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OUTLINES OF CHEMISTRY

WITH PRACTICAL WORK

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OUTLINES OF CHEMISTRY
WITH PRACTICAL WORK

by

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PREFACE

FOR many years it has been the writer's custom to give a course of instruction in General and Physical Chemistry to students who are candidates for the Natural Sciences Tripos at Cambridge. Many students are unable, at this stage, to devote more than one complete year to the study of Chemistry, and, in view of the rapid development of the science, it becomes a matter of no little difficulty to devise a scheme of instruction which will advance the chemical knowledge of the student in the most advantageous way under the conditions which exist. Complete and exhaustive treatment even of a single department is of course out of the question; yet the ground must be covered and superficiality has to be discouraged. The plan of recommending an exclusive reliance upon any single text book has not been found successful, no matter how excellent the book may be. The student, under such circumstances, comes to regard the 'getting up' of this book as the main object of his study and to consider that his progress is measured by the number of pages which he has succeeded in 'finishing.' As the result of a very long experience a method has been adopted, the nature of which is outlined in the present volume.

A special feature of the course is the interdependence of the practical and theoretical teaching, the students, after each lecture, performing a series of experiments which illustrate as far as possible the general principles, laws or facts which have been

discussed. In nearly all cases it is found possible to arrange the experiments so that they bear directly upon the day's lecture; in the few instances where the subject does not admit of practical illustration, there is, of course, always ample material for laboratory work in the subjects of the previous lectures. At the time when the course was initiated this method of practical illustration had scarcely been attempted, and considerable difficulty was experienced in devising experiments suitable for a large class which could be performed in the limited time available.

The method adopted in this course of instruction is to lead the student to regard the subject of the lecture, for the time being, as a specialised study, and to require him, in the interval before the introduction of the next subject, to obtain all the additional information he can from the various text books, and occasionally from original papers. An informal class is also held after each lecture, with the object of encouraging discussion of the more difficult problems and of suggesting sources of further information.

The students have at their disposal nearly all the well known standard text books on the subject—including those of Ostwald, Nernst, van 't Hoff, Arrhenius, Walker, Jones, Whetham, in addition to Sir William Ramsay's series of text books on Physical Chemistry—and to these constant reference is made in the lectures. The present book is in no sense intended as a substitute for any of these excellent works; it is to be regarded rather as an epitome of a particular course of instruction designed to suit the requirements of a certain class of students.

The intention has been to introduce the fundamental principles in a concise and somewhat condensed form and afterwards to convey just so much information as, it is hoped, may create an interest in each of the subjects and stimulate further individual inquiry; full and detailed explanations are, usually, not given, the object being to induce the student to do some of the thinking for himself.

As regards those subjects about which there is any reasonable difference of opinion, the attempt is made to adopt a wholly impartial attitude. It will be generally admitted that one of the peculiar advantages of a chemical education lies in the opportunity and encouragement that it affords for originality and independence of thought. But it appears to the present writer that nothing can be more detrimental to the attainment of this desirable end than that the teacher should take upon himself the combined offices of advocate, jury and judge in a debateable question.

In the instructions given for practical work, the experiments are, in most cases, merely outlined; the importance of inculcating the habit of self-reliance in this part of the study is obvious, and the aim has been to induce the student, as far as possible, to devise his own method, to plan and fit up suitable apparatus, and to regard the work rather in the light of a research than as an exercise. It is necessary at the same time to take into consideration the requirements of weaker and less serious students, and for these it is generally found possible to suggest suitable modifications of the work.

To give an idea of the high pressure at which this teaching has been carried on, it may be mentioned that the subject-matter indicated in the present volume had to be covered in less than two terms. In the two succeeding terms the work is continued on similar lines; the outlines of electrochemistry, thermal chemistry, and photochemistry, are briefly introduced and subjects such as diffusion, colloids, alloys, allotropy, isomerism, etc., are also dealt with. The periodic classification is considered at some length and a descriptive account of the elements and their more important compounds is incorporated with this part of the subject, as far as time allows. If it should happen that the present book is found to be of assistance to students, it is the author's intention to publish this later part of the course as a second volume.

The author desires to express his deep sense of gratitude to the friends who have given him assistance in the production of the book. Professor Larmor most kindly undertook to read certain chapters and his criticisms and suggestions have been of the greatest value. Mr L. A. Levy, B.A., B.Sc., of Clare College, assisted in the preparation of the manuscript for the earlier chapters and it was largely owing to his enthusiasm and encouragement that the task, which at first appeared to be rather a thankless one, was originally undertaken. Mr W. A. R. Wilks, B.A., of Caius College, has carefully read all the proof sheets, and the valuable suggestions which he has offered afford additional evidence of his originality and ability.

The figures have all been executed by Mr F. Shillington Scales, M.A., of Jesus College, to whom the author's most hearty thanks are due; the drawings were made by him from the apparatus actually in use at the demonstrations in the Chemical Laboratory.

H. J. H. F.

CAMBRIDGE,
May 1909.

IN preparing the second edition, it has been considered desirable to introduce two new chapters dealing, in outline, with the subjects of Diffusion and the Colloidal State. Several minor corrections have been made in the text. With these exceptions, no material alteration has been made in the book.

April. 1910.

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CHAPTER I.

MOLECULAR WEIGHTS.

1. In order to assign a formula to a given chemical compound it is necessary in the first instance to determine its exact elementary composition by analysis; the numbers so obtained, when divided by the atomic weights of the respective elements, give values for the simplest empirical formula. Thus the simplest formula for ferric oxide is Fe_2O_3 and for benzene CH; similarly the formula CH_2O represents the simplest formula for grape sugar, lactic acid, acetic acid, formaldehyde and several other compounds.

The problem then is to ascertain what multiple of this empirical formula should be adopted for the compound in question, and the methods which have been employed for the purpose of solving this problem depend upon two entirely distinct principles, which for the sake of reference may be classified as the 'chemical' and the 'physical' methods.

The first named method, it must be confessed, has often been applied in a loose and somewhat unscientific fashion and the older definition of molecular weight as 'the least weight of the substance which can take part in a chemical change' is obviously wanting in precision. It would probably be better to use the term 'reacting weight' to denote the formula-weight which is most consistent with the chemical relationships of the compound. The reacting weight, as so defined, happens to coincide in the great majority of cases with the value found by the physical methods; but the coincidence is by no means universal as will be seen in the examples mentioned later on.

The determination of the 'reacting weight,' i.e. of the 'molecular weight' from chemical considerations, will be best understood

by reference to a few examples. First of all it must be mentioned that it has hitherto been customary to assign the simplest formula to a compound when there is no direct chemical or physical evidence available to indicate the true value. Such formulae as Fe_2O_3 and SiO_2 for example are assigned to solid ferric oxide and silica respectively although there is no direct chemical or physical evidence to shew their degree of complexity.

Acetic acid has the formula $(CH_2O)_x$; but $\frac{3}{4}$ of the hydrogen present can be replaced by chlorine, hence $x = 2$ at least. Further it is only possible to replace $\frac{1}{4}$ of its hydrogen by a univalent metal, by action of metallic hydroxides or carbonates, to form stable and well-defined salts (i.e. the acid is monobasic or unibasic). The latter fact indicates that x is not greater than 2; if it were one would expect to be able to obtain salts in which say $\frac{1}{8}$ of the hydrogen was replaced by metal. [It is true that the substance $C_2H_4O_2C_2H_3OK$ or 'potassium binacetate' *can* be obtained under certain conditions but this is generally regarded as a 'molecular compound' (**39**); the alternative is to consider it a salt of polymerised acetic acid $C_4H_8O_4$.] The formulae for sulphuric acid and oxalic acid are written H_2SO_4 and $C_2H_2O_4$ because they yield two and only two stable salts with a univalent metal.

If the basicity of an acid is known, it is evident that its molecular weight may be determined by neutralisation with a base of known formula weight; thus the molecular weight of an acid whose basicity is n will be that weight of it which can neutralise $n \times 56$ parts by weight of caustic potash. (In other words equivalent wt. × basicity = molecular weight, see page 53.)

Similarly one may analyse the normal salt of an acid of known basicity and a metal whose atomic weight and valency are also known. Thus the normal silver salt of an n-basic acid is formed from the acid by replacing n parts by weight of hydrogen by $n \times 107{\cdot}12$ parts by weight of silver (taking the atomic weight of $H = 1$); so that the weight of silver salt taken stands to the silver it contains as $(M + n\,107{\cdot}12 - n)$ to $n\,107{\cdot}12$ when M = the molecular weight of the acid.

Many nitrogen bases form hydrochlorides which combine with platinic chloride to form crystalline so-called double salts of the type $(B'HCl)_2PtCl_4$, $B''2HCl.PtCl_4$, etc. where B′ and B″ repre-

sent monacid and diacid bases respectively. (These in reality must now be looked upon as single salts of H_2PtCl_6.) If therefore the 'acidity' of the base is known, the molecular weight of the latter can be determined by estimating the amount of platinum contained in a given weight of the salt.

If W grams of platinum salt contain W_1 grams of platinum, then for a monacid base,

$$W : W_1 = (2M + 2 + 193{\cdot}3 + 6 \times 35{\cdot}18) : 193{\cdot}3.$$

The hydrogen in hydrochloric acid, water, ammonia and marsh gas can be replaced by at most one, two, three and four univalent elements (or groups) respectively. This fact is in accordance with the simplest formulae HCl, H_2O, H_3N and CH_4. Any higher multiple of these formulae would indicate that a larger number of substitution derivatives should be obtainable.

The empirical formula for cellulose and also for starch is $C_6H_{10}O_5$. When cellulose is fully nitrated, by means of nitric and sulphuric acids, the tri-nitrate $C_6H_7O_2(NO_3)_3$ is produced; but under varying conditions it is possible to obtain nitrates having, for example, the composition $C_{24}H_{29}O_9(NO_3)_{11}$ and $C_{24}H_{31}O_{11}(NO_3)_9$. The minimum formula for cellulose which would be consistent with the formation of such nitrates (supposing that these are true compounds and not merely mixtures) would evidently be $C_{24}H_{40}O_{20}$. Somewhat similar arguments have been advanced as proof of the complexity of the starch molecule. On hydrolysis by means of enzymes, starch yields maltose $C_{12}H_{22}O_{11}$ and dextrine $(C_6H_{10}O_5)_x$ and the least formula which would account for the production of these in the various proportions experimentally determined is said to be $(C_6H_{10}O_5)_{40}$.

Reasoning of a somewhat different character was at one time employed in deciding the molecular formulae of chlorine or cyanogen. Since by the action of chlorine on cold caustic alkalis one obtains a chloride and a hypochlorite, it was argued that the minimum formula for free chlorine must be Cl_2 because each of the above-named products contains at any rate one atom of chlorine. But although the conclusion here arrived at happens to be correct, it is evident that the reasoning is faulty. One might similarly argue, as pointed out by L. Meyer, that nitric

acid should be represented by a multiple of the formula HNO_3 because by its action on metals it can yield a nitrate together with some oxide of nitrogen. If such reactions were explained by a polymerisation of the nitric acid, the same assumption could be made with regard to actions mentioned of chlorine or cyanogen.

The formula for potassium permanganate is often written $K_2Mn_2O_8$ instead of $KMnO_4$ because the double formula is the least which conveniently represents many of its reactions (e.g. $K_2Mn_2O_8$ by action of sulphuric acid yields 5 atoms of oxygen). The alums for somewhat similar reasons are sometimes represented as $M'_2M'''_2(SO_4)_4 24H_2O$ instead of by the single formula, in order to indicate their formation from the two sulphates M'_2SO_4 and $M'''_2(SO_4)_3$. If the object of the formula is merely that of conveniently illustrating its relationships by means of equations such doubled formulae are free from objection; but it must not be supposed that such reasons are sufficient to decide the true molecular magnitude in the physical sense.

When amorphous carbon is oxidised by means of nitric acid, mellitic acid is obtained. The formula for this acid is shewn, by a variety of its chemical reactions, to be not less than $C_6(COOH)_6$. Hence it is argued that the molecular formula for carbon cannot be less than C_{12}. This argument is supported by the general observation that in the oxidation of carbon compounds one obtains products containing the same or a smaller number of carbon atoms, but never more complex compounds.

If 'albumen' is regarded as a definite chemical compound it is evident that its molecular weight cannot be less than about 1612, since this is the weight of it in which 32 parts by weight of sulphur are contained. Similarly the formula for so-called arabic acid, which was at one time represented as $C_{12}H_{22}O_{11}$, must be a high multiple of this (approximate) formula since a salt $C_{89}H_{142}BaO_{75}$ has been obtained.

2. When the formulae arrived at from these 'general chemical considerations' are compared with those indicated by the physical methods, which are explained below, it will be found that in the vast majority of cases the results are in agreement. There are however several notable exceptions and these alone are sufficient

to necessitate the use of some such term as 'reacting unit,' this value not necessarily being identical with the physical molecule.

With regard to some of the examples which have been given above, it may be mentioned that, by recent physical determinations, the molecular weight of potassium permanganate appears to be $KMnO_4$. (By the transition point in hydrated sodium sulphate as solvent (**18**) and by electric conductivity.) The molecular weight of starch has been estimated as about 25,000, of ferric hydroxide as about 6000 and of silicic acid as at least 49,000. [By the cryoscopic method (**16**).] Since, however, the depressions observed were extremely small and the solutions strong, it is evident that the results are untrustworthy.

The molecular weights of complex compounds which can be built up step by step is often inferred from the mode of synthesis, assuming that no polymerisation takes place. Fischer for example has built up numerous highly complex polypeptides by the linking together of the residues of amino-acids. The most complex member so far obtained is built up from the residues of fifteen glycine and three leucine molecules and has a molecular weight, calculated from its formula $C_{40}H_{80}O_{19}N_{18}$, of 1213. The molecular weights of many of these polypeptides have been determined by the cryoscopic method (**16**) and the numbers agree well with the values calculated from the simplest formulae.

Practical Work.

Expt. 1. Determine the molecular weights of the given acids by titration with standard caustic soda.

Standard solutions of the acids are supplied in order to save the time required for weighing.

The basicities of the acids are given; also the molecular weight of sodium hydroxide.

It is advisable to make several determinations in each case and to try various indicators. Note that the method is not applicable in case of acids whose salts readily undergo hydrolysis and so give no sharp end-point with the usual indicators.

EXPT. 2. **Determine the molecular weights of the given bases.** Standard solutions are supplied, as before, and the 'acidity' of the bases given.

EXPT. 3. **Determine the molecular weights of the acids whose silver salts are supplied.** The basicities of the acids are given. Weigh out about 0·5 to 1 gram of the salt into a porcelain crucible (which has been previously heated and cooled in the desiccator in the usual way). Invert the crucible lid and heat over a small Bunsen flame *very cautiously* at first, to avoid loss by spurting, and afterwards ignite strongly until all traces of organic matter have disappeared. Cool under the desiccator and weigh.

EXPT. 4. **Determine the molecular weights of the nitrogen bases whose platini-chlorides are supplied.** The acidities of the bases are given.

Proceed exactly as in the case of the silver salts.

CHAPTER II.

MOLECULAR WEIGHTS (*continued*).

3. THAT matter is not 'continuous' but is made up of individual parts or has a 'grained structure' is fairly obvious when one regards the phenomena of diffusion (of gases, liquids, and even of solids) and the tendency of gases to expand indefinitely. That these parts are in some sort of motion follows from similar considerations. The quantitative laws of combination by weight, discovered by Dalton, lent strong support to the theory that matter was made up of similar indivisible parts or atoms and this term was at first used in connection with both elements and compounds. Chemists spoke then of an atom of water or an atom of hydrogen as the smallest indivisible parts of these substances.

