitate into stock bottles. This roughly $N/2$ solution can be stored in a bottle fitted with a burette and guard-tubes of soda lime as in Fig. 61. The tubes *A A* contain soda lime; by opening the clip *B* and sucking through the tube *C* the burette can be filled without exposing the solution to the air. In order to prevent sticking it is essential that the tap of the burette should be well greased with vaseline.

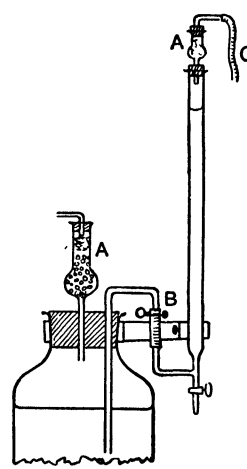


Fig. 61.—Burette and fittings for use with standard sodium hydroxide.

Determine the strength of the caustic soda by titration with a standard acid. From the burette run into a 250 c.c. standard flask the exact volume of caustic soda solution that will make 250 c.c. of $N/10$ NaOH, and make up to the mark with distilled water which has been recently boiled to remove carbon dioxide.

(*b*) *Measurement of velocity of saponification of ethyl acetate.*—Dissolve 4·4 grams of redistilled ethyl acetate in boiled-out water, and make up to 500 c.c. to obtain a tenth-normal solution. Place 200 c.c. of this solution and 200 c.c. of the $N/10$ NaOH in two clean dry corked flasks in a thermostat at 25°. Whilst the flasks are attaining this temperature, place 25 c.c. of $N/10$ HCl in each of five small flasks. After 20 minutes pour the alkali into the ester, and then pour the mixture back into the flask which originally contained the alkali. Withdraw 25 c.c. and run into the hydrochloric acid in one of the small flasks.

Note the time when the pipette is half empty, and estimate the excess of acid by titration with $N/20$ baryta solution, using phenol phthalein as indicator. Withdraw further portions after 15, 30, 45 and 60 minutes, and estimate in the same way the amount of caustic soda remaining.

(*c*) *Calculation of a velocity-coefficient.*—Since equivalent quantities of ester and alkali were used, the velocity-coefficient can be calculated by the formula :

$$k = \frac{1}{at}\frac{x}{a-x} \text{ (see below).}$$

Express a and x in gram-equivalents per litre.

The saponification of ethyl acetate.—The saponification of an ester by an alkali involves a change in concentration of two molecules, since the ester and alkali are both used up in order to produce the alcohol and the sodium salt of the acid. Thus, in the reaction

$$\underset{(a-x)}{CH_3 \cdot CO \cdot OC_2H_5} + \underset{(a-x)}{NaOH} \rightarrow \underset{x}{CH_3 \cdot CO \cdot ONa} + \underset{x}{C_2H_5OH},$$

if we start with a gram-molecules each of ethyl acetate and caustic soda, the rate of change at time t, when the amount of ester saponified is x, will be given by

$$\frac{dx}{dt} = k\,[\text{ester}][\text{NaOH}] = k(a-x)^2. \quad \ldots\ldots\ldots\ldots(6)$$

When integrated this equation becomes

$$k = \frac{1}{at}\frac{x}{a-x}. \quad \ldots\ldots\ldots\ldots(7)$$

The action formulated above proceeds only very slowly in cold dilute solutions, and can be stopped altogether by neutralising the free alkali with a mineral acid. The hydrolysis of the ester in presence of a dilute mineral acid is also a very slow process. The amount of caustic soda which is left over, when a part of the ester has been saponified, can therefore be estimated by running a known volume of the solution into a slight excess of acid, and titrating the excess of acid with standard alkali. Expt. 25, i (*b*) gives details for studying the rate of this change; and some typical results are set out in Table 68. It will be seen that equation 7 gives a constant value for the velocity-coefficient,

although the coefficients of a unimolecular equation in the last column of the table decrease rapidly.

TABLE 68. SAPONIFICATION OF ETHYL ACETATE.
($a = 16{\cdot}00$.)

t (min.).	x.	$k_2 = \frac{1}{at}\frac{x}{a-x}$.	$k_1 = \frac{1}{t}\log\frac{a}{a-x}$.
5	5·76	0·0070	0·089
15	9·87	0·0067	0·077
25	11·68	0·0069	0·060
35	12·59	0·0066	0·050
55	13·69	0·0067	0·039

If unequal amounts of ester and alkali are taken, the formula becomes a little more complicated. Let the initial concentrations be a mols. of ester and b mols. of alkali, and let x mols. of these be used up at a time t. Then the law of mass-action gives for the rate of change at this instant

$$\frac{dx}{dt} = k(a-x)(b-x). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

On integration this becomes

$$k = \frac{1}{t(a-b)} \log_e \frac{b(a-x)}{a(b-x)}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

TABLE 69. SAPONIFICATION OF ETHYL ACETATE.

t (min.).	$a-x$.	$b-x$.	$k = \frac{1}{t(a-b)} \log_e \frac{b(a-x)}{a(b-x)}$.
0	0·5638	0·3114	—
393	0·4866	0·2342	0·00139
669	0·4467	0·1943	0·00142
1010	0·4113	0·1589	0·00140
1265	0·3879	0·1354	0·00144

Table 69 gives some data due to Reicher to illustrate the application of formula 9. The constancy of k shows that the law of mass-action predicts accurately the course of the change, and proves also that the velocity of change is proportional to the concentration of caustic soda as well as to that of the ester.

Actions of a higher order.—The reduction of ferric chloride by

stannous chloride involves the interaction of three molecules and may therefore be taken as an example of a **termolecular reaction** or **reaction of the third order.**

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4.$$

The law of mass-action predicts that the rate of the action will be given by

$$\frac{dx}{dt} = k[FeCl_3]^2[SnCl_2].$$

Thus, if we start with a mols. of each, the rate of the reaction at time t, when x mols. have reacted, will be given by the equation

$$\frac{dx}{dt} = k(a-x)^3. \quad \text{.....(10)}$$

On integration this equation becomes

$$k = \frac{1}{2t}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right) \quad \text{.....(11)}$$

Table 70 gives some data obtained by Noyes, who followed the progress of the reduction by withdrawing samples of the solution at definite intervals of time, adding mercuric chloride to destroy the unchanged stannous chloride, and then estimating the ferrous chloride in the usual way. It will be seen that these data give a very steady value for the termolecular velocity-coefficient.

TABLE 70. REDUCTION OF FERRIC CHLORIDE BY STANNOUS CHLORIDE.

($a = 0{\cdot}0625$.)

t.	x.	$k = \frac{1}{2t}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right)$
1	0·01434	88
3	0·02664	87
7	0·03612	84
11	0·04102	87
40	0·05058	85

The decomposition of potassium chlorate has been found to be **a reaction of the fourth order** in accordance with the equation

$$4KClO_3 = 3KClO_4 + KCl.$$

In the same way, the reaction between potassium ferricyanide

and potassium iodide is said to be a **reaction of the fifth order,** and may be written

$$2K_3Fe(CN)_6 + 3KI \rightarrow 2K_4Fe(CN)_6 + KI_3.$$

Reactions of the fourth, fifth and higher orders are, however, very rare indeed; by far the greater number of reactions which have been studied follow either the unimolecular or the bimolecular law. This is probably due to the action taking place in several successive stages, of which the slowest determines the speed finally measured. Thus the action

$$2FeCl_3 + 6KI \rightarrow 2FeI_2 + 6KCl + I_2$$

would appear to be octamolecular; if written as an ionic equation it would become

$$2Fe^{\cdots} + 2I' \rightarrow 2Fe^{\cdots} + I_2,$$

and would be quadrimolecular. It is actually found to be termolecular, since the rate varies as represented by the equation

$$\frac{dx}{dt} = k[FeCl_3][KI]^2.$$

The action is therefore supposed to take place in two stages, as follows:

$$FeCl_3 + 2KI \rightarrow FeI_2 + 2KCl + Cl \text{ (slow)},$$
$$2KI + 2Cl \rightarrow 2KCl + I_2 \text{ (fast)}.$$

The rate at which free iodine is produced is then determined by the speed of the first slow reaction, and proceeds according to a termolecular equation.

Determination of the order of a reaction.—(i) The first and most obvious method of finding the order of a chemical change is to determine whether the course of the change can be expressed by a unimolecular, bimolecular or termolecular equation. For this purpose it is necessary to measure the amount of substance changed after various periods of time. By substituting the values thus obtained in the expressions for the velocity-coefficient of a unimolecular, bimolecular, or higher reaction, it will readily be seen which of these expressions gives the most satisfactory constant.

An example of this method is given in Table 68, where the column headed k_1 gives the coefficient calculated by a unimolecular formula from the data in the second column, whilst the

column headed k_2 gives the coefficients calculated by means of a bimolecular formula. It will be seen that k_1 decreases rapidly as the action progresses, but that the values of k_2 remain steady throughout, thus showing that the saponification of ethyl acetate is a bimolecular and not a unimolecular reaction.

(ii) Another method is to measure the time required for a given fraction of the change to be completed. Two experiments must be carried out at concentrations c_1 and c_2. Let the times at which the reaction is half-completed be t_1 and t_2; then

$$\frac{t_2}{t_1}=\left(\frac{c_1}{c_2}\right)^{n-1}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

where n is the order of the reaction. Thus, when $n=1$, $t_1=t_2$, *i.e. in a unimolecular reaction the time for half-change is the same at all concentrations.* Similarly, in a bimolecular action, if the concentration is doubled, the time required for the change to be half completed is halved, and so on.

An example of the application of this method is given by the work of Hinshelwood on the reduction of nitric oxide by hydrogen, as represented by the equation

$$2NO+2H_2\rightarrow N_2+2H_2O.$$

This equation shows the ultimate products of the action correctly but indicates that the reaction should be quadrimolecular. Actually, however, the reaction was found to be termolecular. Thus, an equimolecular mixture of the gases at 340·5 mm. initial pressure was half changed in 102 seconds, whilst in another experiment with an initial pressure of 288 mm. the change was half completed in 140 seconds. Since the pressure of a gas is a measure of its concentration, we can substitute in equation (12) the values $c_1=340{\cdot}5$, $c_2=288$, $t_1=102$, $t_2=140$. This gives the equation

$$\left(\frac{340{\cdot}5}{288}\right)^{n-1}=\frac{140}{102}.$$

Taking logarithms, we have

$$(n-1)\log\frac{340{\cdot}5}{288}=\log\frac{140}{102},$$

$$\therefore\ 0{\cdot}0727(n-1)=0{\cdot}1375;$$

$$\therefore\ n=2{\cdot}89 \text{ or } 3 \text{ nearly.}$$

In order to explain this result, Hinshelwood suggests that the change includes a slow action in which nitrous oxide and hydrogen interact to form nitrogen and hydrogen peroxide according to a termolecular equation

$$2NO + H_2 \rightarrow N_2 + H_2O_2$$

followed by a rapid reduction of the hydrogen peroxide to water by the action of a second molecule of hydrogen as shown in the equation

$$H_2O_2 + H_2 \rightarrow 2H_2O.$$

(iii) A third method of determining the order of a complex reaction is known as **Ostwald's Isolation Method.** It depends on making a series of experiments in which all but one of the reacting substances is taken in large excess, so that the rate of the reaction with respect to one substance only is studied. Thus, in the reaction between potassium ferricyanide and potassium iodide, when excess of the latter was taken (so that its concentration was almost constant), the rate of liberation of iodine followed a bimolecular law, *i.e.* two molecules of ferricyanide took part in the change. When excess of ferricyanide was used, the reaction was found to be termolecular, indicating that three molecules of potassium iodide took part. The action is therefore quinquemolecular, since the rate is given by the equation

$$\frac{dx}{dt} = k\,[K_3Fe(CN)_6]^2[KI]^3.$$

Complexity of chemical change.—In the preceding pages we have considered a number of ideal types of chemical change in which a definite number of molecules of the initial materials are converted completely, and without loss, into a definite number of molecules of the various products. These ideal changes are, however, by no means universal, since the simple action, represented by a formal chemical equation, is often complicated by secondary changes of various kinds; and even when the course of the action can be expressed by a simple unimolecular or bimolecular equation, it does not follow that the changes which are actually occurring are anything like as simple as the equations used to represent them. Some of the principal sources of complexity are set out below.

(*a*) *Simultaneous actions.*—In many cases the course of a chemical change is complicated by the fact that two or more reactions may be proceeding simultaneously and independently. Thus, when propyl chloride is acted on by caustic potash, the alkali may either remove hydrogen chloride, or replace the chlorine by hydroxyl according to the schemes set out below.

$$CH_3 \cdot CH_2 \cdot CH_2Cl + KOH \begin{cases} \nearrow CH_3 \cdot CH : CH_2 + KCl + H_2O \\ \searrow CH_3 \cdot CH_2 \cdot CH_2OH + KCl. \end{cases}$$

In practice, both propylene and propyl alcohol are formed. Moreover, the yield of these two products can be varied by changing the conditions. Thus, alcoholic potash gives mainly propylene, whilst aqueous potash gives mainly propyl alcohol.

Again, the isomeric change of N-chloroacetanilide into *p*-chloroacetanilide is complicated by the fact that some of the chlorine set free from the former compound by the action of hydrogen chloride acts upon the latter compound to form N-*p*-dichloroacetanilide $Cl \cdot C_6H_4 \cdot NCl \cdot CO \cdot CH_3$. The addition of phenol to the reaction-mixture in Expt. 24, i. prevents the formation of this reactive product; the iodine titration then records accurately the rate of decomposition of the N-chloroacetanilide, but not that at which the *p*-isomeride is formed, since some of the chlorine set free from the former compound is used up in chlorinating the phenol.

(*b*) *Consecutive actions.*—In other cases the course of the action is complicated by the fact that a number of changes take place consecutively. Thus the mutarotation curves for galactose (p. 284) show that the changes of rotatory power depend on *two* consecutive unimolecular actions. Again, the hydrolysis of ethyl malonate and of the esters of other dibasic acids proceeds in two stages:

$$CH_2\begin{matrix}CO_2Et \\ CO_2Et\end{matrix} + H_2O \rightarrow CH_2\begin{matrix}CO_2H \\ CO_2Et\end{matrix} + EtOH, \quad \ldots\ldots\ldots I$$

$$CH_2\begin{matrix}CO_2H \\ CO_2Et\end{matrix} + H_2O \rightarrow CH_2\begin{matrix}CO_2H \\ CO_2H\end{matrix} + EtOH. \quad \ldots\ldots\ldots II$$

Stage II is usually much slower than stage I, and the existence

of two stages can therefore be detected by measurements of the rate at which the hydrolysis proceeds. When one stage is very much slower than the others, the whole course of the change may be controlled by it, like traffic held up by a " bottle-neck." The reaction may then appear to be of a lower order than that of the simplest chemical equation which can be used to represent it, as in the case of the reaction between ferric chloride and potassium iodide described on p. 289.

(*c*) *Reversible actions.*—Many chemical changes proceed to an equilibrium instead of going completely from left to right. Thus, although saponification of an ester by an alkali proceeds to completion, the hydrolysis of the ester in the presence of an acid is a reversible action and should therefore be represented by an equation with double arrows, thus :

$$CH_3 \cdot CO \cdot OCH_3 + H_2O \rightleftharpoons CH_3 \cdot CO \cdot OH + CH_3 \cdot OH.$$

When the amount of water present is large, the back action may be neglected ; if, however, smaller amounts of water are used, the influence of the accumulating products must be allowed for by adding to the equation a new term to represent the speed of the back action. In practice it is found that, if the forward and back actions taken separately conform to a unimolecular law with velocity-coefficients c_1 and c_2, the combined action *in either direction* can be represented by a unimolecular equation with a velocity-coefficient $c_1 + c_2$.

(*d*) *Catalysed actions.*—A large number of chemical actions, which give a constant velocity-coefficient in a unimolecular equation, are seen on closer examination to be really bimolecular actions, in which the concentration of one reactant remains constant or nearly constant. Thus the hydrolysis of methyl acetate in the presence of acids should be written

$$CH_3 \cdot CO \cdot OCH_3 + H_2O + \overset{+}{H} \rightleftharpoons CH_3 \cdot CO \cdot OH + CH_3 \cdot OH + \overset{+}{H}.$$

In aqueous solution, the concentration of water does not change appreciably, nor does the concentration of the hydrogen ion, so that a unimolecular law is followed.

(*e*) *Surface actions.*—An action which is catalysed by a solid surface may obey the unimolecular law merely because the chemical change is controlled by physical conditions such as

diffusion or absorption. Thus the decomposition of phosphine by heat is represented by the equation,

$$4PH_3 = P_4 + 6H_2,$$

and should therefore obey a quadrimolecular law; but in practice the change is found to follow a unimolecular law. It can be shown, however, that the reaction occurs almost entirely on the surface of the vessel, since the rate of change is largely increased when the vessel is filled with glass-wool in order to increase its surface. In such a case the number of molecules of gas reaching the surface in unit time will be proportional to the pressure, and the rate at which the gas reacts will therefore follow a unimolecular law whatever be the order of the rapid reaction at the glass surface.

Recent work has shown that, although they are very rare, a few genuine unimolecular gas reactions may exist. Thus, the rate of decomposition of nitric anhydride by heat, according to the equation

$$2N_2O_5 = 4NO_2 + O_2,$$

is not affected by increasing the surface of the containing vessel, nor by dilution with an inert gas; the decomposition therefore appears to proceed as a true unimolecular reaction.

It is evident from the cases cited above that the course of a chemical change may be very complex and difficult to interpret. Nevertheless, a study of the rate of a reaction, and in particular of the order of the action under different conditions, may often give important information as to the path by which the action proceeds.

QUESTIONS ON CHAPTER XI.

1. Write a short account of the law of mass-action. Describe any experiments you have performed or seen which show the influence of concentration on *either* reaction velocity *or* equilibrium. (Natural Science Schols., Oxford.)

2. Discuss with examples the influence on the course of a reaction of the concentrations and relative masses of the reactants. (Cambridge Schol.)

3. How can the order of a chemical reaction be determined? What conclusions can safely be drawn from the ascertained order of a reaction as to its mechanism. (B.Sc., Manch.)

4. What is meant by the " order of a reaction." Describe in detail a method of determining the order of a reaction. The data for the conversion of a compound A into its isomeride B are as follows :

Time t =	0	1	2	3	4	6	8
Amount of A: $(a-x)$ =	49·3	35·6	25·75	18·5	13·8	7·3	4·8

Show that the reaction is of the first order and deduce the formula that you employ. (B.A., Bombay.)

5. Malonic acid when heated decomposes according to the equation $CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2$. Hinshelwood followed this reaction by measuring the pressure developed when the acid was heated in a closed vessel at constant volume and obtained following data :

t min. -	10	20	35	56	∞
p mm. -	37·0	67·0	108·0	155·0	302·0

Show that this reaction is of the first order.

6. At 21° the following figures were found for the decomposition of nitrous acid in aqueous solution :

Time (min.) - - -	0	90	135	195
gm. HNO_2 in 100 c.c. -	0·1468	0·1282	0·1247	0·1175

Show that the reaction is unimolecular and calculate the velocity-coefficient.

7. From the following data show that the decomposition of H_2O_2 in aqueous solution is a monomolecular reaction.

Time in minutes -	0	10	20
N	22·8	13·8	8·25 c.c.

where N is the number of c.c. of $KMnO_4$ required to decompose a definite volume of the H_2O_2 solution. (B.Sc. Hons., Punjab.)

CHAPTER XII.

THE MECHANISM OF CHEMICAL CHANGE.

26. Activation.

1. Rate of hydrolysis of methyl acetate in the presence of acids at 15° and 25°.—(*a*) Prepare a solution of hydrochloric acid which is within 1 per cent. of semi-normal strength. Place 100 c.c. of this acid in a corked flask, and immerse in a thermostat at 25°. After half an hour, add 5 c.c. of methyl acetate and shake. Note the time of addition of methyl acetate; then withdraw 5 c.c. immediately with a dry pipette, and run into 20 c.c. of cold distilled water in a small flask. Titrate this solution rapidly with $N/10$ NaOH or $Ba(OH)_2$ solution, using phenolphthalein as indicator. Withdraw further samples of 5 c.c. after intervals of 10, 20, 30, 40, 60, 80 and 100 minutes, and titrate as before. Leave the flask tightly corked in the thermostat for 2 days, and titrate again to get the reading corresponding to complete hydrolysis.

If the apparatus shown in Fig. 61 is not available, the alkali should be re-standardised at the time of the final titration and a correction applied if its strength has altered. Calculate the velocity-coefficient from the formula

$$k = \frac{2{\cdot}303}{t} \log_{10} \frac{c_\infty - c_0}{c_\infty - c_t},$$

where c_0 = titration at the start, c_t = the titration after t minutes, and c_∞ = the final reading when hydrolysis is complete.

(*b*) Repeat the experiment at 15°. Use a large vessel of water as a thermostat and keep the temperature at 15° by adding warm or cold water from time to time. Calculate the ratio k_{25}/k_{15} and deduce a value for the heat of activation by using formula 1, p. 301.

ii. Influence of temperature on velocity of decomposition of hydrogen peroxide.—Determine the velocity of decomposition of hydrogen

peroxide in the presence of potassium iodide at 15° and 25°. For this purpose dilute 10 c.c. of 30 per cent. hydrogen peroxide to about 200 c.c. and add caustic soda from a burette until a drop of the solution gives a neutral reaction with litmus paper.

Dilute the neutralised solution to 1 litre. Place 200 c.c. of this, and a solution of 1 gram of KI in 20 c.c. of water, in separate flasks in a thermostat, or, if a thermostat is not available, in a large tank of water kept at 15° or 25° by adding hot or cold water.

After 20 minutes mix the solutions and note the time. Withdraw 10 c.c. of the solution, run into dilute sulphuric acid, and titrate the H_2O_2 with $N/10$ $KMnO_4$. Take further samples after 10, 20, 30, 60 and 90 minutes and estimate the residual hydrogen peroxide as before. Calculate unimolecular constants for the velocity of decomposition at 15° and 25°, and from the ratio deduce a value for the heat of activation as in Expt. 26, i.

Influence of temperature on the rate of chemical change.—The speed of most chemical changes increases rapidly with a rise of temperature. Thus, a rise of 10° C. often doubles the rate of change. The ratio $\frac{k_{t+10}}{k_t}$, which is described as the **temperature-coefficient of the action,** is set out for a number of chemical changes in Table 71.

TABLE 71. TEMPERATURE-COEFFICIENTS OF REACTION-VELOCITY.

Reaction.	Temperature-coefficient.	Heat of activation
$C_6H_6 + 3Cl_2 \xrightarrow{ICl_3} C_6H_6Cl_6$ - -	$k_{25}/k_{15} = 1{\cdot}05$	911 cal.
$EtAc + KOH \longrightarrow EtOH + KAc$ - -	$k_{35}/k_{25} = 1{\cdot}82$	11,000 ,,
$EtAc + H_2O \xrightarrow{HCl} EtOH + HAc$ -	,, $= 2{\cdot}5$	16,800 ,,
$CH_3{\cdot}CO{\cdot}NH_2 + H_2O \xrightarrow{HCl} CH_3{\cdot}CO\,OH + NH_3$	,, $= 2{\cdot}2$	14,500 ,,
$C_2H_5I + (C_2H_5)_3N \longrightarrow (C_2H_5)_4NI$ - -	,, $= 2{\cdot}2$	14,500 ,,
$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2C_6H_{12}O_6$ - -	,, $= 4{\cdot}13$	26,000 ,,

The temperature-coefficient is usually between 2 and 3; but the chlorination of benzene in the presence of iodine trichloride has

an unusually low coefficient, and low values are also usually found for photochemical actions. The inversion of cane-sugar, on the other hand, gives an abnormally high value. It will be shown below that the influence of temperature on the rate of chemical change is an important factor in determining the mechanism by which the action proceeds, and that a number of interesting theories, including the theory of molecular activation, have been based upon a study of this property.

Kinetic theory of gaseous reactions.—It has already been stated that by far the larger proportion of the reactions hitherto studied are of the first, second or third orders. The rarity of reactions of higher orders is readily understood from the kinetic theory, since interaction can only occur when the right kinds of molecules collide. It is evident that the chances of a simultaneous collision between four or five or more molecules is very small, and that reactions involving smaller numbers of molecules will be much more common.

The simplest theory of chemical change is that which postulates that it is only necessary to bring together the right number and the right kind of molecules, when they will interact immediately to form the products of the reaction. This theory is perhaps correct when applied to ionic reactions (Chapter XIV.), which are in fact almost instantaneous, but the simple **collision theory** breaks down completely when attempts are made to deduce quantitative results, either as regards the *velocity* or as regards the *temperature-coefficient* of chemical changes of other types. Thus (i) in a simple bimolecular action between gases, where the number of collisions per second can be calculated from the kinetic theory, the number of pairs of molecules which undergo chemical change is found to be much smaller than the number which collide ; it is, therefore, obvious that only a small fraction of the collisions are fruitful in the sense that they give rise to the products of the reaction, since if all the collisions were fruitful the action would be complete in a fraction of a second.

(ii) Again, if we assume that the rate of a bimolecular action depends only on the number of collisions in unit time between the reacting molecules, it can be calculated from the kinetic theory that the temperature-coefficient for 10° should be 1·04.

Since in most cases much higher values are found, it is necessary to look for some other factors which may be concerned in bringing about chemical reactions.

(iii) Finally, in the case of unimolecular actions, it is difficult to explain why the change should not be instantaneous if the action is really unimolecular and all the molecules are in a condition to undergo the change which is under consideration.

Arrhenius's theory of molecular activation.—The explanation of these observations which is most widely accepted is due to Arrhenius. He suggested that the large temperature-coefficients of chemical change can be explained by supposing that, in a system undergoing chemical change, there are a few **activated molecules,** which are in a condition to undergo chemical change, and that all the others are inert until they become activated in their turn. The rapid increase of velocity with rising temperature can then be explained by supposing that the proportion of activated molecules increases rapidly with the temperature.

This conclusion is very reasonable if we suppose that the activated molecules differ from the others in that they contain a larger amount of energy, since, according to the theory of probabilities, the number of molecules which have a kinetic energy exceeding a given value increases very rapidly as the temperature rises. Modern theory has indeed gone further and suggested a method by which the **energy of activation** may be calculated. Typical values for the heat of activation are given in the last column of Table 71 (p. 298), whilst the method of deducing these values is discussed in the following paragraph (see below, p. 301).

In the case of unimolecular actions, some form of activation appears to be essential in order to explain why all the molecules do not change simultaneously. An interesting example of this type of selective activation is perhaps provided by the radioactive elements, where the nucleus of the atom appears to pass through an unstable phase at definite intervals of time, so that each element has a definite **half-life period,** at the end of which one half of the atoms have disintegrated; but it is noteworthy that the velocity of this disintegration is not affected by temperature, or by any of the other factors which affect the velocity

of other chemical changes. It is therefore possible, and even probable, that this is the only case in which single atoms or molecules undergo a chemical change without the intervention of other molecules, either of the same sort or of some different kind.

At the present time discussion centres around the question as to how the activated molecules gain their extra energy. Some workers consider that, since chance collisions can give to a few molecules a velocity which is greater than the average, this extra kinetic energy can in some way be transformed into potential energy and make the molecule reactive. Others suppose that the absorption of radiant energy is of great importance, and endeavour to trace a connection between the values of the heat of activation and the absorption spectrum of the reaction mixture. In other cases still it is supposed that the products of the action, which will possess extra energy owing to the heat liberated by the chemical change, can by collision activate molecules which have not yet undergone the change. In the present state of our knowledge we cannot yet say with certainty what part these or other processes play in the activation of molecules.

Calculation of heat of activation from velocity-coefficients.— We have seen (p. 239) that the rate of change of an equilibrium-constant with temperature can be expressed by a formula,

$$\frac{\mathrm{d}\log K}{\mathrm{d}T} = \frac{-U}{RT^2},$$

which van't Hoff derived with the help of rigid thermodynamical reasoning. When the change in reaction-velocity is measured over a wide interval of temperature, it is found by experiment that the variation of the *velocity-coefficient k* with temperature can be expressed by the empirical formula of Arrhenius:

$$\frac{\mathrm{d}\log k}{\mathrm{d}T} = \frac{-E}{RT^2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

If we assume that E, although it determines the value $\frac{\mathrm{d}\log k}{\mathrm{d}t}$, is itself independent of t, this equation on integration becomes

$$\log_e \frac{k_1}{k_2} = \frac{E}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where k_1 and k_2 are the velocity-constants at temperatures T_1 and T_2. If this formula is interpreted on the theory of activated molecules, then E is the **heat of activation** or *the heat required to convert a molecule in its normal condition into an activated molecule.* Values of E are given in Table 71.

27. Catalysis.

i. Catalysis of the mutarotation of glucose.—Repeat Expt. 24, iii. (p. 276), using instead of pure water:

1. Normal potassium chloride.
2. Decinormal hydrochloric acid.
3. Normal acetic acid.
4. M/100 $NaHCO_3$.
5. Normal sodium acetate, which has been approximately neutralised by the addition of N/20 acetic acid.

Calculate the " catalytic-coefficient " of each of these compounds by dividing its concentration into the *increase* in the velocity-coefficient in the solution as compared with that in pure water. Compare the values with those given on p. 309.

ii. Catalysis of the decomposition of hydrogen peroxide by haemase. (Senter.)—Procure a quantity of fresh ox-blood, allow it to stand till a clot forms, and then pipette off 1 c.c. of the clear serum and dilute to 1 litre with distilled water. (*a*) Place in the 25° thermostat, in separate flasks, 200 c.c. of dilute neutral hydrogen peroxide prepared as in Expt. 26, ii., and 20 c.c. of the serum solution, which contains the catalyst haemase. After 20 minutes, mix the solutions and note the time. Withdraw 10 c.c. of the solution, and run into dilute sulphuric acid, which stops the action. Titrate the H_2O_2 with $N/10$ $KMnO_4$. Take further samples after 10, 20, 30, 60 and 90 minutes, and estimate the residual H_2O_2 in a similar manner. From your results calculate the unimolecular velocity-coefficient for this action.

(*b*) The experiment may be repeated, using only half the amount of catalyst, when approximately half the former value will be found for the velocity-coefficient.

(*c*) It may also be repeated, using colloidal platinum (Expt. 36, v.) as a catalyst.

Catalysis.—In 1835, Berzelius directed attention to a number of actions which were accelerated by the presence of an added substance which appeared to play no part in the change. Thus, cane-sugar is converted into glucose and fructose in the presence

of acids, but the acid is all left over at the end of the action, and can be used again repeatedly to invert further quantities of cane-sugar. Berzelius named the phenomenon **catalysis** and gave to the added substance the name of **catalyst.**

Further work has shown that the speed of nearly all chemical changes can be increased by the addition of a catalyst, and the phenomenon is therefore a very general one. Several examples of catalysis have been described in the preceding pages, *e.g.* the isomeric change of N-chloroacetanilide, the inversion of cane-sugar and the hydrolysis of esters *in the presence of acids* (Expts. 24, i. and ii. and 26, i.), whilst Expt. 27, i. deals with the decomposition of hydrogen peroxide by *platinum black*, etc. Berzelius thought that catalytic changes were due to a special catalytic force; later writers have dropped this conception, and Ostwald has defined a catalyst simply as *a substance which alters the velocity of a chemical reaction but does not appear in the end products.*

Characteristics of catalytic actions.—The most important characteristics of catalytic actions are as follows:

(1) *The catalyst remains unchanged at the end of the action.*—This refers only to the chemical composition of the catalyst, since its physical form may be modified profoundly. Thus, when coarsely broken manganese dioxide is used to catalyse the decomposition of potassium chlorate, the pieces are found to be disintegrated to a very fine powder at the end of the action. In the same way, platinum, when used as a catalyst to promote the combination of hydrogen and oxygen, becomes coated with a finely-divided black powder, and this finely-divided platinum is a much more powerful catalyst than the polished metal.

(2) *A small amount only of the catalyst is required.*—In many cases a remarkably small amount of catalyst produces an appreciable effect. Thus Bredig found that a solution containing only 0·00017 gram of colloidal platinum liberated 1·8 c.c. of oxygen per minute from a solution of hydrogen peroxide, and was as active after 10 litres of gas had been evolved as it was originally. Titoff found that copper sulphate at a concentration of only 10^{-12} gram-molecules per litre caused an appreciable increase in the rate of oxidation of sodium bisulphite by air. In

other cases, however, the catalyst is destroyed or removed by secondary actions, *e.g.* in the Friedel-Crafts reaction, where the aluminium chloride forms a compound with the product and is therefore no longer active. In such cases larger amounts of catalyst are obviously necessary.

(3) *A catalyst alters the speed of the action, but does not alter the final state of equilibrium.* Thus the interaction of alcohol and acetic acid to form ethyl acetate and water

$$C_2H_5 \cdot OH + CH_3 \cdot CO \cdot OH \rightleftharpoons CH_3 \cdot CO \cdot OC_2H_5 + H_2O$$

is accelerated by acids, as also is the converse process of hydrolysis of ethyl acetate by water. The final position of equilibrium is, however, unchanged, provided that the amount of acid used is small; *the forward and the backward changes must therefore be accelerated to the same extent.*

It can be shown by thermodynamical reasoning that this proposition must be true whenever the catalyst is present only in small quantity, since the addition of a minute amount of a foreign substance cannot alter to any appreciable extent the energy-constant of a system in equilibrium. When larger amounts of catalyst are used, however, the equilibrium-concentrations of the substances undergoing the change may be altered considerably. Thus Jones and Lapworth have shown that, although the equilibrium-constant for the reversible hydrolysis of ethyl acetate in presence of small amounts of hydrochloric acid has a uniform value of 4·4, which is independent of the concentration of the acid, the value of the constant is raised considerably in presence of large amounts of hydrochloric acid, and is actually doubled when the strength of the acid is raised to about 20 per cent.

TABLE 72. HYDROLYSIS OF ETHYL ACETATE.