Gay-Lussac, in 1808, first clearly pointed out the simple relation which exists between the volumes of gaseous substances which combine or react with one another. His so-called laws of combination by volume, or 'Law of Volumes,' may be stated as follows. The volumes of gaseous elements or compounds which combine or react stand to one another in a simple ratio; and further, if the resulting products are also gaseous, their volumes are again simply related to the volumes of substances from which they were produced.

If the atom is taken as the unit both for compounds and elements, then it follows that equal volumes of different gases contain either the same number of atoms or that the number of atoms in equal volumes is at any rate simply related. That the number is not necessarily equal is at once evident from the experiment illustrating the composition of hydrochloric acid. Since one volume of hydrogen in combining with chlorine yields

two volumes of hydrochloric acid, it would follow that n atoms of hydrogen and n atoms of chlorine give $2n$ atoms of hydrochloric acid—which is obviously absurd, since hydrochloric acid is composed of at least one atom each of chlorine and hydrogen.

The case, however, assumes a much more simple aspect if we make a distinction between the ultimate atom of an element as conceived by Dalton and the physical unit, or molecule, which may be made up of one or many atoms. This important distinction was first suggested by Avogadro in 1811 and he formulated the hypothesis that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. The term molecule (gaseous) was subsequently defined more precisely by Maxwell as that small part of matter which moves about as a whole so that its parts, if it has any, do not part company during the motion of agitation of the gas.

4. The kinetic theory of gases was initiated by D. Bernoulli in 1738 and was developed by Joule (1848), Waterston (1845), Kroenig (1856), Clausius (1857), Maxwell (1860), Boltzmann and others. According to this theory, the pressure of a gas is due to the bombardment of the molecules on the containing envelope and the temperature is measured by their average kinetic energy. In order to account for Avogadro's hypothesis in terms of this theory the following calculation may be referred to.

The gas is contained in a cubical vessel the length of whose side is L. The mass of each molecule is M and its average velocity v*. Consider a single molecule moving in any direction and striking one of the faces; its velocity v may be resolved into three components x, y and z at right angles to one another ($v^2 = x^2 + y^2 + z^2$). Let these three components be parallel to the edges of the cube. Then as regards the effect of the component x, the momentum of the particle due to this component is Mx and, since the particle is perfectly elastic, the change of momentum on impact is $2Mx$. The particle will impinge upon the two parallel faces of the cube $\frac{x}{L}$ times in unit time, so that its total effect as pressure will be $2Mx \times \frac{x}{L}$. Similarly for the components y and z, the total effect being

$$\frac{2Mx^2}{L} + \frac{2My^2}{L} + \frac{2Mz^2}{L} = 2M\frac{(x^2+y^2+z^2)}{L} = \frac{2Mv^2}{L}.$$

This being the effect of a single molecule, the total effect on the interior

* Strictly speaking, v is the square root of the mean square of all the velocities.

faces of the cube will be $\frac{2NMv^2}{L}$, where N is the number of molecules contained in the vessel. The pressure will therefore be

$$P = \frac{2NMv^2}{L \times 6L^2} = \frac{2NMv^2}{6V},$$

where V is the volume of the vessel.

We may therefore write $PV = \frac{1}{3}MNv^2$.

In equal volumes of two different gases at the same pressure

$$MNv^2 = M'N'v'^2.$$

If the temperatures are also equal the average kinetic energy of the molecules is (with every degree of probability) also equal, or

$$\frac{Mv^2}{2} = \frac{M'v'^2}{2},$$

from which it follows that $N = N'$.

5. If the hypothesis of Avogadro be accepted, it follows that the densities of gases, i.e. the masses in a given volume, must be proportional to their molecular weights, or

$$\frac{\text{Density of gas } A}{\text{Density of gas } B} = \frac{\text{Mol. wt. of } A}{\text{Mol. wt. of } B}.$$

When chemists apply this principle to the determination of molecular weights they in reality *compare* the molecular weights of different substances, that is to say the value found represents a ratio and of course not the absolute molecular mass. If the atomic weight of hydrogen is taken as unity and if densities of gases are expressed in grams per 11110 c.c. (measured at 0° and 760 mm.), the density of hydrogen = 1. By what follows it will be seen that the molecular weight of hydrogen is twice its atomic weight. Therefore if the density of any other gas is D and M is its molecular weight,

$$1 : 2 :: D : M \text{ or } M = 2D.$$

The reasoning by which it is assumed that the molecular weight of hydrogen is twice its atomic weight is briefly as follows: When hydrogen combines with chlorine the volume of hydrogen chloride produced is double that of the hydrogen used, and therefore n molecules of hydrogen, by Avogadro's hypothesis, yield $2n$ molecules of hydrogen chloride. But each molecule of hydrogen chloride must contain at least one atom of hydrogen; therefore each molecule of hydrogen must contain at least two atoms of hydrogen. That the molecule of hydrogen chloride does

not contain more than one atom of hydrogen is evident, or is at any rate highly probable, from the fact that in a given volume of any hydrogen compound there is never found a smaller weight of hydrogen than that which is present in the same volume of hydrogen chloride, at the same temperature and pressure. (Compare **32**). Further, experiment shews hydrochloric acid to behave as a monobasic acid; its hydrogen can all be replaced by metals in one stage only. Hence the molecule of hydrochloric acid contains but one atom and the molecule of hydrogen contains two atoms.

The term *density* of a gas has been often used somewhat incorrectly by chemists to signify the specific gravity referred to hydrogen at the same temperature and pressure. The number which expresses the density, i.e. $\frac{\text{mass}}{\text{volume}}$, will evidently depend on the units chosen.

If however the unit of volume is taken as 11110 c.c. measured at 0° and 760 mm. and the unit of mass as the gram, the density will be numerically equal to the specific gravity referred to hydrogen. The density of hydrogen then = 1 and its molecular weight = 2. The density of oxygen will be 15·88 and its molecular weight 31·76.

For reasons which will be discussed later on, some chemists prefer to take the molecular weight of oxygen as 32 and its atomic weight as 16. In this case the molecular weight of hydrogen will be 2·016 and its atomic weight 1·008.

The expression 'molecular weight of a substance in grams' or 'gram molecular weight' is often used for practical purposes. It is that weight of the substance in grams which, as a gas or vapour, would fill 22·22 litres (or 22·4 litres if O = 16) at 0° and 760 mm. This quantity is often termed the molar weight, or simply mole or mol.

[Note that one often uses this term for substances which are solids or liquids at 0° and 760 mm. The number merely indicates that *if* the substance remained as a gas, and obeyed the gas laws, at this temperature and pressure, its molar weight would fill this volume. In this respect the alternative expression 'specific gravity referred to hydrogen at the same temperature and pressure' is preferable to density. The molar weight may however be determined in most cases by methods other than the vapour density.]

A solution which contains one mole of a substance per litre is called a 'molar solution' of that substance. This is not necessarily the same as a 'normal' solution, the latter term being generally used for a solution containing one gram equivalent of the active substance per litre.

[Ostwald proposes to refer the weights of gases to the weight of an equal volume of an imaginary gas which is 32 times lighter than oxygen. The ratio so obtained would of course be identical with the molecular weight, referred to the oxygen standard, as above defined.]

It will be evident from what has been said that densities expressed in grams per c.c. at 0° and 760 mm. must be multiplied by 11110 (or 11200) if it is desired to bring them to the so-called 'chemical' standard. Specific gravities referred to air as standard must be multiplied by 14·4.

[The expression 'one volume' is often used in chemistry to mean the space filled by one part of hydrogen at the stated temperature and pressure, and molecular formulae are then called 'two volume' formulae. Thus it is said that H, Cl, Br, N, etc. fill one volume, P half a volume, Hg two volumes, H_2O two volumes and so on. Some confusion may arise in this way owing to the fact that others speak of the molecular volume as 'one volume.']

6. The laws of Boyle and of Charles and Gay-Lussac, may be combined in the relation $PV = RT$ where T denotes the absolute temperature. If now we take V to be the volume occupied by one gram molecular weight, i.e. the molar volume, it is evident that by Avogadro's hypothesis R will have the same value for all gases which obey the laws mentioned. [V will be 22·22 litres at 0° and 760 mm. on the hydrogen standard, 22·400 on the oxygen standard. For 'ideal' gases the number is 22·412.]

If P is expressed in grams per square centimetre,

$$R = \frac{22400 \times 76 \times 13{\cdot}6}{273} = 84800.$$

In many calculations involving this relation, PV measures work done. For example, the work done in producing a gram molecule of a gas at the absolute temperature T, under a pressure

of one atmosphere, will be $84800 \times T$ gram centimetres. The heat equivalent of this will be

$$\frac{RT}{J} = \frac{84800}{42640} \times T = \text{about } 2T \text{ cal.}$$

Or, if the pressure is expressed in dynes per square centimetre, $R = 83{\cdot}18 \times 10^6$ and $PV = 83{\cdot}18 \times 10^6 \times T$ ergs or $1{\cdot}99\,T$ cal.

In calculating the molecular weight from the vapour density it must be clearly understood that, in the usual mode of procedure, the *exact* formula-weight has previously been determined by analysis, etc. From the density, one only decides what whole-number multiple of the simplest formula represents the molecular weight. Density determination alone, as usually carried out, is not sufficiently accurate to decide the exact value. But by the more refined methods this, in some cases, is possible, if correction be applied for deviation from the gas laws. [Compare D. Berthelot, *Zeit. Electrochem.* 1904 (10) 621. Guye, *Journ. Chim. Phys.* 1905 (3) 321.]

Practical Work.

Expt. 1. Determine the density of carbon dioxide.

A round-bottomed flask of about 200—250 c.c. capacity is drawn off at the neck and closed with pressure-tubing and a clip.

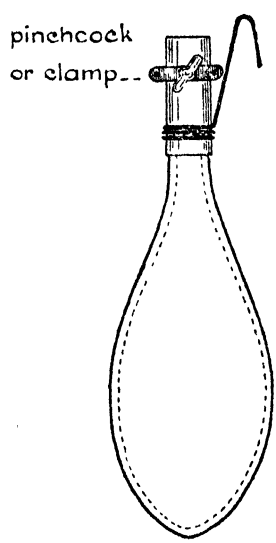


Fig. 1.

The flask (Fig. 1), full of air, is weighed being suspended, if necessary, by a wire. The temperature and pressure are noted. Carbon dioxide, generated in the usual manner, is washed with water and dried by sulphuric acid and then passed into the flask, taking care that the current of gas is not too rapid for efficient drying. The delivery tube should reach nearly to the bottom and the current of gas should be continued for about a quarter of an hour. The delivery tube is taken out, keeping the flask upright. The latter is then closed, weighed and opened

under a solution of caustic soda (about 1 in 3). On shaking, the solution enters slowly at first, then rapidly, finally nearly filling the flask. (The residual air-bubble at the top is now under reduced pressure so that it is advisable to sink the flask below water and level the air-bubble before measuring the liquid.)

The solution is now poured out into a measuring cylinder and its volume noted*. (Observe that according to the method of calculation which follows, it is not necessary to know the total volume of the flask. It is however assumed that the temperature and pressure do not change during the operations and that the minute difference due to vapour pressure of soda solution is negligible. The residual air may in fact be regarded as part of the flask.)

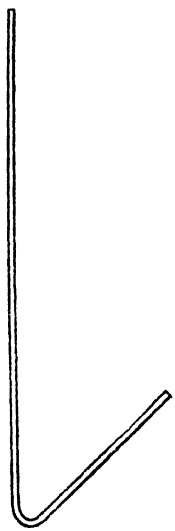


Fig. 2.

Volume of solution $= V$ c.c.
Temperature $= t°$ C.
Pressure $= P$ mm.
Weight of flask full of air $= W_1$ gms.
carbon dioxide and residual air $= W_2$ gms.

Corrected volume of carbon dioxide

$$= V \frac{273}{273+t} \times \frac{P}{760} = V_0.$$

Let x = density of carbon dioxide in gms. per c.c. at 0° and 760 mm.

Its calculated mass will be $V_0 x$.

Similarly the calculated mass of the displaced air is $V_0 \times \cdot 00129$.

$$\therefore \quad W_2 - W_1 = V_0(x - \cdot 00129).$$

To express this result as the density in the sense commonly used by chemists (see above) the result must be multiplied by 11110, H = 1 (or 11200, O = 16).

The density of ammonia, sulphur dioxide, hydrogen chloride, etc. may be similarly determined.

* Owing to the smallness of the orifice, this operation is often attended with difficulty. The following device of Mr Hall overcomes this. A thin glass tube shaped as shewn in the sketch (Fig. 2) is closed at the shorter end with the finger and the longer limb is inserted up the flask so that it reaches the air-bubble; the finger is then removed.

EXPT. 2. **Determine the density of the vapour of a pure liquid** (chloroform, benzene, etc.)

(*a*) *By Dumas' method.*

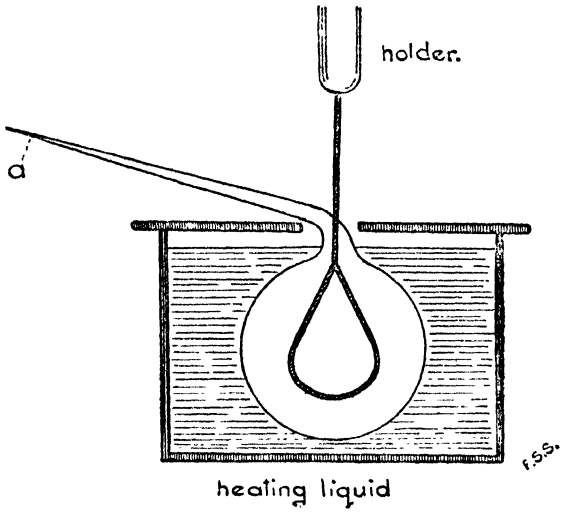


Fig. 3.

A clean dry flask of the form shewn in the sketch is weighed full of air, noting the temperature and pressure. A convenient quantity of the liquid is introduced in the usual manner and the flask is heated by a bath to a known temperature which must be sufficiently above the boiling point of the liquid. The liquid in vaporizing expels the air and finally the flask is full or nearly full of the vapour, the last drop of the liquid having disappeared. This point may be approximately ascertained by holding a cold piece of metal in front of the orifice, observing when the deposition of dew ceases. The flask is then sealed. Experience shews that this can be most efficiently done by drawing off the narrow part (*a*) and sealing, instead of merely sealing the extreme end as is commonly done. The piece of glass which is drawn off is of course retained for weighing. The flask full of vapour is cooled, weighed, and the end is then opened under water which enters and nearly fills the flask. In order to determine the volume of the water, the whole is weighed to a centigram on a *rough balance.*

The calculation is the same in principle as that given above except that two temperature corrections are necessary and consequently the volume of the residual air-bubble must be determined. Where accuracy is required it is also necessary to correct for the expansion of the envelope.

(*b*) *By Victor Meyer's first method.*

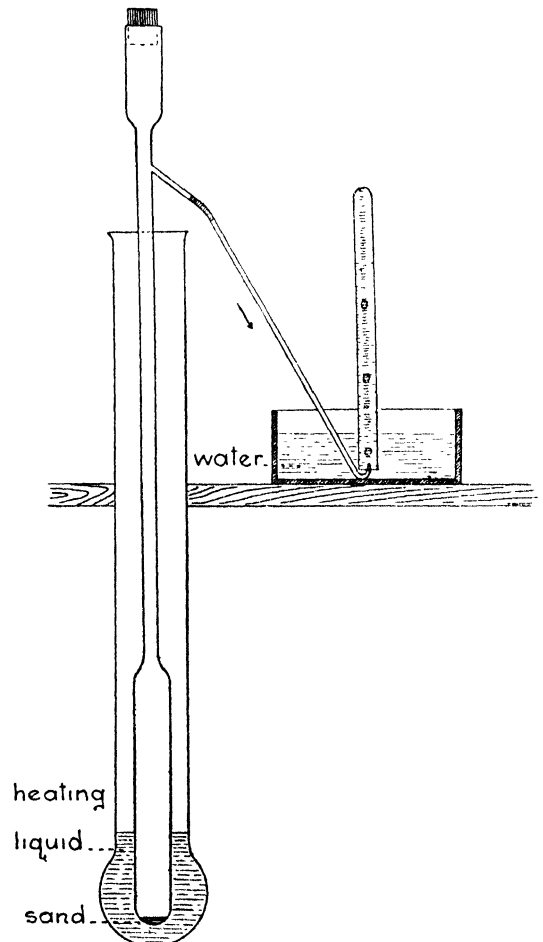


Fig. 4.

The apparatus is arranged as shewn in the figure. The heating is continued until thermal equilibrium results as shewn by the

fact that bubbles are no longer expelled nor is air forced back. The cork is withdrawn, the weighed quantity of the liquid which is contained in a small stoppered tube is quickly dropped in, the cork being immediately replaced. A little sand at the bottom of the flask will prevent any breakage. The expelled air is collected in the measuring tube *B*, levelled and corrected for temperature, pressure and vapour pressure.

Corrected volume of air $= V_0$ c.c.

Weight of substance $= W$ gms.

Density of gas in gms. per c.c. $= \frac{W}{V_0}$.

The weight of substance taken should be chosen so that a convenient volume of air is collected.

The formation of vapour and consequent expulsion of air must be fairly sudden. The result will of course be vitiated if the vapour has time to diffuse into the colder part of the apparatus.

It is necessary therefore to employ, as heating liquid, a substance whose boiling point is considerably above that of the compound to be examined. Observe however that it is not necessary to know the temperature of the heating bath.

Substances commonly employed for the heating bath are: water, amyl alcohol (about 130°), xylene (about 140°), aniline (184°), nitrobenzene (210°), β naphthol (286°), diphenylamine (310°). Also molten fusible metal, molten lead and hot air.

EXPT. 3. **Determine the density of atmospheric air.**

A round bottomed flask (200—300 c.c.) is drawn out at the neck, fitted with a piece of thick pressure tubing and closed with a screw clip.

About 30—50 c.c. of distilled water are introduced and boiled over a small flame for about 10 minutes. The clip is closed and flame removed simultaneously, while the water is boiling fairly vigorously. The whole is cooled and weighed (W_1 grams).

The screw clip is then opened so as freely to admit the air. Temperature (t) and barometer (P) are noted, and the flask, etc. again weighed (W_2 grams). The remaining water is decanted into a measuring cylinder, its volume (V_1 c.c.) is read, and the

flask is then completely filled with water and the contents measured (V_2 c.c.).

$$\text{Corrected volume of air} = (V_2 - V_1) \times \left(\frac{273}{273+t}\,\frac{P-P'}{760}\right) = V_0.$$

$$\text{Weight of air} = W_2 - W_1.$$

$$\text{Density in grams per c.c.} = \frac{W_2 - W_1}{V_0}.$$

EXPT. 4. **Determine the density of ammonia.** The following illustrates a method of density determination in which no direct weighing is necessary. Standard solutions are provided. A flask of the kind described in Expt. 1 is filled with dry ammonia by displacement, as before. The orifice is then opened under a measured excess of standard sulphuric acid (say 100 c.c. of normal acid) contained in a dish and diluted with a convenient volume of water (so that there is more liquid than is necessary to fill the flask). The volume of solution which enters is noted by means of a label or other mark on the flask. The solution is poured back into that remaining in the dish, the flask washed out, and the whole liquid titrated with normal caustic soda, using methyl orange as indicator. From this result the weight of ammonia is calculated in the usual way. The flask is then filled up to the mark with water, the residual air bubble levelled as in the previous case, and the volume of water in the flask measured. In this case again, if it be assumed that no change of temperature or pressure has occurred during the operation, the residual air bubble may be regarded as part of the flask and the volume measured will represent that of the ammonia.

The densities of many other gases (such as HCl, H_2S, SO_2) may be determined in a similar way, the quantities being determined by titration with appropriate standard solutions and with the usual precautions.

If time allows, determinations of vapour density are also made by Hofmann's method (Fig. 5) and by Victor Meyer's second method (Fig. 6) the details of which have been referred to in the Lecture.

The latter observation was contradicted by Than but was upheld by Deville. Marignac, on the other hand, found that the heat necessary to vaporize solid ammonium chloride was equal to the heat evolved when ammonia and hydrogen chloride combine.

An experiment usually quoted in support of the above-mentioned hypothesis is that in which the vapour given off from heated ammonium chloride is allowed to diffuse through a porous partition.

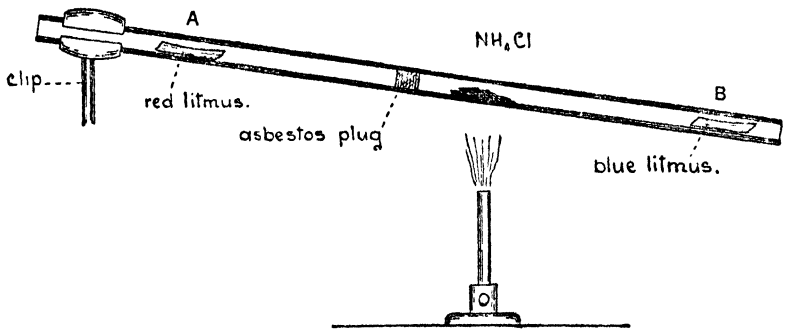


Fig. 7.

If dissociation does occur, a partial separation would be effected owing to the greater rapidity of diffusion of the ammonia. Consequently the litmus paper in *A* will be turned blue and that in *B* will be reddened. This is found to be the case, and the experiment is often considered as conclusive. It must be remarked however that the actual density observed requires that practically all shall be dissociated; whereas the result here mentioned would be also realized if only a minute portion were dissociated: the equilibrium being disturbed by the diffusion, further dissociation would occur. Evidence is also afforded by the fact that the observed density is greater when taken in an atmosphere of one or other product of dissociation.

According to Baker the density of specially-dried ammonium chloride gives a value twice as great as that found under ordinary conditions. It has been suggested that the vapour, in this case, is not in a condition of true equilibrium and that dissociation is taking place with extreme slowness; when traces of moisture are present this change is accelerated catalytically. See pages 155 and 186.

8. Phosphorus pentachloride again gives the following values:

Temperature.	Density (air = 1).	Density (O = 16).	Percentage of dissociated pentachloride.
182	5·08	73·4	41·7
200	4·85	70·0	48·5
250	4·00	57·6	80
300	3·65	52·7	97·3

The calculated value for undissociated PCl_5 is 104·12 (O = 16), consequently for complete dissociation the value is 52·06.

If we explain this apparent abnormality in the same way as in the previous example, the percentage of dissociation from any other observed density (d) may be calculated in the following way:

Let $x =$ percentage of dissociated part

then $100 - x =$ percentage of undissociated part.

The volume of the first will be $\frac{x}{52{\cdot}06}$ and the volume of the combined part will be

$$\frac{100 - x}{104{\cdot}12}.$$

Therefore $$\frac{x}{52{\cdot}06} + \frac{100 - x}{104{\cdot}12} = \frac{100}{d}.$$

Wurtz in order to test this hypothesis made his celebrated experiment of determining the density of the pentachloride in the presence of excess of trichloride, arguing that the presence of one of the products of dissociation would diminish the degree of dissociation and hence higher values should be obtained. This he found to be the case when *the volume was kept constant*, and numbers were obtained approximating to the theoretical value 104·25. [Note that if the addition of phosphorus trichloride is made at the same partial pressure, allowing the mixture to increase in volume, the dissociation would not be prevented. (See page 149.)]

Further evidence is also afforded in this case from the colour of the vapour, which becomes more and more yellowish green as the temperature increases. By comparing the tints obtained with mixtures containing known amounts of free chlorine, the percentage of dissociation can be approximately determined (Wanklyn).

9. Chloral hydrate. The density of Chloral hydrate is found to be approximately one quarter of the simplest formula-weight, corresponding therefore to the impossible formula CCl_3H_3O. This again was held by some to be an exception to Avogadro's hypothesis. Experiments were made in order to ascertain whether a thermal change occurred on mixing the vapours of chloral and water. According to the first observers, heat *was* evolved, this result appearing to support the supposition that chloral hydrate existed as a chemical compound under the conditions of the experiment; this observation however was afterwards contradicted.

Troost suggested the following experiment in order to test the question. If we take a hydrated compound which has a definite dissociation pressure p at a given temperature, then this compound will dissociate in a dry atmosphere or in one containing water vapour at a pressure less than p, but will not dissociate if this value is reached or is exceeded. Chloral hydrate was vaporized at a temperature $t°$ C. and a pressure P. It was found that hydrated potassium oxalate $K_2C_2O_4 . H_2O$ at the temperature $t°$ has a dissociation pressure less than $\frac{P}{2}$. If therefore the space contains chloral hydrate as a chemical individual, the oxalate can give off water since the space contains no aqueous vapour as such. If however dissociation has occurred, as required by the above density, the pressure exerted by the chloral will be $\frac{P}{2}$ and that exerted by the water will also be $\frac{P}{2}$, since equal volumes of these two substances will be produced. In this case therefore the potassium oxalate hydrate could not dissociate. Experiment shewed that no dissociation of the hydrated salt occurred, i.e. the pressure remained constant on introducing the salt.

10. Many other examples of so-called 'abnormal' vapour density have been observed and in every case the results can be accounted for by dissociation or association. An interesting example in which the influence of temperature is clearly shewn is that of *amylene hydrobromide*, $C_5H_{11}Br$, which gives a vapour density of about

37·7 at 360° and approximately double this value at 155°; at intermediate temperatures the density gradually diminishes as the temperature rises, corresponding to the gradual dissociation into amylene and hydrogen bromide. The vapour of *Mercuric sulphide* at 1560° has a density of about 77, corresponding to complete dissociation into mercury and sulphur $\left(\frac{200+32}{3}\right)$. At 670° the density is about 85; complete dissociation probably occurs here also, the higher density being due to the fact that the sulphur molecules are more complex (See page 74.)

Ammonium carbamate $CO(NH_2)ONH_4$ yields a vapour whose density is about 13 and corresponds therefore to complete dissociation into $2NH_3 + CO_2$ $\left(\frac{34+44}{6}\right)$.

11. Calomel. The vapour density of mercurous chloride was found by experiment to be $\frac{235{\cdot}5}{2} = 117{\cdot}75$, corresponding therefore to the molecular formula HgCl. This result gave rise to considerable discussion, since it appeared to contradict the so-called 'Law of even numbers.' (See page 94.) It was suggested however that if the formula could be doubled, there would be no contradiction to the law, since the two chlorides of mercury would be represented as Cl – Hg – Cl and Cl – Hg – Hg – Cl, the mercury being in reality divalent in both cases.

Odling made the important observation that gold leaf became amalgamated when immersed in the vapour of calomel, and later Victor Meyer shewed that when calomel was heated in a porous vessel, metallic mercury diffused through. These experiments shew qualitatively that *some* dissociation has taken place; if we assume that complete dissociation into mercury and mercuric chloride has occurred, the above-mentioned value for the density will be accounted for. The density of mercury is 100 and that of mercuric chloride 135·5; since equal volumes would be produced the density would be the mean, namely $\frac{100+135{\cdot}5}{2} = 117{\cdot}75$. It must be remarked however that the experiments mentioned are merely qualitative, shewing that *some* dissociation has occurred, whereas the observed density would require complete dissociation.

Victor Meyer also made the following experiments:—Sticks of solid potash, previously heated to the same temperature, were plunged into the vapour of calomel and the formation of red mercuric oxide was observed. Had the calomel existed as such one would have expected the formation of black mercurous oxide. Objection was made to this experiment on the ground that, at the temperature in question, mercurous oxide dissociates into the red oxide and metallic mercury. Meyer shewed however that the red compound was produced instantaneously, whereas the black oxide takes an appreciable time to dissociate.

Fileți afterwards stated that the vapour density of calomel was the same, namely 117·75, when taken in an atmosphere of excess of mercury or mercuric chloride. He argued that, as in Wurtz's experiment on phosphorus pentachloride, the dissociation should have been prevented and the density consequently increased by the presence of either of these substances. Hence he concluded that no dissociation takes place and that the formula for calomel is HgCl. Victor Meyer however suggested a way out of this difficulty by drawing attention to the fact that the principle referred to only applies to reversible systems, and that, in the present case, dissociation may be quite complete, i.e. the original substance may not be present, sensibly, beyond a certain temperature. Familiar instances of this limitation are afforded, for example, by phosphonium chloride and the hydrate of hydrogen sulphide, etc. He finally concluded that dissociation does occur when calomel is vaporized, but that we had no evidence as to the molecular state of calomel vapour since it could not be vaporized as such.

Baker subsequently stated that the vapour density of specially-dried calomel is approximately equal to twice the value given above, i.e. 235·5, i.e. in the absence of water vapour the compound appears to have the formula Hg_2Cl_2. (See page 20.)

Compare V. Meyer, *Ber.* 1894, 1482 and 1895, 364.
Fileti, *Jour. Pr. Chem.* 1894, 222 and 1895, 197.
Baker, *Trans. Chem. Soc.* 1900, 646.
Beckmann, *Zeit. Anorg. Chem.* 1907 (55) 175.
Foote and Martin, *Amer. Chem. Jour.* 1909 (41) 451.

CHAPTER IV.

DETERMINATION OF THE MOLECULAR WEIGHTS OF SUBSTANCES IN SOLUTION.

12. UNTIL a comparatively recent date, it was only possible to determine molecular weight with certainty in the case of those substances which could be vaporized without decomposition. In other cases the values could only be fixed (or conjectured) by the general chemical considerations referred to in the first chapter.

The researches of Raoult, Van 't Hoff and others have now given us command of various methods by which it is possible to determine the molecular weights of substances in solution, and, in some cases, of solid and liquid substances themselves.

Osmotic pressure.

A glass vessel is filled with a solution of copper sulphate, and its opening is tightly closed with a bladder. If the latter be immersed in water, the contents of the vessel tend to increase so that the bladder is extended and may even burst. This experiment was described by Dutrochet in 1726, and a similar experiment was made by the Abbé Nollet in 1750, using alcohol in place of copper sulphate solution.

Pringsheim in 1854 noticed that the protoplasmic contents of certain vegetable cells contracted when placed in a strong salt solution. With a weaker solution of the salt the contraction is less, and in pure water the cell maintains its form, since expansion is prevented by the rigid outer cell-wall which is pervious to both water and the substances in solution. The protoplasmic contents are enclosed in a membrane which has the property of allowing pure water to pass, but which is impervious to most dissolved substances.

By carefully diluting a strong solution of a salt and making trials with similar cells, a concentration is eventually obtained which just causes no change of form in the cell-contents. A number of solutions of different salts may thus be adjusted in strength so that each is in equilibrium with similar cells. These solutions are then said to have equal *osmotic pressure* or to be *isotonic*. This statement assumes that two solutions isotonic with a third solution are isotonic with one another. Quantitative experiments of this nature were made by de Vries in 1884 and 1888. He shewed, for example, that solutions of potassium nitrate, potassium chloride, and sodium nitrate were isotonic, in the above sense, with one another when they had chemically equivalent (or molecular) concentrations But with certain organic substances, such as cane sugar, inverted sugar and malic acid, a greater molecular concentration was required to produce the same effect as that given by the salts mentioned.