HCl.	H_2O.	$K_{25} = \frac{[H_2O][EtAc]}{[EtOH][HAc]}$.
1	381	4·45
1	360	4·35
1	6·24	6·35
1	5·76	7·09
1	4·61	8·83

(4) Ostwald's suggestion that *a catalyst cannot start a reaction but only increases or decreases its speed* is probably incorrect, since there are many cases in which a catalyst appears to be merely *a reagent which is reproduced as a product of the reaction*, and is therefore essential to its progress.

Ostwald compared a catalyst to a lubricant which enables a machine to move faster, or to a whip which urges on a reluctant horse. Thus, he supposed that the interaction of hydrogen and oxygen gas proceeds at ordinary temperatures, and in the absence of any catalyst, although the rate is far too slow to measure. The introduction of platinum black is then supposed merely to increase the speed of this pre-existing charge.

Definite evidence in favour of this view is difficult to find, since common experience shows that it is almost impossible to eliminate all catalytically active substances in a given reaction. Thus, even when we do not introduce any platinum black, the glass walls of the containing vessel may prove to be catalytically active, although in a much smaller degree. It has, however, been found possible by drastic purification to arrest the progress of many of the commonest chemical changes so completely as to leave no experimental foundation for the suggestion that the action can still proceed when no catalyst at all is present. Thus Baker has shown that carbon and sulphur will not burn in oxygen when thoroughly dried, dry ammonia and dry hydrochloric acid will not combine, nor will dry ammonium chloride dissociate on heating.

In these and many other actions water appears to be an essential catalyst, without which the reactions cannot proceed. Further, pure water formed from highly purified hydrogen and oxygen will not initiate an explosive combination of these gases, so that *four* components appear to be needed to set this action going.

In the same way, Lowry has shown that the facile isomeric changes which give rise to the changes of optical rotatory power in freshly prepared solutions of nitrocamphor or of tetramethylglucose can be arrested by working with pure materials, in inert solvents and in alkali-free silica vessels, but that these reactions are catalysed by very minute traces of acids and bases.

The conclusion from these observations, that catalysts can initiate (instead of merely accelerating) a chemical change, is in harmony with Armstrong's dictum that "*Chemical action is reversed electrolysis*," since, according to this view, the removal of a catalyst may be compared with taking away the conducting wire from an electric circuit, or removing the copper pole from a Daniell cell. There are, indeed, many indications that even the simplest chemical changes can only proceed with the help of a definite mechanism, and must therefore be brought to a complete standstill unless all the component parts of the machine are provided.

Homogeneous and heterogeneous catalysis.—It is convenient to divide catalytic actions into two groups, namely **homogeneous catalysis**, in which all the substances concerned are in one phase, and **heterogeneous catalysis**, in which two or more phases are present. Examples of homogeneous catalysis are found in the action of water-vapour in promoting the burning of a gaseous mixture of hydrogen and oxygen; also in the influence of acids in promoting the hydrolysis of an ester in aqueous solutions. Examples of heterogeneous catalysis are found in the use of *solid* platinum black to promote the combustion of *gaseous* hydrogen and oxygen, or the decomposition of *aqueous* hydrogen peroxide.

Catalysis by acids.—Acids are often used as catalysts to promote chemical changes in aqueous solutions, *e.g.* the hydrolysis (or "inversion") of cane-sugar (Expt. 24, ii.), the formation or the hydrolysis of an ester (Expt. 26, i.) or the isomeric change which gives rise to "mutarotation" in a freshly-prepared solution of a reducing sugar. The inversion of cane-sugar by acids is a homogeneous catalysis, since the acid forms a part of the liquid phase which contains the sugar. All acids are able to produce this effect, but strong acids are much more efficient than weak acids. The velocity-coefficient of the unimolecular action can therefore be used as a measure of the "strength" of the acid. Thus the velocities set out in Table 73 for a series of acids in $N/2$ solutions are approximately proportional to the strengths of the acids as determined by other methods of measurement (Chap. XIII.).

TABLE 73. CATALYTIC EFFICIENCY OF ACIDS IN THE INVERSION OF CANE-SUGAR. (Ostwald.)

Acid.	k/k_{HCl}.	Acid.	k/k_{HCl}.
Hydrochloric -	1·000	Monochloracetic	0·0484
Nitric - -	1·000	Formic - -	0·0153
Trichloracetic -	0·754	Acetic - -	0·0040
Sulphuric - -	0·536	—	—

It was formerly supposed that the catalytic activity of an acid was proportional to the extent to which it is dissociated into ions $HX \rightleftharpoons \overset{+}{H} + \overset{-}{X}$ (see Chap. XIV.), and that the catalysis is effected only by the free hydrogen ions $\overset{+}{H}$ in solution. This hypothesis is obviously incorrect, however, since the catalytic activity of a given weight of a strong acid *increases* as its concentration increases, whilst the proportion which is dissociated into ions *decreases* (compare the last column of Table 77, p. 331). In direct contradiction, therefore, to the view advocated by Ostwald, the undissociated molecules of a strong acid must have a greater catalytic activity than the ions. The catalytic activity of a given weight of a weak acid, on the other hand, increases with the dilution, since the ions are more efficient catalysts than the undissociated molecules of the acid.

Influence of neutral salts on catalysis by acids.—The catalytic activity of an acid is generally increased by the presence of a salt. Thus Arrhenius found that the rate at which sugar was inverted by $N/40$ acetic acid was increased by 12·6 per cent. in presence of $N/8$ potassium chloride. These effects may be accounted for in part by combination of water with the salt, so that some of the water is no longer available to act as solvent. This would increase the concentration of the acid in relation to the free solvent water, and so increase its efficiency as a catalyst. We can also express this fact by saying that the neutral salt has increased the "activity" of the acid, and perhaps of the sugar, since the solubility of an organic compound is generally diminished and its "activity" increased by the

addition of a salt; but in other cases the effects are much too large to be explained in this indirect way, and we must attribute a direct catalytic activity to the ions of the salt, as described in the following paragraph.

Catalysis by neutral salts.—In order to determine the part played by neutral salts in catalysis, Dawson has investigated the influence of mixtures of acetic acid and sodium acetate, etc., on the velocity with which acetone is attacked by halogens. Lapworth showed in 1904 that the velocity with which bromine acts on acetone is independent of the concentration of the bromine. It is, however, proportional to the concentration of the acetone and of the acid which is formed as a product of the action. It therefore appears to be determined by the velocity with which the ketone is converted into the isomeric enol under the catalytic action of acids, thus:

$$\text{(i)} \qquad CH_3 \cdot CO \cdot CH_3 \overset{HX}{\rightleftharpoons} CH_3 \cdot C(OH) : CH_2.$$

$$\text{(ii)} \quad CH_3 \cdot C(OH) : CH_2 + Br_2 \rightarrow [CH_3 \cdot C(OH)Br \cdot CH_2Br] \rightarrow CH_3 \cdot CO \cdot CH_2Br + HBr.$$

By studying the velocity of iodination of acetone (20 gm. per litre) at 25° in presence of a weak acid and of its sodium salt, Dawson showed that the observed effects could be explained by assigning a definite **catalytic coefficient** to (i) the hydroxyl ions (present only in solutions containing very little acid), (ii) the hydrogen ions, (iii) the undissociated molecules of the acid, (iv) the anion of the weak acid and of its salts (but not the cation of the salt). Water itself exhibited no catalytic activity, apart from that of the hydrogen and hydroxyl ions in the solution, but values for the catalytic coefficients of the other components were deduced as follows:

	Acetic acid and Sodium acetate.	Chloracetic acid and Sodium chloracetate.
k_{OH}	$= 10{,}000{,}000 \times 10^{-6}$	$10{,}000{,}000 \times 10^{-6}$
k_H	$= 442 \times 10^{-6}$	442×10^{-6}
k_{ACID}	$= 1{\cdot}5 \times 10^{-6}$	$24{\cdot}5 \times 10^{-6}$
k_{ANION}	$= 4{\cdot}5 \times 10^{-6}$	$0{\cdot}12 \times 10^{-6}$

The velocity of the action was then given by the equation

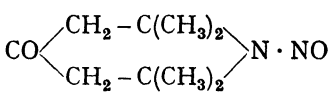
$$v = k_H[H]^+ + k_{ACID}[HA] + k_{ANION}[A]^- + k_{OH}[OH]^-$$

In the mutarotation of glucose, the catalytic coefficients are as follows:

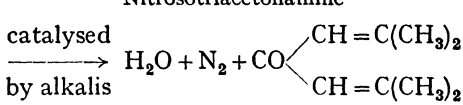
Molecules.	Cations.	Anions.
$k_{HCl} = 0{\cdot}55$	$k_{H^{\cdot}}$ } 0·36	$k_{OH'}$ 8,000
$k_{HAc} = 0{\cdot}0065$	$k_{OH_3^{\cdot}}$ }	$k_{Ac'}$ 0·069
$k_{OH_2} = 0{\cdot}00026$	$k_{NH_4^{\cdot}}$ 0·0012	

It will be found that all the substances which are catalytically active in these two isomeric changes can be classed as acids or bases in terms of the definitions given in Chap. XIV. (p. 358), and that $Na^{\cdot}$ and Cl', which have no appreciable catalytic activity, are also lacking in acidic and basic properties, as there defined.

Catalysis by alkalis.—A number of actions are known which are catalysed by alkalis. Thus, Francis has studied the decomposition of nitrosotriacetonamine into phorone, nitrogen and water, in presence of alkalis.



Nitrosotriacetonamine



Phorone

This reaction obeys the unimolecular law and can be followed readily by measuring the nitrogen evolved.

Other reactions which are catalysed by the alkalis are the mutarotation of glucose, the condensation of acetone to form diacetonyl alcohol

$$2CH_3 \cdot CO \cdot CH_3 \rightarrow CH_3 \cdot CO \cdot CH_2 \cdot C(CH_3)_2 \cdot OH$$

Diacetonyl alcohol

and the inter-conversion of the enolic and ketonic forms of ethyl acetoacetate and similar substances

$$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot OEt \rightleftharpoons CH_3 \cdot C(OH) : CH \cdot COOEt.$$

Autocatalysis.—Some reactions are known in which the products of the action act as catalysts. Thus, the hydrolysis of ethyl acetate by water is accelerated by the acetic acid produced by the hydrolysis; and the value of the unimolecular

velocity-coefficient k (which is very small at first) therefore increases rapidly as the action proceeds. This phenomenon is known as **autocatalysis.**

A case of autocatalysis which is of technical importance is the decomposition of the organic nitrates, such as nitro-cellulose, which are used as explosives. This action takes place very slowly, but is accelerated by the oxides of nitrogen, which are formed in the decomposition. If, therefore, decomposition once sets in, it may proceed more and more rapidly until a spontaneous explosion takes place. In order to prevent this decomposition, *stabilisers* are added, usually derivatives of urea, which react with any trace of oxides of nitrogen produced by incipient decomposition, and thus make the explosive safe and stable.

Heterogeneous catalysis.—Cases of heterogeneous catalysis, in which the catalyst forms a separate phase from the bulk of the reaction-mixture, are very numerous, and are of great technical importance. Thus, finely-divided platinum is a very effective catalyst for changes such as the oxidation of sulphur dioxide to the trioxide, or the oxidation of ammonia to nitric oxide. On the other hand, finely-divided nickel promotes the addition of hydrogen to unsaturated compounds, and is largely used for the hardening of oils by combination with hydrogen. Other important industrial applications of heterogeneous catalysis are the use of copper chloride to promote the oxidation of hydrochloric acid by air in the Deacon process, the use of mercuric sulphate as a catalyst in the oxidation of naphthalene to phthalic acid by the action of hot sulphuric acid, and of vanadic oxide to bring about the oxidation of naphthalene to phthalic anhydride by means of air.

Catalysis by enzymes.—Another important group of catalysts of this class are the **enzymes.** These are complex organic compounds which are produced by living plants and animals, but are readily destroyed by heat. They form colloidal solutions in water and are very effective catalysts for a number of reactions. For example, the enzyme **diastase** (which can be extracted from malt by the action of water and precipitated by the addition of alcohol), can be used to convert starch to maltose by a process of hydrolysis; but a different enzyme, known as **maltase**, is

required in order to effect the further hydrolysis of maltose to glucose.

Anti-catalysts or catalyst-poisons.—It is characteristic of a catalyst that it is reproduced as a product of the reactions in which it takes part, and can therefore be used over and over again without being consumed. For this very reason, however, catalytic actions are extremely sensitive to the presence of any substance which will interact with the catalyst in such a way as to prevent it from playing its usual part, since, for every molecule of the catalyst which is thus "put out of action," many hundreds of other molecules may be prevented from undergoing chemical change. Substances which retard chemical change by destroying the efficiency of a necessary catalyst, are generally described as **anti-catalysts** or **catalyst-poisons.** Thus, when hydrogen peroxide is decomposed under the influence of colloidal platinum or of the enzyme haemase (Expt. 27, i.), it is found that the platinum and the enzyme are both rendered inactive by the presence of certain "poisons," although the effects produced are often widely different in two cases. Table 74 shows the amounts of these "poisons" which are required in order to reduce the velocity of the decomposition of hydrogen peroxide to half its original value.

TABLE 74. CONCENTRATION OF CATALYST-POISON REQUIRED TO REDUCE THE RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE TO ONE HALF.

Poison.	Catalyst.	
	Colloidal Platinum.	Haemase.
H_2S - - -	3×10^{-6}	1×10^{-6}
HCN - - -	5×10^{-8}	1×10^{-6}
$HgCl_2$ - -	5×10^{-7}	5×10^{-7}
Aniline - -	2×10^{-4}	$2{\cdot}5 \times 10^{-3}$
CO - - -	very poisonous	no poisoning
HCl - - -	3×10^{-4}	1×10^{-5}
HNO_3 - -	no poisoning	4×10^{-6}

Since very small amounts of "poison" have such a marked effect on the velocity of a catalysed process, many industrial operations depend for their success on the complete elimination

of all traces of "poisons" from the raw materials which are used. Thus the technical preparation of sulphuric acid by the "contact" process only becomes possible when the gases (formed by burning sulphur or pyrites in a suitable proportion of air) are freed from every trace of arsenic before being brought into contact with the platinum catalyst.

Retardation of a reaction by traces of a foreign substance may also occur in reactions which are not known to be dependent on the presence of a catalyst. Thus hydroquinone retards the (apparently spontaneous) oxidation of benzaldehyde by air; and the oxidation of alkaline sodium sulphite by air is retarded by many aromatic compounds, by cane-sugar, and by brucine, which produces retardation at a concentration of 10^{-7} gram-molecules per litre. Cases such as these are usually described as examples of **negative catalysis,** since it looks at first sight as if these foreign substances produced a retardation in just the same direct way as a positive catalyst produces an acceleration of the reaction. Further examination has shown, however, that these oxidations are initiated at the surface of the containing vessel, and that retardation is produced when this surface is "poisoned" by the negative catalyst, which therefore acts in much the same way as any other catalyst-poison.

Mechanism of catalytic changes.—Since practically all chemical changes can be catalysed by some substance, it does not appear probable that the manner in which a catalyst acts will always be the same. We can, however, distinguish two broad theories of catalytic change which account fairly well for two main groups of reactions.

(*a*) **The "intermediate compound" theory** postulates that the catalyst combines with one of the reagents to form a more reactive intermediate compound. Thus, in the Friedel-Crafts reaction, aluminium chloride forms an addition-compound with benzoyl chloride of the formula $C_6H_5 \cdot COCl, AlCl_3$. This compound can be isolated and interacts with benzene to form benzophenone.

(i) $C_6H_5 \cdot COCl + AlCl_3 \longrightarrow (C_6H_5COCl), AlCl_3,$

(ii) $(C_6H_5 \cdot COCl), AlCl_3 + C_6H_6 \longrightarrow C_6H_5 \cdot CO \cdot C_6H_5 + AlCl_3 + HCl.$

Explanations of this kind have been suggested for many cases of catalytic action. The existence of an intermediate compound, however, is not of itself evidence that the reaction proceeds through this compound, since cases are known in which the intermediate compound is less reactive than the substance from which it is formed. Thus, the oxidation of ferrous sulphate by air is catalysed by nitric oxide ; but the formation of the dark brown compound, $FeSO_4 \cdot 2NO$, which gives the colour in the " brown ring " test for nitrates, cannot be used to account for the catalytic action, since it is found that the nitric oxide in this compound is less efficient than free nitric oxide in promoting the oxidation. It is indeed obvious that, although the formation of an intermediate compound may be essential to catalytic activity, the progress of the action would be prevented if this compound were too stable. In general, therefore, it is unlikely that the essential intermediate compound will be capable of isolation under the same conditions as those which prevail when it is acting as a catalyst.

(*b*) **The adsorption theory** differs from the intermediate compound theory mainly in that the combination of the catalyst with the reactants is not supposed to give rise to a well-defined chemical compound, but to a mere " adsorption compound " or loose aggregate of atoms or molecules. Thus, in a reaction in which a finely divided metal or other solid substance is used as a catalyst, it is found that the fineness of division and the condition of the surface of the catalyst have an enormous effect upon its activity. It is also well known that solids have the property of " adsorbing " or condensing upon their surface a thin layer, often only one molecule thick, of vapours and gases (see Chap. XVI., where a fuller account is given of the application of adsorption to explain the phenomena of surface-catalysis).

These adsorbed molecules must have a smaller potential energy than the same molecules in a free state, but they may nevertheless have a greater chemical activity. Thus, a molecule of hydrogen condensed on the surface of nickel may be more reactive than a molecule in the gas, if we suppose that one atom is held so strongly by the metal that the other atom is partially released. A molecule of an unsaturated compound coming in

contact with one of these reactive molecules of hydrogen may then unite to form an addition-compound which is held less strongly by the surface of the metal, and therefore volatilises away, thus leaving the surface of the catalyst free to combine with further molecules of the reacting substances. This explanation accounts for the influence of the nature of the metal surface, and also for the action of poisons, since the latter may be regarded as substances which have a greater affinity for the catalyst, and therefore cover its surface so that the reacting molecules cannot reach it.

(*c*) **Ionic theories of catalysis.***—The use of acids as catalysts for the hydrolysis of esters and for sugar inversion (p. 276), and of acids and alkalis as catalysts for the isomeric changes which give rise to mutarotation (p. 302) and to the iodination of acetone (p. 308) has led to various ionic theories of catalysis. Thus, since a strong base can form a *salt* even from a very weak acid, and conversely, it has been supposed that catalysis by acids and bases depends on their ability to convert an inert organic compound into a reactive *salt*. It has therefore been suggested that an alkali may promote isomeric change by producing a reactive *anion*, X′, from an organic compound, HX, which is too weak an acid to yield appreciable quantities of this anion by mere electrolytic dissociation :

$$HX \leftarrow H^{\cdot} + X' \quad \text{but} \quad HX + Na^{\cdot} + OH' \rightleftharpoons Na^{\cdot} + X' + H_2O.$$

Conversely, an acid is supposed to convert a very weak organic base (X or YOH) into a reactive *cation* ($HX^{\cdot}$ or $Y^{\cdot}$), either by the addition of a hydrogen ion, or by the removal of hydroxyl

$$X + H^{\cdot} \rightleftharpoons HX^{\cdot} \quad \text{or} \quad YOH + H^{\cdot} \rightleftharpoons Y^{\cdot} + H_2O.$$

The free ion is then supposed to undergo a change of structure, so that, when the action shown in the preceding equations is reversed, it gives rise to an isomeric product instead of the original compound. In this way it is possible to account for the peculiar efficiency of acids and bases as catalysts in chemical changes of this type.

A more complete interpretation can be given if we suppose that isomeric change is effected by adding a proton to one part

* This paragraph may be postponed until Chapter XIII. has been read.

of the molecule at the same moment as a proton is removed from another part of the same molecule. In that case the phenomenon may be compared with an " electrolysis " of the organic molecule, between " poles " formed by the acid and basic constituents of the solution. This view is supported by the fact that isomeric changes of this type proceed most readily in " amphoteric " solvents, *i.e.* solvents which possess both acid and basic properties and which can therefore (in terms of the definitions of Chap. XIV.) give a proton to the organic compound, or receive a proton from it.

QUESTIONS ON CHAPTER XII.

1. What criteria are applicable to catalysis ? Give an account of the intermediate-compound theory of catalysis, illustrating your answer by reference to reactions to which it has been applied. (B.Sc., Sheffield.)

2. Discuss the attempts that have been made to explain the rapid increase in the velocity of chemical reaction with rise in temperature. (B.Sc. Hons., Sheffield.)

3. Mention the chief theories which have been advanced to explain catalysis and describe one of them in detail. (Inter. Sci., Sheffield.)

4. Write a short essay on the nature and uses of catalytic reactions. (Oxford Higher School Certificate.)

5. What do you understand by the terms " positive catalysis," " negative catalysis," " autocatalysis." Give examples of each.

CHAPTER XIII.

ELECTROLYSIS AND ELECTROLYTIC DISSOCIATION.

28. Electrolysis.

i. Comparison of the electrochemical equivalents of copper, silver and lead.—Cut two electrodes about 3 cm. × 6 cm. from stout copper foil and solder each plate to a stout copper wire to serve as a support. Prepare similar pairs of electrodes from silver foil and from thin sheet lead. Weigh one electrode of each kind, after rinsing with water and with methylated spirit from a small wash bottle, and drying in the steam oven for 20 minutes. Then support the pairs of electrodes in beakers, parallel to one another and about 3 cm. apart. In the first beaker place a 10 per cent. solution of copper sulphate, in the second a 10 per cent. solution of silver nitrate, and in the third a 10 per cent. solution of lead nitrate.

Connect up the cells in series, and connect to a battery of accumulators giving a potential of about 10 volts, taking care that in each case the weighed electrode forms the cathode, by which the current leaves the cell. Allow the current to flow for 3-6 hours (the longer period if possible), then stop the current, remove the cathodes, wash well with distilled water, rinse with spirit, and dry and weigh as before. The increase in weight divided by the chemical equivalent should be constant for all three metals.

Conductors and non-conductors.—Substances differ enormously in the resistance which they offer to the passage of electricity. Thus, if the same voltage is applied to a bar of silver and to a bar of sulphur of the same dimensions, the current through the silver is many million million million times as great as that which flows through the sulphur. The relation between the electrical pressure, the resistance, and the current in a

conductor is given by **Ohm's Law,** which states that *the current flowing through a conductor is proportional to the applied voltage and inversely proportional to the resistance.* This law may be written :

$$I = \frac{E}{R},$$

where I is the current, E is the electrical pressure, and R is the resistance.

The *current* is usually measured in amperes, the **ampere** being defined as *the current which deposits* 1·118 *milligrams of silver per second from a solution of silver nitrate* in a voltameter of specified form (p. 322) ; the quantity of electricity which then passes in one second is called a **coulomb.** The *electrical resistance* is measured in ohms, the **ohm** being defined as *the resistance at* 0° *of a column of mercury* 106·3 *cm. in length and weighing* 14·4521 *grams.** The *pressure* is measured in volts. The **volt** is defined merely as *the pressure which is required to send a current of one ampere through a resistance of one ohm* ; but batteries of high resistance have been devised by Clark and by Weston, which give a very constant pressure of 1·434 and 1·0183 volts respectively at 0° C., and these are often used as secondary standards of pressure.

Specific resistance and specific conductivity.—The resistance of a conductor depends upon its shape as well as upon the material of which it is made. Hence, in order to compare the resistance of different substances, it is necessary to consider a standard form of conductor. The **specific resistance** of a substance is defined as the resistance in ohms of a cube of 1 cm. side, when a difference of potential of 1 volt is applied to two opposite faces. The reciprocal of the specific resistance is named the **specific conductivity** and is usually denoted by the symbol κ. Thus $\kappa = \frac{I}{R}$. Units of conductivity are sometimes termed "reciprocal ohms" or more shortly "mhos" (mho = ohm written backwards) ; in the same way a reciprocal megohm has been called a "gemmho."

* The cross-section of such a column is approximately a square millimetre.

Table 75 gives the specific resistances and conductivities of a number of substances and solutions. It will be seen from the table that metals, fused salts, and certain aqueous solutions (usually solutions of salts, acids and bases) possess an appreciable conductivity and are classed as electrical conductors. On the other hand, substances such as glass and sulphur have only a very small conductivity and are usually termed non-conductors.

TABLE 75. SPECIFIC RESISTANCES AND CONDUCTIVITIES AT 18°.

Substance.	R=Specific resistance. Ohms.	κ=Specific conductivity. Mhos.	Class.
Silver	0·00000166	602,000	Metallic conductor
Copper	0·00000178	562,000	,, ,,
Zinc	0·0000061	164,000	,, ,,
Bismuth	0·000119	8,400	,, ,,
Gas carbon	0·005	200	,, ,,
Fused NaCl	0·30	3·33	Electrolyte
N. H_2SO_4	2·56	0·391	,,
N. KOH	5·00	0·200	,,
N. KCl	10·59	0·0944	,,
Pure water	25×10^{6}	$0{\cdot}04 \times 10^{-6}$	Non-conductor
Soft glass	5×10^{11}	2×10^{-12}	,,
Sulphur	4×10^{15}	$2{\cdot}5 \times 10^{-16}$	,,

Metallic conduction and electrolytic conduction.—Two classes of conductors can be recognised in the substances set out in the preceding table. Thus, when a current is passed through a copper wire, the wire is heated by the passage of the current, but is otherwise unchanged; and, when the current is cut off, it regains its original properties as soon as it has cooled down to its original temperature. When, however, an electric current is passed through dilute sulphuric acid, the passage of electricity through the solution is accompanied by a chemical decomposition, since hydrogen is given off at one electrode and oxygen at the other; and this decomposition continues as long as the current flows.

Substances which conduct electricity without suffering any

permanent change are termed **metallic conductors.** All metals belong to this class and also a few substances which are not definitely metallic, *e.g.* gas carbon, selenium, and arsenic, which all have a small " metallic " conductivity.

Most other pure substances are non-conductors both in the solid and in the liquid state ; but alkalis and salts, which are very poor conductors when solid, are excellent conductors when fused, and are at the same time decomposed by the passage of the current. Substances which conduct electricity and simultaneously undergo a chemical change were described by Faraday as **electrolytes** (*i.e.* decomposed by electricity). To this class belong fused salts and a large number of solutions, *e.g.* aqueous and alcoholic solutions of salts, acids and bases.

It is a remarkable fact that two pure liquids, which are themselves non-conductors, *e.g.* pure liquid hydrogen chloride and pure water, may give a mixture which conducts excellently. The solution is, however, decomposed by the passage of the current, and is therefore (like all transparent conducting media) an electrolyte and not a metallic conductor. On the other hand, it is immediately obvious that all solutions are not electrolytes, *e.g.* a solution of cane-sugar in water has about the same small conductivity as pure water. We may, therefore, divide substances into three classes with respect to their behaviour when an electrical pressure is applied to them as follows :

Metallic Conductors.	Electrolytes.	Non-conductors.
Metals.	Fused salts.	Glass.
Gas carbon.	Aqueous solutions of salts, acids and bases.	Sulphur.
		Most pure substances except metals and fused salts.

Faraday's laws of electrolysis.—From a long study of the phenomena of electrolysis, Faraday arrived at the following results.

(i) *The products of electrolysis appear only at the electrodes, i.e. the points at which the current enters and leaves the solution.* In general, the salt is resolved into two parts, one of which appears at each electrode. The " positive " electrode, at which the current enters the solution (according to the old convention,

which treats the current as a flow of *positive* electricity) is called the **anode**; the "negative" electrode, at which the current leaves the solution, is called the **cathode**. The radicles into which the salt is resolved can be divided into two classes. The metals and hydrogen appear at the cathode or negative electrode, and (since opposite kinds of electricity attract one another) are said to be **electropositive** groups. The non-metals and acid radicles appear at the anode, or positive electrode, and are said to be **electronegative** groups. The following equations indicate the primary products of electrolysis in a number of cases.

		Cathode.		Anode.
$NaCl$	$\rightarrow$	Na	$+$	Cl
NH_4Cl	$\rightarrow$	NH_4	$+$	Cl
$CuSO_4$	$\rightarrow$	Cu	$+$	SO_4
$NaCN$	$\rightarrow$	Na	$+$	CN
$K_4Fe(CN)_6$	$\rightarrow$	$4K$	$+$	$Fe(CN)_6$

When these primary products are liberated, they frequently undergo decomposition or chemical change, giving rise to secondary products by interacting with one another, with the electrode, or with the electrolyte. Thus, in the case of a solution of sodium chloride, the sodium atoms immediately attack the water, giving caustic soda and hydrogen, whilst the chloride atoms unite in pairs to form gaseous chlorine, thus:

Primary decomposition: $NaCl \rightarrow Na + Cl$.

Secondary changes:

At cathode - $2Na + 2H_2O \rightarrow 2NaOH + H_2$.

At anode - - $Cl + Cl \rightarrow Cl_2$.

In other cases the anode is attacked. Thus, if copper sulphate is electrolysed between copper electrodes the following changes occur:

Primary decomposition: $CuSO_4 \rightarrow Cu + SO_4$.

Secondary change:

At anode - $SO_4 + Cu \rightarrow CuSO_4$.

The net result is that copper is dissolved at the anode and deposited at the cathode, whilst the composition of the solution remains unchanged.

(ii) *The amount of chemical decomposition is proportional to the quantity of electricity which passes through the electrolyte.* This law, which is generally known as **Faraday's First Law of Electrolysis**, implies that the amount of decomposition is independent of the temperature of the solution, of the current-density, and of the form or material of the electrodes and vessel. When the conditions are such that the electrolysis is not complicated by secondary reactions, this law holds with great accuracy. Thus the weight of silver deposited from a solution of silver nitrate, under specified conditions, is so strictly proportional to the current, that it has been adopted as the basis of the international definition of the ampere (p. 318).

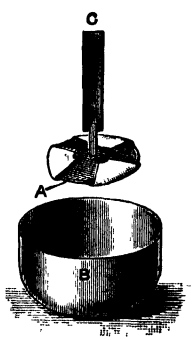


FIG. 62.—Silver voltameter.

The apparatus used for this purpose is known as the **silver voltameter** (Fig. 62). It consists of a weighed platinum bowl *B*, not less than 10 cm. in diameter, which serves as the cathode. The electrolyte in the bowl is an aqueous solution of silver nitrate containing 15 per cent. of the salt. The anode is a silver plate *A*, with a silver strip riveted to it; it is wrapped in filter paper, mounted on a brass rod *C*, and clamped in the centre of the bowl. The filter-paper (secured with sealing wax), is used in order to prevent any particles of metal detached from the anode from falling into the bowl. The deposit on the bowl, after passing a current of about 1 ampere during a period of about 2 hours, is washed, soaked in water for at least six hours, and then rinsed with distilled water and with alcohol and dried at 160° before weighing.

(iii) *When different compounds are decomposed by the same quantity of electricity, the amounts of the products obtained are proportional to their chemical equivalents.* This law is generally known as **Faraday's Second Law of Electrolysis.** Thus when 1 coulomb of electricity (a current of 1 ampere for 1 second) is passed through solutions of silver nitrate, of copper sulphate, and of dilute sulphuric acid, the amounts of silver, copper and hydrogen liberated are: silver 1·118 milligram, copper 0·32935

milligram, hydrogen 0·010446 milligram. These numbers, which represent the amount of the product liberated by unit quantity of electricity, are known as the **electrochemical equivalents** of these elements. Faraday's law states that *the electrochemical equivalents are proportional to the chemical equivalents.* It can be tested by dividing the chemical equivalent by the electro-chemical equivalent.

Silver - -	107·88 ÷0·001118	=96,495
Copper - -	31·78 ÷0·00032935	=96,494
Hydrogen -	1·008÷0·000010446	=96,496

One gram-equivalent of any of these substances is therefore liberated by **96,500 coulombs** of electricity. This important unit of electrical quantity is termed the **Faraday**, and indicated by the symbol F. Thus the number of gram-equivalents of electrolyte decomposed in any electrolytic cell by a total flow of It coulombs is given by It/F, where $F = 96,500$ coulombs.

From the preceding data it is seen that one gram-equivalent of any electrolyte carries a charge of 96,500 coulombs, so that one gram-atom of any metal carries a charge of $n \times 96,500$ coulombs, where n is the valency of the metal. We know also that one gram-atom contains $0·6062 \times 10^{24}$ individual atoms. The charge on the individual atom is therefore

$$\frac{n \times 96,500}{0·6062 \times 10^{24}} \text{ coulombs,}$$

or

$$\frac{n \times 9650}{0·6062 \times 10^{24}} \text{ electromagnetic units,}$$

or

$$\frac{n \times 9650}{0·6062 \times 10^{24}} \times 3 \times 10^{10} \text{ electrostatic units}$$

(where 3×10^{10} is the velocity of light).

The value of this unit charge, which can be regarded as an atom of electricity, is therefore $4·774 \times 10^{-10}$ electrostatic units. In practice, the electrostatic charge of the electron has been determined directly from a study of electrically-charged oil drops, and the Avogadro number has been deduced from these data by a converse process to that used in the preceding calculation.

29. Ionisation and Electrolytic Dissociation.

i. Measurement of electrical conductivity.—(*a*) The *apparatus* used for measuring the resistance of a solution is shown diagrammatically in Fig. 63. The accumulator *A* works the small induction coil, *I.C.*, which supplies from its secondary coil an alternating current to the Wheatstone bridge. The latter consists of a uniform wire stretched over a metre scale and attached at each end to stout brass strips *B*, *B*. The circuit is completed by bridging the gaps between these strips, with (1) the *conductivity cell*, *X*, containing the solution to be tested, and (2) a *resistance-box*, *R*. A pair of head-telephones is connected to the centre strip, *B*, and to a contact, *C*, which can be moved to any desired position along the bridge wire.

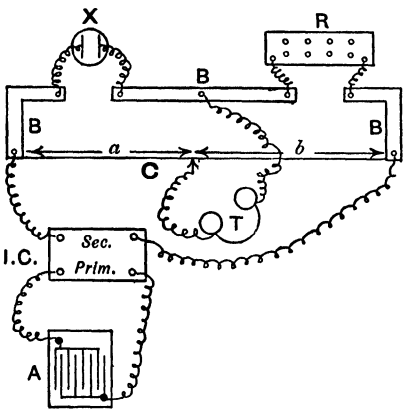


Fig. 63.—Apparatus for measuring electrolytic conductivity.