Semi-permeable membranes (i e. those which allow freely the passage of water, but which are impervious, or nearly so, to dissolved substances) were first artificially prepared by Traube in 1867. Pfeffer in 1877 succeeded in depositing a semi-permeable membrane in a rigid support and made extensive quantitative observations upon the subject. This property of semi-permeability is possessed by several substances such as cupric ferrocyanide, Prussian blue and calcium phosphate; but the first-named is the most efficient.

An unglazed earthenware pot is thoroughly soaked with water in a vacuum to remove air. It is then filled with a solution of copper sulphate and immersed in a solution of potassium ferrocyanide or *vice versa*. The film of cupric ferrocyanide is produced where the solutions meet in the wall of the pot. (For particulars see Adie, *J. C. S.* 1901; Morse and Horn, *Am Chem. Jour.* 1901, 80; Berkeley and Hartley, *Proc. Roy. Soc.* 1904 (73) 436 and *Phil. Trans.* 1906 (206) 481.) The vessel is then fitted with a manometer, filled with a solution to be examined and immersed in water, the temperature being kept constant: water passes from outside into the solution and increases the pressure. The maximum pressure thus produced is called the osmotic pressure of the solution at that temperature. If the volume of the solution

is kept constant by pouring mercury into the open limb of the manometer, the hydrostatic pressure of the mercury column is a measure of the osmotic pressure of the solution.

Considerable difficulties are encountered in making these measurements, chiefly owing to the following circumstances:

(*a*) The maximum pressure is only reached after a very long time—several months in some cases.

(*b*) The pressures produced may be very great. A 17% solution of ammonia, for example, could give at 0° a pressure of about 224 atmospheres. It is difficult therefore to prevent bursting or leaking of the membrane or other part of the apparatus.

(*c*) No perfect semi-permeable membrane has yet been obtained, that is, one which is completely impervious to solute but is pervious to water.

13. Laws of Osmotic Pressure.

Pfeffer's investigations on the osmotic pressure produced by solutions of cane sugar of different concentrations, shewed that the maximum pressure produced is proportional to the concentration. The analogy with Boyle's Law for gases is obvious if for gas pressure we substitute osmotic pressure. The osmotic pressure was also found to increase with rise of temperature and the results obtained, considering the difficulties of the experiment, were consistent with the assumption that the law of Gay-Lussac or of Charles is obeyed, namely, that at constant volume the pressure varies as the absolute temperature. It is found moreover that solutions of different non-electrolytes which are isotonic at one temperature are also isotonic at another temperature. So far then it would appear that the relation $VP = RT$ is applicable to substances in dilute solution, P being the osmotic pressure.

It was further shewn by Van 't Hoff that the value of R has actually the same value as in the case of gases, that is that the solute exerts the same osmotic pressure in solution as the pressure it would exert if it were gasified at the same temperature and confined in the same volume. It follows therefore that one molar weight of solute will exert an osmotic pressure at 0° of 760 mm. when the volume of the solution is 22·4 litres. In other words the law of Avogadro is applicable to substances in solution,

and equal volumes of all (non-electrolytic) substances at the same temperature and osmotic pressure contain the same number of molecules.

Evidently then if the experimental difficulties could be satisfactorily overcome, the measurement of the osmotic pressure of a solution of known concentration would afford a direct method for determining the molecular weight of a solute.

If w grams of solute are contained in V c.c. of solution at $t°$ and the osmotic pressure produced is P mm. one can perform the calculation exactly as in the case of gases.

The volume at 0° and 760 mm. will be

$$V \frac{273}{273+t} \times \frac{P}{760} = V_0.$$

Then since V_0 c.c. contains w grams, 22400 c.c. will contain $\frac{22400 \times w}{V_0}$ grams, which gives the molecular weight in grams.

Pfeffer found, for example, that a 1 per cent. solution of cane sugar at 13·5° produced an osmotic pressure of 521 mm. Here $w = 1$ and $V =$ about 100 c.c. so that the molecular weight of cane sugar = about $\frac{22400}{65{\cdot}3} = 343$. The calculated value for $C_{12}H_{22}O_{11}$ is 342.

Note that the volume considered here is that of the *solution*. Recent work of Morse and Frazer [*Am. Chem. Jour.* 1905 (34) 1 and 1906 (36) 1] point to the conclusion that, in the case of cane sugar at any rate, better results are obtained if the volume is referred to that of the *solvent* in the pure state. It would appear, in fact, that cane sugar dissolved in water exerts an osmotic pressure equal to that which it would exert if it were in the gaseous state at the same temperature and were contained in the volume not of the *solution* but of the *solvent* in the pure state. In other words, in comparing osmotic pressures the solutions should perhaps be made 'weight normal' instead of 'volume normal.' It is usually the custom in osmotic pressure calculations to regard the volume of the solution as being analogous to the volume of the vessel containing a gas. But the other view is at any rate worth consideration, namely that the effects may be due to an attraction by, or combination with, the solvent and that comparison should

be made with solutions containing equal quantities of the pure solvent. Compare Bancroft, *Journ. Physical Chem.* 1906 (10) 319.

The laws of osmotic pressure, above mentioned, thus refer only to very dilute solutions. In stronger solutions considerable deviations occur. In the case of gases, deviation from the relation $PV = RT$ can be accounted for if one takes into consideration the size of the molecules and their mutual attraction; the well-known equation of van der Waals, $\left(P + \frac{a}{V^2}\right)(V - b) = RT$, gives a close approximation to the experimental facts*. It does not necessarily follow that the deviations from the laws of osmotic pressure should be of the same magnitude, or in the same direction, as the deviation from the gas laws, but a relation on similar lines might be expected. This problem has recently been investigated by Lord Berkeley [*Proc. Roy. Soc.* 1907 (79) 125] and he deduces equations which agree well, within certain limits, with his experimental observations on strong solutions of cane sugar.

14. The nature or cause of osmotic pressure has formed a subject of considerable discussion and final agreement has not been arrived at. Some consider that it may be due to an attraction between solute and solvent, these tending, for example, to form hydrates. Others refer the phenomenon to purely physical causes and compare the tendency of a gas to expand, so as to fill any vessel containing it, with the expansion tendency of a solute to fill the liquid space at its disposal. This expansion tendency of gas or solute is evidenced by the gas pressure or osmotic pressure respectively and is the same in both cases for equal molecular concentrations at the same temperature. The osmotic pressure, according to this view, may be due to the bombardment of solute molecules; the solvent molecules can pass the diaphragm freely and so produce no pressure on it.

Another simple way of looking upon the matter, is to consider that the effect originates from the greater pressure of the pure solvent outside the cell. The diaphragm is subjected on the outside to the bombardment of pure solvent molecules only and on the inside to that of both solute and solvent. A greater

* Compare, for example, Poynting and Thomson's *Heat*, p. 152.

number therefore of pure solvent molecules strike the surface, in unit time, on the outside and pure solvent will flow in until its pressure is the same on both sides.

An experiment suggested by Arrhenius and carried out by Ramsay shews clearly the analogy between the pressure of a gas and the osmotic pressure of a solute. Two vessels of equal volume are separated by a wall of palladium. One is filled with nitrogen and the other with hydrogen—both being at the same pressure P. If the apparatus is now heated to 600°, the palladium acts as a semi-permeable membrane, allowing the hydrogen, but not the nitrogen, to pass. The hydrogen will therefore distribute itself equally between the two vessels and the nitrogen will remain enclosed in the one compartment. On cooling to the original temperature, there will therefore be a pressure of $\frac{1}{2}P$ in one vessel and $1\frac{1}{2}P$ in the other. The excess of pressure in the latter may be regarded as the 'osmotic pressure' of the nitrogen; just as in the experiments previously described, the excess of pressure was due to the solute.

Poynting [*Phil. Mag* 1896 (42) 298] considers that the solvent molecules inside the cell become impeded by their combination or association with the solute molecules and that their mobility is thus diminished. The mobility of the pure solvent molecules being greater, there will be a flow from outside to inside and the pressure within the cell will increase. But it is also shewn that the mobility of the liquid molecules becomes greater as the pressure increases so that, when the pressure reaches a certain value, the mobility of the molecules inside will become equal to that of the pure solvent molecules outside and the flow will then cease.

Armstrong [*Proc. Roy. Soc.* 1906 (78) 264] considers that the primary or main osmotic effect is exerted by the solvent, not by the solute. In pure water there is an equilibrium between the associated and single molecules [see **24**], and the effect of introducing molecules of the solute (non-electrolyte) is to cause dissociation of the complex water molecules to an extent which is in proportion to the amount added. The osmotic pressure, on this view, is a measure of the extent to which the equilibrium is thus disturbed, that is, in the direction $(H_2O)_n \longrightarrow nH_2O$. The single molecules, or 'monads,' are regarded as the attracting element in

the region of the solution, causing a flow of similar molecules from the pure solvent, or from a more dilute solution, until the two regions are in equilibrium*.

15. We have further to enquire what constitutes semi-permeability. Some have considered that the membrane has a sieve-like structure, through the pores of which the simple water molecules can pass, but which does not allow the passage of the larger molecules of solute (presumably hydrated).

A second explanation which has been suggested is that the solvent forms loose chemical compounds with the membrane which dissociate on the side on which the concentration of *solvent* is less.

That colloidal substances can probably form such loose compounds with water appears probable from the researches of Graham.

This explanation has been applied to the well-known experiment of filling an indiarubber tube with carbon dioxide and exposing it to air, when carbon dioxide diffuses out and air scarcely passes in—hence the tube collapses.

Another explanation is that offered by J. J. Thomson, who ascribes the mechanism to differences of surface tension. (See Thomson, *Applications of Dynamics to Physics and Chemistry*, page 190. Also Traube, *Phil. Mag.* 1904 (VI) 8. 704.)

A perfect semi-permeable membrane, available for experiments of the nature described above, has not yet been obtained; but such a membrane may be considered to exist in the case of the space separating solution and solvent when the two latter are placed in separate vessels under a bell-jar. This space is completely permeable to the vapour of the pure solvent but is impermeable to the (non-volatile) solute. The laws that would hold for a perfect membrane are the same however it may be formed. [Compare Larmor, *Phil. Trans.* 1897, 205.]

Practical Work.

Some simple qualitative experiments may be made in illustration of certain effects of **osmotic pressure.**

1. A particle of solid ferric chloride is added to a dilute aqueous solution of potassium ferrocyanide. A film of Prussian

* Compare also Callendar. *Royal Institution Address* Feb. 26, 1909. *Nature* 1909 (81) 235.

blue is thus formed, round the solid, through which pure water can pass. The ferric chloride inside dissolves forming a strong solution and consequently water passes in from the weaker solution outside. The Prussian blue cell becomes expanded and may assume remarkable forms. ('Chemical garden.')

2. A drop of a fairly strong solution of potassium ferrocyanide is added to a dilute solution of copper sulphate. A semi-permeable cell is formed round the drop and pure water passes in as in the last experiment. The solution just outside the cell is consequently strengthened and blue striæ may be seen to descend owing to the greater density of the solution.

3. An ordinary egg is immersed for a short time in hydrochloric acid so as to remove the outer shell; it is then washed and placed in pure water. After some hours the volume will have considerably increased owing to the entrance of water since the outer membrane has, to some extent, a semi-permeable character. A second egg similarly treated is immersed in a strong solution of common salt; water passing out into the strong solution, the egg will undergo considerable contraction if left for a few hours.

4. Experiments may also be made illustrating (*a*) the deposition of the copper ferrocyanide membrane in a porous pot, (*b*) the diffusion of carbon dioxide through indiarubber, and (*c*) the rise of liquid in a tube, closed by a bladder at the lower end, which contains a solution of sugar, as in Dutrochet's experiment.

5. A strong aqueous solution of calcium nitrate saturated with phenol is placed in a cylinder; on this is poured a layer of liquid (hydrated) phenol and, above this layer, a saturated aqueous solution of phenol. The phenol layer is impervious to calcium nitrate but pervious to water; the result is, that water enters the calcium nitrate solution and dilutes it, and the phenol layer gradually rises.

CHAPTER V.

DETERMINATION OF THE MOLECULAR WEIGHTS OF SUBSTANCES IN SOLUTION (*continued*).

16. Depression of the Freezing point. The fact that the freezing point of a solvent is lowered when a substance is dissolved in it has been known for a great length of time, and is apparent in many familiar phenomena such as the comparative difficulty of freezing sea-water.

Blagden already in 1788 and Rüdorff independently in 1861 shewed that the lowering of the freezing point was directly proportional to the quantity of substance dissolved. So that if w grams of solute, dissolved in a given mass of solvent, lower the freezing point by $t°$, $\frac{t}{w}$ represents the lowering for one gram dissolved. (Blagden's Law.)

The quantity $\frac{t}{w}$ is sometimes called the coefficient of depression. de Coppet in 1871 shewed that the lowering of the freezing point was in many cases related to the molecular concentration, but the more exact and general relationships were first pointed out by Raoult in 1883.

For dilute solutions of all non-electrolytes investigated he found that, taking 100 grams of solvent, the value of $\frac{t}{w}$ when multiplied by one molecular weight is constant for that particular solvent; or $\frac{t}{w} \times M = C$.

The number of gram-molecules of solute taken (n) is equal to the $\frac{\text{weight taken}}{\text{molecular weight}} = \frac{w}{M}$. The relation might therefore be written $t = Cn$.

In practice one does not necessarily use 100 grams of solvent but say, S grams. Since the lowering of the freezing point is inversely proportional to the quantity of solvent taken, we then have

$$\frac{S}{100} \times \frac{t}{w} \times M = C.$$

The value of C for the various solvents which are commonly used is as follows:

Substance	F.P.	Constant.
Water	0°	18·6
Acetic acid	16·6°	39
Benzene	4·9°	50
Nitrobenzene	5·7°	70·7
Formic acid	8·5°	27·7

These constants have been obtained by making experiments with substances whose molecular weights have already been determined by other methods. (Vapour density or chemical considerations.) It does not necessarily follow, without further evidence, that the molecular weight determined by the vapour density is identical with that in solution; but nevertheless by using the values obtained by such methods, Raoult obtained remarkably concordant results. In the majority of cases, the molecular weights calculated from the freezing-point method generally (but not always) do agree with those obtained from vapour-density determinations and from general chemical considerations.

Later it was shown by van 't Hoff that, reasoning from the hypothesis that the gas laws and Avogadro's law are applicable to solutions, one may calculate the value of Raoult's constant from the latent heat of fusion of the solvent.

17. The following is a brief outline of the method of proof stated in the most elementary way. Note that when a dilute solution freezes the pure solvent separates (except when solid solutions are formed, see page 320). This may be illustrated by observing the separation of colourless ice from a dilute solution of

a coloured solute such as potassium permanganate. A stronger solution is therefore left behind, work being done against the osmotic pressure as the volume is diminished.

A solution containing n gram molecules of solute in S grams of solvent is contained in a cylinder fitted with a semipermeable partition at one end and a movable piston. The freezing point of the pure solvent is T (absolute) and its latent heat of fusion, L.

The solution is cooled until it begins to freeze at $T-t$; the lowering of the freezing point being t. An amount of pure solvent which contained one gram molecule of solute is allowed to solidify; this will be $\frac{S}{n}$ grams. The solid is separated and the whole system brought to the temperature T. The separated solid solvent melts and $\frac{SL}{n}$ units of heat are absorbed. The resulting liquid solvent is then allowed to pass slowly into the remainder of the solution through the semipermeable partition, the pressure on the piston remaining constant at the osmotic pressure P because the volume of this solution is great. If the increase of volume is V, the work done is PV. The system is afterwards cooled to the temperature of freezing $(T-t)$ to complete the cycle of operations. Since this process is reversible, it follows that $\frac{SL}{n} : PV = T : t$. Or, since $PV = RT$ and R in thermal units is approximately 2,

$$\frac{SL}{n} = \frac{2T^2}{t} \text{ or } \frac{t}{n} = \frac{2T^2}{SL}.$$

But by Raoult's relation, when 100 grams of solvent are taken (i.e. $S=100$),

$$C = \frac{t}{n}$$

and this, in terms of the above quantities, $= \frac{2T^2}{100L}$.

18. Although Raoult obtained such remarkably consistent results in the case of non-electrolytes such as cane-sugar, urea, etc., it was found that aqueous solutions of metallic salts always gave a depression of the freezing point which was much too great. Quite similar results were obtained, it will be remembered, in the measurement of the osmotic pressure of solutions of electrolytes. These supposed abnormalities have been fully explained by the hypothesis of ionization, which will be discussed later on.

In other cases the values obtained for the freezing points are smaller than those calculated. In the first case the molecular weights will appear too small, and in the second case, too large. These apparent irregularities have a complete parallel in the so-

called abnormal vapour densities which give, for example, too small a molecular weight for ammonium chloride, etc. and too great a value for acetic acid near its boiling point.

Instead of the observation of freezing-point depression one may employ in a similar manner, the change of transition point (see page 350). This has been done for example in the following cases:—

Löwenherz [*Zeit. Physikal. Chem.* 1895 (18) 70] has determined the molecular weights of various substances by observing the change in the transition point of the system—

$$Na_2SO_4 . 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O.$$

The constant was determined by trial with non-electrolytes of known molecular weight and also by Van 't Hoff's method, as above. It was found that sodium salts do not ionise when dissolved in this solvent, and Crofts [*Trans. Chem. Soc.* 1898, 593] has applied the method to the determination of the molecular weight of permanganates. It is shewn that sodium permanganate has the simple formula $NaMnO_4$. [See also Dawson and Jackson, *loc. cit.* 1908, 344.]

J. Meyer [*Chem. Centr.* 1906 (2) 1231] has attempted to determine the molecular weights of metals in the solid state by dissolving them in pure tin and observing the change of transition point in the system—white tin, stannous chloride, grey tin. The method of calculation is similar to that mentioned in the previous examples, the constant $\frac{2T^2}{100L} = 17{\cdot}8$, being calculated from the heat of transformation. Mercury was found, in this way, to dissolve in tin in the unimolecular condition.

Practical Work.

1. Determination of the molecular weights of the given (non-electrolytic) **substances A and B by the freezing-point method,** using water as solvent.

[Those who have not previously worked in this direction should make preliminary qualitative experiments on the super-cooling of

liquids and the freezing of coloured solutions (**17**). The method of adjusting the Beckmann's thermometer must also be studied.]

The freezing tube (*A*) (Fig. 8) clean and dry is fitted with corks at the two openings and weighed. A convenient quantity (12 to 15 c.c.) of water is then introduced, the corks replaced and the whole weighed. The outer freezing bath, which contains water and lumps of ice, is brought to about $-2°$ or $-3°$ by the addition of common salt. The thermometer and stirrer are now placed in position in the weighed solvent and the tube is immersed in the outer freezing bath until ice just begins to separate. It is then warmed by the hand, until the temperature rises about one degree and all ice disappears, and inserted in the outer air jacket which is surrounded by the cooling mixture. The stirrer is moved slowly up and down to keep the temperature uniform and when the thermometer has fallen to about 0·5 degree below the freezing point (which has been roughly ascertained previously) the stirring is continued more rapidly and sharply in order to promote freezing. As soon as ice begins to form the temperature will rise rapidly to the normal freezing point. The liquid is gently stirred while the temperature is rising and the highest point is read off, the thermometer being lightly tapped with the fingers. The temperature should be read to $\frac{1}{100}$ of a degree or less; for the sake of accuracy it is best to make a second observation, removing the tube, melting the ice and again freezing. The tube is again removed; a weighed quantity (about 0·1 to 0·2 gram) of the solute is then introduced (from a suitable weighing tube) by the side opening, the cork replaced and the mixture stirred until the solid is completely dissolved. The freezing operation is then carried out as before.

A second and a third determination may then be made, using the same solution and adding further weighed quantities of solute. [Note that where great accuracy is required many further precautions are necessary. (Compare, for example, Nernst and Abegg, *Zeit. Physikal. Chem.* 1894 (15) 681).]

When great accuracy is not required and a Beckmann's thermometer is not available, a good thermometer of the ordinary type, reading to tenths of a degree, may be employed. In such cases the simpler form of apparatus (Fig. 9) is generally sufficient.

2. Determine the molecular weights of the given substances *A'* and *B'* by the same method using glacial acetic acid (F.P. about 16·6°) as solvent.

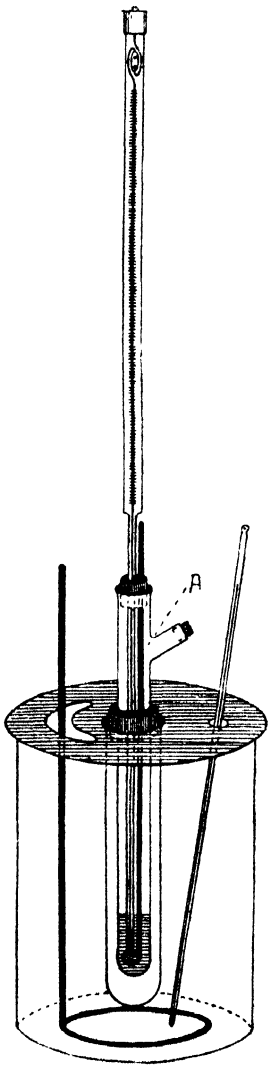


Fig. 8.

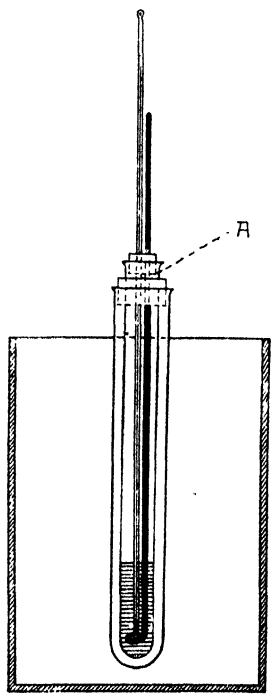


Fig. 9.

Lowering of the vapour pressure.

19. The influence of dissolved substances in raising the boiling point of water was first investigated by Faraday in 1822 and Griffiths in 1824, but no general laws were arrived at. Gay-Lussac and Prinsep afterwards made experiments on the same subject but in a different way, namely by measuring the vapour pressure of a solution of common salt at different temperatures. Babo in 1848, and Wüllner in 1856 extended such observations to a number of salts, and the last-named author came to the conclusion that the diminution of the vapour pressure of water caused by the dissolution in it of a non-volatile substance is proportional to the quantity of substance dissolved (Wüllner's Law).

It was subsequently shewn by Tammann about 1883 that the diminution of the vapour pressure caused by different salts, of the same type, is nearly the same if the molecular concentrations are equal. Ostwald had previously drawn a similar inference from the results of Wüllner.

A most important advance in the knowledge of this subject was made by Raoult in 1886 who used the barometric method of measuring the vapour pressure and also extended the observations to solvents other than water.

He arrived at the conclusions that:—

(i) The relative lowering of the vapour pressure $\left(\frac{P-P'}{P}\right)$ of ether has the same value between 0° and 20°, i.e. that it is independent of temperature.

(This had been previously suggested by Babo, but was not entirely confirmed by later observers.)

(ii) For solutions which are not too concentrated, the relative lowering is proportional to the concentration.

(iii) The value of $\frac{P-P'}{P}$ for one molecular weight of various non-electrolytic substances in 100 gms. of solvent is constant for that particular solvent.

Raoult's experiments afterwards led him to the conclusion that the results would be best expressed by the relation

$$\frac{P-P'}{P} = \frac{n}{N+n}c$$

where n = number of molecules of solute,

N = " " " " solvent,

and c is a constant which is approximately equal to unity.

Evidently this relation may be made use of for the determination of molecular weights.

Suppose w gms. of solute, molecular weight x, be dissolved in S gms. of solvent, molecular weight m,

$$n = \frac{w}{x}, \text{ and } N = \frac{S}{m},$$

$$\therefore \frac{P - P'}{P} = \frac{\frac{w}{x}}{\frac{S}{m} + \frac{w}{x}}.$$

Hence $$x = \frac{wmP'}{S(P - P')}.$$

Raoult soon discarded the method of measuring the vapour pressure in barometer tubes, owing to difficulties, such as the removal of the last traces of air and errors due to the evaporation of the solution on the sides of the tubes, etc. Various other more or less direct methods of measuring the lowering of the vapour pressure have since been devised but have not been employed to any great extent. Amongst these later methods may be mentioned the following:—

20. Ostwald's method as modified by Will and Bredig. A slow current of dry air is passed at the rate of about 1 litre per hour first through a solution of w gms. of solute in S gms. of solvent and then through the pure solvent.

The vapour becomes saturated in the first case to P', the maximum vapour pressure of the solution, and passing through the pure solvent becomes further saturated to P, the maximum vapour pressure of the pure solvent, at the given temperature.

Therefore the loss of weight experienced by the solution is to the loss experienced by the solvent as $P' : P - P'$.

Hence $$x = \frac{wm}{S} \times \frac{\text{loss in solution}}{\text{loss in solvent}}.$$

The air, which must be carefully dried before entering the solution, is caused to circulate through a coil of leaden pipe placed in a bath at constant temperature. In this the weighed bulbs containing the solution and solvent are also placed; an empty U tube follows, the object of which is to prevent any condensation of vapour which might diffuse back.

Each series of bulbs may be made by sealing together three potash bulbs, such as those used for combustions, as follows:—

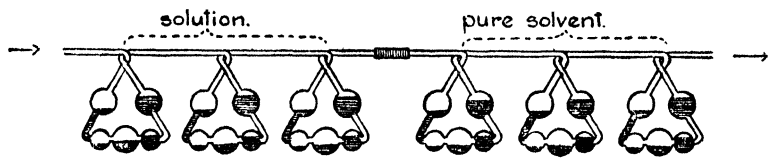


Fig. 10.

Lord Berkeley and Hartley [*Proc. Roy. Soc.* 1906 (77) 156] improve the accuracy of this method by passing the current of air *over* instead of through the solution and solvent.

Barger's method [*Trans. Chem. Soc.* 1904, 286] has the advantage that it may be employed when only a minute quantity of the substance is available. It depends upon the principle that isotonic solutions have the same vapour pressure and will therefore remain in equilibrium with one another when placed side by side in a closed vessel. If however one has a greater molecular concentration than the other, distillation of the solvent will take place; the volume of the solution of greater concentration will therefore increase at the expense of the other. Solutions of known concentration are prepared of the substance to be investigated and of some substance whose molecular weight is known. A series of drops of each of these solutions is placed, alternately, in a capillary tube, which is afterwards closed. The size of the drops is measured under the microscope and the relative increase or diminution is observed, the temperature of course being kept constant. The concentration of one or other solution is then adjusted until, on making a similar experiment, the two solutions are found to be in equilibrium.

21. Raoult's empirical relation $\frac{P-P'}{P}=\frac{n}{N+n}$ was obtained from the results of experiments on solutions of finite strength. When calculated for infinitely dilute solutions, the relation will be $\frac{P-P'}{P}=\frac{n}{N}$; practically the two are almost identical since n is very small compared to N.

A simplified outline of the proof of this relation, which is due to Arrhenius, may be briefly indicated in the following way.

A long funnel-shaped tube, closed at the lower end by a semi-permeable diaphragm, contains a solution of n molecules of solute in N molecules of solvent. It is placed upright in a basin containing the pure solvent, the whole is covered by a bell-jar and the air is exhausted. We have here two semi-permeable media, namely the diaphragm and the vacuous space between the liquids.

When equilibrium is attained, the osmotic pressure of the solution will be measured by the hydrostatic pressure of the column of liquid (height h) in the tube*. The vapour pressure of the solution at the surface (H) of the liquid in the tube will be equal to the vapour pressure of the solvent at this place; if it were not so vaporisation or condensation would take place. The vapour pressure of the solvent at the point H ($=P'$) is less than that at the surface of the liquid in the basin ($=P$) by the weight of a column of vapour of height h. Or,

$$P'=P-hd$$

where d is the density of the vapour. (This would not hold for stronger solutions, since d varies with h, and when the latter has a high value this variation can no longer be neglected.)

To calculate h. Let V be the volume of the solution in the tube, F the osmotic pressure, M the molecular weight of the solvent in the gaseous state† and S the density of the liquid solvent. Then $V=\frac{MN}{S}$ and since $FV=RT\times n$, $F=\frac{nRTS}{MN}$. But $h=\frac{F}{S}$. [The density of the very dilute solution may be regarded as practically identical with that of the solvent.]

Hence $$h=\frac{nRT}{MN}.$$

To calculate d. If v is the volume of one gram molecule of the vapour,

$$d=\frac{M}{v} \text{ and } Pv=RT, \text{ so that } d=\frac{MP}{RT}.$$

* For the sake of simplicity the pressures are expressed in gravitation measure.

† Note that if the molecules of the solvent were more complex in the liquid than in the gaseous state the product MN would be unaltered since if, for example, the molecular weight was doubled the number of molecules would be halved.

Substituting these values for h and d in the first equation we have

$$P' = P - \frac{nRT}{M\bar{N}} \cdot \frac{MP}{RT} \text{ or } P' = P - \frac{nP}{\bar{N}} \text{ or } \frac{P-P'}{P} = \frac{n}{\bar{N}}.$$

Poynting [*Phil. Mag.* (42) 298] shews that the result may be explained in an extremely simple way on the assumption that unstable molecules are formed by combination of solvent and solute and that these are effective for condensation but not for evaporation. Compare also Callendar [*Proc. Roy. Soc.* 1908 (80) 466].

22. Rise in the Boiling Point. Owing to obvious experimental difficulties, it is not possible to obtain results of great accuracy by any of the methods of molecular weight determination which depend upon the direct observation of the lowering of vapour pressure. It was shewn however by Beckmann in 1889, that good results can be easily obtained if instead of observing the actual pressures we determine the temperature at which the vapour pressures are equal, e.g. the boiling points under atmospheric pressure. The method is applicable only to non-volatile solutes or at any rate to those which give an inappreciable vapour pressure at the temperature employed. In order to calculate the results in the manner described above, when the pressures were directly observed, it would of course be necessary to know the vapour pressures of the solvent corresponding to different temperatures, i.e. to map out the vapour pressure curve. Since this has been done for comparatively few liquids (and since there is probably no practically reliable formula known connecting the vapour pressures and temperature) the calculation is made in an empirical manner analogous to that employed by Raoult in the freezing point method. If we assume that the rise in boiling point is proportional to the concentration, we may determine a constant (c) for each solvent representing the rise in boiling point produced by the addition of one gram molecule of solute to any specified mass or volume of solvent; so that, if w grams of solute produce a rise of $t°$,

$$t = \frac{cw}{x},$$

where x is the molecular weight of the solute (or $t = cn$ where n is the number of molecules of solute).