When the apparatus is connected up in this manner a sound will be heard in the telephones; but in one position of the movable contact *C* the sound will be reduced to a minimum. When this adjustment has been made, then

$$\frac{\text{resistance of } X}{\text{resistance of } R} = \frac{a}{b},$$

$$i.e. \quad \text{resistance of } X = \frac{a}{b} R,$$

where *R* is the known resistance corresponding with the plugs which have been removed from the resistance box, whilst *a* and *b* are the lengths of wire between the movable contact and the ends of the bridge wire. The most accurate results are obtained when *a* is nearly equal to *b*. Plugs should therefore be removed from the resistance-box until the point of adjustment comes near the centre of the wire, *e.g.* between 40 cm. and 60 cm. on the scale.

(*b*) The *conductivity cell* for the experiments described below is preferably of the form shown in Fig. 64. The electrodes are of platinum and are welded to stout platinum wires which are sealed through two glass tubes supported by an ebonite cap. A little mercury is placed in each tube, so that contact can be made with the electrodes by means of copper wires dipping into the mercury. The electrodes should extend nearly to the wall of the outer vessel, which is preferably made of resistance glass.

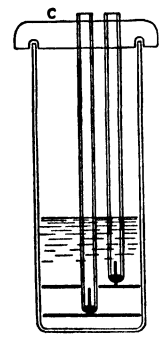


FIG. 64.—Cell for measurement of electrolytic conductivity.

One of the chief difficulties in measuring the resistance of a solution is that products of electrolysis collect on the electrodes, causing "polarisation" and giving high and irregular values for the resistance. This difficulty is largely overcome by using an alternating current and by coating the electrodes with platinum black. Before use, therefore, the electrodes should be cleaned by washing with warm chromic acid and with distilled water, and then coated with platinum black. This is done by filling the cell with a solution of 3 grams of chloroplatinic acid and 0·02 grams of lead acetate in 100 c.c. of water, and connecting the electrodes through a reversing switch to a 4-volt accumulator battery. Electrolysis is allowed to proceed for 20 minutes, the current being reversed every minute.

When the electrodes have thus been coated with an even layer of platinum black, the platinising liquid is poured back into the stock bottle and the electrodes are rinsed with water. The cell should then be filled with dilute (5 per cent.) sulphuric acid, and the electrolysis continued for 30 minutes, reversing the current every minute. (This treatment removes impurities occluded by the platinum black). Finally the electrodes are well washed with distilled water and are left immersed in distilled water until required.

(*c*) *Conductivity-water.*—The distilled water used in the laboratory is not usually pure enough for use in measurements of conductivity. A combined still and water-oven in continuous operation will, however, often be found to produce water with a conductivity of 2 to 4 $\times 10^{-6}$ mhos at 25°, which is good enough for the experiments described below. If the conductivity is greater than this, the water should be redistilled after adding a little potassium hydrogen sulphate; a condenser of resistance-glass should be used and the middle third of the water collected

in a large bottle of resistance-glass and used within a few days. Obviously the water must be distilled and kept in a part of the laboratory that is free from fumes ; absorption of carbon dioxide from the atmosphere may also be checked by means of soda-lime tubes.

(*d*) *Determination of the constant of the cell.*—Prepare a solution of potassium chloride of $N/50$ concentration, using fused potassium chloride and conductivity-water. Wash out the cell two or three times with this solution, then fill the cell with the solution so that both plates are covered, and see that there is no air bubble between them. Place the cell (and the flask containing the solution) in a thermostat at 25° and after 15 minutes measure the resistance of the cell. Refill the cell with more of the solution, take another reading, and repeat until a constant value R_{KCl} is obtained.

Wash the cell thoroughly with distilled water, and soak the plates over-night in distilled water. Then fill the cell with conductivity-water and determine its resistance, which will be high. Refill with conductivity-water and redetermine the resistance. Let the steady value be R_{H_2O} ; then the true conductivity of the solution (apart from impurities in the water) is

$$\kappa = X\left(\frac{1}{R_{KCl}} - \frac{1}{R_{H_2O}}\right),$$

where X is the **cell-constant.** But the specific conductivity of $\frac{N}{50}$ KCl at 25° is 0·002768 (see Table 76 for values at other temperatures) ;

$$\therefore X = \frac{0{\cdot}002768}{\frac{1}{R_{KCl}} - \frac{1}{R_{H_2O}}}.$$

Then if R_Y is the resistance of any other solution Y measured in this cell, the specific conductivity of X is given by

$$\kappa_X = X\left(\frac{1}{R_Y} - \frac{1}{R_{H_2O}}\right)$$

The conductivity of the water is given by the ratio $\frac{X}{R_{H_2O}}$, and should not be greater than 4×10^{-6} mhos.

Care must be taken in handling the cell to avoid distorting the plates, since this would alter the value of X. It is advisable to redetermine the cell-constant from time to time in order to make sure that no such alteration has occurred.

TABLE 76. CONDUCTIVITY OF $N/50$ KCl AT DIFFERENT TEMPERATURES.

0°	0·001522	15°	0·002243
5°	0·001752	20°	0·002501
10°	0·001996	25°	0·002768

(*e*) *Conductivity of aqueous solutions of copper sulphate.*—Check the calibrations of two 100 c.c. flasks and of a 50 c.c. pipette. If the etched marks are not correct, make new marks with a diamond to indicate the correct calibration.

In one of the flasks prepare a normal solution of copper sulphate by dissolving 12·49 grams of $CuSO_4$, $5H_2O$, and filling up to the mark with conductivity-water. Rinse the conductivity-cell twice with a few cubic centimetres of this solution; fill the cell with the solution and place it in the thermostat at 25°. Whilst it is attaining the temperature of the bath, transfer 50 c.c. of the solution by means of the pipette to the second flask and make up to the mark with conductivity-water, thus obtaining a solution of $N/2$ concentration. Measure the resistance of the N solution in the cell, then rinse out and fill the cell with the $N/2$ solution.

Clean out the first flask, transfer to it 50 cubic centimetres of the residual $N/2$ solution, make up to the mark with conductivity-water, and determine its resistance as before. In the same way, prepare and measure the resistance of $N/4$, $N/8$, $N/16$, $N/32$, $N/64$, $N/128$, solutions, etc. From the results calculate the specific and equivalent conductivities of the solutions. Set out the results as follows:

Concentration. C.	Dilution. V.	Resistance. R.	Specific conductivity. κ.	Equivalent conductivity. Λ.
N	1000 c.c.	R_1	$\kappa = X\left\{\frac{1}{R_1} - \frac{1}{R_{H_2O}}\right\}$	$\Lambda = \kappa \times 1000$
$N/2$	2000 c.c.	R_2	$\kappa = X\left\{\frac{1}{R_2} - \frac{1}{R_{H_2O}}\right\}$	$= \kappa \times 2000$
$N/4$	4000 c.c.	R_4	$\kappa = X\left\{\frac{1}{R_4} - \frac{1}{R_{H_2O}}\right\}$	$= \kappa \times 4000$
etc.	etc.	etc.	etc.	etc.

ii. Titration, using conductivity as an indicator.—Place 10 c.c. of $N/10$ HCl in the cell and measure its conductivity. From a burette add 2 c.c. of $N/10$ NaOH and measure the conductivity

again. Repeat, adding the alkali 2 c.c. at a time until 16 c.c. have been added. Plot the conductivities against the amount of NaOH added. The points will fall on two straight lines, the intersection of which gives the end-point. This is because the ions $H^{\cdot}$ and OH' have much larger mobility that other ions, so that a minimum conductivity is reached at the neutral point. This method is useful for titrating coloured solutions in which indicators cannot be used.

Decomposition of electrolytes into ions.—In order to account for the facts that (i) the products of electrolysis are liberated only at the electrodes and, (ii) a definite amount of electricity is associated with each equivalent of salt decomposed, Faraday supposed that the current was carried by particles charged with positive or negative electricity. These were called **ions** (Greek ἴω, I go), because they moved to the electrodes under the influence of the current.

The ions with their charges travel unchanged through the bulk of the solution, but become reactive when their charges have been neutralised by contact with an oppositely-charged electrode. Thus, the positively-charged sodium ions and the negatively-charged chloride ions, which are formed by the electrolysis of a solution of common salt, develop the normal reactivity of atoms of sodium and of chlorine only at the electrodes, where their electric charges are neutralised. In the same way a solution of copper sulphate is decomposed by the current into copper ions and sulphate ions.

The copper ions are positively charged, but since two Faradays of electricity are needed to deposit one gram-atom of copper, each atom of bivalent copper carries *two* units of positive charge, whereas each atom of univalent sodium or chlorine carries only a single positive or negative unit. The negatively-charged bivalent sulphate ions also carry two negative charges. When the solution is electrolysed, the positively-charged copper ions are attracted to the negative electrode or kathode and there neutralise an equal amount of negative electricity, and deposit a corresponding quantity of metallic copper. Similarly, the negative sulphate ions are attracted towards the positive electrode, or anode, and, when discharged, attack either the

electrode or the solvent. Thus, when a copper electrode is used, copper sulphate is formed at the anode,

$$SO_4 + Cu \rightarrow CuSO_4,$$

whilst with an electrode of platinum, which is not attacked by the sulphate ions, the water is decomposed and oxygen is evolved :

$$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2.$$

The electric charges on the ions are generally represented by + and − signs, but for convenience of printing we may add a dot to the symbol of the element or radical for each positive charge or a dash for each negative charge. Thus the ions in a copper sulphate solution are printed as $Cu^{\cdot\cdot}$ and SO_4'', instead of $\overset{++}{Cu}$ and $\overset{--}{SO_4}$. Positively-charged ions which are attracted to and discharged at the cathode are termed **cations**, *e.g.* $Na^{\cdot}$, $Ag^{\cdot}$, $NH_4^{\cdot}$, $Cu^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, etc. Negatively-charged ions which are attracted to the anode and there liberated are termed **anions**, *e.g.* Cl', Br', NO_3', SO_4'', CO_3'', PO_4''', etc.

Dissociation of electrolytes into ions. (*a*) *Faraday's theory of ions.*—Faraday supposed that ions were produced by the action of the electric current on the electrolyte, and that when no electric current was passing an aqueous solution of a salt or acid did not contain any ions. Clausius pointed out, however, that, since electrolytes obey Ohm's Law accurately, all the electrical energy of the current must be used up in driving ions through the solution, and that none of it could be expended in splitting up neutral molecules into ions. The latter must, therefore, already be free in the solution. Clausius supposed that a small fraction of the salt was ionised by molecular collisions and that a condition of equilibrium resulted as shown by the equation :

$$NaCl \rightleftharpoons Na^{\cdot} + Cl',$$

the smallness of the dissociation being indicated by the broken line of the upper barb.

(*b*) *Arrhenius's theory of electrolytic dissociation.*—In 1887 Arrhenius suggested that, instead of only a trace of the electrolyte being ionised, most salts were already very largely dissociated in solution, and tended to dissociate completely at great dilutions $NaCl \rightleftharpoons Na^{\cdot} + Cl'$.

This revolutionary doctrine was introduced in order to account for the observation of Kohlrausch, that *the efficiency of a salt in carrying the electric current increases with dilution*, when allowance is made for the quantity of salt available for electrolysis.

This effect can be shown very easily by converting the specific conductivity into an **equivalent conductivity** in order to correct for the dilution of the solution. For this purpose the specific conductivity is multiplied by the number of cubic centimetres which contain 1 gram-equivalent of the solute. Thus if κ is the specific conductivity, and Λ the equivalent conductivity:

$$\Lambda = \kappa V = \kappa/c,$$

where V is the volume in c.c. containing 1 gram-equivalent, and c is the concentration in gram-equivalents per c.c. The **molecular conductivity** is defined in a similar way, but the volume used is that containing *one gram-molecule* of the substance instead of *one gram-equivalent.*

An alternative way of picturing the equivalent conductivity of a salt is to think of a pair of electrodes 1 cm. apart, forming the walls of a large parallel-sided trough. One gram-equivalent of salt is dissolved in any desired quantity of water, say V c.c., and poured into the trough. The specific conductivity κ is then defined by the conduction through a single centimetre cube of the solution, whilst the equivalent conductivity Λ is given by the conduction over the whole area covered by the solution, *i.e.* by κV. Kohlrausch's discovery can be expressed by saying that the conductivity of the salt increases progressively when the volume of liquid in the trough is increased by the addition of pure water.

An illustration of this phenomenon is given in Table 77, which shows the specific and equivalent conductivities of potassium chloride in aqueous solutions. It will be seen that as the dilution increases, the equivalent conductivity Λ rises at first rapidly and then more slowly, and approaches a constant value in very dilute solutions. This limiting value is called the **equivalent conductivity at infinite dilution** and is written Λ_∞.*

* When the strength of the solution is expressed as a *concentration* instead of a dilution, the symbols Λ_c and Λ_0 are used instead of Λ_v and Λ_∞. We then write $\alpha = \Lambda_c/\Lambda_0$ instead of $\alpha = \Lambda_v/\Lambda_\infty$.

TABLE 77. SPECIFIC AND EQUIVALENT CONDUCTIVITIES OF POTASSIUM CHLORIDE SOLUTIONS AT 18°.

Concentration Equivalent/litre.	Dilution V c.c.	Specific conductivity. κ	Equivalent conductivity. $\Lambda = \kappa V$.	$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$.
1	1,000	0·09824	98·2	0·757
0·5	2,000	0·05100	102·0	0·784
0·1	10,000	0·01120	112·0	0·861
0·02	50,000	0·002395	119·8	0·921
0·01	100,000	0·001220	122·0	0·938
0·0001	10,000,000	0·00001291	129·1	0·993
0	∞	—	130·1	1·000

Arrhenius assumed that in electrolytic conduction the current was carried only by the ions. The limiting conductivity corresponded therefore to a complete dissociation of the molecules of the salt into ions, and the fraction of the salt which was dissociated at a given dilution V was given by $\alpha = \Lambda_v/\Lambda_\infty$.* The ratio α is termed the **degree of dissociation** of the salt, and it will be seen from the last column of Table 77 that, according to Arrhenius's theory, in a normal solution of potassium chloride, more than three-quarters of the salt is dissociated into ions.

The osmotic pressure of electrolytes.—The increased conducting power of a salt in dilute solutions, as deduced from the measurements of Kohlrausch, was quite contrary to the theories of electrolysis then existing. Thus Grotthuss had supposed that the conductivity of the solution was due to the formation of chains of molecules of the salt, which carried the current from one electrode to the other, and that the liberation of ions at the electrodes was effected by an interchange of acid and basic radicals along the chain.

Grotthus's theory, however, was obviously incompatible with an increase of efficiency on dilution, since this would make it more difficult to form the chains of salt molecules and easier to break them up. Arrhenius therefore fell back on a theory of activation (compare Chapter XII.), and suggested that some of the molecules of the electrolyte were active in electrolysis, whilst all the others were inactive. Since dilution with water

* See footnote on opposite page.

increased the proportion of active molecules, he suggested in 1883 that these were perhaps hydrated; but in 1887 he developed the idea that they were molecules which had already been split up into ions.

An experimental basis for this new theory was found in van't Hoff's observations on osmotic pressure, which have already been described in Chapter VII. It was there stated that abnormally low values are obtained for the molecular weights of many dissolved salts, as deduced from the depression of the freezing-point or from the osmotic pressure of the solution. In order to express these anomalous molecular weights, van't Hoff tabulated the values of a factor $i = \frac{\text{calculated mol. wt.}}{\text{observed mol. wt.}}$. Some values of i for approximately $N/5$ solutions are given in Table 78.

TABLE 78. VAN'T HOFF'S FACTOR.

Substance.	i from Osmotic pressure.	i from Freezing-point.
KCl - - - -	1·82	1·81
$MgCl_2$ - - -	2·68	2·79
$Ca(NO_3)_2$ - - -	2·47	2·48

These abnormally low molecular weights are shown only by electrolytes. Thus, cane-sugar and urea, which give non-conducting solutions, show a normal molecular weight in solution, so that $i = 1$; and even when abnormalities are observed in substances of this type, they are in the opposite direction and can, therefore, be attributed to polymerisation. The abnormal molecular weights of salts, which give large values of i, can only be explained by supposing that the molecules have been broken down into some smaller units; they can, therefore, be accounted for by the dissociation of the salt into the ready-formed ions which give to the solution the property of conducting the electric current.

This view is confirmed when the actual values of i are studied. Thus salts such as potassium chloride, which are decomposed by the electric current into two ions, give in dilute solutions a value $i = 2$, approximately, *i.e.* the average molecular weight is

approximately half that of the undissociated salt, as would be expected if the dissociation is nearly complete. On the other hand, salts such as $MgCl_2$, and $Ca(NO_3)_2$ give values of i which approach 3 in dilute solutions, a result that is readily understood if they are almost completely split up into three ions, thus

$$MgCl \rightarrow Mg^{\cdot\cdot} + 2Cl',$$
$$Ca(NO_3)_2 \rightarrow Ca^{\cdot\cdot} + 2NO_3'.$$

The most conclusive test of the theory of the large dissociation of salts was made, however, by showing that the electrical conductivity could be accounted for quantitatively by the progressive dissociation of the salt. Thus there is a broad general agreement between the values of α calculated from conductivity measurements by means of the ratio $\alpha = \Lambda_v/\Lambda_\infty$ and those deduced from the freezing-points of the solutions by means of the equation $i = (n-1)\alpha + 1$, where n is the number of ions produced from each molecule of the electrolyte. For instance, Table 79 gives the values of α for solutions of potassium chloride and potassium nitrate as calculated on the one hand from the freezing-point determinations of Adams (1916), and on the other hand from conductivity measurements. It will be seen that, except in the more concentrated solutions of potassium nitrate, there is very fair agreement between the values of α obtained by the two methods. This is very important evidence in favour of Arrhenius's theory of dissociation into ions, since, apart from this theory, no correlation between the electrical properties and the osmotic properties of the solutions had been foreseen.

TABLE 79. DEGREES OF DISSOCIATION FROM FREEZING-POINT DEPRESSION AND FROM CONDUCTIVITY MEASUREMENTS.

Concentration (Equivalents per litre).	Potassium chloride.		Potassium nitrate.	
	α (f.p.).	α (cond.).	α (f.p.).	α (cond.).
0·1	0·861	0·860	0·787	0·824
0·05	0·888	0·889	0·848	0·867
0·02	0·922	0·922	0·908	0·911
0·01	0·943	0·941	0·937	0·935
0·005	0·961	0·956	0·958	0·953
0·002	0·969	0·971	0·967	0·970

The theory of complete ionisation.—Arrhenius's theory of electrolytic dissociation postulates that in dilute solutions the free ions of a salt are enormously in excess of the neutral molecules. It therefore implies that a pair of atoms of potassium and chlorine, carrying opposite electric charges and therefore attracted to one another by electrical as well as by chemical forces, are actually in a more stable condition than when united to form a neutral molecule. Since the heat of formation of potassium chloride from metallic potassium and chlorine gas is more than 100,000 calories,

$$K\ (\text{metal}) + \tfrac{1}{2}Cl_2\ (\text{gas}) = KCl + 106{,}000\ \text{cal.},$$

it was almost incredible that the salt should decompose spontaneously into free atoms on mere dissolution in water, and even less credible that it should decompose into free atoms carrying opposite electric charges.

A partial explanation of the electrolytic dissociation of the salt could be found by reviving the original idea of Arrhenius, that the electrolytically-active salt is hydrated, *i.e.* that the ions have a greater affinity for water than has the neutral salt, since the addition of water must then promote the ionisation of the salt. This explanation is in harmony with the fact that electrical conductivity is only developed in a limited group of **ionising solvents,** including, in addition to water, liquid sulphur dioxide, liquid hydrogen cyanide, and liquid ammonia. Moreover, these solvents possess a large amount of residual affinity, and form a large number of addition-compounds. The amount of energy liberated in the formation of these addition-compounds is not large, however, and would scarcely be expected to suffice for the complete decomposition of a stable salt into its component atoms.

Ostwald attempted to get over this difficulty by describing the ions as " allotropic forms " of the element ; but this phrase was a mere gloss, which did not explain in the least degree why oppositely-charged atoms of sodium and chlorine should persist in a free state to the extent of perhaps 90 per cent., when the stable forms in which the metal and gas are prepared and used combine so vigorously with one another. It was Ostwald,

however, who made the daring suggestion that the atoms might perhaps liberate energy *by combination with their electric charges.* This suggestion was in complete opposition to the experimentally observed facts that the charging of a condenser always absorbs energy, and that, if the condenser is a conducting sphere, the energy required to impart a given charge to it is inversely proportional to the radius, and would therefore be enormous in the case of a sphere of atomic dimensions. Modern physics, however, has endorsed this daring suggestion so completely that it is now generally admitted that, *even in the solid state,* potassium chloride is merely an aggregate of ions of potassium and chlorine, and that these ions are so stable that they are incapable of discharging their opposite electric charges to form a neutral molecule of the salt.

According to this modern view a crystal of potassium chloride is merely an orderly assemblage of alternate potassium and chlorine ions; and the only "molecules" that can be formed (*e.g.* in strong solutions or in the vapour of the salt) are pairs of ions, forming electrically neutral "doublets." Since, however, the ions in these doublets are held together only by the electrostatic attraction of their opposite charges, and are not united by any real chemical "bond," they are perfectly free to interchange partners, and thus to undergo very rapid "double decomposition."

The theory of complete ionisation is not incompatible with Arrhenius's theory of electrolytic dissociation, since this term is a perfectly valid description of the separation from one another of pairs of pre-existing ions under the influence of an ionising solvent. Thus the **Nernst-Thomson Rule** postulates that, since the work required to separate two opposite electric charges is inversely proportional to the dielectric constant of the medium, the dissociation of the ions must be promoted by using a solvent of high dielectric capacity. This is obviously true if these ions are already in existence, whereas, if the atoms in the neutral molecule were united by a chemical bond (as Arrhenius supposed), this effect should be only of secondary importance. On the other hand, the theory of complete ionisation postulates that the variations of molecular conductivity

and of osmotic activity in dilute solutions are not due to variations in the *number* of ions, as Arrhenius supposed, but to variations in their *activity*, resulting from the phenomenon of **electro-striction**, *i.e.* the mutual attraction of oppositely-charged ions, giving rise to a modified distribution of these ions in the solution. The existence of ionic doublets in strong solutions is admitted, since there must be some tendency for oppositely-charged ions to cling together in pairs, but their concentration is supposed to be very much smaller than that of the neutral molecules postulated by Arrhenius's theory of electrolytic dissociation.

Complete and reversible ionisation.—Although many electrolytes retain their ionic structure in the crystal, others form real molecules, in which the opposite electric charges of the ions are neutralised by one another, and the radicals of the ions are united by chemical bonds. In these cases, we must suppose that molecules as well as ions can persist in solution, especially at high concentrations; the progressive ionisation of the salt in dilute solutions must then be attributed to an electrolytic dissociation of neutral molecules, exactly as postulated in Arrhenius's theory. Some examples of complete and reversible ionisation are set out below.

Complete Ionisation.		Reversible Ionisation.	
$Na^{\cdot}Cl'$	$\rightleftharpoons Na^{\cdot} + Cl'$	HCN	$\rightleftharpoons H^{\cdot} + CN'$
$K^{\cdot}OH'$	$\rightleftharpoons K^{\cdot} + OH'$	HCl	$\rightleftharpoons H^{\cdot} + Cl'$
$NEt^{\cdot}_4OH'$	$\rightleftharpoons NEt^{\cdot}_4 + OH'$	$NH_3 \cdot H \cdot OH$	$\rightleftharpoons NH^{\cdot}_4 + OH'$
$Ba^{\cdot\cdot}Cl_2''$	$\rightleftharpoons Ba^{\cdot\cdot} + 2Cl''$	$HgCl_2$	$\rightleftharpoons Hg^{\cdot\cdot} + 2Cl''$

Compounds of the first type, which includes the *alkalis* and the majority of the *metallic salts*, usually behave as "strong electrolytes" (p. 361) when fused, or when dissolved in a good ionising solvent. The second type includes a large number of "weak electrolytes"; but compounds of this type may behave as strong electrolytes if the bond between the radicals is too weak to serve as an effective check on the ionisation of the molecule. This second class includes the *acids*, which are all capable of forming real molecules. These molecules persist in the liquid state, but are ionised by contact with water, probably according to a scheme such as $H_2O + HCl \rightleftharpoons H_3O^{\cdot} + Cl'$, where the cation

is not a free proton, but an "oxonium ion," possessing all the properties that are commonly attributed to a hydrogen ion in aqueous solution.

The nitrogenous *bases* are also included in the second group as examples of reversible ionisation, since Moore and Winmill have suggested that the hydroxyl ion may be linked to nitrogen through a bivalent hydrogen atom, as shown in the symbol $NH_3 \cdot H \cdot OH$. In the case of the quaternary ammonium hydroxides, however, *e.g.* $NEt_4^{\cdot}|OH'$, this is no longer possible, and these quaternary hydroxides are, therefore, strong bases like the alkalis. Some *mercury* salts are also included in the list, since X-ray analysis has shown that compounds of this element may have a molecular instead of an ionic structure.

Whilst therefore the theory of complete ionisation applies to nearly all metallic salts, including the metallic hydroxides, the theory of electrolytic dissociation is still valid in its original form in the case of weak acids and weak bases, as well as in the limited group of weak salts.

30. The Transport of Ions.

i. Transport number for silver in silver nitrate.—The *transport apparatus* is shown in Fig. 65. The anode *A* consists of a stout silver wire soldered to a copper lead and sealed into the end of a glass tube with sealing wax. The cathode *C* is a small plate of platinum foil. The apparatus is filled, to a point a little above the bridge joining the two tubes, with a dilute solution of silver nitrate. Slots should be cut in the corks to allow any gases evolved to escape.

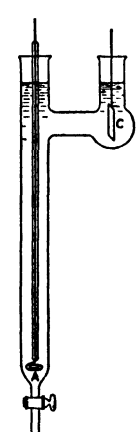


Fig. 65.—Transport apparatus.

The transport-apparatus is connected in series with a simple *silver voltameter*, Fig. 66. This consists of a wide-necked bottle closed by a rubber-stopper pierced with three holes. Two of these hold glass tubes into which the wires from the electrodes are sealed; the third is left open to allow gases to escape. The electrodes consist of sheets of platinum foil, about 3 cm. × 2 cm., mounted on platinum wires, and should be fixed parallel and about 3 cm. apart.

Prepare a solution containing one-tenth of a gram-equivalent of silver nitrate in 1000 *grams* of solution. Fill the transport apparatus with this solution, and weigh 100 grams of the solution into the voltameter. Connect the two pieces of apparatus in series and apply direct current from the lighting circuit (if available) for 1 to 2 hours. If direct current from the mains is not available, use a battery of accumulators (giving a pressure of about 50 volts) for 3 to 6 hours.

FIG. 66.—Voltameter.

Meanwhile, weigh out two 50 gram lots of the solution of silver nitrate, and titrate with decinormal potassium thiocyanate (Volhard's method). When the electrolysis is complete, run off through the tap into a weighed flask a volume of the solution corresponding roughly with that which would fill the long anode-limb of the transport-apparatus up to the bridge; weigh the flask and solution, and titrate with $N/10$ KCNS. Also transfer the liquid from the voltameter to a suitable flask, rinse out the bottle and electrodes with distilled water, and titrate the whole with the $N/10$ KCNS solution. The method of calculation is shown by the following example:

50 grams of the original solution required 48·7 c.c. of $N/10$ KCNS.

100 grams of this solution was placed in the voltameter; after electrolysis this solution required only 28·6 c.c. KCNS. The total current is therefore proportional to

$$2 \times 48{\cdot}7 - 28{\cdot}6 = \mathbf{68{\cdot}8} \text{ c.c. } N/10 \text{ KCNS.}$$

The anode solution weighed 39·5 gm. and required 74·9 c.c. of $N/10$ KCNS. Of this, however, 68·8 c.c. is due to the silver dissolved from the anode by NO'_3 ions. The amount of the original silver nitrate left at the anode is therefore proportional to $74{\cdot}9 - 68{\cdot}8 = 6{\cdot}1$ c.c. But silver originally present in this weight of solution is

$$\frac{39{\cdot}5}{50} \times 48{\cdot}7 = 38{\cdot}5 \text{ c.c.}$$

$$\therefore \text{ Loss of silver} = 38{\cdot}5 - 6{\cdot}1 = 32{\cdot}4 \text{ c.c.}$$

The transport number for silver $(1 - n)$ is given by

$$1 - n = \frac{\textit{loss at anode in equivalents}}{\textit{total current in equivalents}} = \frac{32{\cdot}4}{68{\cdot}8} = \mathbf{0{\cdot}471.}$$

The transport number for the nitrate ion is therefore **0·529.**

ii. Demonstration of movement of hydrogen ion. (Lodge.)—Shake 3 grams of powdered agar-agar with 100 c.c. of boiling water, and heat in a water-bath until solution is complete. Add phenol phthalein to the hot solution and then caustic soda drop by drop till a deep purple colour is produced. Pour the hot solution into the tube bent twice at right angles (Fig. 67), until the vertical limbs are half-filled, and allow the solution to set. When cold, support the tube in a dish of cold water, place dilute sulphuric acid over the jelly in the left-hand limb, and a solution of common salt in the right-hand limb. Close the tubes with corks, carrying small spirals of platinum wire to serve as electrodes, and with a groove cut in each cork to permit gases to escape. Connect to the lighting circuit, if direct current is available, taking care that the limb containing the acid is the anode. As the hydrogen ions are attracted towards the cathode, the phenol phthalein is decolorised, and the boundary between the colourless and coloured jelly will be seen to move steadily from the anode to the cathode. The speed depends upon the dimensions of the apparatus and the applied voltage. With a tube about 8 mm. diameter and 25 cm. distance between the electrodes, a pressure of 200 volts gives a speed of several centimetres per hour. It is necessary to immerse the tube in a bath of water, since otherwise the heat developed by the passage of the current may melt the jelly.

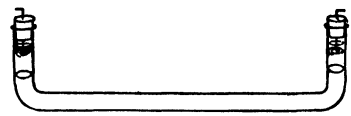


FIG. 67.—Lodge's apparatus for demonstrating the movement of ions.

The independent migration of ions.—From a long study of the conductivity of salt solutions, Kohlrausch found a very simple relation between the conductivities of a number of salts at infinite dilution. Thus, there is a *constant difference* between the values of Λ_∞ for sodium and potassium salts of the same ions:

KCl	130·1	KNO_3	126·5	KI	131·2
NaCl	109·0	$NaNO_3$	105·3	NaI	110·0
$K' - Na'$ =	21·0		21·2		21·2

There is also a constant difference between the values for the chloride and nitrate of a given metal.

KCl	130·1	NaCl	109·0	$\frac{1}{2}CaCl_2$	117·2
KNO_3	126·5	$NaNO_3$	105·3	$\frac{1}{2}Ca(NO_3)_2$	113·5
$Cl' - NO'_3$ =	3·6		3·7		3·7

In general, the equivalent conductivity at infinite dilution is an additive function, and can be predicted by adding together numbers which are characteristic of the ions in the solution.

The reason for this additive relationship is seen when the process of conduction by ions is considered a little more closely. The ions in a solution which is not undergoing electrolysis will be moving at random in all directions; when the electrodes are connected to the battery, however, the anions will be attracted towards the anode and will begin to move towards it, and similarly the cations will begin to move towards the cathode. Those which are nearest to the electrodes will arrive first and give up their charges, but others will be drawn from different parts of the solution as electrolysis proceeds. The passage of the current through the solution is therefore due to the neutralisation at the electrodes of the electric charges of the ions, and depends, not only upon the number of ions and the charge which they carry, but also upon the speed at which they move through the solution under a given electric potential.

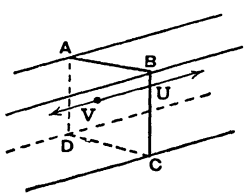


FIG. 68.—Diagram to illustrate the movement of ions.

It might seem at first sight that, since equal numbers of positive and negative ions are neutralised, the anions and cations must move with the same speed. This is not usually the case, and it is readily seen that, if the ions have different speeds, the salt as a whole will drift in the direction of the faster-moving ion. In Fig. 68, let *ABCD* be a section across a tube of solution undergoing electrolysis, under the action of a current flowing from left to right. Let us suppose that cations move to the right with a velocity U, which is twice as great as V, the velocity with which the anions move to the left. As soon, however, as a few positively-charged ions have crossed the plane *ABCD*, in excess of the number of negatively-charged ions which have crossed in the opposite direction, the solution to the right of this plane will become positively-charged and that to the left negatively-charged. There will therefore be strong electrostatic forces set up which will prevent the anions going to the left and will drag them to the right in the train of

the faster-moving cations. As a result, the salt as a whole will drift in the direction of the faster-moving ion.

It was shown by Hittorf that this drifting or transport of the electrolyte can be used to calculate the relative velocities of the anion and cation. This can be seen diagrammatically in Fig. 69. Line *I* of this diagram represents the solution of a salt *BA* which splits up into ions B' and A'. The thick lines represent the electrodes, and the dotted lines are imaginary planes which cut off the central portion of the liquid from the portions around the electrodes.

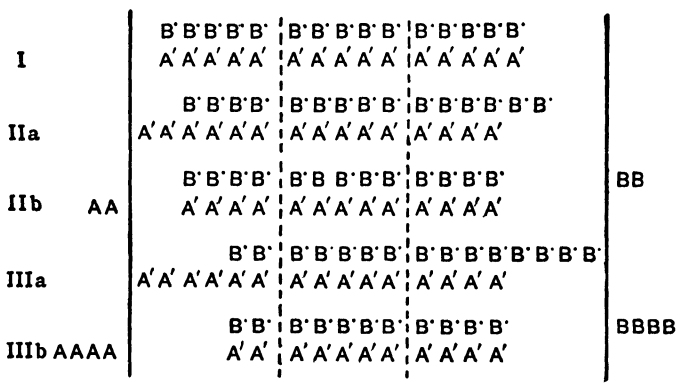


FIG. 69.—Diagrams to illustrate the migration of ions.