If the constant is determined for one gram of solvent (a), and experimentally we use S grams of solvent, the molecular weight will be

$$x = \frac{cw}{St}.$$

Or if the constant refers to 1 c.c. of solvent (b) at its boiling point, and we take V c.c.

$$x = \frac{cw}{Vt}.$$

Some of the solvents commonly used for these determinations and their constants referred to the two systems, are as follows:—

Ethyl alcohol (a) 1150, (b) 1560 Ether (a) 2110, (b) 3030. Benzene (a) 2670, (b) 3280. Acetone (a) 1670, (b) 2220. Water (a) 520, (b) 540.

The values of the constants were obtained in the first instance by the experimental method, using substances of known molecular weight. They can also be calculated theoretically from the latent heat of vaporisation of the solvent in a manner very similar to that sketched in (**17**). In this way it can be shewn that the boiling point constant for 100 grams of solvent $= \frac{2T^2}{100L}$, where T is the boiling point of the solvent on the absolute scale and L is the latent heat of vaporisation.

In Beckmann's original apparatus, the operation of determining the rise of boiling point is carried out by boiling the weighed or measured quantity of the pure solvent in a flask, connected with an upright condenser, which is fitted with a delicate thermometer and side tube for the introduction of the solute. The flask is partly filled with glass beads or pieces of platinum foil and a platinum wire is sealed through the bottom of the flask; these precautions are taken in order to make the liquid boil uniformly and without superheating. The boiling point of the solvent is first determined, the thermometer bulb being immersed in the liquid; a weighed quantity of the solute is then introduced and the boiling temperature again recorded.

Sakurai [*Trans. Chem. Soc.* 1892, 989] uses a different form of apparatus in which the solution is heated by passing in the vapour of the same solvent and also by a small flame. The heating is so

arranged that the quantity of vapour which enters the solution is approximately equal to that which distils away. In this method unweighed quantities of solvent and solute are employed and the concentration of the solution, after the temperature observations are completed, is ascertained by analysis or by other means.

In Landsberger's method [*Ber.* 1898 (31) 458] the solution is heated and kept at its boiling point by the vapour of the boiling solvent, no external flame being used as in Sakurai's process. In this way superheating is altogether avoided. The concentration of the solution is determined by using a known weight of solute and weighing the solution after the experiment is finished.

Walker and Lumsden [*Trans. Chem. Soc.* 1898, 502] have somewhat modified Landsberger's apparatus and they read the volume of the solution, after equilibrium has been attained, instead of ascertaining its weight. (The volume constants (*b*) are then employed in the calculation.) Details of this method are given below.

Practical Work.

Determination of the molecular weights of substances by the boiling point method. Walker and Lumsden's modification of Landsberger's method is employed and ethyl alcohol is used as solvent.

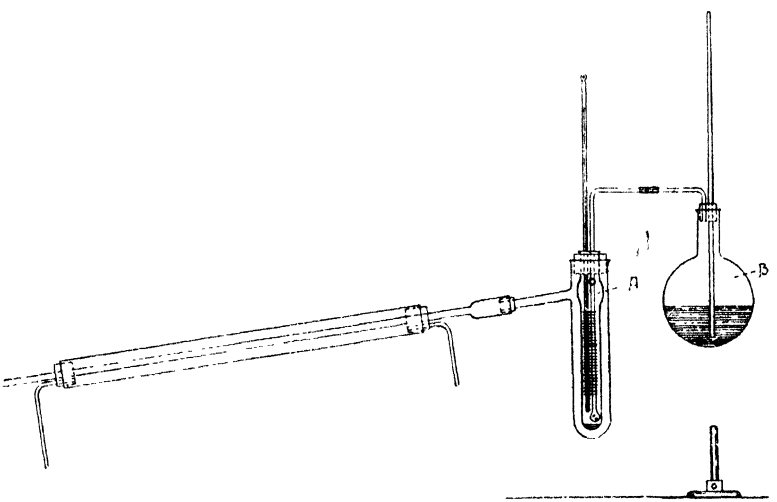


Fig. 11.

The boiling point of the solvent is first determined by placing about 12 c.c. of the liquid in the graduated boiling tube *A* and passing in the vapour from the solvent boiling in the flask *B* until drops fall from the condenser at the rate of at least one or two a second. The highest stationary temperature on the thermometer is then recorded. Some of the liquid is then removed from the tube (leaving say 5 to 7 c.c.) and a weighed quantity (0·5 to 1 gram) of the solute is introduced. The apparatus is again connected up, the vapour passed in as before and the temperature noted. The tube is then quickly removed, supported in an upright position and the volume of liquid read off. A second and a third determination may then be made by again passing the vapour into the same solution and recording the boiling temperatures and volumes. Landsberger recommends the introduction of a piece of porous tile to the liquid in the boiling flask in order to ensure regularity in the boiling; a fresh piece of tile should be added each time the boiling is interrupted. The thermometer employed should have a small bulb and light stem. For determinations of approximate accuracy a thermometer of the ordinary type, reading to $\frac{1}{10}$ degree, may be employed.

23. *Method based on the lowering of solubility.*

It has been pointed out by Nernst that there is great similarity between the vaporisation of a liquid and the solubility of a solute in a solvent. Just as a liquid tends to give off vapour until, at a given temperature, the vapour pressure reaches a definite maximum value, so the solute tends to throw off its particles into solution and will go on dissolving until the osmotic pressure of its molecules in solution balances this tendency to dissolve. This maximum osmotic pressure of the saturated solution at a given temperature is called the 'solution pressure' of the solute.

If a foreign substance be dissolved in the solute, its solution pressure, at a given temperature, will be lowered, in a manner quite analogous to the lowering of the vapour pressure which has been referred to above (**19**). [In fact the solution pressure and the vapour pressure will both be lowered and in the same proportion.]

If, for example, we first determine the solubility of pure ether in water at a given temperature and then repeat the experiment with ether in which a small quantity of some substance (which is soluble in ether and not in water) has been dissolved, we shall obtain a lower result in the second case.

Generally, suppose we have two solvents *A* and *B* which dissolve one another only to a limited extent and a solute' *C* which dissolves in *A* but not in *B*. It is then possible to determine the molecular weight of *C* by observing

the lowering of solubility of A in B when the solute is dissolved in A. The method of calculation is quite analogous to that employed in the determination of molecular weights by the vapour pressure method.

We first determine the solubility of pure (A) in (B) ($=P$) by shaking up a sufficient excess of (A) with (B) and determining the concentration of the resulting saturated solution (by titration, or by freezing point determination etc.). A solution of w gram of the solute (C) in S grams of the solvent (A) is then shaken with (B) as before and the solubility of (A) in (B) again determined ($=P_1$). Then if x is the molecular weight of (C) and M that of (A),

$$x = \frac{wMP_1}{S(P-P_1)} \qquad \text{(compare (19)).}$$

Nernst* in the first instance determined the molecular weights of several compounds which are soluble in valeric acid but not in water. valeric acid being only slightly soluble in water. The solubilities in water of pure valeric acid and of valeric acid in which the solute was dissolved, were determined by titration. A single example may here be given in illustration.

0·182 gram of benzene dissolved in 4·13 grams of valeric acid at 13° lowered the solubility of the latter in water, the ratio of the solubilities being as 10·48 to 9·90. The molecular weight of valeric acid being 102 that of benzene is

$$\frac{0{\cdot}182 \times 102 \times 9{\cdot}9}{4{\cdot}13 \times 0{\cdot}58} = \text{about } 76,$$

the theoretical value being 78.

24. Molecular weights of pure substances in the liquid state.

The problem of ascertaining the molecular weight of a pure substance in the liquid state is of course entirely distinct from that of finding the molecular weight of a dissolved substance. It has often been the custom to assume that the value is always the same in the liquid as in the gaseous condition; but that such a conclusion is by no means justified is evident if one considers the tendency of many substances, such as acetic acid or hydrofluoric acid, to form vapours of greater molecular complexity near the boiling point.

Several methods have been suggested for ascertaining the degree of complexity of the molecules of liquids, but the only one which has been thoroughly investigated, in a practical way, is the surface tension method of Eötvös [*Wied. Annalen* 1886 (27) 448]. If M is the molecular weight of a liquid, assumed to be in spherical form, and V is the specific volume, the 'molecular' surface will be proportional to $(MV)^{\frac{2}{3}}$ (since the volume varies as the cube and the surface as the square, of the radius). This value multiplied by the surface tension, γ, is called the molecular surface energy. The surface tension of all liquids diminishes as the temperature increases and becomes zero at about the critical temperature of the liquid. The work necessary to produce one mole of a substance in the gaseous state, at constant pressure, varies with the temperature in the same way for different substances, i.e. it is proportional to the temperature reckoned from absolute

* *Zeit. Physikal. Chem.* 1890 (6) 16.

zero (6). In a similar way, it appeared probable that the work required to produce a molecular surface (i.e. one over which an equal number of molecules are distributed) might vary with the temperature in the same way for different liquids. Eötvös found that for many liquids the rate of change of molecular surface energy with temperature is constant for different liquids. But in certain cases abnormal results were obtained and these were ascribed to association in the liquid molecules.

The method has been exhaustively tested by Ramsay and Shields [*Trans. Chem. Soc.* 1893, 1089; *Phil. Trans.* 1893 (184) 647] and they have somewhat modified the original formula of Eötvos.

Their results may be very briefly referred to in the following way :—

For a large number of liquids such as ethyl acetate and many other esters, ether, benzene, nitrobenzene, carbon disulphide, carbon tetrachloride, and phosphorus trichloride, it is found that

$$\frac{\gamma_1 (M V_1)^{\frac{2}{3}} - \gamma_2 (M V_2)^{\frac{2}{3}}}{t_2 - t_1} = K \text{ (about } 2{\cdot}12),$$

where γ_1 and V_1 are the surface tension (in dynes per cm.) and the specific volume $\left(\frac{1}{D}\right)$ at t_1, and γ_2 and V_2 are the respective values at t_2. M is the molecular weight of the substance as determined by its vapour density.

The molecular surface energy is therefore a linear function of the temperature. The line representing the variation with temperature however has its origin not at the critical temperature but at about 6° below. Good agreement was generally obtained at temperatures between the ordinary temperature and about 25° below the critical.

But in certain other cases, such as water, fatty acids, alcohols and acetone the value of K is found to be too small, i.e. the value of M must be multiplied by some factor (the association factor) in order to obtain the number 2·12. This factor (greater than 1) gives the average number of simple molecules which have united to form a complex molecule.

Calculated in this way, the results of experiment indicate that the molecular weights of the liquids last mentioned, at about the ordinary temperature, correspond to the formula greater than the normal, the degree of association becoming smaller as the temperature rises.

It must be remembered however that the degree of association arrived at by this method is only relative; that is, it indicates the degree of molecular complexity only if one assumes that the substances which behave 'normally' have, in the liquid state, the single or unassociated formulae which have been arrived at by vapour density determination. Further, it may be mentioned that in certain cases the value of K is *greater* than 2·12 and on the foregoing assumption this would imply that such liquids are dissociated. Compare Dutoit and Majoïu, *J. Chim. Phys.* 1909 (7) 169.

25. *Polymeric compounds* are defined as those which possess the same empirical formulae but different molecular weights. It is generally understood, however, that the compounds in question must be obtainable from one another in one direction at any rate,

if not in both. Thus paracyanogen, paraformaldehyde and cyamelide have formulae more complex than C_2N_2, CH_2O and HCNO respectively, and can all be obtained by condensation of the simple compounds mentioned. For the same reason benzene is often regarded as a polymer of acetylene; but acetic acid $C_2H_4O_2$ is not regarded as a polymer of formaldehyde CH_2O since there is nothing more than the numerical relation between them.

In the case of acetic acid vapour near its boiling point, nitrogen tetroxide vapour, sulphur vapour, liquid water, liquid alcohols, etc. (**24**) and of many hydroxy-compounds when dissolved in benzene and similar solvents, we observe a similar aggregation, that is to say the formulae indicated, by the methods already described, are more complex than the 'normal' formulae. But in these cases the values continuously vary with the temperature or with the volume, within certain limits. The name *association* is usually applied in such cases, a distinction therefore being implied between polymerisation and association. Such a distinction is evidently convenient, but it is not always easy to draw a hard and fast line between the two classes. Perhaps the most practical distinction lies in the fact that association is always reversible by means of the conditions—temperature or volume as the case may be—whereas the class of condensation-products known as polymers require, in most cases, something more than mere temperature or volume alteration to effect the transformation in both directions. The polymeric modifications can generally each exist, separately, in a pure state at the same temperature through a considerable range. Probably, however, in many cases one is to be regarded as the stable form, the other being a state of false equilibrium; or the stable condition may correspond to an equilibrium mixture of the two. On this view the distinction between polymeric and associated compounds would be concerned only with a difference in reaction-velocity. A distinction between the two classes appears to be more justifiable when an actual difference in chemical constitution can be shewn. Compare for example the instance of paraldehyde (**36**).

26. Molecular weights of solids.

It is generally the custom to represent the formulae of solid

substances by the same symbols as are used for molecular formulae. We write the formulae for solid sodium chloride and ferric oxide as NaCl and Fe_2O_3 in the same equations as we write carbon dioxide or hydrogen as CO_2 and H_2. Yet the latter formulae have been established by molecular weight determination and the former have not. More correctly we should write $(Fe_2O_3)_x$ $(NaCl)_x$ to express the fact that the values are unknown.

Very few methods have yet been suggested by which it is possible to determine the molecular weights of solids. There are some cases in which a certain amount of information can be gained by application of the partition law. If, for example, a solid substance *A* dissolves in another solid *B*, to form a true solid solution, and also in another solvent *C* in which *B* is not soluble, one may at any rate ascertain whether the molecular state of *A* is the same in both solvents or not (see page 321).

Another method, which is applicable to either liquid or solid solvents, depends on the lowering of solubility, in a given solvent, which a substance experiences when a small quantity of another substance is dissolved in it; this has been referred to in (**23**). Compare also (**18**).

It must be observed that these methods refer only to the molecular state of the solid when dissolved in a solid solvent, not to that of the solid itself in a pure state.

CHAPTER VI.

LAWS OF COMBINATION BY WEIGHT.

27 THE law of *conservation of mass*, which states that the total mass of the substances taking part in a chemical change is constant, appears to have been first formulated by Empedocles in the year 500 B.C. The law was practically demonstrated in a quantitative way by Lavoisier towards the end of the 18th century. This law is generally accepted as an axiom and is for practical purposes as well established as any so-called law in chemistry. It must be remembered however that the recent advances in radioactivity, and the modern theories of the nature of matter, may necessitate a modification in the way of stating the generalisation. Reference may also be made to the researches of Landolt and Heydweiller [*Ann. der Physik.* 1901 (5) 394] who obtained indications of a loss of weight in certain reactions such as in the reduction of silver solutions by ferrous salts. They have more recently shewn however that these results may be explained by the slow recovery of the vessels from disturbing effects, such as thermal expansion*.

The law of *definite proportions* which appears to have been arrived at simultaneously by several chemists in Lavoisier's time, states that the same compound always contains the same elements united in the same proportion. This law was called in question by Berthollet, who thought that in some cases the proportions might be continuously varied; but since the more exact investigations of Proust and later, the classical researches of Stas, the law has been regarded as absolute and unconditional.

[Note that the converse proposition, that invariability of composition must of necessity indicate a chemical compound, does not

* Compare however Zengelis, *Zeit. Physikal Chem.* 1909 (65) 341 and Tollens, *Ber.* 1909 (42) 2013.

at all follow, and many mistakes have from time to time been made owing to this assumption. See pages 318 and 345.]