(i) Let us suppose that B' and A' have the same velocity. We therefore move the B' ions one place to the right, and the A' ions one place to the left. The result is shown in *II* (*a*). The unpaired ions will then be discharged at the electrodes, and the condition of affairs will be that represented in *II* (*b*), where the discharged ions are shown outside the electrodes.

In this diagram, each compartment contained 5 molecules of the salt in stage *I*; the anode and cathode compartments in *II* (*b*) have each lost one molecule of salt; and the losses in these two compartments are the same, because we have supposed that the anion and cation move with the same velocity.

(ii) Now let us suppose that the cation B' moves three times as rapidly as the anion A'. Stepping B' three places to the

right, and A' one place to the left, we get the condition in *III* (*a*), and when unpaired ions are discharged *III* (*b*) results. Here the anode compartment has lost three molecules of salt and the cathode compartment only one. Thus it follows that:

$$\frac{\textit{loss at anode}}{\textit{loss at cathode}} = \frac{\textit{speed of cation}}{\textit{speed of anion}}.$$

Note that the loss at each electrode is proportional to the speed of the ion which is *leaving* it. It is obvious from the diagram that this will only be true when the concentration in the central compartment is unchanged and the experiment must be carried out so that all the losses occur in the anode and cathode compartments.

Since the greater speed of an ion assists the passage of the current, we may suppose that a fraction n of the total current is carried by the anion and a fraction $1-n$ is carried by the kation. It follows from the diagram that

$$n = \frac{\textit{fall in concentration round cathode}}{\textit{total fall in concentration round anode and cathode}}.$$

Transport numbers.—The ratio n was termed by Hittorf the **transport number** of the anion. Obviously $1-n$ is the transport number of the cation. Let U = velocity of the cation, and V = velocity of the anion. Then

$$\frac{n}{1-n} = \frac{\textit{loss at cathode}}{\textit{total loss}} \times \frac{\textit{total loss}}{\textit{loss at anode}} = \frac{V}{U}.$$

If $U = V$, $\quad \frac{n}{1-n} = 1$ and $n = 0{\cdot}5$.

Experimental details for the determination of the transport number of NO'_3 in silver nitrate are given in Expt. 30, i. The following example of a similar experiment with copper sulphate will show the method of calculation.

A solution of copper sulphate containing 10 grams of copper per litre was electrolysed between copper electrodes. After electrolysis the cathode had gained in weight 1·886 grams and the anode had lost the same weight. The solution was divided into three parts; the cathode solution, with a volume of 500 c.c., contained 3·831 grams of copper; the middle solution was

unchanged in composition; the anode solution, with a volume of 500 c.c., contained 6·169 grams of copper.

The cathode solution contained originally $10 \times \frac{500}{1000} = 5{\cdot}000$ grams of copper, hence loss at cathode $= 5{\cdot}000 - 3{\cdot}831 = 1{\cdot}169$ grams. The transport number of the SO_4'' ion is therefore

$$n = \frac{\textit{loss at cathode}}{\textit{total loss electrolysed}} = \frac{1{\cdot}169}{1{\cdot}886} = \mathbf{0{\cdot}620.}$$

Similarly at the anode we have,

Copper present originally - -	5·000 grams
Copper dissolved from anode - -	1·886 ,,
Total copper - - - - -	6·886 grams
But copper found - - - -	6·169 ,,
∴ loss at anode - - - -	= 0·717 grams

Hence the transport number for copper =

$$1 - n = \frac{\textit{loss at anode}}{\textit{total electrolysed}} = \frac{0{\cdot}717}{1{\cdot}886} = \mathbf{0{\cdot}380.}$$

The ratio of the velocities of the sulphate and copper ions given by

$$\frac{V}{U} = \frac{n}{1-n} = \frac{0{\cdot}620}{0{\cdot}380} = \mathbf{1{\cdot}62.}$$

Kohlrausch's Law. Mobilities of ions.—Returning now to the regularities discussed on p. 339, it is possible by the aid of transport numbers to divide the equivalent conductivity of a salt into two parts, which are proportional to the speeds of the anion and of the cation. Thus, for KCl, we can take the experimentally determined values $\Lambda_\infty = 130{\cdot}1$ and $n = 0{\cdot}503$ for the limiting conductivity of the salt and the transport number of its anion. The fraction of this limiting conductivity due to the anion Cl' is therefore $130{\cdot}1 \times 0{\cdot}503 = \mathbf{65{\cdot}5}$, and that due to the cation $K^{\cdot}$ is $130{\cdot}1 \times 0{\cdot}493 = \mathbf{64{\cdot}6}$. These values are termed the **mobilities** of the ions.

When one pair of mobilities is known, others may be calculated from the relation, discovered by Kohlrausch, that the

difference between the values of Λ_∞ for two anions is independent of the cation and *vice-versa*. Thus in general,

$$\Lambda_\infty = \Lambda_\kappa + \Lambda_a$$

where Λ_κ and Λ_a are the mobilities of the cation and anion respectively.* Thus, using the figures on p. 339, Λ_∞ for NaCl is 109·0; then since $\Lambda_{Cl} = 65{\cdot}5$, $\Lambda_{Na} = 109{\cdot}0 - 65{\cdot}5 = \mathbf{43{\cdot}5}$. We can now get two independent values for the nitrate ion, since

$$\Lambda_{KNO_3} = 126{\cdot}5,\ \Lambda_K = 64{\cdot}6;\ \therefore\ \Lambda_{NO_3} = \mathbf{61{\cdot}9},$$

$$\Lambda_{NaNO_3} = 105{\cdot}3,\ \Lambda_{Na} = 43{\cdot}5;\ \therefore\ \Lambda_{NO_3} = \mathbf{61{\cdot}8}.$$

TABLE 80. IONIC MOBILITIES AT 18°.

Cations.		Anions.	
$H^\cdot$	313·9	OH'	174
$Na^\cdot$	43·4	Cl'	65·5
$K^\cdot$	64·6	Br'	67·7
NH_4	64·7	I'	66·6
$Ag^\cdot$	54·0	NO_3'	61·8
$\frac{1}{2}Ca^{\cdot\cdot}$	51·9	$\frac{1}{2}SO_4''$	68·5
$\frac{1}{2}Cu^{\cdot\cdot}$	45·9	$\frac{1}{2}CrO_4''$	72·0

Table 80 gives the **ionic mobilities** for a number of ions at 18°. By adding together the numbers for the ions concerned, the equivalent conductivity of any salt at infinite dilution can be predicted. Thus the calculated value of Λ_∞ for calcium chloride is $\frac{1}{2}CaCl_2 = 51{\cdot}9 + 65{\cdot}5 = 117{\cdot}4$; the observed value is 117·2.

Absolute velocity of ions.—Consider a cube of side 1 cm., in which electrolysis is taking place between two opposite faces with a difference of potential of 1 volt. The ions which will be discharged per second will be those which are U cm. from the anode and those which are V cm. from the cathode, where U and V are the velocities in centimetres per second of cation and anion under the unit potential gradient of 1 volt/cm. If the solution has a concentration of c equivalents per c.c., then the number of gram-equivalents discharged $= c \times (U + V)$, since this is the number of ions within the given distances from the two electrodes. Since each gram-equivalent of ions carries one faraday, or 96,500 coulombs, the total quantity of electricity which is

* These are commonly represented by the symbols u and v, so that $\Lambda_\infty = u + v$.

discharged at the electrodes per second is $96{,}500\,c \times (U+V)$. This is equal, however, to the current passing through the unit cell under a pressure of 1 volt, and is numerically equal to the *specific conductivity* κ of the solution as defined on p. 318 above. It therefore follows at once that

$$\kappa = 96{,}500c(U+V).$$

The *equivalent conductivity* of the solution is

$$\Lambda = \frac{\kappa}{c} = 96{,}500(U+V).$$

If the solution is very dilute $\Lambda = \Lambda_\infty = \Lambda_\kappa + \Lambda_a$.

$$\therefore\ U = \frac{\Lambda_\kappa}{96{,}500} \quad \text{and} \quad V = \frac{\Lambda_a}{96{,}500}$$

or $$\Lambda_\kappa = 96{,}500U, \quad \Lambda_a = 96{,}500V.$$

For the hydrogen ion $\Lambda_H = 313{\cdot}9$;

$$\therefore\ U = \frac{\Lambda_H}{96{,}500} = \frac{313{\cdot}9}{96{,}500} = 0{\cdot}00325 \text{ cm./sec.}$$

Thus this ion, which has a much larger mobility than others, only moves at a very slow speed through water when driven by a potential gradient of 1 volt per centimetre. This very slow movement is due to the resistance offered by the liquid, *i.e.* to its viscosity. It is found in fact that, when the viscosity of a liquid is lowered by heating, the conductivity increases almost proportionately (p. 346).

The movement of ions can be observed directly in certain cases. An arrangement due to Lodge for measuring the velocity of the hydrogen ion is described in Expt. 30, ii. Similar arrangements, in which the movement of a coloured boundary (*e.g.* between solutions of $K_2Cr_2O_7$ and K_2CO_3) is measured, have been used by other workers in order to determine the absolute velocities of the ions. In general, the velocities measured directly in this way agree approximately with the values calculated from the ionic mobilities.

Influence of temperature on conductivity.—The *resistance* of a metallic conductor usually increases when the temperature is raised, and falls when the temperature is lowered. In the case of certain pure metals, indeed, the resistance is roughly propor-

tional to the absolute temperature, although it falls abruptly to zero at the boiling-point of liquid helium, a few degrees before the absolute zero is reached. On the other hand, the *conductivity* of aqueous electrolytes is found to increase rapidly as the temperature is raised. Since this increase (about 3 per cent. per degree at 0°) corresponds roughly with the increase in the fluidity of the water, it is probably due to the increasing *mobility* of the ions and not to an increase in the *number* of free ions.

TABLE 81. VARIATION OF CONDUCTIVITY AND VISCOSITY WITH TEMPERATURE. $N/100$ KCl.

Temperature. t.	Specific Conductivity. κ.	Viscosity. η.	$\eta\kappa$.
0	$7{\cdot}76 \times 10^{-4}$	0·01793	$1{\cdot}392 \times 10^{-6}$
5	$8{\cdot}96 \times 10^{-4}$	0·01522	1·364
10	10·19	0·01311	1·336
15	11·47	0·01142	1·310
20	12·78	0·01006	1·286
25	14·12	0·00893	1·260
30	15·52	0·00800	1·240

Table 81 gives some data for $N/100$ KCl solution; the conductivity increases and the viscosity decreases rapidly as the temperature rises. If the influence of the lowered viscosity were the only factor to be considered, and the effect were a proportional one, then the product of viscosity and conductivity should be constant. The last column of the table shows that this quantity $\kappa \times \eta$ is nearly constant, but decreases slowly as the temperature rises. The diminution in the value of the product can be explained by supposing that the ratio $\alpha = \Lambda/\Lambda_\infty$ is less at higher temperatures.

The decrease of conductivity, which results from a fall in the degree of dissociation as the temperature rises, can be observed in badly conducting non-aqueous solutions, where the conductivity drops rapidly, tending towards a zero value *at the critical temperature*. There is, however, evidence that, when the viscosity of the solution is increased (*e.g.* by the addition of sugar), the increase of resistance is not directly proportional to the increase of viscosity, but to some lower power, *e.g.* $\kappa \propto \eta^{0{\cdot}7}$.

Non-aqueous solutions.—The properties of aqueous electrolytes, are in many respects abnormal, if only because of the formation of hydrated ions. Thus, Ciamician suggested in 1890 that an *anion* is surrounded by molecules of water with the hydrogen atoms facing the negative radical, whilst a *cation* is surrounded by molecules of water with the oxygen atoms facing the positive radical.

Walden sought to avoid these abnormalities by studying the behaviour of electrolytes in a large range of organic solvents, and in particular by making use of salts of the type of tetra-ethylammonium iodide, $N(C_2H_5)_4I$, where the nitrogen of the cation is already surrounded by a hydrocarbon " atmosphere " and is therefore unlikely to acquire an atmosphere of water, and where the anion also appears to have no great residual affinity. He was thus able to discover a number of simple laws, which could not have been deduced from a study of aqueous solutions alone. Thus :

I. *The limiting value* Λ_∞ *of the equivalent conductivity of a salt is inversely proportional* (i) *to the square root of its molecular weight and* (ii) *to the viscosity of the solvent.*

$$\Lambda_\infty = \frac{11{\cdot}15}{\eta_\infty \sqrt{M}}.$$

Table 82 gives the value of this numerical constant for fifty-five solutions, including aqueous solutions of two salts in which the tendency to form hydrates is at a minimum.

TABLE 82. EQUIVALENT CONDUCTIVITY IN NON-AQUEOUS SOLUTIONS.

Salt	Molecular weight. M.	Mean value. $\Lambda_\infty \eta_\infty$.	$\Lambda_\infty \eta_\infty \sqrt{M}$.
$N(CH_3)_4I$ -	201	0·745 in 9 solvents	10·6
$N(C_2H_5)_4I$ -	257	0·700 in 29 solvents	11·2
$N(C_3H_7)_4I$ -	313	0·624 in 10 solvents	11·1
$N(C_5H_{11})_4I$ -	425	0·557 in 5 solvents	11·5
RbI - -	212·4	0·806 in water	11·7
$RbNO_3$ - -	147·4	0·907 in water	11·0
		Mean -	11·2

II. *A dissolved salt gives a definite value for the ratio Λ/Λ_∞ at a dilution which is inversely proportional to the cube of the dielectric constant.*

Table 83 shows the value of $\epsilon\sqrt[3]{v}$ when $\Lambda/\Lambda_\infty = 0{\cdot}5$ for a series of strong electrolytes in various solvents at 25°.

TABLE 83. ELECTROLYTIC DISSOCIATION AND DIELECTRIC CONSTANT.

	ϵ.	v.	$\epsilon\sqrt[3]{v}$.
$AgNO_3$ in water - - -	81·7	0·7	73
NaCl in formic acid - -	62	2·1	79
NEt_4I in furfurol - -	42	5·0	72
KI in acetonitrile - -	36·4	11·0	81
$LiNO_3$ in methyl alcohol -	35·4	9·0	74
LiCl in ethyl alcohol - -	25·4	35	83
$NaNO_3$ in ammonia (at −33°)	22	70	90
KI in acetone - - -	21·2	60	83
KI in pyridine - - -	12·4	300	83
$N(C_3H_7)_4I$ in isobutyl alcohol	6·1	1700	73
			Mean 79

III. *The degree of dissociation of a dissolved salt is approximately constant for saturated solutions in any anhydrous solvent.*

Table 84 shows the degree of dissociation of tetraethylammonium iodide in nearly-saturated solutions at 25°.

TABLE 84. DISSOCIATION OF TETRAETHYLAMMONIUM IODIDE IN SATURATED SOLUTIONS AT 25°.

Solvent.	Solubility (gram. mol. in V litres).	Equivalent conductivity.			
		V.	Λ_v.	Λ_∞.	Λ_v/Λ_∞.
Methyl alcohol -	2·41	3·0	47·85	124	0·40
Glycol - -	3·40	4·0	4·26	8·3	0·51
Furfurol - -	4·82	5·0	26·83	50	0·52
Acetonitrile -	8·46	10·0	96·4	200	0·48
Ethyl alcohol	29·2	30·0	24·53	59·0	0·42
Acetone - -	103·3	103·8	112·0	225	0·50
Ethyl nitrite -	415	428	68·67	140	0·49
				Mean	0·47

By using compounds of the type of tetraamylammonium iodide, $N(C_5H_{11})_4I$, Walden was also able to prepare solutions

of a number of salts in hydrocarbon solvents with dielectric constants of 10 or less. These solutions behaved as electrolytes, but the effect of dilution was abnormal, since the molecular conductivity often passed through a minimum value, from which it increased at higher concentrations as well as at higher dilutions.

These peculiar solutions may be compared with colloidal electrolytes (p. 414). Thus the solubility in water of a soap, such as sodium palmitate, $C_{15}H_{31} \cdot CO \cdot ONa$, can be attributed to the affinity for water of the metallic cation, which is strong enough to compel the hydrocarbon radical of the fatty acid to enter into the aqueous solution. In the same way the solubility of tetraamylammonium iodide in hydrocarbon solvents can be attributed to the fact that the cation, $NC_{20}H_{44}$, has very nearly the composition of a hydrocarbon, and might therefore be expected to dissolve in a medium of similar composition, thus compelling the iodide ion also to dissolve in the same solvent. It is, therefore, not surprising that the properties of the solution should be abnormal, in marked contrast to the regularities which are generally observed in non-aqueous electrolytes.

QUESTIONS ON CHAPTER XIII.

1. Explain what takes place when an electric current is passed between two plates of copper immersed in copper sulphate solution, and indicate carefully the difference between the way in which the current is conducted by the solution and by a metal. What is the relation between the quantity of metal deposited and the current passed ? How may equivalent weights be determined by an application of this relation ? (B.A., Madras.)

2. What are the principal characteristics of electrolytic conduction ? How far do you consider they are to be explained by the hypothesis of ionic dissociation ?
(Natural Science Schols., Oxford.)

3. What observations have led to the view that salts are ionised in solution ? What is meant by the degree of dissociation, and how is it measured ? (School Certificate, Joint Matric. Board.)

4. In what sense is the osmotic pressure of a solution comparable with the pressure of a gas ? Calculate the osmotic pressure of a $0{\cdot}1N$ acetic acid solution at 20° C., assuming that the acid is non-ionised. Explain why the osmotic pressure of a $0{\cdot}1N$ solution of sodium chloride is nearly twice as great. (Higher School Cert.)

5. A one per cent. solution of glucose $C_6H_{12}O_6$ in water has a freezing-point of $-0{\cdot}103°$ C. A one per cent. solution of sodium chloride freezes at $-0{\cdot}604°$ C. and a one per cent. solution of potassium iodide at $-0{\cdot}213°$ C. Explain what conclusions can be drawn from these data. (C = 12, O = 16, Na = 23, K = 39, Cl = 35·5, I = 127.) (Natural Science Schols., Oxford.)

6. State Faraday's laws of electrolysis and show how they may be experimentally verified.

Explain on the basis of the ionic hypothesis the reactions which take place during the electrolysis of (i) dilute sulphuric acid, (ii) a hot solution of sodium chloride, (iii) a solution of potassium iodide.
(Higher School Certificate, Joint Matric. Board.)

7. An electric current is passed between platinum plates through solutions of copper sulphate, silver nitrate and dilute sulphuric acid, the solutions being placed in series. Explain what happens in each case. If 0·105 gm. of copper is deposited in the first cell, calculate (*a*) the weight of silver separated from the second solution, (*b*) the volume of hydrogen, measured at 15° C. and 740 mm., which is liberated from the third solution. H = 1, Cu = 63·5, Ag = 108.
(Higher School Certificate, Joint Matric. Board.)

8. The molecular conductivity of a five per cent. solution of chromium trioxide is not increased by further dilution; its freezing-point is $-1{\cdot}34°$ C. What conclusions can you draw as to the condition in which the oxide exists in solution (K for water = 19).
(B.A., Bombay.)

9. When the solution of the sulphate of a certain metal was electrolysed (secondary reactions being avoided) it was found that for every gram of the metal deposited at the cathode 146 c.c. of oxygen at 0° and 760 mm. were evolved at the anode. The specific heat of the metal was about 0·058. Find its atomic weight. Mention further experiments which might be tried to confirm the place of the element in the periodic classification.
(Pembroke College, Entrance Schol.)

10. Describe and explain on the basis of the theory of electrolytic dissociation the changes which occur when an electric current is passed between platinum electrodes immersed in aqueous solutions of the following substances, (*a*) when the products of electrolysis are allowed to recombine, (*b*) when they are kept apart; silver nitrate, sodium chloride, hydrochloric acid, copper sulphate. (Inter. Sci., Manchester.)

11. Summarise the developments in electrochemistry associated with the names of Faraday, Hittorf and Arrhenius.
(B.Sc., Sheffield.)

12. Explain the significance and inter-relationship of the following: transport numbers; equivalent conductance at infinite dilution; ionic mobilities.

The velocity of migration of the silver ion at 18° C. is 0·000577

cm. per sec. and of the NO_3 ion 0·000630 cm. per sec. The specific conductance of 0·1*N* $AgNO_3$ solution at 18° is 0·00947 reciprocal ohms. What is the degree of dissociation of silver nitrate ? (Inter. Sci., Sheffield.)

13. Describe what happens when a current of electricity is passed through the following cells:

(*a*) Copper nitrate solution with platinum electrodes.
(*b*) Concentrated hydrochloric acid with platinum electrodes.
(*c*) Dilute sulphuric acid, lead anode, cathode of lead coated with lead peroxide.
(*d*) Sodium sulphate solution with platinum electrodes.
(Inter. Sci., Sheffield.)

14. Write an essay on the determination of transport numbers and their application to the elucidation of the state of solutes in solution. (B.Sc. Hons., Sheffield.)

15. Give an account of the effect of (*a*) viscosity, (*b*) temperature on the conductivity of a solution of an electrolyte.
(B.Sc. Hons., Sheffield.)

16. The absolute velocity of the silver ion is 0·00057 cm. per second, and of the nitrate ion 0·00069 cm. per second, both at 25° C. Calculate the conductance of a normal silver nitrate solution at 25° C. given that van't Hoff's factor for this solution is 1·58. (B.Sc., Sheffield.)

CHAPTER XIV.

APPLICATIONS TO ELECTROLYTES OF THE LAW OF MASS-ACTION.

31. The Strength of Acids and Bases.

i. Comparison of the strength of acids.—By the method outlined in Expt. 26, i., determine the velocity coefficients at 25° of the hydrolysis of methyl acetate by (1) $N/2$ hydrochloric acid, (2) $N/2$ sulphuric acid, (3) $N/2$ monochloracetic acid. Compare the relative strengths of the acids as given by the ratios of the velocity coefficients with the relative strengths deduced from conductivity measurements, as given in Table 85.

The "strength" of acids and bases.—An **acid** was first defined by its sour taste, and then by its power of changing the colour of certain vegetable colours (which could therefore be used as "indicators"), and its ability to decompose carbonates, giving rise to "neutral salts." A **base** was merely a substance—alkali, earth or metal—which could neutralise an acid, and thereby give rise to a **salt**. Since all acids contain *hydrogen* (and not oxygen, as Lavoisier supposed) and this hydrogen is replaced by a metal when the acid is converted into a salt, the acids were regarded by Davy (1816) as compounds in which the hydrogen may be considered as "acting the part" played by a metal in the salts derived from it. The view that acids are merely "hydrogen-salts" is confirmed by the fact that, when an acid is electrolysed, hydrogen is set free at the cathode, just as copper is set free when a copper salt is electrolysed.

According to the theory of electrolytic dissociation, an acid is dissociated reversibly in solution giving rise to hydrogen ions, *e.g.*

$$HCl \rightleftharpoons H^{\cdot} + Cl',$$
$$H_2SO_4 \rightleftharpoons 2H^{\cdot} + SO_4'',$$
$$H_2C_2O_4 \rightleftharpoons 2H^{\cdot} + C_2O_4'', \text{ etc.}$$

The formation of a hydrogen ion is therefore a characteristic property of an acid, and the view was advanced that the acidity of a solution can be measured in precise terms by the concentration of hydrogen ions which it contains. This concentration can be deduced from measurements of electrical conductivity, since (if the mobility of the ions is constant), the degree of dissociation of an electrolyte is given by the ratio $\alpha = \Lambda_v/\Lambda_\infty$ (p. 331). Table 85 shows the degree of dissociation deduced in this way for a number of acids at concentrations of $N/2$ and $N/1000$.

TABLE 85. DEGREE OF DISSOCIATION OF ACIDS AT 25°.

	Degree of dissociation.	
	at $N/2$.	at $N/1000$.
(*a*) *Strong acids.*		
Hydrochloric acid	0·862	0·993
Nitric acid	0·862	0·997
Sulphuric acid	0·536	0·960
Trichloracetic acid	0·760	0·990
(*b*) *Weak acids.*		
Monochloracetic acid	0·054	0·692
Formic acid	0·020	0·368
Acetic acid	0·006	0·126
Carbonic acid	0·0008	0·017
Hydrocyanic acid	0·00005	0·0011

It will be seen that the degree of dissociation varies greatly both with the nature of the acid and with the concentration; but the **strength of an acid** can be stated in terms of its degree of dissociation *at a given concentration.* It is then clear that this method of measurement enables us to divide the acids roughly into two groups, namely **strong acids**, which are largely dissociated, and **weak acids**, which are feebly dissociated in aqueous solutions of a given concentration. It should be noted, however, that the individual acids in each group vary widely in strength; thus acetic acid, although a weak acid, is more than a hundred times as strong as hydrocyanic acid.

Since the degree of dissociation of an electrolyte increases with dilution, all acids tend to become equal in strength at very high dilutions. This is illustrated by the figures in the last column of the table, from which it will be seen that at a dilution of $N/1000$ all the strong acids are nearly equal in strength, and

that even some of the weaker acids are now dissociated to a considerable extent.

Displacement of weak by strong acids.—The earliest method of judging the strength of an acid was by its ability to liberate other acids from their salts. Thus, sulphuric acid was regarded as a stronger acid than nitric or hydrochloric acid because the latter acids could be set free from their salts by the action of sulphuric acid. We now know that this method is untrustworthy, because these reactions give rise to a chemical equilibrium, and the ultimate course of the action depends much more on the relative volatility of the acids than on their strengths. Thus in the reversible actions represented by the equations :

$$KNO_3 + H_2SO_4 \rightleftharpoons KHSO_4 + HNO_3,$$
$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl,$$

the change proceeds to completion in the sense of the upper arrow *when the mixture is heated.* This displacement is almost inevitable in view of the fact that nitric acid and hydrogen chloride are much more volatile than sulphuric acid, and can therefore be driven off as fast as they are formed, without boiling off the less volatile sulphuric acid. When, however, nitric acid is added to potassium sulphate *in the cold*, potassium nitrate crystallises out and the action proceeds in the reverse direction. In the same way when hydrochloric acid is added to a solution of silver sulphate, the action proceeds from left to right in the equation $2HCl + Ag_2SO_4 \rightarrow 2AgCl + H_2SO_4$,

i.e. hydrochloric acid displaces sulphuric acid from silver sulphate and gives rise to a quantitative yield of silver chloride.

In reality, these actions are all reversible, and it is the sparing solubility of the potassium nitrate and the insolubility of silver chloride which cause the action to proceed in the opposite direction from that of the actions which serve for the commercial preparation of nitric and hydrochloric acids, which in their turn are determined by the volatility of the acids.

It is therefore obvious that no conclusions as to the relative strengths of acids can be drawn from experiments in which one of the acids is allowed to vaporise, since, if this classification were adopted, ordinary sand would be classed as one of the very

strongest acids, in view of the fact that sodium sulphate can be converted into sodium silicate by fusion with sand, as in the manufacture of glass. Nor can we use methods in which one of the products is allowed to crystallise out from the mixture. We must therefore employ methods in which the equilibrium between the undissociated acid and its ions is not disturbed either by the separation of a solid or gaseous phase or by reagents introduced as tests of acidity.

Thus titration with an alkali can be used to measure the total concentration of an acid, but not the concentration of its ions, since a weak acid will produce more hydrogen ions as fast as those initially present are neutralised, and the process will go on till all the acid is neutralised.

Avidity of acids and bases.—The strength of acids and bases in dilute solution can be compared most readily by making them compete for a base, and determining by some physical method the proportion of the base which each obtains. In such solutions there is no disturbance of the equilibrium by separation of a solid or a gas. Julius Thomsen first used heats of neutralisation in the following manner, and arranged acids in the order of their **avidity** (*i.e.* their relative affinity) for a base. In dilute solution (about $N/5$) the heats of neutralisation by potash of hydrochloric and sulphuric acids are 13,700 cal. and 15,700 cal. It follows from Hess's law that if 1 equivalent of sulphuric acid, when added to a solution of 1 equivalent of potassium chloride, displaced all the hydrochloric acid, there should be an evolution of 2000 calories of heat. It was found by experiment that only 700 calories were evolved, indicating that the reaction

$$KCl + \tfrac{1}{2}H_2SO_4 \rightleftharpoons \tfrac{1}{2}K_2SO_4 + HCl$$

reached an equilibrium when $700/2000 = 0{\cdot}350$ of the sulphuric acid had combined with the base. The relative avidities of hydrochloric acid and sulphuric acid were assumed to be proportional to the amounts combined with the base at equilibrium, *i.e.* as $0{\cdot}650 : 0{\cdot}350$ or $100 : 54$.

Ostwald measured also the small changes in volume and in refractive index which accompany neutralisation and found that the order of the avidities was the same. In 1884 he showed

that the order of avidities was also the order of the electrical conductivities of the acids, and this proportionality was confirmed by the other methods described below.

Methods of measuring the strength of acids.—The most important methods of measuring the strengths of acids, apart from the method which depends on the measurement of their electrical conductivity, are set out below.

(*a*) *Determination of degree of dissociation by depression of the freezing-point.*—It is obvious that, if the property of acidity is due to the presence of hydrogen ions, any method of determining the degree of dissociation of an acid may be used to measure the acidity of the solution. For instance, the depression of the freezing-point can be measured quite easily, and gives values for the strength of an acid which are in good general agreement with the results of a study of electrical conductivity. This method can only be used, however, when no other substances but the acid itself are present in the solution.

(*b*) *Hydrolysis of salts.*—It is found by experience that salts of strong bases with a strong acid are neutral in aqueous solution, whilst salts of a strong base with a weak acid give alkaline solutions. Thus sodium chloride and sulphate give solutions which are neutral to litmus, whilst solutions of sodium carbonate and of sodium cyanide are strongly alkaline. The liberation of alkali in the latter cases may be regarded as due to a splitting up of the salt by water which is therefore described as the **hydrolysis** of the salt, thus:

$$NaCN + HOH \rightleftharpoons NaOH + HCN.$$

This hydrolysis is shown, in § 33 below, to be due to the tendency of the anion of a weak acid to form undissociated molecules, by combination with hydrogen ions produced by the electrolytic dissociation of water. The extent of the hydrolysis is therefore a measure of the *weakness* of the acids, as judged by the criterion set on p. 354 above.

Acids as proton-donors.—The two preceding methods of measuring the strength of an acid depend on the electrolytic dissociation of the acid, $HX \rightleftharpoons H' + X'$. They therefore give similar values to those deduced from measurements of electrical conductivity; but this is no longer true when the strength of the

acid is measured by its catalytic activity in isomeric change or in hydrolysis. In these processes, the function of the acid is to give a hydrogen ion $H^{\cdot}$ (or, more accurately, a positively-charged hydrogen nucleus, or "proton") to the organic compound, *i.e.* the acid acts as a **proton-donor,** and not as an electrolyte.

The "hydrogen ions" produced by the electrolytic dissociation of an acid are not free protons, since these are much too active to exist in a free state in solution. The ionisation of the acid should therefore be represented as an interaction with water and not as a mere dissociation

$$OH_2 + HCl \rightleftharpoons OH^{\cdot}_3 + Cl' \text{ not } HCl \rightleftharpoons H^{\cdot} + Cl'.$$

The "oxonium ions" $OH^{\cdot}_3$ shown in this equation then play the part generally assigned to "hydrogen ions," and in particular are responsible for a large part of the conductivity of the acid solution. They can also act as proton-donors, but only by a highly endothermic action

$$OH^{\cdot}_3 \rightleftharpoons OH_2 + H^{\cdot} - 180{,}000 \text{ cal.}$$

In the case of a strong acid, however, the undissociated molecules of the acid can also act as proton-donors, since they can give a proton directly to the organic compound, instead of first passing it on to the water to form an oxonium ion. These molecules contribute nothing to the conductivity of the solution, but are even more efficient catalysts than the (hydrated) "hydrogen ions." The molecules of a weak acid are less active than those of a strong acid, since they are less ready to dissociate into ions; but they can also act as proton-donors and possess small but definite catalytic-coefficients.

It is also clear that the cation of a weak nitrogenous base can act as a proton-donor, provided that the neutralisation of the base is reversible, *e.g.*

NH_3	+	HCl	$\rightleftharpoons$	$NH_4^{\cdot}$	+	Cl'
Basic molecule		Acidic molecule		Acidic cation		Basic anion

The cation of a weak base must therefore be classed as an acid; conversely, the anion of a weak acid must be classed as a base, since it possesses the power of accepting a proton, as shown in the equation $X' + H^{\cdot} \rightleftharpoons HX$. We therefore find that the

cation of a weak nitrogenous base, *e.g.* NH'_4 and the anion of a weak acid, *e.g.* $CH_3 \cdot CO \cdot O'$, have a definite catalytic activity of their own, which can be measured in terms of an independent "catalytic-coefficient" (p. 308). On the other hand, a metallic cation, such as Na', which can neither give nor take a proton, has no direct catalytic activity. In the same way the anion, *e.g.* Cl', of a strong acid, which is almost completely ionised in solution, has little if any catalytic activity, since its ability to hold a proton is much less than in the case of the anion of a weak acid.

Properties of bases.—A base is a substance which possesses the property of neutralising an acid. It may therefore be defined as a "proton-acceptor," *i.e.* as a substance which can combine with or eliminate hydrogen ions. In aqueous solutions, where hydrogen and hydroxyl ions are always in equilibrium with one another, union with hydrogen ions results in the liberation of hydroxyl ions from the water, in accordance with the laws of mass-action as applied to the equation

$$H_2O \rightleftharpoons H' + OH'.$$

The **strength of a base** can therefore be defined in terms of the alkalinity of the solution, as measured by the concentration of hydroxyl ions, just as the acidity of a solution is measured by the concentration of hydrogen ions. According to this definition the strength of an alkali is proportional to its degree of dissociation at a given concentration, *e.g.*

$$NaOH \rightleftharpoons Na' + OH',$$
$$Ba(OH)_2 \rightleftharpoons Ba'' + 2OH'.$$

The strength of a nitrogenous base, such as ammonia, which contains no oxygen, and cannot therefore liberate hydroxyl by electrolytic dissociation, is a more complex property, since the alkalinity of its aqueous solutions depends on the ability of the base to liberate hydroxyl ions from water. It is therefore a function both of the readiness of the base to unite with water to form a hydrate, and of the "degree of dissociation" of this hydrate in terms of an equation such as

$$NH_3 + H_2O \rightleftharpoons NH_4 \cdot OH^* \rightleftharpoons NH'_4 + OH'.$$

* The formation of intermediate hydroxides is discussed on p. 337.

TABLE 86. DEGREE OF DISSOCIATION OF BASES.

		α at $N/2$.	α at $N/1000$.
(*a*) *Strong bases.*			
Potassium hydroxide	KOH	0·826	0·981
Sodium hydroxide -	NaOH	0·795	0·966
Barium hydroxide -	$Ba(OH)_2$	0·90 (at $N/10$)	0·977
(*b*) *Weak bases.*			
Methylamine: $CH_3 \cdot NH_2 + H_2O \rightleftharpoons CH_3 \cdot \overset{+}{N}H_3 + \bar{O}H$		0·313	0·500
Ammonia: $NH_3 + H_2O \rightleftharpoons \overset{+}{N}H_4 + \bar{O}H$		0·0068	0·141
Aniline: $C_6H_5 \cdot NH_2 + H_2O \rightleftharpoons C_6H_5 \cdot \overset{+}{N}H_3 + \bar{O}H$		0·000030	0·00068

Table 86 gives the degree of dissociation of a number of bases as determined by a study of the electrical conductivity of their aqueous solutions. It will be seen that there are again two well-marked groups, namely, **strong bases,** which are largely dissociated at moderate dilutions, and **weak bases** which are only feebly dissociated at moderate dilutions.

Determination of strength of bases.—The strength of bases can be determined by a series of methods which are precisely similar to those described for acids. Thus the degree of dissociation of an alkali can be deduced from the depression of the freezing-point of an aqueous solution, and the values found in this way are in good agreement with those obtained from measurements of conductivity.

The strength of an alkali can also be deduced from the velocity of saponification of an ester, as represented by the equation

$$CH_3 \cdot COOCH_3 + OH' \rightarrow CH_3 \cdot COO' + CH_3 \cdot OH,$$

where the metallic ion of the alkali (which remains unchanged) is omitted from the equation and only the hydroxyl ion is shown. This hydroxyl ion is used up as the reaction proceeds, so that the change follows a bimolecular law; but, if a large excess of ester is used, its concentration remains nearly constant, and the rate of hydrolysis gives a measure of the strength of the alkali.

Finally, a weak base can be detected by the hydrolysis of its salts. Salts of strong acids and strong bases give neutral solutions whilst salts of strong acids and weak bases are acid in

solution. This acidity can scarcely be detected in a solution of ammonium chloride, but it is very marked in the salts of very weak bases, *e.g.* in aluminium chloride and in aniline hydrochloride.

Catalysis by bases.—It was formerly supposed that catalysis in alkaline solutions depended exclusively on the hydroxyl ions, just as catalysis by acids was attributed exclusively to hydrogen ions. It was therefore believed that the concentration of hydroxyl ions in an alkaline solution could be deduced from experiments on catalysis, such as have been described in Chap. XII. (p. 309). This is now known to be untrue, since other components of the solutions also act as catalysts. Thus an alkaline mixture of boric acid and borax is a powerful catalyst for the mutarotation of glucose; but this effect is due mainly to the borate ions, and not to the small proportion of hydroxyl ions, which are present in solution as a product of hydrolysis of the salt. Again, bases can act as catalysts for *isomeric change* in non-aqueous solutions, *e.g.* in benzene, where there can be no hydroxyl ions, since there is no oxygen in the system. On the other hand, *hydrolysis*, which depends on the addition of the elements of water to the substance hydrolysed, is only possible in media which can yield both hydrogen and hydroxyl ions.

Strong and weak electrolytes.—Strong acids and strong bases resemble metallic salts in being largely dissociated at moderate dilutions. These three classes of substances are therefore spoken of as **strong electrolytes.** On the other hand, weak acids and bases, which are only feebly dissociated at moderate dilutions, are described as **weak electrolytes.** In the next section it will be shown that a significant difference between these two classes is disclosed when the effect of dilution upon the degree of dissociation is studied quantitatively.

32. The Dilution Law.

1. Dissociation-constant of acetic acid.—By the methods described in Expt. 29, determine the molecular conductivity at 25° of acetic acid at concentrations of $N/10$, $N/20$, $N/40$, $N/80$,

$N/160$, $N/320$, etc. For this experiment it is convenient to calibrate two pipettes, one to deliver 10 c.c. and the other to withdraw 10 c.c. Place 20 c.c. of $N/10$ acetic acid in the cell, and, after measuring the conductivity, withdraw 10 c.c. of the acid and add 10 c.c. of conductivity water. Mix the solutions by moving the electrodes slowly up and down, and measure the resistance again. Repeat the dilution and measurement until at least six observations have been made. The conductivity of the water must be determined, since the correction for this becomes important at the higher dilutions. At 25°, Λ_∞ for acetic acid is 398. Using this value, calculate from your results the degree of dissociation at each dilution and the dissociation-constant of the acid.

Ostwald's dilution law.—The law of mass-action was applied by Ostwald to the dissociation of an electrolyte in the following manner. Let us suppose that we are dealing with a binary electrolyte, that is, one that dissociates into two ions. The electrolytic dissociation of an acid such as acetic acid may then be expressed as a reversible action as follows :

$$\underset{1-\alpha}{CH_3 \cdot COOH} \rightleftharpoons \underset{\alpha}{CH_3COO'} + \underset{\alpha}{H^{\cdot}}.$$

Let the fraction dissociated at a dilution V be α; the proportion of undissociated acid is then $1-\alpha$. By the law of mass-action :

$$\frac{[CH_3COO'][H^{\cdot}]}{[CH_3 \cdot COOH]} = K. \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The concentration of $CH_3 \cdot COO'$ and of $H^{\cdot}$ is, however, α/V; and the concentration of $CH_3 \cdot COOH$ is $(1-\alpha)/V$, so that

$$K = \frac{\alpha^2}{V(1-\alpha)}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Formula (2) is usually described as **Ostwald's dilution law.**

To test the accuracy of this formula it is necessary to determine α for a number of values of V. This can be done by measurements of freezing-point depression ; but more accurate values are obtained from conductivity measurements. Table 87 contains some of the data found by van't Hoff and Reicher for acetic acid.

TABLE 87. DISSOCIATION OF ACETIC ACID AT 14·1°.

V.	Λ.	$\alpha = \frac{\Lambda}{\Lambda_\infty}$.	$K = \frac{\alpha^2}{V(1-\alpha)}$.
2·02 litres	1·94	0·00614	$1·88 \times 10^{-5}$
15·9 ,,	5·26	0·0166	1·76 ,,
1500 ,,	46·6	0·147	1·69 ,,
3010 ,,	64·8	0·205	1·76 ,,
7480 ,,	95·1	0·301	1·73 ,,
15000 ,,	129·0	0·408	1·87 ,,
∞	316·0	—	—

It will be seen that the dilution law holds for acetic acid over a range of dilutions from 2 to 15,000 litres or more for each gram-molecule of acid. In the same way it has been found that a large number of *weak acids* and *weak bases* in aqueous solution obey the dilution law with a high degree of accuracy.

The numerical value of the constant K in Ostwald's equation gives a very convenient measure of the strength of a weak acid. From formula (2) it follows that

$$\alpha^2 = KV(1-\alpha); \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

but, since α is very small for a weak acid at moderate dilutions, $1-\alpha$ is practically equal to unity, so that

$$\alpha = \sqrt{KV}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

This formula is very useful for calculating the degree of dissociation at moderate dilutions. Thus, when the dilution is 1 litre, so that

$$V = 1,$$
$$\alpha = \sqrt{K}.$$

The "strength" of a weak acid in a normal aqueous solution is therefore proportional to the square root of its dissociation-constant.

Dissociation-constants of acids.—Table 88 gives the values of K for a number of organic acids, and in particular shows the effect of substitution upon the dissociation-constants of certain acids. Thus the effect produced on the strength of the acids of the acetic series by substituting chlorine for hydrogen is remarkable. In the homologous series of fatty acids, however, although formic acid is much stronger than acetic acid, the decrease in

K becomes insignificant as the series is extended further. The position of a substituent in the molecule is also of importance. Thus *o*-nitrobenzoic acid has a much larger dissociation-constant, and is therefore a much stronger acid, than the isomeric *m*- and *p*-nitrobenzoic acids, whilst *m*-cresol is definitely stronger than *o*- and *p*-cresol.

TABLE 88. DISSOCIATION-CONSTANTS OF ACIDS.

Acid.	t.	$k \times 10^5$.
Acetic acid	25°	1·86
Monochloracetic acid	25°	155·
Dichloracetic acid	25°	5,000·
Trichloracetic acid	18° about	20,000·
Formic acid	25°	21·4
Acetic acid	25°	1·86
Propionic acid	25°	1·4
Benzoic acid	25°	6·6
o-Toluic acid	25°	12·5
m-Toluic acid	25°	5·6
p-Toluic acid	25°	4·3
o-Nitrobenzoic acid	25°	630
m-Nitrobenzoic acid	25°	35
p-Nitrobenzoic acid	25°	40
Carbonic acid	18°	0·0304
Hydrogen sulphide	18°	0·0057
Hydrocyanic acid	18°	0·00013
Phenol	18°	0·000013
o-Cresol	25°	0·0000063
m-Cresol	25°	0·0000098
p-Cresol	25°	0·0000067

The dibasic organic acids would not perhaps be expected to obey the dilution law, but in practice it is found that the conductivities give a steady value for K. This is explained by a two-stage dissociation, *e.g.* for succinic acid.

$$\begin{array}{l} CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{array} \rightleftharpoons \begin{array}{l} CH_2 \cdot COO' \\ | \\ CH_2 \cdot COOH \end{array} + H'$$

followed by

$$\begin{array}{l} CH_2 \cdot COO' \\ | \\ CH_2 \cdot COOH \end{array} \rightleftharpoons \begin{array}{l} CH_2 \cdot COO' \\ | \\ CH_2 \cdot COO' \end{array} + H'$$

The ion $COOH \cdot CH_2 \cdot CH_2 \cdot COO'$ is such a very weak acid that it does not show any appreciable dissociation until very high dilutions are reached, and at moderate dilutions the value found for K is that corresponding to the first stage of the dissociation.

Dissociation of strong electrolytes.—Strong electrolytes (p. 361) do not obey Ostwald's dilution law. Thus the values of α, calculated from the conductivities of aqueous solutions of potassium chloride, give rise to the dissociation-constants shown in Table 89.

TABLE 89. ELECTROLYTIC DISSOCIATION OF POTASSIUM CHLORIDE.

V.	α.	K (Ostwald).	K (van't Hoff.).
10	0·861	0·533	3·31
20	0·888	0·352	2·79
50	0·922	0·218	2·58
100	0·943	0·156	2·58
200	0·961	0·118	2·92

The third column headed K (Ostwald) shows a rapid increase in the values of K calculated by formula (2) as the dilution decreases, showing that the electrolytic dissociation falls off much less rapidly in strong solutions than it should do according to the law of mass-action. The last column of the table gives the values of K calculated from the empirical formula of van't Hoff,

$$K = \frac{\alpha^3}{V(1-\alpha)^2}.$$

The values of K (van't Hoff) are more nearly constant than those of K (Ostwald), but even this formula is only valid over a middle range of concentrations.

The most successful formula for the conductivity of strong electrolytes is probably that of Kohlrausch, according to which $1-\alpha \propto C^{\frac{1}{2}}$ when α is small. This law can be verified by plotting α against $\sqrt{C}$, as in Fig. 70, where a linear relation is seen to exist in the case of potassium iodide dissolved in four different solvents.

The theory of Debye and Hückel.—A theoretical foundation for Kohlrausch's formula has been derived by Debye and

Hückel from the theory of complete ionisation, according to which the variations of molecular conductivity in dilute solutions are due to changes in the *mobility* and not in the *number* of the ions. These authors suppose that the forces of interionic

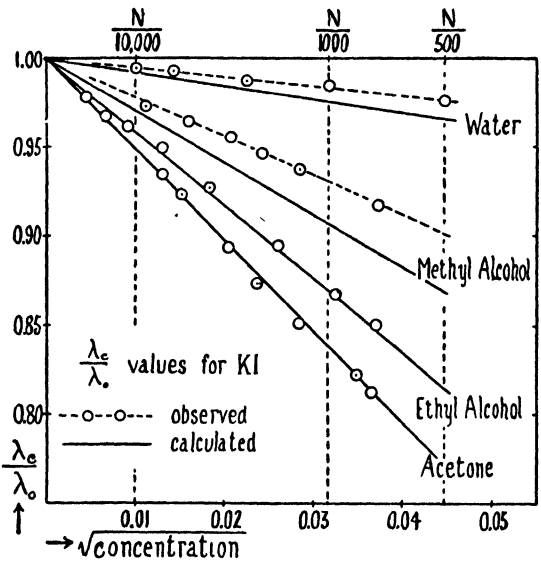


FIG. 70.—Coefficient of ionisation of potassium iodide in different solvents.

attraction gives rise to an unequal distribution of ions in a solution, so that there is an excess of negative ions in the neighbourhood of a positive ion, and conversely, just as there is in a crystal of rock salt. Two effects follow from this unequal distribution.

(i) When an ion moves through the solution, the atmosphere of oppositely-charged ions lags beyond, and produces a retarding electrostatic force, which opposes the E.M.F. under which the ion is moving.

(ii) Since the ion drags through the solution an atmosphere of oppositely-charged ions, the frictional resistance to its migration is increased.

By a difficult calculation, the details of which need not be

quoted, Debye and Hückel show that in each case *the retardation is proportional to the square root of the concentration.* Kohlrausch's Law can therefore be explained by supposing that the total *number* of ions remains unchanged, but that Λ_c/Λ_0* is diminished by a *reduction of mobility* resulting from interionic attraction as described above.

The two terms which represent the electrical retardation, and that due to " electrophoresis " of the solvent (compare p. 411), are shown in the equation

$$\frac{\Lambda_c - \Lambda_0}{\Lambda_0} = \{K_1 D^{-\frac{3}{2}} w_1 + K_2 D^{-\frac{1}{2}} w_2 b\} \sqrt{\nu m},$$

where

K_1, K_2 are constants for a given solvent at a given temperature

D is the dielectric constant of the solvent.

b is the average radius of the ions.

ν is the number of ions in the molecule.

m is the molecular concentration of the electrolyte and

w_1 and w_2 are universal constants depending only on the valency of the ions.

In each case, the retardation includes the term $\sqrt{\nu m}$, which is the square root of the ionic concentration, as required by Kohlrausch's equation; but the numerical agreement between theory and experiment (as shown in Fig. 70) is less satisfactory than the general concordance of theory and experiment as regards the *form* of the dilution law for strong electrolytes.

33. Ionisation of Water.

i. Hydrolysis of urea hydrochloride.—Prepare an $N/2$ solution of urea hydrochloride by dissolving the calculated amount of urea in $N/2$ HCl. By the method outlined in Expt. 26, i., determine the velocity of hydrolysis of methyl acetate in this solution. From the ratio of the velocity-coefficient found to that observed for $N/2$ HCl, calculate the degree of hydrolysis of urea hydrochloride and the dissociation-constant of urea. (K_w at 25° is $1{\cdot}1 \times 10^{-14}$).

* See footnote, p. 330.

ii. Hydrolysis of aniline acetate, by method of partition.—Determine the partition-coefficient of aniline between benzene and water as in Expt. 22, i. Prepare a specimen of aniline hydrochloride by passing dry hydrogen chloride into a solution of aniline in benzene. Wash the precipitate with benzene until colourless, and dry in the air-oven at 60°. Dissolve about 3 grams of the product in 1000 c.c. of water, add 60 c.c. of benzene, immerse in a thermostat and shake repeatedly. Estimate the aniline in 25 c.c. of the layer of benzene by precipitating the hydrochloride with dry hydrogen chloride gas.

Calculate the hydrolysis-constant $K = \frac{[C_6H_5 \cdot NH_2][HCl]}{[C_6H_5NH_2, HCl]}$ and deduce the percentage hydrolysis when aniline and hydrochloric acid are present at a concentration of 1 molecule per litre of water.

The ionisation of water.—When the equation for the neutralisation of a strong acid by a strong base is expressed in terms of the theory of electrolytic dissociation, the only chemical change is the union of hydrogen and hydroxyl ions to form water, *e.g.*

$$H^{\cdot} + Cl' + K^{\cdot} + OH' = H_2O + K^{\cdot} + Cl'.$$

This conception of the process of neutralisation affords an immediate explanation of the experimental fact, noted in Chapter IX. (p. 207), that the heat of neutralisation of a strong acid by a strong base in a dilute solution is always 13,700 calories.

It is of interest to enquire whether this action is reversible, *i.e.* whether pure water itself is ionised to any extent into hydrogen and hydroxyl ions :

$$H_2O \rightleftharpoons H^{\cdot} + OH'.$$

The electrical conductivity of ordinary distilled water (about 10×10^{-6} mhos) cannot be cited as evidence, since this is obviously due for the most part to traces of impurities, chiefly dissolved carbon dioxide and ammonia; these can be eliminated by distillation from alkaline potassium permanganate, when much lower conductivities are observed. The lowest value yet recorded was obtained by Kohlrausch, by repeated distillation in a sealed vessel, in which the water was kept in contact with platinum electrodes for long periods of time, and then poured back again and redistilled. In this way he reduced the conductivity of the water to $0{\cdot}0384 \times 10^{-6}$ mhos at 18°, but he was

not able to reduce the conductivity any further. This residual conductivity may be attributed to the dissociation of water itself; it can only be regarded as an upper limit, however, since lower values might be recorded at any time as a result of more successful purification.

Assuming, however, that Kohlrausch's value represents the real conductivity of pure water, it is easy to deduce from it a value for the dissociation-constant. Thus, the mobilities u and v of the hydrogen and hydroxyl ions at 18° are 318 and 174 respectively. The number of gram-ions per 1000 c.c. is therefore given by

$$c = \frac{1000K}{u+v} = \frac{38{\cdot}4 \times 10^{-6}}{492} = 0{\cdot}78 \times 10^{-7},$$

that is, the number of gram-ions of hydrogen or hydroxyl in a litre of pure water is $0{\cdot}78 \times 10^{-7}$. By applying the law of mass-action (since water is a weak electrolyte), it is evident that in water and in any aqueous solution

$$[H^{\cdot}][OH'] = K[H_2O].$$

Since water is so slightly ionised, the concentration of undissociated water is constant; the right-hand side of this equation is therefore a constant and may be written

$$[H^{\cdot}][OH'] = K_w.$$

where K_w is the **ionic product** for water. At 18°

$$[H^{\cdot}] = [OH'] = 0{\cdot}78 \times 10^{-7},$$

whence $K_w^{18°} = 0{\cdot}61 \times 10^{-14}$. This ionic product, K_w, must be distinguished clearly from the dissociation-constant K of the balanced action, which would be 55 times smaller, since

$$[H_2O] = 1000 \div 18 = 55 \text{ (approx.)}.$$

Kohlrausch found that the conductivity of pure water increased rapidly with temperature, so that at 25°, $K_w = 1{\cdot}06 \times 10^{-14}$. Since K_w is a multiple of the equilibrium-constant for the dissociation of water, we can use the equation of van't Hoff (p. 254) in order to calculate the heat of the reaction $H^{\cdot} + OH' = H_2O$ from values of the equilibrium-constant at two temperatures. van't Hoff's equation may be written

$$2{\cdot}303 \log_{10} \frac{K_1}{K_2} = \frac{U}{2} \frac{T_2 - T_1}{T_1 T_2}.$$

Inserting the values given above for K_w at 18° and 25°,

$$U = \frac{2 \times 2{\cdot}303 \times 291 \times 298 \log_{10} \frac{1{\cdot}06}{0{\cdot}61}}{298 - 291}$$
$$= 13{,}670 \text{ cal.}$$

This is practically identical with the value found experimentally for the heat of neutralisation of a strong acid by a strong base, a reaction which, according to the ionic theory, consists only of the combination of hydrogen and hydroxyl ions. The good agreement between these numbers, calculated from very different experimental data, is strong evidence of the validity of the theory of electrolytic dissociation as applied to this particular case.

Hydrolysis.—The very small dissociation of water might perhaps be thought to be of little importance, but it provides an explanation of many of the properties of aqueous electrolytes which would otherwise be difficult to understand, and, in particular, of the hydrolysis of metallic salts. Suppose we have a solution of a metallic salt, MA, derived from a strong alkali MOH and a weak acid HA. We may regard the metallic salt (at least in dilute solution) as being completely ionised as at (*a*) whilst the weak acid and the water of the solution are feebly ionised as at (*b*) and (*c*).

(*a*) $MA \rightarrow M' + A'$.
(*b*) $H_2O \rightleftharpoons H' + OH'$.
(*c*) $HA \rightleftharpoons H' + A'$.

It is obvious that there will be a competition for the possession of hydrogen ions between the hydroxyl ions of the water and the anions of the acid; and this will ultimately reach a condition of equilibrium, depending upon the relative tendencies of water and the acid to dissociate. Thus, if the acid is very weak, the anion A′ of the salt will unite with a large proportion of the hydrogen ions of the water; the equilibrium $H_2O \rightleftharpoons H' + OH'$ will therefore be disturbed and more molecules of water will dissociate, giving rise to a further supply of hydrogen and hydroxyl ions. The net result is that the concentration of the hydroxyl ions in the solution will exceed that of the hydrogen

ions, some of which have been used up to form undissociated molecules of the weak acid. The solution will therefore be *alkaline* in reaction, and in terms of ions the **hydrolysis** may be written

$$A' + H_2O \rightleftharpoons OH' + HA. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

It is evident from this discussion that the extent of hydrolysis depends upon the relative degrees of dissociation of water and of the acid. Salts of acids with dissociation-constants greater than water will only be hydrolysed to a small extent, whilst those with smaller dissociation-constants will be largely hydrolysed. This can be expressed quantitatively by applying the law of mass-action to the hydrolysis-equation (1). This gives

$$\frac{[\text{acid}][\text{base}]}{[\text{unhydrolysed salt}]\,[\text{water}]} = K, \quad \ldots\ldots\ldots\ldots\ldots (2)$$

or, since the concentration of water is practically constant in a dilute solution,

$$K_H = \frac{[\text{acid}][\text{base}]}{[\text{unhydrolysed salt}]}, \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where K_H, the hydrolysis constant, takes the place of K [water] in equation (2).

If we have 1 gram-molecule of the salt in V litres, and a fraction x is hydrolysed

$$K_H = \frac{x^2}{V(1-x)}. \quad \ldots\ldots\ldots\ldots\ldots (4)$$

It is evident from this formula that, as V increases, the proportion x of the salt that is hydrolysed must increase.

Determination of the ionic product of water.—The relation between the hydrolysis-constant K_H and the dissociation-constants of the acid and water can readily be expressed in a quantitative form. Thus the law of mass-action gives for the dissociation of the weak acid

$$[H'][A'] = [HA]\,K_A,$$

where K_A is the dissociation-constant of the acid. But since the acid is feebly dissociated $[HA] = \frac{x}{V}$ and $[A'] = \frac{1-x}{V}$, so that $[H'] = K_A \frac{x}{1-x}$. Also, since the strong base MOH can be

regarded as completely dissociated, $[OH'] = \frac{x}{V}$. But, in any aqueous solution, $[OH'][H'] = K_W$, whence

$$K_W = \frac{x}{V} \cdot \frac{x}{1-x} \cdot K_A$$

or

$$\frac{K_W}{K_A} = \frac{x^2}{V(1-x)} = K_H. \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The hydrolysis-constant of the salt is therefore equal to the ratio of the ionic product of water and the dissociation-constant of the acid. This relation provides a quantitative explanation of the fact that only salts of acids which have dissociation-constants smaller than the ionic product K_W will be largely hydrolysed.

It is obvious that if K_W and K_A are known, we can predict the extent of the hydrolysis in a given solution. Conversely, from measurements of K_A and the degree of hydrolysis, we can obtain an independent determination of K_W. The measurement of the degree of hydrolysis presents, however, the same difficulties as the measurement of the degree of dissociation of an acid. For instance, direct titration of the free alkali cannot be employed, for this would disturb the equilibrium and cause progressive hydrolysis of the salt. Thus borax is only 0·50 per cent. hydrolysed in $N/10$ solution, yet the whole of the base can be titrated with acid using methyl orange as indicator.

The method which is most suitable is to utilise the catalytic activity of the hydroxyl ion for certain reactions (cf. p. 309). Thus Shields, from measurements of the rate of saponification of methyl acetate by sodium acetate solutions and by very dilute solutions of caustic alkali, found that this salt is hydrolysed to the extent of 0·008 per cent. in $N/10$ solution at 25°. That is, $x = 0{\cdot}00008$ when $V = 10$, so that

$$K_H \frac{(0{\cdot}00008)^2}{10(1-0{\cdot}00008)} = 6{\cdot}4 \times 10^{-10}.$$

But K_A is known from measurements of the conductivity of acetic acid to be $1{\cdot}8 \times 10^{-5}$;

$$\therefore \quad K_W = K_H \cdot K_A = 6{\cdot}4 \times 10^{-10} \times 1{\cdot}8 \times 10^{-5}$$
$$= 1{\cdot}15 \times 10^{-14}.$$

When the smallness of the quantities measured is considered, this is remarkably close to the value deduced from the conductivity of pure water ($1{\cdot}06 \times 10^{-14}$). Several other methods of determining K_W have been devised, and the values found for this important constant are given in Table 90.

TABLE 90. DETERMINATION OF THE IONIC PRODUCT OF WATER.

Method.	Value of K_W at 25°.
Conductivity of pure water - - - -	$1{\cdot}06 \times 10^{-14}$
Hydrolysis of sodium acetate - - - -	$1{\cdot}15 \times 10^{-14}$
Hydrolysis of methyl acetate by pure water, etc.	$1{\cdot}4 \times 10^{-14}$
E.M.F. of hydrogen-oxygen cell - - - -	$1{\cdot}0 \times 10^{-14}$

For the calculations in the remainder of this chapter we shall use the convenient approximation $K_W = 1{\cdot}0 \times 10^{-14}$.

Hydrolysis of salts. (*a*) *Salts of weak acids.*—Using the value of K_W set out above, the degree of hydrolysis of some sodium salts of weak acids has been calculated and the results are given in Table 91.

TABLE 91. DEGREE OF HYDROLYSIS OF SODIUM SALTS.

Salt.	Dissociation-constant of acid.	Hydrolysis of sodium salt in normal solution.
Sodium acetate - -	$1{\cdot}8 \times 10^{-5}$	0·0024%
Sodium carbonate - -	$3{\cdot}0 \times 10^{-7}$	0·0185
Sodium sulphide - -	$5{\cdot}7 \times 10^{-8}$	0·042
Sodium cyanide - -	$1{\cdot}3 \times 10^{-9}$	0·28
Sodium phenate - -	$1{\cdot}3 \times 10^{-10}$	0·88

(*b*) *Salts of weak bases.*—The hydrolysis of salts of a weak base with strong acids can be calculated in a similar fashion. Here there is a competition for hydroxyl ions between the kations of the salt and the hydrogen ions of the water, *e.g.*

$$NH_4 \cdot OH \rightleftharpoons NH_4^{\cdot} + OH',$$
$$H \cdot OH \rightleftharpoons H^{\cdot} + OH'.$$

This gives rise to the reversible action shown in the equation

$$NH_4Cl + H_2O \rightleftharpoons NH_4 \cdot OH + HCl.$$

The solution is *acid*, because the ionisation of the acid exceeds that of the base. At equilibrium we can write

$$K_H = \frac{[\text{acid}][\text{base}]}{[\text{unhydrolysed salt}]} = \frac{x^2}{V(1-x)} = \frac{K_W}{K_B},$$

where K_B is the dissociation-constant of the base. Thus for ammonium chloride, where $K_B^* = 2{\cdot}3 \times 10^{-5}$, the degree of hydrolysis in normal solution is only 0·002 per cent., whilst with aniline hydrochloride, where K_B^* for aniline is $3{\cdot}9 \times 10^{-10}$, the hydrolysis reaches 0·5 per cent. in normal solution and the solution is strongly acid. In the same way, the acidity or neutrality of solutions of metallic salts enables us to draw conclusions about the strength of bases which are too insoluble for direct measurements. Thus the chlorides of aluminium, antimony and bismuth give acid solutions (the last two form precipitates of basic chlorides), so that alumina and the hydroxides of antimony and bismuth are weak bases. On the other hand, silver nitrate and mercuric chloride give neutral solutions, so that the oxides of these metals must be regarded as strong bases.

(*c*) *Salts of weak acids and weak bases.*—The hydrolysis of a salt of a weak acid and a weak base, *e.g.* aniline acetate, can also be calculated by the same method. The equation for hydrolysis can be written :

$$M' + A' + HOH \rightleftharpoons MOH + HA,$$

whence by the law of mass-action

$$K_H = \frac{[MOH][HA]}{[M'][A']} \frac{[\text{acid}][\text{base}]}{[\text{unhydrolysed salt}]^2} = \frac{x^2}{(1-x)^2},$$

since [MOH] and [HA] are both proportional to x/v, and [M'] + [A'] to $(1-x)/V_1$ if the salt is ionised completely, whilst $[H_2O]$ is a constant. Here the dilution V, which would appear as a square in the numerator and denominator, cancels out of the expression for K_H, so that *the degree of hydrolysis is independent of the dilution.* Further, it can be shown that

$$K_H = \frac{K_W}{K_A \cdot K_B}.$$

* These are the "apparent dissociation-constants," in which no allowance is made for the thermal dissociation of the hydroxide, *e.g.* $NH_4 \cdot OH \rightleftharpoons NH_3 + H_2O$ (compare p. 337).

Thus, for aniline acetate $K_A = 1{\cdot}8 \times 10^{-5}$ and $K_B = 3{\cdot}0 \times 10^{-10}$ so that $K_H = 1{\cdot}9$. This corresponds to a hydrolysis of 58 per cent. It is not easy to determine experimentally the degree of hydrolysis of aniline acetate, but, from a study of the partition coefficient of aniline between benzene and solutions of aniline acetate, a hydrolysis of 45 per cent. has been deduced, in fair agreement with the theoretical value.

It will be noted that a large amount of hydrolysis occurs with salts in which both acid and base are weak, and in some cases such salts cannot exist in aqueous solutions, *e.g.* aluminium carbonate and aluminium sulphide. Another interesting point in connection with solutions of salts of this type is that the acidity or alkalinity depends upon the relative values of the dissociation-constants of the acid and of the base. If these are of the same order of magnitude, the solution, although largely hydrolysed, will be neutral in reaction.

34. Neutralisation and the Theory of Indicators.

i. Preparation of buffer solutions.—Prepare a litre of each of the following solutions:

(1) $N/5$ Acetic acid.
(2) $N/5$ Sodium acetate.
(3) $M/20$ Borax. (19·11 gm. $Na_2B_4O_7$, $10H_2O$ in 1 litre).
(4) $M/5$ Boric acid + NaCl (12·40 gm. H_3BO_3 + 2·93 gm. NaCl in 1 litre).

Clean and dry six stoppered bottles of about 250 c.c. capacity and label them $p_H = 4$, $p_H = 5$, ... to $p_H = 9$. Run into the bottles from a burette the following quantities of the stock solutions.

$p_H = 4$	164 c.c.	$N/5$ acetic acid	+	36 c.c.	$N/5$ sodium acetate.
$p_H = 5$	59 ,,	,,	,,	+ 141	,,	,,	,,	,,
$p_H = 6$	9 ,,	,,	,,	+ 191	,,	,,	,,	,,
$p_H = 7$	12 ,,	$M/20$ borax	+	188 c.c.	$M/5$ boric acid + NaCl
$p_H = 8$	55 ,,	,,	,,	+ 145	,,	,,	,,	,,
$p_H = 9$	160 ,,	,,	,,	+ 40	,,	,,	,,	,,

ii. Working range of indicators.—Place 10 c.c. of these 6 buffer solutions, in a series of six clean dry test-tubes. Add three drops of methyl orange to each test-tube. Note in which of the tubes a marked change of colour occurs. Repeat with other indicators, *e.g.* methyl red, litmus, cresol red, and phenol phthalein, and record the working range of each indicator.

iii. Measurement of the hydrolysis of potassium cyanide.—Prepare an $N/10$ solution of potassium cyanide and place 10 c.c. in a clean test-tube. Add three drops of litmus (or cresol red) and compare the tint with those of a series of buffer solutions tinted with the same indicator. From the colour of the solution, estimate its p_H, and compare with the value predicted from the dissociation constant of HCN ($K_A = 1{\cdot}3 \times 10^{-9}$).

iv. Measurement of "hydrogen-ion concentration" by means of the hydrogen electrode.—(*a*) *Measurement of electromotive forces of a cell.* —The *potentiometer* (Fig. 71) consists of a uniform wire *RR* of fairly high resistance (about 100 ohms) stretched over a metre scale. The ends of the wire are connected to a 2 volt accumulator which maintains a steady fall of potential along it. The left-hand end of the wire is connected to the negative terminal of a *standard Weston cell W*, which gives an E.M.F. of 1·0183 volts at room temperature, and also to the negative terminal of the cell under investigation *C*. The positive terminals of these cells are connected to two points on the *switch S*. This consists of a block of paraffin wax containing three cavities filled with mercury, and a copper wire, which can be moved from the position shown in the diagram to that shown by the dotted line. By means of this switch, either the Weston cell or the experimental cell can be connected rapidly to the *galvanometer G*. A moving-coil instrument with a resistance of about 100 ohms is suitable and should be fitted with a lamp and scale. The circuit is completed by a flexible wire from the galvanometer which can make contact with the resistance wire at any point on the scale.

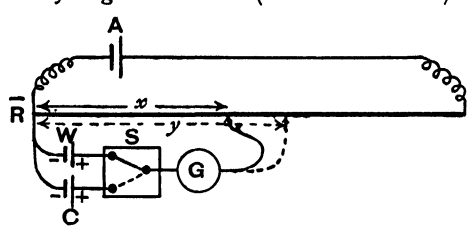


FIG. 71.—Potentiometer.