The law of *multiple proportions*, due to Dalton, states that when two elements, A and B, unite together in more than one proportion the quantities of A which unite with a given weight of B, stand to one another in a simple ratio (or are multiples of a common factor). This was interpreted to mean that the atoms unite in proportions which may be expressed as simple whole numbers. Although this law is sufficiently evident in most of the simple inorganic substances it can scarcely be said to apply to the more complex series of compounds such as the hydrocarbons. Compare for example the paraffins such as $C_{21}H_{44}$ and $C_{31}H_{64}$.

With these laws it is usual to include the law of reciprocal proportions, which states, that if there are compounds AB, AC and BC, the quantities of A and B which respectively combine with a given weight of C are in the proportion in which A unites with B or are simply related to that proportion.

[For example: 35·45 parts of chlorine unite with 8 parts of oxygen or with 23 parts of sodium; 8 parts of oxygen unite with 23 parts of sodium. But 8 parts of oxygen may also unite with 11·5 parts of sodium.]

28. Equivalent weights.

The weights of two substances which exactly combine with, react with or replace one another, are said to be chemically equivalent. Thus 39·15 parts of potassium combine with 35·45 parts of chlorine; 56·16 parts of caustic potash react with 49·03 parts of sulphuric acid, and 39·15 parts of potassium replace 1·008 parts of hydrogen. In determining equivalent weights therefore one in reality finds the ratio between two quantities although in practice it is the custom to refer the values to a common standard. We can in fact assign to each element A, B, C... numerical constants c_1, c_2, c_3... representing their combining ratios. The composition of a compound of A with B will then be $n_1c_1 + n_2c_2$ where n_1 and n_2 are, in general, small whole numbers.

In assigning these numbers there is a certain obvious advantage, as regards simplicity, in taking hydrogen as unity. But

practically there are very few elements whose equivalent weights can be determined accurately by combination with, reaction with, or replacement of, hydrogen. Oxygen, or the halogens, are far more suitable for this purpose and if the equivalent weight has then to be referred to hydrogen, it becomes necessary to determine with the greatest accuracy the ratio between the equivalent weights of oxygen and hydrogen, or the halogen and hydrogen.

The ratio between the equivalent weights of oxygen and hydrogen is 7·94 : 1. We might therefore choose to define the equivalent weight of an element as that weight of it which can combine with or replace one part by weight of hydrogen or 7·94 parts of oxygen. There are reasons, however, which will be referred to later, which make it desirable to fix the equivalent weight of oxygen as 8 exactly. In this case the equivalent weight of hydrogen will be 1·008. [More exactly 1·00775. Noyes, *J. Am. Chem. Soc.* 1907, 1718.]

Similarly we may refer equivalent weights to 35·18 or 35·45 parts of chlorine, and so on.

Strictly speaking, the number assigned to an element as the equivalent weight refers only to its combining ratio as regards the particular compound employed in the determination. If, for example, we determine the equivalent weight of hydrogen from the composition of water, taking the equivalent weight of oxygen as 8, we obtain the value 1·008; but if hydrogen dioxide were employed instead of water, the value for hydrogen would be 0·504.

The term equivalent weight is often employed for compounds as well as for elements. Here again it is important to notice that the value refers only to the particular reaction or property of the compound which is under consideration. If we are considering the neutralisation of acids and bases we may take the equivalent weight of an acid as that weight of it which contains one part by weight of replaceable hydrogen. The equivalent weight of a base, again, is that weight of it which can neutralise one formula-weight of a monobasic acid. But when we say that the equivalent weight of potassium permanganate is 31·6 we refer to its oxidising capability, i.e. to that weight of it which can perform functions equivalent to the oxidation of one part by weight of hydrogen.

The following are some of the principal methods which have been employed in the determination of equivalent weights.

I. *The replacement of hydrogen in acids by metals.*

It is necessary of course to employ acids which are not reduced under the conditions, e.g. nitric acid is not applicable.

[The replacement of a metal in a salt by another metal should theoretically answer a similar purpose, but in this case complications are liable to occur, such as the formation of basic salts or the evolution of hydrogen from water employed.]

II. *Direct oxidation of the element.*

This is usually effected by treatment with nitric acid; the resulting nitrate, hydrated oxide or acid being afterwards decomposed by heat.

III. *Double decomposition of salts* (e.g. silver salts and chlorides or bromides. Barium salts and sulphates, etc.).

IV. *Reduction of oxides by hydrogen* (e.g. CuO to Cu).

V. *Decomposition of salts by heat* (e.g. $KClO_3$ to KCl, $KAuCl_4$ to KCl and Au, etc.).

VI. *Electrolytic method based on Faraday's law.*

VII. *Accurate determination of the gaseous densities and ratio of combination by volume* (e.g. hydrogen and oxygen).

The ratio of the equivalent weights of oxygen and hydrogen which is of such fundamental importance, was first determined by Berzelius and by Dulong in 1819, the method employed being the reduction of cupric oxide by hydrogen. More exact determinations were afterwards made by Dumas, and by Erdmann and Marchand (1842) who used a similar method. But in more recent years it has been shewn that various sources of error existed in the earlier method of conducting this experiment, and important modifications have since been introduced by Cooke and Richards [*Am. Chem. Journ.* 1887 (10) 81], Keiser [*ibid.* 1888 (10) 249], Dittmar and Henderson [*Proc. Phil. Soc. Glasgow*, 1891 (22) 33], and Morley [*Am. Chem. Journ.* 1896 (17) 267]. Lord Rayleigh [*Proc. Roy. Soc.* 1889 (45) 425] determined the ratio by direct combination of the weighed gases.

The ratio of combination by volume was accurately determined by Scott [*Proc. Roy. Soc.* 1888, 396], and later by Morley and by Leduc. These results, in conjunction with accurate determinations of the relative densities by Lord Rayleigh and by Morley, afford independent means of arriving at the ratio of combination by weight.

Practical Work.

Determination of the ratio between the reacting equivalent weights of certain compounds.

For example (*a*) ferrous sulphate and potassium permanganate, (*b*) iodine and sodium thiosulphate, (*c*) silver nitrate and sodium chloride.

Determination of the equivalent weights of certain metals.

(*a*) *By replacement of hydrogen in acids.*

An appropriate quantity of the metal, very accurately weighed, is introduced into one of the following forms of apparatus (Figs.

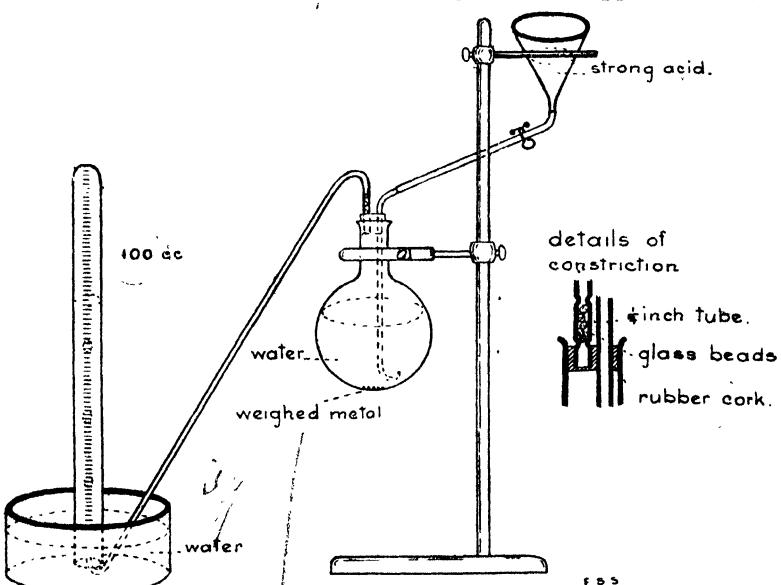


Fig. 12.

12 and 13) and acted upon by dilute hydrochloric acid. The resulting hydrogen is collected in the measuring tube, levelled,

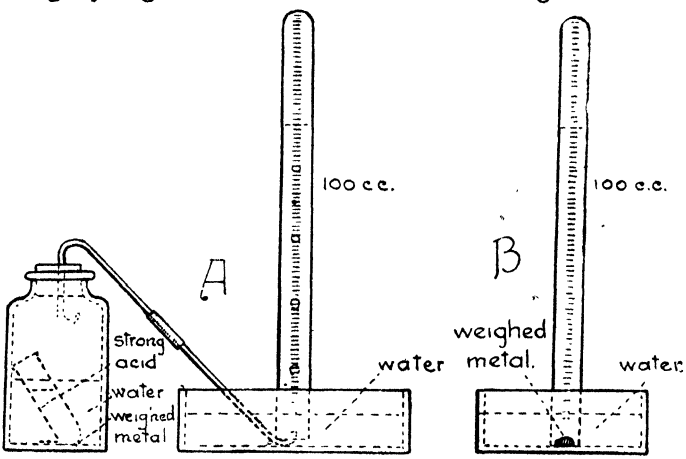


Fig. 13.

allowed to stand for a few minutes, the temperature of the surrounding air being noted, as follows:

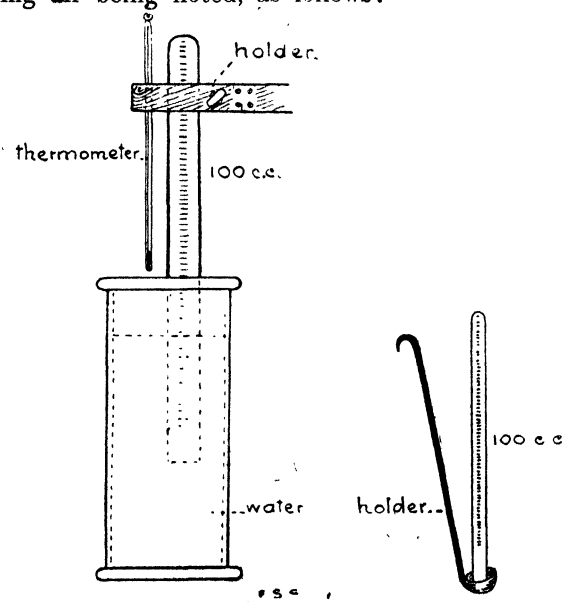


Fig. 14.

The weight of the metal taken must be adjusted to the capacity of the measuring tube employed—usually about 0·1 gram is sufficient.

Weight of metal taken = W gram.

Volume of hydrogen = V c.c.

Temperature = $t°$.

Barometer pressure = P.

Maximum pressure of aqueous vapour at $t° = p$.

Corrected volume of hydrogen $V \times \frac{273}{273+t} \times \frac{P-p}{760} = V_0$.

Weight of hydrogen = $\frac{V_0}{11110}$; therefore equivalent weight of the metal = $\frac{W \times 11110}{V_0}$. [Equivalent weight of hydrogen = 1.]

(*b*) *By oxidation.*

The metal (e.g. tin) is weighed out into a porcelain crucible. Strong nitric acid is carefully added drop by drop by means of a pipette, the crucible being partly covered by the inverted lid in order to prevent loss by spurting. The crucible is very gently warmed and the addition of nitric acid is continued until the violent action ceases. The crucible is then tilted, the small pointed flame directed towards the upper part and the acid evaporated off as carefully as possible. The whole is then strongly heated. The crucible is cooled in a desiccator and weighed. It is advisable now to repeat the treatment with nitric acid and weigh again in order to ascertain if the oxidation is complete. Weight of metal taken = W.

Weight of oxide obtained = W_1; therefore equivalent weight of metal = $\frac{W}{W_1 - W} \times 8$. [Equivalent weight of oxygen = 8.]

Determination of the ratio between the equivalent weights of substances by the electrolytic method, based on Faraday's law.

The nature and arrangement of the necessary apparatus will be apparent from the following sketch.

The two copper plates are cleaned by immersing them for a few seconds in strong nitric acid. They are then carefully washed with water and one of them is further washed with alcohol and

dried in a steam oven and weighed. The whole apparatus is then fitted up as illustrated and a current is passed under such conditions that about 50 c.c. of hydrogen are collected in half an hour.

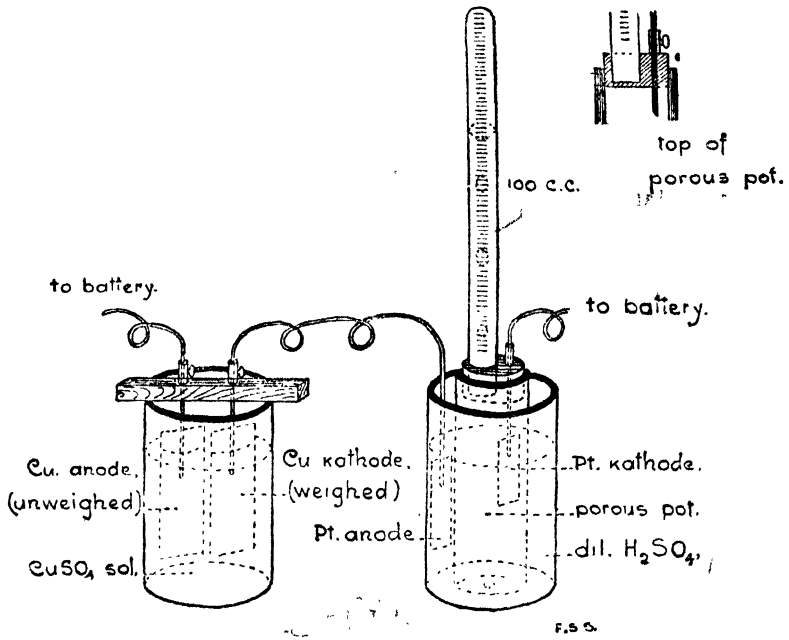


Fig. 15.

The following points may be noticed:

(i) If the current density is too high low results will be obtained, since a little hydrogen may be evolved at the kathode. On the other hand, if it is too low, some copper appears to dissolve as cuprous salt. The best results require a current density of about ·01 ampere per sq. cm. of kathode.

(ii) The solution of copper sulphate employed should be about 15%. (Some recommend the addition of 5% of sulphuric acid and 5% of alcohol.)

(iii) After the operation, the kathode copper plate is washed first with water, then with alcohol, then dried and weighed as before. Theoretically the loss of weight of the anode plate should be equal to the gain in weight of the kathode, but the former is

not suitable for measurement since some oxidation invariably takes place.

(iv) The hydrogen in the measuring tube is transferred to the levelling vessel and its volume corrected for temperature, pressure, etc. Care must of course be taken, in order to avoid the retention of gas bubbles, that the measuring tube does not project quite through the stopper in the porous pot.

By Faraday's Law the increase of weight on the kathode stands to the weight of hydrogen obtained in the ratio of the equivalent weights.

In a similar way the ratio between the equivalent weights of other elements such as copper and silver may be determined. In the silver voltameter, one uses a platinum crucible as kathode and a rod of silver as anode, the latter being surrounded by a porous pot. The electrolyte is a 10% solution of silver nitrate. The silver deposited must be thoroughly washed with water, then with alcohol, and dried at about 160° C.

Determination of the ratio of the equivalent weights of oxygen and hydrogen.

This ratio being of fundamental importance requires the greatest possible accuracy in determination, and many special precautions have to be taken. The following way of conducting the experiment must be regarded merely as a general illustration of the method.

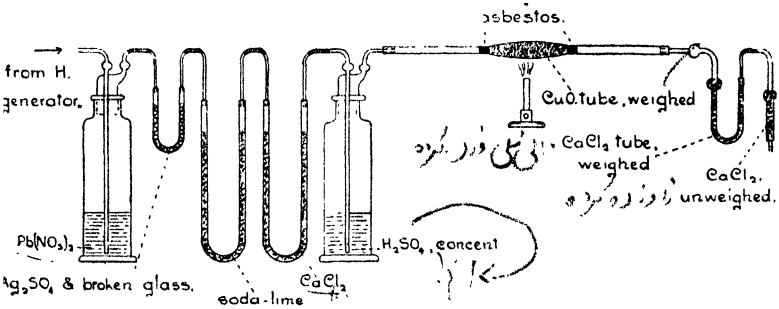


Fig. 16.