To measure the E.M.F. of the cell, first put the switch in the position shown, and find the point (near the middle of the scale) where there is no deflection of the galvanometer on making contact between the flexible wire and the potentiometer wire. A light tap on the wire should be made until the balance-point is nearly reached, so that very little current is drawn from the cell. Let the scale-reading be x. Then move the switch to bring the cell *C* into the circuit, and find the new balance-point with a scale reading of y. The E.M.F. of *C* is given by $E = 1{\cdot}0183\ y/x$.

Since the E.M.F. of the accumulator may change slightly during the experiment, it is best to make alternate determinations of x and y as rapidly as possible and use the mean values.

(*b*) *The hydrogen and calomel electrodes.*—In order to determine the E.M.F. of a hydrogen electrode, a cell is prepared, in which the *negative* pole is formed by the hydrogen electrode, and the *positive* by a calomel electrode. A convenient form of hydrogen electrode is shown on the left hand of Fig. 72. It consists of a small platinised platinum plate, enclosed in a glass tube, through which a slow stream of pure hydrogen is blown for at least 15 minutes before taking a reading. The hydrogen is best obtained from a cylinder of electrolytic hydrogen, as otherwise an elaborate purification of the gas is desirable to obtain accurate results.

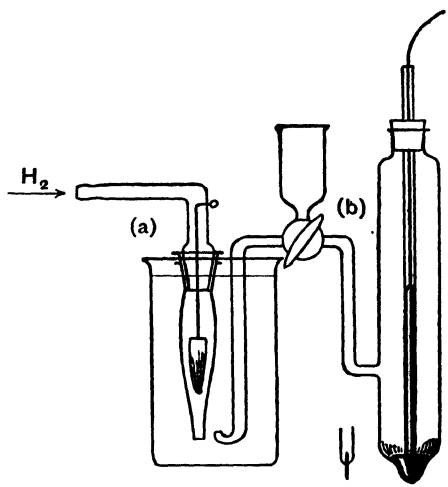


FIG. 72.—(*a*) Hydrogen electrode; (*b*) calomel electrode.

The *calomel electrode* is shown on the right-hand side of Fig. 72. It contains a little pure mercury, to which contact is made by means of a platinum wire sealed through a glass tube passing through the stopper. This tube is partially filled with mercury, to which contact is made by means of a copper wire. The mercury in the outer tube is covered with calomel, and the electrode vessel is filled with a solution of $N/10$ KCl, which has been saturated with finely-powdered calomel by shaking and standing for several hours. The solid calomel ensures that the solution shall remain saturated when current passes through the electrode. The syphon tube is filled with $N/10$ KCl, which can be run in through a three-way tap.

(*c*) *Measurement of electromotive force of a hydrogen electrode.* Set up the cell shown in Fig. 72, placing 10 c.c. of N/HCl in the beaker. Connect to the potentiometer and measure the E.M.F. of the cell. Let this be E'. The $N/10$ calomel electrode has been found to have a potential of +0·3351 volts on an

arbitrary scale known as the "hydrogen scale" (p. 388). The E.M.F. of the hydrogen electrode on this scale is therefore $0{\cdot}3351 - E'$.

The concentration C of the hydrogen ions can be calculated by equation

$$0{\cdot}3351 - E' = 0{\cdot}058 \log_{10} C.$$

Therefore $$p_H = -\log_{10} C = -\frac{0{\cdot}3351 - E'}{0{\cdot}058}.$$

Thus, if $E' = 0{\cdot}3441$, $0{\cdot}3351 - E' = -0{\cdot}0090 = 0{\cdot}058 \log_{10} C$.

Therefore $$\log_{10} C = -\frac{0{\cdot}0090}{0{\cdot}058} = -0{\cdot}0155 = \bar{1}{\cdot}845;$$

and $$C = 0{\cdot}70.$$

Also $$p_H = -\frac{0{\cdot}3351 - E'}{0{\cdot}058} = -\frac{0{\cdot}0090}{0{\cdot}058} = 0{\cdot}155.$$

To the solution in the beaker add 5 c.c. of N/KOH from a burette and measure the E.M.F. again. Repeat after adding 7, 8, 9, 9·5, 9·8, 10·0, 10·2, 10·5, 11, 12, 13 and 15 c.c. In each case calculate the p_H of the solution. Plot the p_H against the number of c.c. of alkali added and compare your curve with that on p. 384.

v. Measurement of "hydrogen-ion concentration" by the quinhydrone electrode.—(*a*) A piece of well-cleaned bright platinum foil about 1 cm. × 2 cm. is welded to a platinum wire sealed through the end of a glass tube. The latter contains mercury into which dips a copper wire leading to the potentiometer. The platinum foil dips into a small beaker of the solution to be examined and takes the place of the hydrogen electrode in Fig. 72.

Make 10 c.c. of the buffer solution of $p_H = 4$ (Expt. 34, i.) with about 0·5 gm. of quinhydrone, which can be prepared in the form of greenish-brown needles by boiling quinol (hydroquinone) with aqueous ferric chloride. (It is essential that some crystals remain undissolved.) Complete the cell by means of the N/10 calomel electrode and measure its E.M.F. The calomel electrode will now be the negative terminal of the cell. From the E.M.F. of the cell calculate the p_H of the solution.

Example.—If the E.M.F. of the cell is 0·1360 volts, then, since the calomel electrode has a potential of 0·3351 volts, on the hydrogen scale, the E.M.F. of the quinhydrone electrode is $0{\cdot}1360 + 0{\cdot}3351 = 0{\cdot}4711$.

The E.M.F. of this electrode is given by

$$E = 0{\cdot}704 + {\cdot}058 \log_{10} [H^{\cdot}].$$

$$p_H = -\log_{10} [H^{\cdot}] = \frac{0{\cdot}704 - E}{{\cdot}058}$$

$$= \frac{0{\cdot}704 - 0{\cdot}4711}{0{\cdot}058}$$

$$= \frac{0{\cdot}2329}{0{\cdot}058}$$

$$= 4{\cdot}02.$$

(*b*) Repeat the experiment with the other buffer solutions up to $p_H = 7$.

(*c*) As a further experiment determine the hydrolysis-constant of aniline hydrochloride. Prepare an *N*/10 solution of the hydrochloride by dissolving the right amount of redistilled aniline in *N*/10 HCl. Add quinhydrone and set up the cell as before. From the E.M.F. of the cell calculate the concentration of hydrogen ions and the hydrolysis constant and apparent dissociation-constant of aniline hydrochloride. Compare your results with the values given on p. 374.

Neutralisation.—It is readily seen from the ionic theory that the process of neutralisation consists of the combination of the hydrogen ions of an acid with the hydroxyl ions of a base, and that neutrality is attained when the concentrations of these two ions are equal. Further, since we know the value of

$$K_w = 1 \times 10^{-14},$$

we can predict that in a strictly neutral solution the concentration of hydrogen ions will be 10^{-7} gram-equivalents per litre.

Hydrogen-ion concentration.—In discussing problems of neutralisation, a special method is often employed for stating the concentration of hydrogen ion. The acidity or alkalinity is defined by a quantity known as p_H, where

$$p_H = -\log_{10} [H^{\cdot}] = \log_{10} \frac{1}{[H^{\cdot}]} \cdot \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Thus a solution in which $[H^{\cdot}] = 10^{-6}$ is said to have $p_H = 6$, and one in which

$$[H^{\cdot}] = 2 \times 10^{-10} = 10^{+0{\cdot}30} \times 10^{-10} = 10^{-9{\cdot}7}$$

is said to have a p_H of 9·7. The neutral point, at which $[H^+] = 10^{-7}$, is of course $p_H = 7$.

It is instructive to calculate the changes in concentration of hydrogen ion around the neutral point when a strong base is titrated by a strong acid. Let us assume complete dissociation of both acid and base, and suppose that normal alkali is being added to 50 c.c. of normal acid, the volume in all cases being made up to 1000 c.c. When 49·5 c.c. of alkali have been added, the residual acid has a concentration of $0{\cdot}5 \times 10^{-3} = 5 \times 10^{-4}$ gram-equivalents per litre, and (assuming complete dissociation) this number also gives the concentration of hydrogen ions remaining in the solution. On the alkaline side, when 50·5 c.c. of alkali have been added the concentration of hydroxyl ions is similarly 5×10^{-4}; and since

$$[H^+][OH^-] = K_w, \quad [H^+] = 1 \times 10^{-14} \div 5 \times 10^{-4} = 2 \times 10^{-11}.$$

Table 92 is calculated in this way. In this table the second column shows the change in $[H^+]$ as the neutral point is reached and passed; the last column shows the corresponding changes in p_H.

TABLE 92. CHANGES OF HYDROGEN-ION CONCENTRATIONS DURING NEUTRALISATION.

c.c. *N.* NaOH.	$[H^+]$.	p_H.
45	5×10^{-3}	2·3
49	1×10^{-3}	3·0
49·5	5×10^{-4}	3·3
49·9	1×10^{-4}	4·0
49·95	5×10^{-5}	4·3
50·0	1×10^{-7}	7·0
50·05	2×10^{-10}	9·7
50·1	1×10^{-10}	10·0
50·5	2×10^{-11}	10·7
51·0	1×10^{-11}	11·0
55·0	2×10^{-11}	11·7

In the first place it should be noticed that there is a very rapid change in the concentration of hydrogen ions in the neighbourhood of the neutral point, where a variation of ±0·1 c.c. produces a million-fold change in the concentration of hydrogen ions from 10^{-4} to 10^{-10} gram-equivalents per litre. It is evident that solutions with hydrogen ion concentrations between

$p_H = 4$ and $p_H = 10$, cannot be prepared with accuracy by mixing strong acids and bases, since slight errors of concentration or the presence of traces of acid or alkaline impurities would have an enormous effect on the acidity of the solution.

Influence of neutral salts.—We have neglected so far the influence, upon the dissociation of the acid or base, of the salt formed by their neutralisation. This is justifiable when strong acids and bases are concerned, but not when weak acids and bases are used. As an example we may discuss the neutralisation of a weak acid (*e.g.* acetic acid) by a strong base (*e.g.* caustic soda). As before, we will commence with 50 c.c. of normal acid and add normal NaOH from a burette, the solution in each case being made up to 1000 c.c. Since the dissociation of the weak acids obeys the law of mass-action, as expressed by Ostwald's "dilution law," we have

$$\frac{[H^{\cdot}][A']}{[HA]} = K_A = 1{\cdot}8 \times 10^{-5}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Hence

$$[H^{\cdot}] = K_A \frac{[HA]}{[A']} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and

$$p_H = \log_{10} \frac{1}{[H^{\cdot}]} = \log_{10} \frac{[A']}{K_A[HA]}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

We may regard the sodium acetate as completely dissociated, so that [A′] corresponds to the amount of alkali added; also the acid is so feebly dissociated that we may suppose that [HA] corresponds to the whole of the residual acid. Thus, when 10 c.c. of alkali have been added $[A'] = 10^{-2}$ and $[HA] = 4 \times 10^{-2}$, so that

$$p_H = \log_{10} \frac{10^{-2}}{1{\cdot}8 \times 10^{-5} \times 4 \times 10^{-2}} = 4{\cdot}14.$$

Table 91 gives the values calculated in this way for the variation of p_H during the titration. It should be noted that there is a region in which the concentration of hydrogen ion changes only slowly, and that, when exactly half the acid is neutralised, the change of p_H with added base is least. At this point, where [HA] = [A′], it will be seen from equation (3) that the concentration of hydrogen ions [H·] is numerically equal to

the dissociation-constant K_A of the acid, namely, $1{\cdot}8 \times 10^{-5}$ or $p_H = 4{\cdot}74$.

TABLE 93. NEUTRALISATION OF A WEAK ACID BY A STRONG BASE.

Volume of normal acetic acid	Volume of normal sodium hydroxide.	p_H.
50 c.c.	10 c.c.	4·14
,,	15	4·38
,,	20	4·57
,,	25	4·74
,,	30	4·92
,,	35	5·11
,,	40	5·35
,,	45	5·70
,,	50	7·22
,,	50·05	9·70
,,	50·1	10·0
,,	50·5	10·7

This characteristic behaviour of a mixture of a weak acid with an equivalent amount of one of its salts provides a ready means of preparing a solution of known hydrogen-ion concentration, since slight errors in the concentration of the acid or of the salt have very little effect on the concentrations of the hydrogen ions. Further, if small amounts of acid or alkali are added, the change in p_H is very small. Such solutions, which resist a change in p_H on the addition of acid or alkali, are termed **buffer solutions.** Other mixtures used as buffer solutions are:

Citric acid + sodium citrate,
$Na_2CO_3 + NaHCO_3$,
$Na_2HPO_4 + NaH_2PO_4$,
Borax + boric acid.

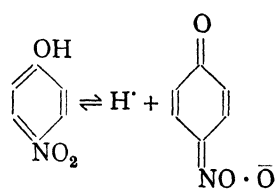
The theory of indicators.—We are now in a position to discuss the action of indicators. Practically all indicators are weak acids, so that in aqueous solution they are very little dissociated into ions. Thus phenol phthalein may be regarded as dissociating slightly thus:

$$HP \rightleftharpoons H^{\cdot} + P^{\cdot}.$$

From the law of mass-action it follows that, if other hydrogen ions are added, so that the p_H of the solution is less than corresponds to the dissociation-constant of the indicator, then this dissociation will be almost entirely repressed. On the other hand, if the solution is made more alkaline, *i.e.* if p_H rises, then the indicator (if present in small amount) will be very largely ionised in the form of its sodium salt, thus:

$$Na\ P \rightleftharpoons Na^{\cdot} + P'.$$

The second important property of an indicator is that the anion must possess a different colour from the undissociated acid. Thus phenol phthalein is colourless but gives a red anion, methyl orange is red and gives a yellow anion, *p*-nitrophenol is colourless and gives a yellow anion. These changes of colour are probably due to a change in structure when the anion is produced. Thus, in the case of *p*-nitrophenol the formation of a salt probably involves a change from a benzenoid to a quinonoid structure.



Similar changes occur in indicators of more complex constitution, but all these changes have as their essential characteristic the fact that it is the *concentration of hydrogen ions* in the solution which determines the change in constitution and therefore in colour, since it is only the anions and not the undissociated molecules that are converted into the quinonoid form.

Like any other weak acid, an indicator is half-converted into anions when the concentration of hydrogen ions is numerically equal to its dissociation-constant. For phenol phthalein this occurs at $p_H = 9{\cdot}5$. It can readily be shown that at $p_H = 8{\cdot}5$ only 10 per cent. of the indicator is in the form of anions whilst at $p_H = 10{\cdot}5$ more than 90 per cent. of it is ionised. Hence over a range from p_H 8·5 to p_H 10·5 phenol phthalein changes from an almost colourless solution to deep red. In the same way, the change of colour in any other indicator takes place over

a narrow working range on either side of the value of p_H corresponding with its dissociation-constant. Table 94 gives the working range of a few common indicators.

TABLE 94. WORKING RANGE OF INDICATORS.

Methyl orange	$p_H = 3{\cdot}1 - 4{\cdot}5$
Methyl red	$4{\cdot}7 - 6{\cdot}4$
Litmus	$5{\cdot}0 - 7{\cdot}0$
Cresol red	$7{\cdot}2 - 8{\cdot}8$
Phenol phthalein	$8{\cdot}5 - 10{\cdot}5$

Choice of an indicator.—From a knowledge of these values a decision can readily be made as to the indicator that is most suitable for a particular titration.

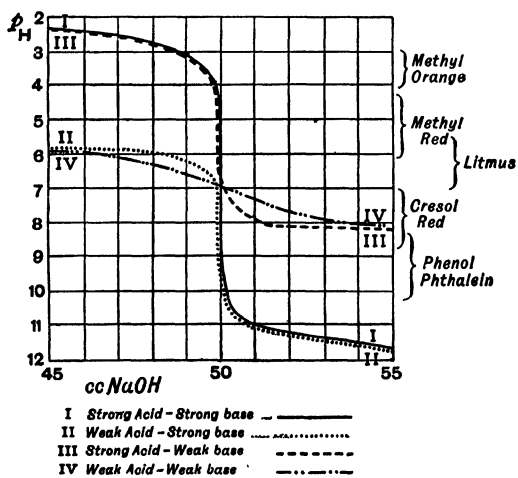


FIG. 73.—Variation of concentration of hydrogen ions during titration.

In Fig. 73 the working range of the indicators is shown on the right-hand side of the diagram.

(*a*) The continuous curve I. shows the variation of p_H during the titration of a strong acid by a strong base. This curve shows a rapid change in p_H from 4 to 10 for very small additions of base, so that all the indicators would give very nearly the same end-point and might be used with satisfactory results.

(*b*) Curve II. represents the titration of a weak acid by a

strong base. p_H is seen to change gradually until the neutral point is reached and then falls rapidly, following nearly the same course as curve I. It is evident from the diagram that methyl orange and litmus would not be satisfactory indicators as their working range corresponds to a large excess of acid. On the other hand phenol phthalein, the working range of which corresponds with a steep part of the curve, could be used with good results.

(*c*) Curve III. represents the titration of a strong acid by a weak base. It follows almost the same course as I. up to the neutral point, but then diverges and shows only small changes in p_H for a large excess of added base. It is evident that methyl orange or methyl red would be satisfactory indicators for this titration, whilst phenol phthalein would give a very indefinite end-point, since it would only become coloured in presence of a large excess of weak base.

(*d*) Curve IV. shows the variation of p_H when a weak acid is titrated with a weak base. The curve is shallow on both sides of the neutral point and no indicator will give a satisfactory end-point.

These conclusions may be summarised for practical purposes as follows:

Titration.	Indicator.
Strong acid – strong base.	Any indicator.
Weak acid – strong base.	Phenol phthalein.
Strong acid – weak base.	Methyl red or methyl orange.
Weak acid – weak base.	No indicator is satisfactory.

Measurement of hydrogen-ion concentration : the hydrogen electrode.—The hydrogen-ion concentration of a solution can be determined with fair accuracy by adding a suitable indicator to the solution and comparing the colour produced with that given by the same indicator when added to buffer solutions of known p_H. A more direct and accurate method depends upon the use of the hydrogen electrode or the quinhydrone electrode.

The **hydrogen electrode** consists of platinised platinum dipping into the solution through which a current of hydrogen is bubbled. The platinum catalyses the reactions concerned in the equilibrium.

$$2H^{\cdot} \rightleftharpoons H_2 + 2\theta$$

so that the electrode tends to be charged positively when hydrogen ions are converted into gaseous hydrogen. The electrode will therefore reach a definite electrical potential at which the electrostatic force repelling the hydrogen ions prevents any further discharge of these ions. The potential thus attained will depend upon (*a*) the concentration of hydrogen gas, which is usually kept constant at atmospheric pressure, and (*b*) on the concentration of hydrogen ions in the solution.

To determine the relation between hydrogen-ion concentration and the potential of the hydrogen electrode we can use the thermodynamical principle that the maximum external work done by any change in a system is the same whatever the mechanism by which the change is accomplished (p. 225). Thus, two hydrogen electrodes may be immersed in solutions of hydrogen-ion concentrations C_1 and C_2, which are in contact with one another. This combination is described as a **concentration cell,** and may be represented by the scheme :

$$H_2Pt \;\underset{E_1}{|}\; C_1 \;\underset{e}{|}\; C_2 \;\underset{E_2}{|}\; H_2Pt.$$

The small difference of potential e between the solutions may be neglected for our present purpose. The electromotive force of the cell is then given by $E_1 - E_2$ where E_1 and E_2 are the potentials of the two electrodes. If these electrodes are joined by a wire, current will flow through the wire from E_1 to E_2, if $C_1 > C_2$ so that $E_1 > E_2$. Meanwhile some hydrogen ions will discharge at E_1 to maintain its potential, so that at this electrode the reaction may be written

$$2H^{\cdot} \rightarrow H_2 + 2\theta.$$

Similarly at E_2 the positive electricity carried by the wire is dissipated by the formation of hydrogen ions

$$H_2 + 2\theta \rightarrow 2H^{\cdot}.$$

The hydrogen-ion concentration around E_1 therefore tends to diminish whilst that around E_2 tends to increase.

Suppose the current flows for such a time that dx gram-ions of hydrogen are transferred from the first solution to the second. By Faraday's law this will involve the passage of $dx \times F$ coulombs of electricity. The electrical work done is therefore

$dxF(E_1 - E_2)$. We could bring about the same transfer of hydrogen ions from solution 1 to solution 2 if we had a semi-permeable membrane impermeable to hydrogen ions, and the maximum work done by such a process would be

$$A = dx\ RT \log_e \frac{P_1}{P_2}$$

where P_1 and P_2 are the osmotic pressures of the hydrogen ions (p. 223) in the two solutions. If the solutions are dilute then the osmotic pressure is proportional to the concentration and $P_1/P_2 = c_1/c_2$. Equating the electrical work to the osmotic work

$$dx\ F(E_1 - E_2) = dx\ RT \log_e \frac{c_1}{c_2}.$$

Rearranging and changing to common logarithms,

$$E_1 - E_2 = \frac{2{\cdot}303RT}{F} \log_{10} \frac{c_1}{c_2}. \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Since $R = 8{\cdot}315 \times 10^7$ ergs and $F = 9650$ C.G.S. units, we can calculate the value of the quantity $2{\cdot}303\ RT/F$ for different temperatures with the following results for E in volts

t	=	0°	10°	20°	30°
$\frac{2{\cdot}303RT}{F}$	=	0·0542	0·0562	0·0582	0·0601

At room temperature (15°-20°) the approximate formula

$$E_1 - E_2 = 0{\cdot}058 \log_{10} \frac{c_1}{c_2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

is sufficiently accurate.

This expression for the E.M.F. of a concentration cell can be made general by writing

$$E_1 - E_2 = \frac{0{\cdot}058}{n} \log_{10} \frac{c_1}{c_2}$$

where n is the valency, or the number of charges carried by the ion. Thus, if the cell consists of copper electrodes dipping into solutions of copper sulphate, then $n = 2$, and the E.M.F. of the cell is given by $0{\cdot}029 \log_{10} \frac{c_1}{c_2}$.

It is evident from this equation that if we know the hydrogen-ion concentration in one solution, we can calculate the

hydrogen-ion concentration in the other. The potential of a hydrogen electrode in a solution which is normal with respect to hydrogen ions has a special importance since it is taken arbitrarily as the zero from which electrode potentials are measured. If we put $c_2 = 1$ and $E_2 = 0$ in equation (6) then the E.M.F. of the first electrode on the **hydrogen scale** is given by

$$E_{H_2} = 0{\cdot}058 \log_{10} c_1.$$

A cell with two hydrogen electrodes is sometimes used; but since it is not always easy to adjust to exact normality the concentration of hydrogen ions at the second electrode, this is usually replaced by a **calomel electrode,** which is readily set up and has a known and constant potential on the hydrogen scale. The measurement of hydrogen-ion concentrations by the hydrogen electrode is described in Expt. 34, iv.

The quinhydrone electrode.—When quinone and its reduction product, hydroquinone, are present in a solution containing hydrogen ions, a reversible reaction can take place represented by the equation:

$$\underset{\text{Quinone}}{C_6H_4O_2} + 2H^{\cdot} \rightleftharpoons \underset{\text{Hydroquinone.}}{C_6H_6O_2} + 2\theta$$

For the reaction to proceed, however, it is necessary to remove the liberated positive electricity 2θ. This can be done by immersing a platinum electrode in the solution and using the arrangement as half of an electrical cell. The potential of such an electrode can be obtained by calculating the maximum work to be obtained from the change and equating this to the electrical work. For the reduction of dx molecules of quinone the electrical work done is $2dxFE$ where E is the potential of the electrode. The maximum work to be obtained from the chemical change is given by the equation of van't Hoff (p. 237).

$$A = dx\, RT \log_e K - dx\, RT \log_e \frac{[C_6H_6O_2]_f}{[C_6H_4O_2]_i\,[H^{\cdot}]_i^2},$$

where K is the equilibrium-constant for the reaction, and the quantities in the second term are the initial and final concentrations of the reactants and resultants. Equating the electrical work to the affinity of the change

$$2\,dx\,FE = dx\, RT \log_e K - dx\, RT \log_e \frac{[C_6H_6O_2]_f}{[C_6H_4O_2]_i\,[H^{\cdot}]_i^2},$$

$$\therefore\ E=\frac{RT}{2F}\log_e \mathrm{K}-\frac{RT}{2F}\log_e\frac{[\mathrm{C_6H_6O_2}]}{[\mathrm{C_6H_4O_2}]\,[\mathrm{H^\cdot}]^2},$$

$$E=\frac{RT}{2F}\log_e K-\frac{RT}{2F}\log_e\frac{[\mathrm{C_6H_6O_2}]}{[\mathrm{C_6H_4O_2}]}+\frac{RT}{F}\log_e[\mathrm{H^\cdot}].$$

The first term of this expression is constant, and so is the second term *provided that the ratio of the concentrations of quinone and hydroquinone is kept constant.* This is readily achieved by adding to the solution an excess of the sparingly soluble molecular compound of quinone and hydroquinone, $C_6H_4O_2$, $C_6H_6O_2$, known as quinhydrone. The E.M.F. of the **quinhydrone electrode** is then given by

$$E=\mathrm{E}_k+\frac{RT}{F}\log_e[\mathrm{H^\cdot}],$$

and such an electrode can be used to measure hydrogen-ion concentrations once the value of E_k has been determined. Biilmann has made direct comparisons of the quinhydrone electrode with the hydrogen electrode and finds that at 18°

$$E=0{\cdot}704+0{\cdot}058\ \log_{10}[\mathrm{H^\cdot}].$$

The quinhydrone electrode is simpler to set up than the hydrogen electrode as it does not require a supply of hydrogen. It can, however, only be used for acid solutions $p_{\mathrm{H}}<7$ and gives erroneous results in the presence of certain neutral salts. The latter error is diminished by using a modified form of the electrode in which excess of solid hydroquinone as well as quinhydrone is added to the solution. For this **hydro-quinhydrone electrode** Biilmann finds at 18°

$$E=0{\cdot}618+0{\cdot}058\ \log_{10}[\mathrm{H^\cdot}].$$

For the **quino-quinhydrone** electrode in which an excess of solid quinone is added to the quinhydrone, the E.M.F. is

$$E=0{\cdot}756+0{\cdot}058\ \log\,[\mathrm{H^\cdot}]\ \text{at } 18°.$$

35. The Solubility-product of Electrolytes.

i. Determination of the solubility-product of potassium bromate.—(*a*) Prepare a saturated solution of potassium bromate by cooling a stronger solution to 20°. After half an hour at 20°, decant off the clear solution and estimate the amount of bromate present by running 2 c.c. of the solution into an excess of

potassium iodide solution, acidifying with sulphuric acid and titrating the liberated iodine with $N/10$ thiosulphate.

(*b*) To 100 c.c. of the clear solution add 11·9 grams of potassium bromide, so as to make the solution normal with respect to the bromide. Shake till the bromide has dissolved, let the solution stand at 20° for half an hour, and then determine the amount of bromate in the clear liquid.

(*c*) From your results calculate the concentrations of the potassium and of the bromate radicals in both solutions and note if the product is constant.

ii. Solubility-product of silver acetate.—Shake an excess of silver acetate with 250 c.c. of water at 20° until a saturated solution is formed. Estimate, by titration with potassium thiocyanate, the amount of silver in 25 c.c. of the clear solution. To 100 c.c. of the clear solution add 8·2 grams of anhydrous sodium acetate, so as to make the solution normal with respect to this salt. After standing for half an hour, redetermine the amount of silver in the clear solution. Calculate the concentrations of the silver and of the acetate radicals in the two solutions, and see if the product is constant.

The solubility-product of an electrolyte.—The theory of electrolytic dissociation gives a very interesting explanation of the solubility relations of sparingly soluble substances, and in many cases enables us to determine the conditions under which a precipitate will be formed. Thus, if we consider the equilibria which are set up in a saturated solution of a sparingly soluble substance such as silver chloride, which is completely ionised in the solid state, we may express the main condition of equilibrium by a scheme such as

$$\underset{\text{(Solid)}}{\text{AgCl}} \rightleftharpoons \underset{\text{(Dissolved)}}{\text{Ag}^{\cdot} + \text{Cl}'}.$$

Since the active mass of the solid is constant, it follows from the law of mass-action that

$$[\text{Ag}^{\cdot}][\text{Cl}'] = K[\text{AgCl solid}] = S.$$

This constant S is named the **solubility product** for silver chloride. Its significance may perhaps be appreciated better if we now reverse our reasoning, since it is evident that, when silver ions and chloride ions are brought together in solution, *a precipitate will not form unless the product of the concentration of these ions is greater than the solubility-product S.*

The solubility of silver chloride in water is 1×10^{-5} gram-molecules per litre at room temperature. In this very dilute solution we can assume that ionisation is complete, so that

$$[Ag^{\cdot}] = [Cl'] = 1 \times 10^{-5},$$

whence $S_{AgCl} = 1 \times 10^{-10}$.

If the concentration either of silver ions or of chloride ions is increased, then the concentration of the other type of ion must fall until the product of the concentrations reaches the solubility-product. Since this can only occur by the removal of further silver chloride from the solution, it can be predicted that silver chloride will be less soluble in a solution containing silver nitrate or potassium chloride than in pure water.

The amount of silver chloride precipitated in this manner can readily be calculated. Suppose, to 1 litre of a saturated solution of silver chloride, sufficient silver nitrate is added to make the solution decinormal with respect to this salt. The concentration of silver ions $[Ag^{\cdot}]$ is now 10^{-1}. Hence, since

$$[Ag^{\cdot}][Cl'] = S = 10^{-10},$$

$$[Cl'] = \frac{S}{[Ag^{\cdot}]} = \frac{10^{-10}}{10^{-1}} = 10^{-9}.$$

The amount of silver chloride in solution therefore falls from 10^{-5} to 10^{-9} gram-molecules per litre, and 0·00001 gram-molecule is precipitated. Since the molecular weight of AgCl is 143·5 this amounts to 0·001435 grams per litre. This amount is quite appreciable in atomic weight determinations; a slight excess of silver nitrate is therefore always used in order to complete the precipitation of chloride ions by silver, or *vice versa*.

Applications to qualitative analysis.—The theory of the solubility-product gives an interesting explanation of many of the reactions used in qualitative analysis. The solubility-products of a number of the commoner sulphides in order are, HgS 4×10^{-54}, CuS 8×10^{-45}, CdS 5×10^{-29}, ZnS about 1×10^{-20}, MnS $1{\cdot}4 \times 10^{-15}$. When sulphuretted hydrogen is passed into a solution of the salts of these metals, precipitation will occur when

$$[M^{\cdot\cdot}][S''] > S,$$

where $M^{\cdot\cdot}$ is the ion of the metal.

We cannot vary the concentration of the metallic ion very readily, since we are limited in one direction by the solubility of the salt and, on the other hand, by the necessity of obtaining a sufficient amount of precipitate to handle and use for confirmatory tests. We can, however, vary within wide limits the concentration of sulphide ion present. Sulphuretted hydrogen is a weak acid, and the dissociation

$$H_2S \rightleftharpoons 2H^{\cdot} + S''$$

is readily repressed by hydrogen ions. If therefore the solution is acidified with hydrochloric acid, the concentration of sulphide ions [S''] is lowered so much that the solubility-product is only attained for the very insoluble sulphides, *e.g.* HgS, CuS, and CdS, whilst ZnS and MnS remain in solution. If too much acid is added, CdS may not be precipitated, though here the reaction is complicated by the fact that an unstable orange form of CdS with a greater solubility-product is first produced.

If H_2S is passed into a neutral solution of a zinc salt some ZnS is precipitated, but the reaction is never complete as the acid liberated by the reaction rapidly lowers the concentration of sulphide ions and stops the precipitation. If, however, ammonium acetate and acetic acid are added, so that only a weak acid is present, ZnS can be precipitated completely. Under these conditions, the more soluble MnS is not thrown down and requires the addition of a soluble sulphide, *e.g.* ammonium sulphide, to give a supply of sulphide ions in excess of its solubility product.

In the separation of copper and cadmium the concentration of the metallic ion is varied. On the addition of excess of potassium cyanide to the solution, copper forms a complex ion $Cu(CN)_4''$, so that very little of the ion $Cu^{\cdot\cdot}$ is present. Cadmium does this to a much smaller extent, so that, when sulphuretted hydrogen is passed through the solution, the solubility-product of cadmium sulphide is reached before that of copper sulphide, and cadmium is first precipitated.

An example, in which the dissociation of a base is controlled, is provided by the separation of iron, aluminium and chromium

from zinc, manganese and magnesium. Ammonia is a weak base and its degree of dissociation is lowered markedly by the addition of ammonium chloride. If, therefore, a dilute solution of ammonia is added to a solution containing salts of these metals together with ammonium chloride, only those hydroxides with small solubility-products, namely, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, are precipitated. If, however, too much ammonia is added, or if enough ammonium chloride is not present, or if the concentration of the metallic ions is too large, then the hydroxides of zinc, manganese, and magnesium will also be thrown down, since their larger solubility-products will be exceeded. In this case, ammonium chloride is used to regulate the dissociation of ammonia, and to differentiate between hydroxides with different solubility-products.

The conception of a solubility-product can also be used to account for the solubility relationships of the chromates and sulphates of calcium, strontium, and barium, and for the solubility of salts of weak acids, *e.g.* phosphates and cyanides, in strong acids. In all such cases it must be remembered that the solubility-product can only be regarded as constant for sparingly soluble substances and for reagents in dilute solutions. In stronger solutions of salts, with or without an ion common to the sparingly soluble substance, it has been found that the solubility-product is by no means constant. Silver chloride, for example, is more soluble in concentrated solutions of potassium chloride than in pure water, although in dilute solutions of this salt it is much less soluble than in water, and gives a solubility-product which is nearly constant.

QUESTIONS ON CHAPTER XIV.

1. An acid is a substance which in aqueous solution changes the colour of litmus from blue to red : a base is a substance which effects the converse change.

Criticise these statements as *definitions* of an acid and a base respectively. (Entrance Schols., Cambridge.)

2. Derive the formula for the Ostwald Dilution Law, showing clearly the principles on which it is based. Under what conditions is it found to hold ? Give a formula which agrees more closely with the experimental data. (B.Sc., Manchester.)

3. Explain what is meant by the avidity of an acid. From the following data calculate the relative avidities of the two acids HX and HZ.

HXaq MOHaq = 31·380 cal.
HZaq MOHaq = 27·230 cal.
MXaq HZaq = −2·740 cal.

Explain the action of phenolphthalein as an indicator from the standpoint of avidity. (B.Sc., Manchester.)

4. Describe with full experimental details how you would propose to ascertain (*a*) whether an organic acid, say propionic acid, obeys Ostwald's Dilution Law, (*b*) whether the inversion of cane-sugar can be expressed exactly by the equation for a monomolecular reaction. (B.Sc., Hons.)

5. Explain what is meant by hydrolysis. The following salts undergo hydrolysis in aqueous solution : ferric chloride, potassium cyanide, sodium carbonate, and cupric sulphate. Describe exactly how the existence of this phenomenon may be demonstrated in each case. (Cambridge Higher School Certificate.)

6. Write short notes on three of the following : (i) ionisation and electrolytes, (ii) solubility product, (iii) hydrolysis of salts, (iv) the neutralisation of an acid by a base. Illustrate by examples.
(Joint Matric. Board, Higher School Certificate.)

7. Why is a solution of sodium carbonate alkaline ? Why must phenol phthalein not be used as an indicator for titrations with sodium carbonate ? (Natural Science Schols., Oxford.)

8. Explain what is meant by the dissociation-constant of an acid and point out how it can be determined in the case of acetic acid.

The electrolytic dissociation-constants of formic and acetic acids are $21{\cdot}4 \times 10^{-5}$ and $1{\cdot}8 \times 10^{-5}$ respectively. What is the relative avidity (strength) of the two acids ?
(Trinity College, Senior Schol.)

9. What definitions can be given of a neutral solution ? The following salts when dissolved in water do not give neutral solutions : ferric chloride, borax, potassium cyanide. How do you account for these phenomena ? (Downing College, Minor Schol.)

10. Describe the experiments you would make to determine the relation between the degree of dilution of a solution of acetic acid and its molecular conductivity. How are the results of such experiments explained ? The equivalent conductivity of acetic acid at infinite dilution is 388 ; the equivalent conductivity of a solution containing 0·3 gm. of acetic acid in 50 c.c. of water is 4·6. Calculate the freezing-point of this solution. [A solution containing 34·2 gm. of cane-sugar in 100 gm. of water freezes at −1·85° C., H = 1, C = 12, O = 16.]
(Selwyn College, Entrance Schol.)

11. Explain how to calculate how the hydrogen-ion concentration varies in the titration of 50 c.c. of $N/100$ acetic acid with $N/100$ sodium hydroxide solution as the volume of the alkali added is increased from 49 c.c. to 51 c.c. Plot the p_H of the solution against the volume of alkali added, and with the aid of your curve explain how an indicator with a dissociation-constant of 10^{-5} will behave during the titration (K_{25} for acetic acid is $1{\cdot}8 \times 10^{-5}$, $K_W = 10^{-14}$). (Trinity College, Senior Schol.)

12. By what methods has the ionisation-constant of water been determined ? Describe one method in detail.
(B.Sc. Hons., Manchester.)

13. A pseudo-acid is red in acid solution and yellow in alkaline solution and has an apparent dissociation-constant of 10^{-5}. Calculate roughly what fraction of it will be in the red form in solutions of p_H 4, 5 and 6 respectively.
State what further information would be required to enable you to decide whether the substance in question would be useful as an indicator, and assuming it to be satisfactory in these respects, discuss briefly the types of volumetric estimation for which it could be employed. (Inter. Sci., Sheffield.)

14. Describe in detail the various experimental methods, and their theoretical basis, that are available for determining degree of hydrolysis. (B.Sc. Hons., Sheffield.)

15. Write a brief essay on the theory of indicators.
(B.Sc., Manchester.)

16. Calculate the hydrogen ion concentrations of the following solutions: (*a*) $M/100$ HCl, (*b*) $M/100$ $CH_3 \cdot COOH$, (*c*) 20 c.c. $M/100$ CH_3COOH and 10 c.c. $M/100$ NH_4OH ; also determine in each case what change would be brought about by a ten-fold dilution.
Discuss the differences in behaviour of the three solutions and explain what bearing these results have on analytical technique (K_A for acetic acid is $1{\cdot}8 \times 10^{-5}$, per cent.; ionic dissociation of $0{\cdot}01$ N HCl $= 96{\cdot}4$ and of $0{\cdot}001$ N HCl $= 98{\cdot}2$). (B.Sc., Sheffield.)

17. How may the term solubility product be defined ? Give three examples of the utility of this concept in qualitative analysis. The solubility of barium sulphate is $2{\cdot}3 \times 10^{-4}$ gm. in 100 c.c. of water. What is the percentage error involved in washing a precipitate of $0{\cdot}200$ gm. of barium sulphate with (*a*) a litre of water, (*b*) a litre of $\frac{N}{100}$ sulphuric acid ? Ba = 137, S = 32, O = 16.
(Cambridge Entrance Schols.)

18. An aqueous solution of ammonia is capable of precipitating certain metals as sparingly soluble hydroxides, but in the presence of ammonium chloride this precipitation is often prevented. What explanation can be given of this phenomenon ?
(Downing College, Minor Schol.)

19. Explain the following facts :

(*a*) When hydrochloric acid is led into a saturated solution of sodium chloride, crystals of the salt are precipitated.

(*b*) Many normal salts such as sodium carbonate and ferric chloride are alkaline or acid in solution.

(*c*) Zinc sulphide is precipitated by hydrogen sulphide from a solution of zinc acetate, but not from a solution of zinc chloride.

(Oxford Higher School Certificate.)

20. Explain how the solubility of a sparingly soluble electrolyte may be increased or diminished by the presence of small quantities of other substances.

One litre of a saturated solution of calcium sulphate at 18° contains 0·015 mol. of the salt. Calculate how much calcium sulphate should be precipitated by the addition of 0·025 mol. of potassium sulphate to one litre of this saturated solution, both salts being regarded as practically completely ionised.

(Trinity College, Cambridge.)

CHAPTER XV.

THE COLLOIDAL STATE.

36. Preparation and General Properties of Colloids.

i. Experiments on dialysis.—Make a dialyser by soaking a large filter-cup (as used in a Soxhlet extraction apparatus) in a 5 per cent. solution of collodion in glacial acetic acid. When the excess of collodion has drained off, immerse the cup in water and wash it free from acetic acid, when it will be ready for use. Cups of parchment paper can also be purchased ready for use as dialysers. Place within the cup a 2 per cent. solution of gelatin, to which a little sodium chloride has been added, and immerse in a beaker of water. After 24 hours, test the water in the beaker for salt by adding silver nitrate, and for gelatin by adding a solution of tannic acid. It will be found that the salt has passed through the membrane whilst the gelatin has been retained completely in the inner vessel.

ii. Preparation of colloidal arsenious sulphide.—Finely powder 0·5 gram of pure arsenious oxide, and boil with 500-600 c.c. of distilled water until all is dissolved. Through the cooled solution pass a current of sulphuretted hydrogen which has been filtered from acid spray by means of a U-tube containing cotton wool. When no further deepening of colour occurs, remove the excess of sulphuretted hydrogen by bubbling through the solution, for half an hour, a current of hydrogen or of carbon dioxide, filtered through cotton wool. Filter the solution to remove any large particles of sulphide, and store it in a clean glass bottle.

iii. Preparation of colloidal aluminium hydroxide.—Dissolve about 3 grams of aluminium sulphate in 300 c.c. of water and precipitate the aluminium hydroxide in the usual manner with ammonium chloride and ammonia. Filter off the hydroxide on a large filter paper and wash with five or six lots of 200 c.c. of boiling water. Towards the end of the process the precipitate will become slimy and filtration will be very slow. When this

occurs, transfer the precipitate to a clean flask and boil with 500 c.c. of water for 2-3 hours. A few drops of $N/10$ HCl should be added from a burette every half hour. After 3 hours, practically all the hydroxide will have passed into solution and the sol should be filtered and stored in a clean glass bottle.

iv. Preparation of colloidal copper.—Wind two stout copper wires round strong glass rods to serve as insulating handles. Connect one end of each wire to the secondary terminals of an induction coil and bend the other ends so that the wires are about 1-2 mm. apart and immersed in a beaker of distilled water. Start the induction coil, and if necessary strike the arc between the wires by moving them together for a moment. Brown clouds will be formed round the junction of the wires, and a colloidal solution of copper will be produced in the beaker. This should be filtered from coarse particles, and stored in a clean glass vessel.

v. Preparation of colloidal platinum.—Weld two short pieces of platinum about 2 mm. in diameter to the ends of stout copper wires passing through glass tubes which serve as insulating handles. Connect to the lighting circuit (200 volts) through a resistance of 30–40 ohms. capable of carrying 5 amperes. Place 100 c.c. of conductivity water in a porcelain dish cooled in ice; bring the platinum wires together under the water and separate them about 2 mm. to form an arc, which, however, soon dies out. Repeat the formation of the arc for about 10 minutes, and finally filter the brown solution to remove the larger particles. For use in Expt. 27, ii. (*c*), dilute until the hydrogen peroxide is half decomposed in about 20 minutes.

Crystalloids and colloids.—The terms **colloid** and **crystalloid** were introduced by Graham in 1861 in order to distinguish between two important classes of dissolved substances, which differed widely in the rate at which they diffused into pure water. Some substances, such as salts, sugar, urea, etc., were found to diffuse relatively fast in aqueous solution; these were described as **crystalloids**, in order to recall the fact that the solid substances are crystalline. On the other hand, a large group of amorphous substances, including gelatin, starch, gum, etc., were found to diffuse very slowly in solutions; these were described as **colloids** (from the Greek κολλα = glue), in order to recall the fact that the solids were generally obtained in the form of a sticky paste on evaporating the colloidal solutions.

Table 95 gives some of Graham's figures for the rates of diffusion of members of these two classes.

TABLE 95. RELATIVE RATES OF DIFFUSION IN WATER.

(*a*) Crystalloids.		(*b*) Colloids.	
HCl	1·00	Albumen	0·02
NaCl	0·43	Caramel	0·01
$MgSO_4$	0·14		
Sucrose	0·14		

It has also been found that many substances, such as metallic gold, which (unlike gelatin or gum) are quite insoluble in water, can be brought into a colloidal condition by adopting special methods of treatment. Thus, when gold is precipitated from an aqueous solution of auric chloride by the action of a suitable reducing agent, a red or purple "solution" is obtained which passes completely through filter paper, and contains no particles which are visible to the naked eye or even under a microscope. These "solutions" of insoluble compounds possess the characteristic property of very slow diffusion, but are usually unstable, since the "dissolved" substance is often precipitated on standing, on boiling, or on the addition of an electrolyte.

Later workers have found that the colloidal state can also be produced in other media than water, although the test of diffusibility is not always employed in these other media. Thus it is possible to prepare a colloidal solution of rubber in benzene, or of nitro-cellulose in acetone or in a mixture of alcohol and ether. Even common salt can be brought into a colloidal state in benzene; and soap, which gives colloidal solutions in water, behaves as a crystalloid when dissolved in alcohol. In face of facts such as these, it appears probable that any substance may be obtained in a colloidal state if suitable conditions are employed. It is therefore probably more correct to speak of the **colloidal state** than to describe a particular substance as a colloid or a crystalloid. The term **colloid** can, however, be applied without hesitation to substances such as gelatin or glue, which always give colloidal solutions, and do not even form a crystalline solid when dried by evaporation.

Classification of colloids.—It is evident that the colloidal state covers several totally diverse conditions, and that, for instance,

colloidal gold and a colloidal solution of gelatin have very little in common, except a slow rate of diffusion. In order to understand the behaviour of colloids, therefore, it is necessary in the first instance to consider very carefully how they are to be classified. It is, indeed, immediately obvious that two main groups must be recognised, of which gold and gelatin may be taken as typical examples. These are described below as **colloidal suspensions** and **colloidal solutions**, but it is suggested that the colloidal solutions (like true solutions), may be divided into two sub-groups, according as the colloidal material is an electrolyte or a non-electrolyte.

(*a*) *Colloidal suspensions.*—It has been established clearly by experiment that many colloidal solutions or **sols** are not solutions at all, but mere suspensions, in which an insoluble substance, such as gold, is reduced to such a fine state of subdivision that it behaves almost as if it were *dissolved* in a solvent, instead of being merely "dispersed" or scattered in the liquid medium. A colloidal system of this type contains two phases, namely, (i) **the dispersing medium**, which takes the place of the solvent in a true solution, (ii) **the disperse phase**, which takes the place of the solute. When the disperse phase is completely insoluble in the dispersing medium, and can only be brought into a colloidal condition by special processes, as in the case of metallic gold in water, the system can be described most accurately as a **colloidal suspension.** It is shown below that the minute particles of a colloidal suspension are prevented from settling by the bombardment of the molecules of the solvent, and are prevented from coalescing by the fact that they carry electric charges of the same sign, either positive or negative.

(*b*) *Colloidal electrolytes.*—When a fatty acid of high molecular weight is added to water, it spreads out with great rapidity into a thin layer, which occupies a very large area on the surface of the water. This spreading has been explained by the fact that the carboxyl-radical of the acid is *hydrophilic*, and has a definite affinity for the water, whilst the oily hydrocarbon radical to which it is attached is *hydrophobic* and tends to separate itself from the water. These two tendencies can only be satisfied simultaneously by allowing the acid radicals to

come into direct contact with the water, whilst the hydrocarbon radicals form an outer layer on the surface. Under these conditions the thickness of the film is reduced to that of a single molecule, provided that there is enough surface available for this reduction of thickness to take place. Incidentally, the striving of the molecules to take up a position at the water-air interface tends to stretch the surface and therefore reduces the surface tension of the liquid, in addition to causing the molecules to set themselves in a definite orientation.

When alkali is added, the fatty acid is converted into a soap, which forms a colloidal solution in the water. The chemical change which takes place can be shown for the typical case of palmitic acid by the equation:

$$\underset{\text{Palmitic acid.}}{C_{15}H_{31}\cdot CO\cdot OH} + \overset{+}{N}a\,\vdots\,\overset{-}{O}H \rightleftharpoons \underset{\text{Sodium palmitate.}}{C_{15}H_{31}\cdot CO\cdot \overset{-}{O}\,\vdots\,\overset{+}{N}a} + H_2O,$$

where the sodium hydroxide and sodium palmitate are represented as pairs of ions. The electrolytic dissociation of the salt then permits the sodium ions of the sodium palmitate to escape into the water, and thus creates such a strong pull upon the oppositely-charged palmitate ions that they can no longer remain as an oily film on the surface of the water, but are dragged into the interior. Even there, however, the palmitate ions retain their oily character, and, instead of breaking up into individual anions, they collect into oily aggregates which have been described by the term **ionic micelle.** The colloidal solution then consists of sodium ions which are in true solution and palmitate ions which are merely suspended in the medium without even being dispersed as individual ions. Colloids of this kind are known as **colloidal electrolytes.** They differ from colloidal suspensions on the one hand, and from non-conducting colloidal solutions on the other hand, in that *the molecules are ionised by the solvent.* It is for this reason that the substance passes spontaneously into the colloidal state by mere contact with the solvent, without requiring any other special treatment.

Many dye-stuffs have the structure of a colloidal electrolyte and exhibit the typical properties of this class. These dye-

stuffs are prepared by introducing a salt-forming radical into a coloured compound which is insoluble in water, *e.g.* NH_2 or SO_3H. The negative ion of the salt $-\overset{+}{N}H_3\overset{-}{Cl}$ or the positive ion of the salt $-SO_2 \cdot \overset{-}{O}\overset{+}{N}a$ then passes into solution and compels the oppositely charged ion of the colour-producing complex to follow it, just as the palmitic ion follows the sodium ion into water.

(*c*) *Non-conducting colloidal solutions.*—Substances of high molecular weight are most easily dissolved by converting them into colloidal electrolytes, as when indigo is sulphonated:

$$C_{16}H_{10}N_2O_2 + 2H_2SO_4 = C_{16}H_8N_2O_2(SO_2 \cdot \overset{-}{O}\overset{+}{H})_2 + 2H_2O.$$

In some cases, however, solution can be effected merely by selecting a suitable solvent. Non-conducting solutions are then produced which are colloidal in character only because the solute is of very high molecular weight. Examples of this kind are the solution of rubber in benzene, and of nitrocellulose in acetone, which cannot be classed as colloidal electrolytes, since the solute cannot be ionised and the solution is not an electrolytic conductor. These colloidal solutions are not optically clear, but the scattering of light which takes place appears to be only an exaggerated form of that which can already be detected in aqueous solutions of a crystalline sugar.

It is of interest to notice that the distinction between electrolytes and non-electrolytes, which provides so many contrasts in solutions of crystalloids, is also of predominant importance in colloidal solutions (as distinguished from colloidal suspensions), since these also can be of either type.

Peptisation by salt-formation.—Gelatin, which possesses weak basic and acidic properties, passes spontaneously into colloidal solution only when the water contains a trace of acid or alkali to convert the gelatin into a salt. Thus, pure gelatin is practically insoluble in slightly acid water, in which the concentration of the hydrogen-ions has been adjusted (to $p_H = 4{\cdot}7$), so that the tendency to form a salt is reduced to a minimum. In the same way, aluminium hydroxide, which is insoluble in water, can be prepared in a colloidal form by the action of very dilute hydrochloric acid (Expt. 36, iii.).

This process is sometimes described as **peptisation** (p. 404), and the acid is described as a **peptising agent**; but the action appears to be nothing more than a partial replacement of hydroxl by chlorine, as a result of which an aggregate of molecules of aluminium hydroxide is converted into a colloidal electrolyte, just as a fatty acid can be converted into a colloidal soap by the action of a smaller quantity of sodium hydroxide than is required to convert the whole of the acid into its sodium salt. A similar explanation can probably be given in other cases in which an acid acts as a " peptising agent " for a weak base, or conversely.

Lyophobic and lyophilic colloids.—Colloidal suspensions differ widely from colloidal solutions in their sensitiveness to electrolytes. Thus a gold sol is readily precipitated by traces of electrolytes, and the precipitate cannot be redissolved again by mere contact with the pure solvent. Since there is very little affinity between the disperse phase and the solvent, colloids of this type are termed **lyophobic** (*i.e.* solvent-hating). Colloidal metals and metallic sulphides belong to this group. On the other hand, a solution of gelatin can only be precipitated by very strong solutions of electrolytes, *e.g.* saturated ammonium sulphate, and the precipitate dissolves again readily in moderately pure water. In this type of sol it is evident that the disperse phase has a considerable affinity for the solvent. For this reason colloids of this type are termed **lyophilic** (*i.e.* solvent-loving). Starch, albumen, and gum arabic belong to this class.

It was at one time supposed that the disperse phase in a lyophobic colloid was always a solid, whilst the disperse phase in a lyophilic colloid was always a liquid. An attempt was therefore made to classify colloids as **suspensoids** and **emulsoids** according as the disperse phase was solid or liquid. It has been found, however, that colloidal suspensions, having all the normal characteristics of a " suspensoid," can be prepared with a liquid, *e.g.* oil or mercury, as the disperse phase. This method of classification is therefore unsatisfactory, and it is better to classify the two main groups of colloids as lyophobic and lyophilic. The terms **irreversible sols** and **reversible sols** are sometimes used for this purpose, since the precipitate obtained when a lyophobic colloid is coagulated by electrolytes cannot in general be

re-dissolved directly. This can, however, be effected in many cases by a process of "peptisation," as in the case of the sol of aluminium hydroxide (p. 403), where the addition of an acid converts a lyophobic hydroxide into a basic salt which is lyophilic.

37. Properties of Colloidal Suspensions.

i. Observation of the Tyndall cone.—Set up an ordinary projection lantern in a dark room and prepare a series of round-bottomed flasks of about 20 c.c. capacity filled with (*a*) distilled water, (*b*) filtered salt solution, (*c*) colloidal arsenious sulphide, (*d*) colloidal aluminium hydroxide. For the two latter flasks use the solutions prepared in Expt. 36, ii. and iii., diluted ten-fold with distilled water. Hold each flask in turn in the narrow portion of the projected beam (about 6-8 inches in front of the projecting lens). The track of the beam will scarcely be visible in flasks (*a*) and (*b*), but will stand out vividly as a band of light in flasks (*c*) and (*d*).

ii. Demonstration of cataphoresis.—The apparatus required consists of a U-tube ending in a bent capillary tube which carries a stopcock and funnel (Fig. 74). Clamp the U-tube vertically, and run in distilled water through the stopcock till the limbs are rather less than half filled. Then run in slowly a colloidal solution of arsenious sulphide so as to maintain a sharp interface until the level of the water is near the top of the U-tube. Close the U-tube with stoppers carrying electrodes formed of flat spirals of platinum wire and place an opal glass scale behind each limb to show the position of the interface. Connect the electrodes to a direct-current electric supply at a potential of about 200 volts, and read the position of the interface every 15 minutes for an hour. Arsenious sulphide will be found to move towards the anode, thus showing that the particles are negatively charged.

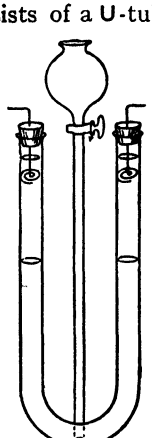


Fig. 74.—Apparatus for demonstration of cataphoresis.

Repeat the experiment with colloidal ferric hydroxide, which will be found to move towards the cathode, since the particles carry a positive charge.

iii. Coagulation of colloidal arsenious sulphide.—Prepare a $2N$ solution of sodium chloride and place 5 c.c. of this in the first of a row of clean test tubes. From the same solution, by successive dilutions, prepare solutions of N, $N/2$, $N/4$, $N/8$, $N/16$, and $N/32$ concentration, and place 5 c.c. of each in successive test-tubes. To each tube add 5 c.c. of the arsenious sulphide sol, mix by inverting the tubes twice, and allow to stand. After 2 hours note the concentration at which precipitation is just produced.

Set up a similar experiment with barium chloride as precipitant, using concentrations of $N/10$, $N/20$, $N/40$, $N/80$, etc., and with aluminium sulphate, using concentrations $N/200$, $N/400$, $N/800$, $N/1600$, etc. Calculate in each case the concentration in millimols per litre which just causes precipitation in 2 hours. Remember that the added electrolyte is diluted to twice its bulk by the sol.

iv. Coagulation of colloidal aluminium hydroxide. — By the method described in the previous experiment, determine the minimum amounts of sodium chloride, of potassium sulphate, and of sodium phosphate which will just coagulate a sol of aluminium hydroxide. Use the following concentrations as a start: NaCl, $2N$, N, $N/2$, etc.; K_2SO_4, $N/10$, $N/20$, $N/40$, etc.; Na_2HPO_4, $N/200$, $N/400$, $N/800$, etc.

v. Mutual coagulation of colloidal suspensions.—Prepare a series of mixtures of colloidal suspensions in pairs, *e.g.* As_2S_3 and $Fe(OH)_3$, and notice which pairs coagulate one another.

Preparation of colloidal suspensions.—Since lyophobic colloids are very unstable in presence of electrolytes, it is usually necessary, when preparing colloidal suspensions, to take special precautions to avoid the presence of salts, and of strong acids and bases, or to remove them from the solution, in order to render the colloid stable. Thus colloidal gold can be prepared most readily by reducing a solution of auric chloride with a reducing agent which is not an electrolyte, as in Faraday's experiments, where a solution of phosphorus in ether was used. A more general method for the preparation of colloidal metals consists of striking an electric arc between two wires of the metal immersed in a suitable solvent (Expt. 36, iv.) The metal is vaporised in the arc and suddenly condensed by the surrounding liquid in extremely fine particles which form a colloidal suspension. By this method Bredig and others have prepared

colloidal solutions of gold, platinum, and many other metals in a series of solvents including water, alcohols and esters.

A further example of the influence of electrolytes is found in the fact that, when sulphuretted hydrogen is passed into an acidified solution of *arsenious chloride*, a yellow precipitate of the sulphide is produced. If, however, the gas is passed into a solution of *arsenious oxide* in water, a clear yellow colloidal solution of arsenious sulphide is produced. In the latter case, there is never any considerable concentration of ions present, since the arsenious oxide and the sulphuretted hydrogen are both weak electrolytes. The colloidal solution thus prepared can be kept for years if the precaution is taken of sweeping out the excess of sulphuretted hydrogen by a current of hydrogen or of carbon dioxide (Expt. 36, ii.). The addition of a little hydrochloric acid to a portion of the yellow solution brings about a rapid precipitation of the sulphide.

Purification of colloids by dialysis.—Since electrolytes differ considerably in their action on colloids, it is possible in some cases to prepare an insoluble substance in the colloidal state by mixing suitable solutions in the right order. Thus, when hydrochloric acid is added to a solution of sodium silicate, a precipitate of silicic acid is formed; if, however, the silicate is poured slowly into excess of dilute hydrochloric acid, a clear solution is obtained, which contains colloidal silicic acid as well as sodium chloride. The latter can be removed by the process of **dialysis.** This process depends upon the fact that crystalloids will diffuse rapidly through a diaphragm of parchment paper or of bladder, whilst the colloid is unable to pass through the membrane. An early form of dialyser (due to Graham) consists of a shallow cylinder with the base closed by a bladder. The solution to be dialysed is placed in the vessel, which is then suspended in a dish of water (Fig. 75). A convenient modern form is a cup of parchment paper suspended in a vessel through which water flows slowly.

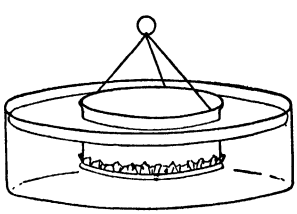


FIG 75.—Apparatus for dialysis.

By repeated dialysis, Graham obtained a colloidal solution of silicic acid of 5 per cent. concentration, which could be concentrated by evaporation until it contained 14 per cent. of silicic acid. Further concentration caused it to coagulate to a jelly, which would not dissolve on adding more water. This colloidal solution was found to be coagulated readily by small amounts of alkalis, but was much less sensitive to acids and to neutral salts.

Colloids can also be separated from crystalloids by **ultrafiltration,** *i.e.* by forcing the liquid through a membrane, such as collodion, which will not allow the colloid to pass. Since the osmotic pressure of colloids is very small, the pressures required for this purpose are not excessive.

Dimensions of colloidal particles.—When a colloidal suspension (which has been filtered to remove coarse particles) is examined under the microscope, no particles can be detected even with the most powerful objectives, and the solution appears to be homogeneous. The size of particle which can be detected by the ordinary microscope is, however, limited by the wave-length of the light used. Particles smaller than 2×10^{-5} cm. in diameter could not be seen with visible light, no matter how excellent the construction of the instrument.

A method of detecting still smaller particles, which was discovered by Tyndall, depends upon their power of scattering light. The path of a beam of light through pure water or through a solution of a crystalloid of small molecular weight is invisible when viewed at right angles to the beam ; if, however, a colloidal sol is substituted for pure water, the path of the beam is shown by a bright column or cone of scattered illumination which is often termed the **Tyndall cone.** (Expt. 37, i.).

The **ultramicroscope** of Zsigmondy consists essentially of an arrangement for examining the Tyndall cone by means of a microscope. A narrow beam of light of considerable intensity is passed horizontally through a small cell containing the colloid, and a portion of the track of the beam is viewed through a vertical microscope. It is then seen that the Tyndall cone is due to a number of scattered points of light which are moving about irregularly with considerable velocity on a dark background. Each little bright star is due to a colloidal particle which scatters

the light falling upon it and so becomes visible. In this way particles which are much too small to be distinguished under the microscope can be detected and counted.

The shape and size of the particles cannot be determined directly, but X-ray analysis has established the fact that the particles of colloidal gold have the same crystalline character as the more ordinary forms of the metal. Moreover, the actual size of these minute crystals can be determined by combining a knowledge of the number of particles present in a given volume of the solution with a determination of the total weight of colloid in the same volume.

Thus Zsigmondy found that a particular colloidal suspension of silver exhibited on the average 30 particles in the field of view of the ultramicroscope. The volume of the solution in the field of view, as calculated from the dimensions of the instrument, was $\frac{1}{100}$ of a cubic millimetre. The solution therefore contained 3000 particles per cubic millimetre or 3×10^6 particles per c.c. This solution was prepared by diluting, in the ratio 1000 : 1, a solution containing 68 milligrams of silver per litre. The diluted solution therefore contained

$$0{\cdot}068 \times 10^{-3} \times 10^{-3} = 6{\cdot}8 \times 10^{-8} \text{ grams of silver per c.c.}$$

Since this is the weight of 3×10^6 particles, each particle weighs

$$\frac{6{\cdot}8 \times 10^{-8}}{3 \times 10^6} = 2{\cdot}3 \times 10^{-14} \text{ grams.}$$

If the particle is supposed to be spherical and of radius r cm., its mass will be $\frac{4}{3}\pi r^3 d$, where d is the density of silver, which under ordinary conditions is 10·5. On this basis the radius of the particle is given by the equation

$$\tfrac{4}{3}\pi r^3 \times 10{\cdot}5 = 2{\cdot}3 \times 10^{-14};$$

$$\therefore\ r^3 = \frac{2{\cdot}3 \times 10^{-14} \times 3}{4\pi \times 10{\cdot}5} = 5{\cdot}2 \times 10^{-16} \text{ c.c.}$$

and $$r = 8{\cdot}1 \times 10^{-6} \text{ cm. or } 810 \text{ Ångström units.}$$

These particles are relatively large, since a study of colloidal solutions of gold has revealed the presence of particles down to about 20 Ångström units in radius. In general, the radii of the particles of colloidal suspensions vary from 20 to about

1000 Å.U. Table 96 shows how the dimensions of colloidal particles are related to those of other well-known systems. It will be seen that colloidal solutions are intermediate between suspensions, containing particles which are visible under the microscope, and true solutions, in which the particles are of molecular dimensions.

TABLE 96. DIMENSIONS OF COLLOIDAL PARTICLES, ETC.

Coarse suspensions :	Blood corpuscles	75,000 ÅU.
	Starch grains	70,000 ÅU.
	Bacteria	about 5,000 ÅU.
	Mastic suspensions	10,000 – 5,000 ÅU.
Wave-length of red light		about 8,000 ÅU.
,, ,, blue ,,		about 4,000 ÅU.
Colloidal suspensions :	from	1,000 ÅU.
	to	20 ÅU.
Molecule of chloroform		8 ÅU.
Molecule of hydrogen		1 ÅU.

Brownian movement of colloidal particles.—The particles seen under the ultramicroscope are in continual motion. This irregular movement has also been observed in many suspensions of small particles which are visible under the microscope. It was first described in 1827 by the botanist Brown, and is therefore known as the **Brownian movement.** It has been observed in particles suspended in a liquid in the interior of crystals of quartz, where it has apparently persisted during the ages which have passed since the crystals were first deposited.

The Brownian movement can be accounted for completely by the irregular bombardment of a particle by molecules of the liquid in which it is suspended. If the particle is large, it receives millions of blows per second on all sides, and the effect of these cancels out. If, however, the particle is small enough, then at a particular instant it may receive a greater impulse on one side than on the other, and so move in a definite direction. The amplitude of the Brownian movement is therefore greatest in the case of very small particles.

This theory of the Brownian movement has been developed mathematically by Einstein, and has been tested experimentally by Perrin. By counting the number of particles in different

layers of an emulsion of gamboge, when a column of the suspension was allowed to settle, Perrin was able to determine Avogadro's number N (*i.e.* the number of molecules in a gram-molecule, p. 19) with considerable accuracy. Other values of N were obtained by measuring the average distance through which the particles moved in unit time, and also from the average rotation of a particle in unit time.

Since all these observations led to similar values of N, and since these were in good agreement with the number determined by other methods, the correctness of this explanation of the Brownian movement is fully established. The study of the Brownian movement has in fact provided the most convincing evidence for the real existence of molecules, and for the perpetual molecular motion which is postulated by the kinetic theory.

The formulae used in this work were as follows:

(i) *Distribution of particles:*

$$\frac{RT}{N} \log \frac{n}{n_0} = V(d-w)g(h-h_0),$$

where n_0 and n are the number of particles in a given volume at heights h_0 and h.

V = volume of granule,

d = density of granule,

w = density of intergranular liquid.

(ii) *Movement of translation:*

$$\frac{X^2}{t} = \frac{RT}{N} \frac{1}{6\pi a\eta},$$

where X is the distance travelled through in time t,

a = radius of granule,

η = viscosity of medium.

(iii) *Movement of rotation:*

$$\frac{A^2}{t} = \frac{RT}{N} \frac{1}{4\pi a^3\eta},$$

where A is the angle turned through in time t.

It will be seen that the movement of translation or rotation does not take place with a definite velocity, but is proportional to the square root of the time.

Electrification of colloidal particles.—One of the most important properties of colloidal suspensions is that the particles carry an electric charge. Thus sols of metallic hydroxides generally carry a positive charge, whilst most other sols (metals, As_2S_3, etc.) carry a negative charge. The presence of the charge is proved by the fact that the particles move in a definite direction when the sol is placed in an electric field. This phenomenon is known as **cataphoresis** (Expt. 37, ii). The sign of the charge can be deduced from the *direction* of the motion of the particles, whilst its magnitude can be deduced from their *velocity* in a given electric field. This velocity is practically constant for all the particles of a given colloid, whatever their magnitude.

Since the electrical capacity of a sphere is proportional to the radius, and the resistance which opposes its motion in a viscous medium is also proportional to its radius, the conclusion can be drawn that a constant difference of electrical potential is set up between the two phases of the colloidal suspension. The electric charges set up by this potential difference give rise to cataphoresis when the particles can move through the medium; but, when the particles are fixed, the medium can be made to move under the influence of the same electrical forces. This movement, which is produced most readily when a potential difference is set up between water on either side of a porous partition, is known as **electric osmose** or **electrophoresis.**

Coagulation of colloidal suspensions.—The sign of the charge on the particles is related closely to the remarkable behaviour of colloidal suspensions towards electrolytes, since the coagulation of a colloidal suspension is generally caused by the absorption of oppositely charged ions from the medium. Table 97 shows the smallest amount of a number of salts which just caused coagulation of an arsenic sulphide sol.

TABLE 97. COAGULATION OF AN ARSENIOUS SULPHIDE SOL BY ELECTROLYTES.

(Millimols per litre required to produce coagulation.)

KCl	49·5	$MgSO_4$	0·81	$AlCl_3$	0·093
NaCl	51·0	$CaCl_2$	0·65	$Al(NO_3)_3$	0·095
		$BaCl_2$	0·69		

It will be seen that, as the valency of the positive ion of the salt increases, its efficiency as a coagulant becomes very much greater. Since this sol carries a negative charge, *the valency of the ion of opposite sign* is the principal (but not the only) factor which determines its efficiency as a coagulating agency.

With a positively-charged sol, such as ferric hydroxide, it is the valency of the negative ion which is important. Thus it will be seen from Table 98 that barium chloride is no more efficient than potassium chloride in producing coagulation, whilst potassium sulphate is much more effective.

TABLE 98. COAGULATION OF A FERRIC HYDROXIDE SOL BY ELECTROLYTES.

(Millimols per litre required to produce coagulation.)

NaCl	-	9·3	K_2SO_4	-	0·20
KCl	-	9·0	$MgSO_4$	-	0·22
$BaCl_2$	-	9·6			

These results suggest that the coagulation of a lyophobic colloid by electrolytes is due to the neutralisation of the charge on the particles by the ions of opposite sign. It is found experimentally that, as increasing amounts of an electrolyte are added, the rate of movement in an electric field becomes smaller and smaller, and is practically zero in the neighbourhood of the point at which rapid coagulation occurs. In accordance with this result, it is found that two oppositely-charged colloids will coagulate each other if mixed in such proportions that their charges are mutually neutralised (Expt. 37, v.).

38. PROPERTIES OF COLLOIDAL SOLUTIONS.

i. Reversible precipitation of albumen.—Mix the white of an egg with about 100 c.c. of water and filter at the pump to remove fibrous matter. To 30 c.c. of the clear solution add powdered ammonium sulphate and shake the mixture continuously. As the solution approaches saturation, a white curdy precipitate of albumen is formed. Allow this to settle and pour off the supernatant liquid. Shake the precipitate with about 30 c.c. of water. The precipitate will redissolve, showing that the precipitation of albumen by ammonium sulphate is readily reversible.

Soap solutions.—The best examples of colloidal electrolytes are to be found in aqueous solutions of soaps. The sodium salts of the lower fatty acids, *e.g.* sodium acetate, show the normal behaviour of a crystalline salt; but when the fatty acid contains more than 8 or 10 carbon atoms, the sodium and potassium salts begin to behave as colloids. The soaps, of which sodium palmitate, $C_{15}H_{31} \cdot CO \cdot ONa$, and sodium stearate, $C_{17}H_{35} \cdot CO \cdot ONa$, are typical examples, therefore exhibit all the properties of lyophilic colloids. Thus the viscosity of a soap solution increases rapidly with concentration and ultimately a jelly may be formed on cooling. On the other hand, soap solutions have a large electrical conductivity and a considerable osmotic pressure (deduced from observations of lowering of the vapour-pressure and freezing-point); so that some of the soap is evidently in true solution.

A quantitative study of soap solutions by McBain and his collaborators has revealed an interesting and complex series of changes, in which both neutral colloids and a special type of electrically-charged colloid are concerned. Solutions of pure sodium palmitate were found to be hydrolysed to a very small extent, except in very dilute solutions, but exhibited a high equivalent conductivity which changed very little with dilution.

TABLE 99. HYDROLYSIS AND CONDUCTIVITY OF SODIUM PALMITATE AT 90°.

Concentration.	Hydrolysis.	Equivalent conductivity.	
		(i) Sodium hydroxide.	(ii) Sodium palmitate.
1·0*N*	0·20 %	1·10	83·6
0·75*N*	0·30	1·65	85·8
0·50*N*	0·37	2 1	87·4
0·10*N*	1·28	7·0	75·5
0·05*N*	2·22	12·2	76·4

Table 99 shows that the observed conductivity may be divided into two parts, (i) the conductivity due to the NaOH produced by hydrolysis, $NaX + H_2O \rightleftharpoons NaOH + HX$, and (ii) the conductivity due to the unchanged soap. In the stronger solutions the

conductivity is almost entirely due to the soap, yet the solution is very viscous and sets to a jelly on cooling. Further, its osmotic activity is considerably less than the value to be expected from its concentration, even assuming the soap to be wholly undissociated.

It is evident, therefore, that, in addition to a colloidal neutral soap, there must be present an ionised form with a high conductivity. McBain explains this behaviour by assuming (i) that a portion of the soap is aggregated to form neutral colloid $(NaX)_x$, and (ii) that the anions combine with one another, and with neutral colloid to form charged aggregates, termed **ionic micelles,** which are hydrated $(NaX)_x(X')_y(H_2O)_z$. Although the micelles are larger than the simple anions, they move faster in an electric field because of their larger charge, thus accounting for the comparatively high conductivity of the solutions.

McBain has been able to determine approximately the proportions of each constituent in such a solution. Thus potassium oleate at 18° in 0·6*N* solution contains 0·17*N* of free sodium ions and not more than 0·01*N* of other crystalloidal matter. The ionic micelle is composed of 0·43 *N* neutral colloid together with 0·17*N* of aggregated oleate ion. When such a solution is diluted, the amount of colloid decreases, at first slowly and finally more rapidly ; at each concentration, however, a definite equilibrium is set up between sodium ions, neutral colloid and micelle.

Perhaps the most remarkable feature of this work is the discovery that the electrical conductivity is unaffected by large changes in the viscosity of the solution and is not altered when the liquid sets to a jelly. Similar observations have been made by Hatschek with solutions of copper sulphate in agar-agar jelly. It seems necessary therefore to regard a jelly as a very loose structure through which the ions can pass freely.

Colloidal electrolytes and non-conducting colloidal solutions.— Lyophilic colloids can be divided into two groups, namely, those which are electrolytes and those which are not. Colloidal electrolytes are dispersed spontaneously in the medium in virtue of the fact that the molecules are ionisable (either in the pure state or when contaminated with a " peptising agent ") and that one of the ions is readily diffusible in the medium, so that it is able to

drag the non-diffusible ion after it into a quasi-solution. The non-conducting colloids appear to be brought into quasi-solution by the same forces as those which cause analogous substances with small molecules to pass into true solution. Thus the formation of a colloidal solution of starch may be compared with the dissolution in water of glucose or of cane-sugar.

Viscosity of lyophilic colloids.—The viscosity of a liquid is dependent, at least in part, on the average size of the molecules. When, therefore, the anions of a soap aggregate together to form an " ionic micelle," or when molecules of gelatin with a molecular weight of about 10,000 are brought into colloidal solution (in the form either of a sodium salt or of a chloride), solutions of great viscosity may be produced. In the same way, colloidal solutions of compounds of high molecular weight, *e.g.* starch in water or nitrocellulose in acetone, are usually very viscous. Indeed, in many cases the viscosity becomes so great that the liquid acquires the elasticity of a solid, and the solution sets to a jelly. A colloidal solution which has thus set to a jelly is commonly described as a **gel**, and the formation of the jelly is sometimes described as **gelation**. This property does not appear in colloidal suspensions, which are usually quite mobile and do not form jellies, and for this reason yet another method of classifying colloids is to divide them into two groups as **gelatinising colloids** and **non-gelatinising colloids**.

The viscosity of a colloidal solution often depends on the treatment to which it has been subjected as well as upon its composition. Thus, if a 3 per cent. solution of gelatin is prepared by heating, and is then cooled to 10°, its viscosity will be found to increase steadily as time passes, and in a few hours becomes enormously great as the solution sets to a jelly. It appears very probable that the jelly is produced by the interlacing of tendrils of the disperse phase, which grow slowly on standing by a process similar to crystallisation.

In other cases, although a jelly is not formed, the changes in the viscosity of the solution show that slow changes are proceeding in the sol. Thus a solution of the dye known as " night blue " gave the following values for its viscosity in arbitrary

units. Freshly prepared: 0·852; after one day: 0·913; after 6 days: 1·026. Vigorous shaking reduces the viscosity of the aged sol to its original value.

It is indeed the slowness of changes of this type, and those involved in reactions such as peptisation, which differentiate the chemistry of colloids from that of crystalloids. Reactions in true solutions often proceed rapidly, whilst in colloidal solutions slow changes in physical and chemical properties may proceed for many days.

Coagulation of colloidal solutions.—Lyophilic colloids can often be precipitated by putting them into competition with a substance which has a greater affinity for the solvent. Thus soaps can be " salted out " from water by addition of salt, which represses the electrolytic dissociation of the sodium soaps and weakens the grip of the water upon them. The soaps dissolve again, however, quite freely in water. Again, albumen can be precipitated by ammonium sulphate (Expt. 38, i.), but dissolves again in ordinary water. This process can be used in the purification of lyophilic colloids; thus several fractions of albumen with distinctive properties can be separated from blood serum by fractional precipitation with ammonium sulphate.

Protective colloids.—Lyophilic colloids also possess the important property of protecting lyophobic colloids from precipitation by electrolytes. Thus, if a little gelatin is added to a gold sol, the latter is no longer precipitated on the addition of sodium chloride. There is an enormous variation in the protective powers of different colloids. Zsigmondy measured this by a **gold number,** which is the weight in milligrams of the protective colloid which will inhibit the coagulation of 10 c.c. of a given gold sol by 1 c.c. of a 10 per cent. solution of sodium chloride. The gold numbers of a few colloids are given in Table 100. It will be seen that gelatin and egg albumen are much more effective than purified albumen and starch.

TABLE 100. GOLD NUMBERS.

Gelatin	0·005	Crystalline albumen	2–8
Egg albumen	0·08	Starch	3
Gum arabic	0·10	Dextrin	6–12

QUESTIONS ON CHAPTER XV.

1. What are crystalloids and colloids. Give instances. Discuss some of the most important properties of a colloid. Describe carefully a process by which a colloid can be obtained in a pure state. (B.A., Bombay.)

2. Describe any method by which the size of a colloidal particle can be determined.

3. Give two methods by which the sign of the electrical charge on a colloidal particle can be determined. Discuss the part played by the charge in controlling the stability of the solution.

4. Give a brief account of *either* (*a*) the preparation and properties of colloidal solutions, *or* (*b*) the supposed analogy between gases and dilute solutions.
(Joint Matric. Board, Higher School Certificate.)

5. Gelatin, silicic acid, arsenious sulphide and ferric hydroxide can all be obtained in a colloidal state. Which of these would you class as lyophobic and which as lyophilic colloids ? State the properties of the colloidal systems on which you base your classification.

6. Write a brief account of the preparation and properties of colloidal solutions. In what respects do the physical properties of a colloidal solution of silicic acid differ from those of an aqueous solution of sodium chloride ?
(Joint Matric. Board, Higher School Certificate.)

7. Discuss the following :—" Any substance whatever, whether elementary or compound, may be a colloid since the question as to whether it is or is not a colloid is settled, not by its chemical composition or constitution, but by its physical condition."
(B.Sc. Hons., Punjab.)

8. Define the terms " hydrolysis," " neutralisation," " oxidation," " reduction," " colloid," " allotropy," and give an example of each. (B.A., Madras.)

CHAPTER XVI.

ADSORPTION.

39. Adsorption.

i. Adsorption of acetic acid by charcoal.—Prepare 1 litre of normal acetic acid and from it by dilution prepare 250 c.c. of each of the following concentrations, $N/2$, $N/4$, $N/8$, $N/16$. Titrate each solution against $N/10$ baryta contained in the apparatus described in Expt. 25, i.

Select five bottles of about 200 c.c. capacity closed by tightly fitting rubber stoppers, and weigh into each 5 grams of animal charcoal. With a pipette add 100 c.c. of the normal solution to bottle 1, 100 c.c. of the $N/2$ solution to bottle 2, and so on. Shake in a shaking machine for 3-4 hours, when adsorption will be practically complete. If a shaking machine is not available, allow the bottles to stand for 5-6 days, shaking them vigorously three or four times a day. Then open the bottles, filter off the charcoal and titrate measured volumes of the filtered solutions with $N/10$ baryta. Calculate c, the weight of acetic acid per c.c. of the equilibrium solution, and from the fall in concentration, calculate $\frac{x}{m}$, the weight of acid adsorbed by a gram of charcoal.

Plot $\log_{10}\frac{x}{m}$ against $\log_{10}c$. The points should lie roughly on a straight line, from which the constants a and b in the formula

$$\frac{x}{m} = ac^b$$

can be determined.

Adsorption at solid surfaces.—It is well known that many surfaces have the power of retaining a film of moisture or gas which can only be removed with considerable difficulty. Thus in experiments in which a very high vacuum is required, it is

necessary to heat the glass apparatus almost to redness before the film of moisture on the glass can be removed by the vacuum pump.

Except in special experiments of this kind, the surface film on a vessel can usually be neglected, as the total amount of substance in the film is very small compared with the weight of the reacting substances. If, however, we are dealing with a finely divided substance, then unit weight of it may possess such a large surface area that the amount of substance retained on the surface needs to be considered. Thus a cube of 1 cm. side has a surface area of 6 cm.^{2} and the ratio $\frac{\text{surface}}{\text{volume}} = 6$. If it be subdivided into cubes of 1 mm. side, this ratio becomes 60, and so on. Table 101 shows that this ratio (often termed the " degree of dispersion ") becomes very large when the subdivision is extended to particles of the order of those found in colloidal solutions, namely 10^{-5} to 10^{-6} cm. in diameter. The surface-area per gram may then be several million square centimetres. Thus the properties of surfaces play an important part in determining the behaviour of colloidal solutions.

TABLE 101. DEGREE OF DISPERSION.

Side of cube (cm.).	Surface (cm.^{2}).	Volume (cm ^{3}).	Surface/Volume.
1	6×1	1	6
1×10^{-1}	6×10^{-2}	10^{-3}	60
1×10^{-2}	6×10^{-4}	10^{-6}	600
1×10^{-3}	6×10^{-6}	10^{-9}	6,000
1×10^{-4}	6×10^{-8}	10^{-12}	60,000
1×10^{-5}	6×10^{-10}	10^{-15}	600,000
1×10^{-6}	6×10^{-12}	10^{-18}	6,000,000

Many porous substances, such as charcoal, possess the property of absorbing gases, and also of absorbing substances from solution. Thus freshly ignited charcoal placed in ammonia gas confined over mercury rapidly absorbs the gas and causes the level of the mercury to rise. Similarly, charcoal is able to remove colouring matters from solution, and this property is frequently utilised in the purification of sugar and other organic compounds. This phenomenon is termed **adsorption,** since it differs in many respects from simple *absorption*, such as the solution of ammonia by water.

The adsorption isotherm.—A quantitative study of adsorption shows that in most cases a condition of equilibrium is rapidly attained. Thus, if a fixed amount of charcoal is placed in ammonia at constant pressure, a definite amount of gas is adsorbed; if the pressure is lowered gas is evolved until a new point of equilibrium is reached; or, if the pressure is raised, more gas is adsorbed. Since this equilibrium is attained rapidly, it is scarcely possible that the process can consist of solution in the solid charcoal, for the rate of diffusion of molecules through a solid is very slow. It is therefore probable that the gas forms a condensed film on the surface of the charcoal, and that the high adsorptive power of charcoal and of other porous substances is due to the large surface-area which these substances possess. On the other hand, the slow further absorption may be due to diffusion of the adsorbed substance into the bulk of the adsorbing agent.

When the amount of adsorption at different pressures is studied, it is found that the following relation holds with fair accuracy

$$\frac{x}{m} = ap^b.$$

Here x is the weight of gas adsorbed by m grams of solid at a pressure p; a is a constant determined by the condition of the solid adsorbent, and b is a constant (always less than unity) which is in general characteristic for each gas absorbed. Thus in the adsorption of gases by charcoal, $b = 0{\cdot}44$ for ammonia, 0·39 for carbon dioxide and 0·12 for chloroform. This formula resembles in some respects the formula for the *absorption* of gases by liquids (Henry's Law) which may be put in the form

$$\frac{x}{m} = ap,$$

where x is the amount of gas dissolved by m grams of liquid at a pressure p. By analogy with the results obtained from a study of partition coefficients, it might be supposed that the exponent b was due to a difference in molecular weight of the gas when condensed on the charcoal. Since, however, b is always less than unity, this would mean that the adsorbed gas had a smaller molecular weight than that in the gas phase, and in the examples

quoted above this is impossible. The adsorption equation has therefore no theoretical significance and merely provides an empirical formula for summarising experimental results. It is found, in fact, that at high pressures and at low pressures this equation does not hold.

The adsorption of substances from solution can also be represented roughly by the same formula, if p is replaced by the equilibrium-concentration in solution, c. Thus, in an experiment on the adsorption of iodine from alcoholic solution by charcoal, the following figures were obtained :

TABLE 102. ADSORPTION OF IODINE BY CHARCOAL.

$\frac{x}{m}$ - -	0·30	0·46	0·50	0·59	0·71
c - - -	1·65	5·10	8·60	14·4	27·0
$a=\frac{x}{m}c^{-0·33}$ -	0·254	0·267	0·244	0·243	0·237

Here again it has been found that the formula does not hold accurately for strong solutions and that the amount of substance adsorbed tends towards a definite maximum or saturation-value as the concentration in the solution increases.

Mechanism of adsorption.—In recent years a much clearer understanding of the nature of adsorption has been obtained by the development of Langmuir's theory of surface forces. We have seen in Chapter IV. that the atoms in a crystalline solid are held in definite positions in a space lattice by forces of attraction between adjacent atoms. At the surface of a crystal, however, the surface molecules are only held on one side by adjacent atoms and must be supposed to possess a certain affinity or force of attraction on the outer surface. If a molecule of a gas impinges on such a surface it may be held by one of the attracting atoms and so be adsorbed. If the adsorbed molecule has little affinity for the atom, then it will soon obtain sufficient energy from thermal agitation to evaporate off again. On the other hand, if it has a great attraction for the atom of the adsorbing agent, its " life " on the surface will be comparatively long. Thus arsenic, phosphorus and sulphur, which adhere even more firmly than oxygen to the surface of platinum, act as catalyst-

poisons, since they prevent the access of more active molecules to the metal.

Langmuir compares the surface of the adsorbent with a chess board on which the squares can be covered by adsorbed molecules. With any particular gas, the proportion of the spaces covered at a given instant (*i.e.* the amount of gas adsorbed) will depend upon the pressure and upon the affinity of the gas molecules for the atoms of the adsorbent. As the pressure is increased the number of vacant spaces will become fewer, and ultimately a limit will be reached when the surface of the solid is covered by a layer one molecule thick. It has been found in a number of cases that the maximum adsorption of a gas at temperatures well above its boiling-point does indeed correspond to a unimolecular layer.

The process need not of necessity end at this stage of " primary adsorption," for if the pressure and temperature are such that the gas is nearing liquefaction, it is evident that attractive forces between the gas molecules themselves can come into play. A second and third and further layers can be built up, and the high degree of " secondary adsorption " observed with easily liquefied gases can thus be accounted for. Langmuir's theory has been applied with considerable success to the discussion of the mechanism of catalytic reactions at the surface of solids, and many other surface phenomena, some of which are described below.

Adsorption and catalytic oxidation of carbon monoxide by platinum.—Langmuir found that when a platinum wire is heated in a mixture of carbon monoxide and oxygen at a temperature below 500° C. and at a pressure of less than a millimetre, the velocity of oxidation is *proportional to the pressure of the oxygen*, as we should expect, but *inversely proportional to the pressure of carbon monoxide*, whereas, from the law of mass-action we should expect it to be *proportional to the square of the pressure of carbon monoxide*, $2CO + O_2 = 2CO_2$. Bodenstein and Fink found a similar relationship when carbon monoxide was oxidised at about atmospheric pressure on surfaces of fused quartz, but they explained their results by supposing that the access of oxygen to the solid surface was checked by a

cushion of carbon monoxide, the thickness of which was proportional to the pressure of this gas. Langmuir considers that the protective film of carbon monoxide is monomolecular. He suggests that the carbon monoxide combines with the platinum to form a stable complex, *e.g.* $>Pt=C=O$, which is not decomposed by the impact of oxygen molecules, since only the oxygen of the complex is exposed; the gas therefore acts as a catalyst-poison by blocking the surface of the metal. This effect is proportional to the area of the surface which it covers, and the retardation of the action is therefore proportional to the pressure of carbon monoxide. When the surface is occupied by oxygen, on the other hand, the atoms of this element can interact with the molecules of carbon monoxide which strike them; and the molecules of carbon dioxide which are formed escape quickly from the surface, since they are much more nearly "saturated" than the molecules of oxygen or of carbon monoxide. This mechanism would therefore lead to a velocity of reaction proportional to the pressure of oxygen, and inversely proportional to the pressure of carbon monoxide.

In the range of temperatures below 500° the reaction-velocity has a large temperature-coefficient, the velocity increasing in the ratio 1·6 to 1 for a rise of 10° at about 320°; but at about 500° the reaction-velocity reaches a maximum, which is almost independent of the temperature up to 800°. The velocity is then *proportional to the pressure of carbon monoxide* when oxygen is in excess, and *proportional to the pressure of oxygen when* carbon monoxide is in excess. Langmuir, however, assigns a different function to the two gases, on the ground that the carbon monoxide begins to evaporate from the platinum surface at temperatures as low as 250°, whereas there is no appreciable evaporation of oxygen from the surface even at 1200° C. Thus, when oxygen is present in excess, the velocity of reaction depends on the number of molecules of carbon monoxide which strike the fully-oxidised surface-film, and is proportional to the pressure of *carbon-monoxide.* When carbon monoxide is in excess, however, the surface is largely bare on account of the greater volatility of the carbon monoxide in this higher range of temperature; the velocity therefore depends on the

concentration of *oxygen*, since every molecule of this gas which strikes the surface remains there until it is struck by a molecule of carbon monoxide and converted into a volatile molecule of carbon dioxide.

Adsorption and catalysis by tungsten filaments.—(*a*) When a filament of tungsten is heated in an atmosphere of *hydrogen*, the loss of heat from the filament proceeds with greatly increasing rapidity at temperatures above 1500°. When this experiment is carried out at low pressures, hydrogen disappears from the bulb, but remains adsorbed on the walls, in a chemically active form, which is capable of interacting with gaseous oxygen at room temperature, long after the tungsten filament has been allowed to cool. These effects can be explained most readily by supposing that the molecules of hydrogen are dissociated into atoms by the action of the hot tungsten filament.

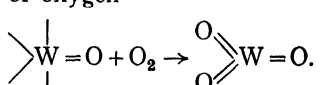
The mechanism of this action appears to be as follows. The molecules of hydrogen which strike the hot filament are condensed on the metal to the extent of at least 68 per cent. In this process the molecules are probably broken up into atoms, which have only a slow rate of evaporation, since they are very strongly unsaturated. If these atoms occupy adjacent positions on the metal, they can combine with one another to form hydrogen molecules, which evaporate rapidly on account of their much greater saturation; but, since this can only occur when two atoms are contiguous, a large proportion of the hydrogen which evaporates from the surface is in the atomic form. This "atomic hydrogen" is adsorbed on the walls of the vessel and disappears. The proportion of the gas dissociated into atoms was calculated to be 0·0033 at 1700°, 0·031 at 2200° and 0·34 at 3200°. The heat of reaction $2H = H_2$ at 2700° was calculated to be 84,000 calories at constant volume or 90,000 cal. at constant pressure.

(*b*) When the filament is heated to a high temperature in presence of a trace of *water-vapour*, the oxygen unites with the metal to form a volatile tungstic oxide, whilst the hydrogen is liberated in atomic form. The volatile oxide is deposited on the walls of the bulb, where it is reduced to the metallic state by the atomic hydrogen. The water-vapour produced by this

reduction returns to the filament, and causes the action to be repeated indefinitely. A minute quantity of water-vapour may therefore cause the deposition on the bulb of an indefinitely large proportion of metallic tungsten.

(*c*) When the tungsten filament is heated in *oxygen*, under low pressure, an oxidised film is formed, which reduces the emission of electrons from the metal many thousandfold even at temperatures as high as 1600° C. It also inhibits the normal action of the filament in dissociating molecular hydrogen at temperatures of 1200° or above, and thus acts as a powerful anti-catalyst (p. 311) for this dissociation. The stability of the film is shown by the fact that it does not interact with hydrogen to form water, even at these high temperatures, and does not catalyse the chemical combination of hydrogen and oxygen in the gas. When the filament is heated in a mixture of hydrogen and oxygen, therefore, the only action which proceeds is a progressive vaporisation of tungstic oxide, WO_3, from the filament, as oxygen enters into combination with the metal; but when the oxygen has nearly all been used up in this way, the oxidised film is suddenly stripped off by the hydrogen, and the filament recovers its power to dissociate the latter gas.

This surface film is neither tungstic oxide nor oxygen gas, but probably consists of atoms of oxygen held to the tungsten surface by chemical forces, just as the oxygen in carbon dioxide is attached to the carbon, O=C=O, but without detaching the tungsten from the other atoms in the film. The formation of tungstic oxide can be accounted for by the impact on this film of molecules of oxygen



The metal then becomes saturated by combination with two additional atoms of oxygen, and the trioxide sublimes from the filament. The efficiency of this action is so high that, even at 3000°, half the molecules of oxygen which strike the filament are converted into tungstic oxide.

Practical applications.—Adsorption has many applications in practice. Thus a very good method of obtaining a high vacuum

is to connect a bulb of charcoal, cooled in liquid air, to a vessel which has already been evacuated as far as possible by a mercury pump, since at this low temperature all gases except hydrogen and helium are adsorbed almost completely. Animal charcoal is employed as a decoloriser in the manufacture of cane-sugar and many other substances, whilst the special adsorbent power of vegetable charcoal is utilised in the construction of respirators for adsorbing gases and vapours, including those which are chemically inert and which cannot therefore be removed by chemical agents such as lime and potassium permanganate. Another interesting adsorbing agent used in technical practice is bauxite, which is found to have the power of adsorbing traces of sulphur compounds from crude petroleum.

Adsorption of ions.—Adsorption is also frequently involved in the reactions of colloidal solutions, *e.g.* the high efficiency of polyvalent ions as precipitants is due to the ease with which these ions are adsorbed. Thus, it has been found that when colloidal arsenious sulphide is precipitated by potassium ions only one per cent. of the added potassium ion is carried down by the precipitate, whilst over 50 per cent. of the very much smaller amount of aluminium ion added to produce coagulation is thus removed from the solution. These adsorbed ions cannot be washed out from the precipitate, but can be replaced by equivalent amounts of other ions.

Adsorption phenomena must also be taken into account in analysis. Many colloidal precipitates, *e.g.* $Zn(OH)_2$ and $Fe(OH)_3$, are good adsorbents, and, unless the precipitation is carried out under favourable conditions, the colloidal precipitate may carry down other substances from solution and thus produce considerable errors in gravimetric estimations. In qualitative analyses the colloidal hydroxides of iron, aluminium, and chromium are good adsorbing agents for some succeeding elements, notably zinc and calcium, and these may be missed entirely in later tests if the precipitation of the hydroxides of the iron group is not carried out in dilute solution and under correct conditions, namely, in the presence of a slight excess only of ammonia and a considerable amount of ammonium chloride.

QUESTIONS ON CHAPTER XVI.

1. When chloroform is shaken with an aqueous solution of iodine it extracts some of the iodine; charcoal shaken with an alcoholic solution of iodine will also extract some iodine. What are the main points of difference found when these two phenomena are studied over a range of concentrations?

2. Finely divided insoluble substances, *e.g.* $BaSO_4$, often retain $\frac{1}{2}$ per cent. to 1 per cent. of water when dried in the air at ordinary temperatures. How is this water held? What would be the effect of (*a*) fineness of division of the solid, (*b*) temperature of drying, and (*c*) humidity of the atmosphere upon the amount of water retained by the precipitate.

3. In an investigation of the adsorption of acetic acid from its aqueous solutions by charcoal the following results were obtained:

Solution c -	0·00365	0·0084	0·0206	0·0350 gm./c.c.
Charcoal $\frac{x}{m}$ -	0·0182	0·0223	0·0286	0·0324 gm./gm.

Show that these figures are in agreement with the formula $\frac{x}{m} = ac^b$.

4. Chromium hydroxide precipitated from a solution containing calcium chloride was found on analysis to contain 2 per cent. of CaO. The precipitate was redissolved in acid and reprecipitated and then contained only 0·05 per cent. of CaO. How do you account for this behaviour?

ANSWERS TO PROBLEMS

CHAPTER I

2. No, for $\frac{P}{T}$ is not constant. **5.** 25·2.

7. 39,350 cm./sec. at 0°, 84,950 cm./sec. at 1000°; $5{\cdot}49 \times 10^{-14}$ ergs at 0°, $2{\cdot}56 \times 10^{-13}$ ergs at 1000°.

CHAPTER III

6. $k = 2{\cdot}09$, hence M.W. is normal.

7. (P) obs. 217·2, 218·3, (P) calc. 219·0 (semipolar), 243·8 (nonpolar). Hence double bond is semipolar.

CHAPTER IV

4. 81·37°. **5.** 0·207 cal./gm. **6.** 52·967°.

CHAPTER VI

9. Transition temp., 33·0°.

13. Maximum at −38° and 25% NH_4NO_3 molecules. Hence compound $NH_4NO_3 \cdot 3NH_3$ formed.

17. 80·5% ethylene dibromide.

CHAPTER VII

2. 3·46 atm. **3.** 2·04 atm. **4.** 6·91 atm.

6. Let x = wt. of substance; then M.W. as vapour = $3{\cdot}12x$ and in solution = $5{\cdot}35x$. Hence either vapour is dissociated or substance is associated in solution.

CHAPTER VIII

2. 157.

3. 75% dissociated. Since the acid is strong, dissociation will be practically complete at N/100 (cf. p. 354).

4. 236. **5.** 342. **6.** 30·1.

7. 341, normal; 42·2, largely dissociated; 48·5.

8. 311, 313, mean 312.

10. 1·677°/1000 gm.; 129·3 cal./gm.

11. (*a*) $k = 5{\cdot}13, 5{\cdot}18, 5{\cdot}17$. Mean 5·16°/1000 gm.
(*b*) $M = 205, 206, 205$.
(*d*) $M = 196, 220, 255, 276, 351$.
Since $C_4H_4O_6(C_2H_5)_2 = 206$, this substance is normal in formamide and associated in benzene.

CHAPTER IX

1. $H_2S + I_2 \rightarrow 2HI + S - 7800$ cals. ∴ reaction is endothermic. In aqueous solution the heat of solution of HI makes the reaction exothermic.

3. 1032K.

4. (*a*) 21,750, (*b*) 21,170

5. −16,000.

8. 321,960.

9. (*a*) 129,040 (C_6H_6 liquid at 17°); (*b*) 130,800.

10. 29,650.

11. 9385 cal./gm.

12. 99,420.

13. 287·5 cals./gm. mol. H_2O.

15. 8172 cals./gm. mol.

16. 5995 cals./gm. mol., 18·3° C.

17. $k_p = 3{\cdot}743$, $A = 7980$ cals./gm. mol. O_2 (Products at 1 atm.).

18. $A = 21{,}250$.

21. 52·950° C.

CHAPTER X

1. 0·9449 mols. ester and water, 0·0551 mols. alcohol, 4·0551 mols. acid.

3. 79·9%.

7. 0·8% monatomic molecules (by weight).

8. 79·7%.

11. 17·66%, 16·63%, 16·00%, 17·20%, 19·47%, 20·93%. Degree of dissociation shows a minimum about 320°. Below this temperature dissociation is exothermic; above it, endothermic.

18. 29·07 gm./*L*.

CHAPTER XI

4. $k_{mono.} = 0{\cdot}141, 0{\cdot}141, 0{\cdot}142, 0{\cdot}138, 0{\cdot}138, 0{\cdot}119$.

5. $k_{mono.} \times 10^3 = 5{\cdot}68, 5{\cdot}45, 5{\cdot}49, 5{\cdot}59$.

6. $k_{mono.} \times 10^4 = 6{\cdot}55, 5{\cdot}26, 4{\cdot}91$. Mean 5·57.

7. $k_{mono.} \times 10^2 = 2{\cdot}18, 2{\cdot}21$.

CHAPTER XIII

4. 2·40 atm.

5. From glucose expt. f.p. depression constant = 1·854°; NaCl M obs. = 30·7, M calc. = 58·5; KI, M obs. = 87·1, M calc. = 166 hence the halides are highly dissociated.

7. 40·1 cc.

8. M obs. = 70·9. CrO_3 = 100 (calc.). If present as $H_2Cr_2O_7$ completely dissociated into 3 ions M should be $100 \times \frac{2}{3} = 66{\cdot}7$.

9. Equiv. = 38·33, approx. at. wt. = 109. Accurate at. wt. = $3 \times 38{\cdot}33$ = 115·0.

12. 81·3%.

16. 0·0705 mhos.

CHAPTER XIV

3. HX : HZ = 1 : 1·94.

8. Formic : acetic = 3·45 : 1.

9. −0·187°.

11. NaOH = 49, 49·5, 49·9, 50·0, 50·1, 50·5, 51·0 cc.
p_H = 6·44, 6·74, 7·44, 8·22, 9·00, 9·70, 10·00.
(At 50·0 cc. solution is alkaline by hydrolysis of NaAc.)

13. 0·909, 0·500, 0·091.

16. (*a*) $9{\cdot}64 \times 10^{-2}$, $9{\cdot}83 \times 10^{-3}$; (*b*) $4{\cdot}15 \times 10^{-4}$, $1{\cdot}26 \times 10^{-4}$; (*c*) $1{\cdot}8 \times 10^{-5}$, $1{\cdot}8 \times 10^{-5}$.

17. 1·15%, 0·0023%.

21. 0·816 gm. $CaSO_4$.

CHAPTER XVI

3. $\frac{x}{m} = 0{\cdot}0785c^{0{\cdot}262}$ gives $\frac{x}{m}$ = 0·0180, 0·0224, 0·0284, 0·0326.

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