The copper oxide is first heated to low redness in a current of dry air in order to remove all traces of moisture. The ends of

the tube are then closed with the stoppers and the tube allowed to cool. The stoppers are quickly removed and the tube is accurately weighed, the stoppers being immediately replaced. The chloride of calcium tube is weighed with similar precautions.

In the meantime a current of hydrogen is being passed through the purifying and drying tubes in order to remove all traces of air. The apparatus is then put together as shewn in the sketch and the current of hydrogen is passed for a sufficient time to remove all the air from the weighed tubes. This is essential, not only in order to avoid danger from explosion, but also because any residual oxygen would, if combined with the hydrogen, vitiate the result. The current of hydrogen must not be too rapid, otherwise the purification is incomplete.

The oxide of copper is now heated to redness and the slow current of hydrogen continued until the reduction is complete, or nearly so. Care must be taken that the junction between the copper oxide and calcium chloride tubes is 'flush,' or drops of water might be condensed between the two.

The hydrogen generating apparatus is now removed and a current of nitrogen, from a gas holder, is passed through the apparatus while the tube cools. The object of this is (*a*) that the reduced copper may cool in an atmosphere of nitrogen, so as to avoid the occlusion of hydrogen, and (*b*) that the hydrogen in the weighed tubes may be replaced by a gas whose density is approximately the same as the air which they originally contained.

The tubes are then weighed as before. The loss of weight in the copper oxide tube represents the oxygen consumed, and the gain of weight in the chloride of calcium tube the weight of water produced. Note that in the determination of the ratio by this method the weight of hydrogen is obtained only by difference and all errors are consequently thrown on the hydrogen.

Determination of the ratio of the equivalent weights of carbon and oxygen in carbon dioxide.

This experiment may also be regarded as a proof of the composition of carbon dioxide and therefore serves as an illustration of a method of ascertaining the weight of an element present in a

molecule of one of its gaseous compounds, the molecular weight having been previously determined. (Compare **32.**)

Pure carbon in the form of graphite is extremely difficult to burn, consequently one is obliged to employ purified charcoal. This therefore necessitates the determination of the hydrogen as well as carbon. The process is in fact quite analogous to an organic combustion. If pure carbon were employed one could directly determine the ratio of carbon burnt to carbon dioxide produced.

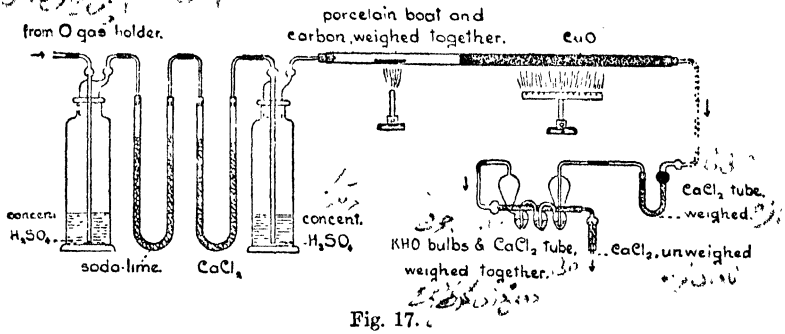


Fig. 17.

The charcoal, contained in a porcelain boat, is introduced into the combustion tube heated to low redness, a current of pure dry oxygen is passed over it and the products collected in the weighed calcium chloride tube and potash bulb respectively. The charcoal, together with the boat, are weighed before and after the experiment. It is not absolutely necessary that all the charcoal should be consumed.

Loss of weight in boat = carbon and hydrogen consumed
$= W.$

Gain of weight in calcium chloride tube = water formed
$= W_1.$

Gain of weight in potash bulb = carbon dioxide produced
$= W_2.$

Weight of hydrogen consumed is $\frac{W_1}{9}$; therefore weight of carbon consumed is $W - \frac{W_1}{9}$.

Observe that

(i) The products of the combustion are passed over copper oxide, which has been previously heated to low redness, before they enter the absorption vessels. The object of this is to ensure the oxidation of any carbon monoxide which might be formed.

(ii) After the operation is complete, a slow current of dry air is passed through the whole apparatus whilst the tube is cooling in order completely to displace the oxygen. This process takes about twenty minutes.

(iii) The current of oxygen should not be too rapid, else the products may not be completely absorbed.

(iv) The absorption tubes should be removed, the ends closed with the stoppers, and allowed to remain for half an hour in the balance room before they are weighed.

Proofs of the composition by volume of certain common gaseous substances.

I. *Carbon dioxide.*

Charcoal is supported in the jar of oxygen connected with a water-valve. It is ignited by an electric spark. A layer of oil is floated on the top of the water in the valve to prevent absorption of the gas. After cooling it is observed that no change in volume has occurred, showing that the volume of the carbon dioxide produced is equal to that of the oxygen from which it was formed. The composition of sulphur dioxide may be illustrated in a similar way.

II. *Ammonia.*

Pure dry ammonia is subjected to the action of electric sparks till the volume, after cooling, no longer increases. The increase of volume is noted, the mercury of course being levelled when the readings are taken. A portion of the resulting gas is transferred to a bent eudiometer filled with water, mixed with a suitable volume of oxygen and exploded by a spark from the induction coil. Two-thirds of the diminution in volume represents the hydrogen present.

(Note that the decomposition by sparking is not complete but that the residual ammonia is practically removed when the gas is transferred over water.)

III. *Air.*

A known volume of air is exploded with a measured excess of hydrogen in a bent eudiometer over water, the usual precautions being taken. Other methods of removing the oxygen may also be employed as, for example, absorption by an alkaline solution of pyrogallol, a stick of moist phosphorus, etc. It is usual at this stage to estimate the carbon dioxide by Pettenkofer's method by shaking a known large volume of air with a measured excess of standard baryta water and titrating back with oxalic acid, using phenol phthalein as indicator.

The hygrometric method of estimating the water by observation of the dew-point in various forms of apparatus and reference to table of 'vapour tension' is also illustrated.

The volume composition of the following gases has been illustrated in the lecture.

(*a*) Hydrochloric acid gas by the usual synthetical and analytical methods.

(*b*) Water by Cavendish's experiment and by Hofmann's modification of the latter.

(*c*) Hydrogen sulphide, marsh gas and ethylene by decomposition with a series of electric sparks.

(*d*) Ammonia by decomposition with chlorine according to Hofmann's method.

CHAPTER VII.

ATOMIC WEIGHTS.

29. THE hypothesis that matter is built up of small individual, indestructible, particles, or atoms, is often attributed to Democritus; others give the credit to Leucippus (428 B.C.) of whom Democritus was a pupil. It is probable however that the idea originated at a much earlier date. This mere vague conception of the ancient philosophers was transformed by Dalton (1804) into a concrete scientific theory, based on quantitative measurements. The laws of combination by weight and particularly the law of multiple proportions, are evidently easily accounted for if we attribute a fixed unalterable mass to each individual atom of the same kind and assume that atoms of different kinds, having different masses, combine together in a simple way to form compounds.

If now we define the equivalent weight of an element in the manner above suggested (**28**) taking, for example, the equivalent weight and atomic weight of hydrogen as unity, it is evident that the atomic weights of elements must be either identical with their equivalent weights, or multiples of them by a whole number. That is,

$$\text{Atomic weight} = \text{Equivalent weight} \times n,$$

where n is generally a small whole number*.

Observe that n may have more than one value since the same element may have more than one equivalent weight. Experience

* Because in general one deduces the equivalent weights from the composition of the simpler compounds. If the equivalent weight of carbon, for example, were derived from the composition of some of the more complex hydrocarbons, n would not necessarily be a whole number.

shews that if the equivalent weight is determined by analysis or synthesis of *hydrogen* compounds the value of n never exceeds 4. The equivalent weight deduced from *halogen* compounds seldom gives a value for n greater than 5 and never greater than 6*, whilst from *oxygen* compounds the maximum value is 8.

The first step in determining the atomic weights is to find the value of the equivalent weight with the greatest possible accuracy. In order to gain some insight into the extraordinary care and attention to minute detail which is necessary in making equivalent weight determinations for this purpose, the student is advised to refer to the Stas Memorial Lecture, *Trans. Chem. Soc.* 1893 (1).

It remains then to discover the value of n—that is, the whole number by which the exact equivalent weight has to be multiplied in order to give the atomic weight. [The value sought for the atomic weight is of course not an absolute mass but the ratio between the atomic weight of the element in question and that of hydrogen, the latter being taken as unity. (Or as 1·008, according to the system adopted.)]

There are several ways of ascertaining this value. Some of these depend on generalisations made from empirical observation, while others are based upon theoretical considerations which involve the molecular hypothesis. It is because of these last named methods that it becomes necessary to deal with the subject of molecular weights before attempting to give a summary of the methods used in fixing the value of the atomic weights; although the atomic theory came into existence long before the molecular hypothesis assumed a definite shape.

The principal methods are the following:

30. I. Application of the observed relationship between the specific heat of solid elements and their atomic weights.

Dulong and Petit in 1818 having determined the specific heats of several elements (Cu, Au, Fe, Pb, Ni, Pt, S, Sn, Zn, Bi, Co, Ag, Te) in the solid state, noticed that the values diminished as the atomic weights increased and, in many cases, the product obtained by multiplying the specific heat by the atomic weight appeared to be constant and equal to about 6·25. They concluded from their results that the atoms have all the same capacity

* Osmium octafluoride OsF_8 has been isolated by Ruff, *Ber.* 1913, 920.

for heat [*Ann. Chim. Phys.* 1819 (10) 403]. Many exceptions were noticed but these were attributed to errors in the atomic weights which were assigned at that time to the elements in question. Neumann in 1831 extended this 'law' in such a way as to include compounds, stating in effect, that the specific heats of compounds of similar composition are inversely as their formula weights. Later investigations of Regnault and of Kopp and others shewed that although the law is approximate only, it is generally applicable. The average value of the constant is about 6·4 but in the case of non-metallic elements of low atomic weight the value is 'abnormal.' For example, P 5·5, F 5·0, O 4·0, Si 3·8, B 2·7, C 1·8, H 2·3. (The values for F, O and H were obtained by subtraction from the atomic heats of their compounds.)

For practical purposes the laws may be stated thus:

Dulong and Petit's law—At. wt. × S.H. = a constant = about 6·4.

Neumann's law—Mol. wt. × S.H. = 6·4 × a where a is the number of atoms in the molecule. [Or, more strictly, the number of atoms indicated by the formula employed. Obviously the last named law cannot be used for finding molecular weights, since unless we know the molecular formula we do not know the number of atoms in the molecule.]

The specific heats of the elements mentioned were usually determined as mean values between temperature intervals from 100° downwards. Weber in 1875 shewed however that the mean specific heats rise with the temperature and that in the cases of carbon, boron and silicon the rise is very rapid. The mean values are therefore unsuitable for comparison and he calculated the true specific heats at various temperatures. The specific heat of carbon was determined at temperatures from −80 to 1060° and it was shewn that the value increased rapidly at first, then more slowly and at about 600° the rise became insignificant. With silicon the limit was reached at about 200°. The atomic heats calculated from the specific heats at the temperatures at which the rise becomes insignificant, give numbers which are still low but are not far removed from the common constant. It appeared therefore that Dulong and Petit's law is universally applicable if the specific heats are taken at the temperature above which the rapid rise ceases. Weber also shewed that the specific heats of the

different allotropic modifications of an element, such as carbon, which are very different at low temperatures, approximate more as the temperature rises and become almost equal at the limiting temperature referred to.

A similar rapid rise of specific heat with temperature was observed in the case of beryllium, the value increasing from 0·3756 at 0° to 0·6206 at 500°. Beyond this temperature the value becomes nearly constant.

The more recent investigations of Tilden [*Phil. Trans.* 1900 (194) 233; *Trans. Chem. Soc.* 1905, 551, etc.] indicate that there is no one condition under which the law of Dulong and Petit is true for all elements. The specific heats of nickel and cobalt for example both rise with temperature, and that of nickel increases more rapidly, so that the values become more divergent as temperature rises. They approach each other at temperatures of -78 to $-182°$ and the mean atomic heats calculated for this range are about 4. It is further shewn that even in the case of several metals whose specific heats are taken at temperatures where the change with temperature is slow, the value of the 'common' constant may vary from 5·64 to 7·90. The author considers that it would be best for practical purposes to take the mean specific heats between 0° and 100° and to recognise carbon, boron, silicon and beryllium as exceptions.

It is quite evident from what has been said that the law of Dulong and Petit is *by itself* entirely useless as a means of finding the exact value of the atomic weights. [This has been recognised from the first, but mention is here made of the circumstance since the mistake is so frequently made of regarding the constant as an exact number.] But if the equivalent weight of an element has already been exactly determined we can make use of this approximate law in deciding the value of n, since the product S.H. $\times nE$ must give a number approximating to 6·4. The equivalent weight of aluminium for example was found to be 9 and its specific heat 0·218; evidently the whole number n must be 3 and the atomic weight 27.

The equivalent weight of beryllium is 4·55; if the value of the specific heat is taken as 0·6206, the nearest value for n will be 2 and the atomic weight will be 9·1. But the atomic heat will

still, as in the cases of carbon, boron and silicon, be considerably below the mean value.

As an example of the application of Neumann's law we may take the case of lead bromide, whose specific heat is 0·0533. The formula weight of $PbBr_2$ is, in round numbers, 367 and

$$0{\cdot}0533 \times 367 = 19{\cdot}56,$$

that is, approximately three times the common constant.

31. II. The law of isomorphism.

Mitscherlich, from a study of the crystalline forms of certain arsenates and phosphates, came to the conclusion that substances of a similar chemical constitution crystallise in the same, or nearly the same, form. Substances which not only crystallise in the same form but are capable of forming a continuous series of homogeneous mixed crystals are said to be isomorphous, and in this sense the generalisation of Mitscherlich is usually called the law of isomorphism*. Practically the property may be indicated by ascertaining whether the one substance can act as a nucleus in bringing about crystallisation from a supersaturated solution of the other, i.e. a crystal of one may continue to grow in a solution of the other without alteration of form. Familiar examples are the alums $M'M'''(SO_4)_2 12H_2O$ or the 'vitriols' $M_2'M''(SO_4)_2 6H_2O$. Thus we may obtain a complete series of crystals, identical in form, from chrome alum $KCr(SO_4)_2 12H_2O$ and aluminium alum $KAl(SO_4)_2 12H_2O$. Regarding the Cr as replacing the Al, or *vice versa*, the one metal may replace any proportion of the other provided always that the weights which replace one another are chemically equivalent, i.e. in the proportion of 52 parts of chromium to 27 of aluminium. The resulting homogeneous crystals are to be looked upon as solid solutions, since the two substances are miscible in all proportions, i.e. the relative composition is continuously variable. [Compare page 320.] [In certain cases however the miscibility is limited; for example,

$MgSO_4 . 7H_2O$ and $FeSO_4 . 7H_2O$; $BeSO_4 . 4H_2O$ and $BeSeO_4 . 4H_2O$;

$NaClO_3$ and $AgClO_3$.]

*. See article on Isomorphism by Hutchinson in Watt's *Dictionary of Chemistry*, III. 88, and *An Introduction to Chemical Crystallography*, by Groth, translated by Marshall, London, 1906. Also Retgers *Zeit. physikal. Chem.* 1890 [5] 436.

When in the above cases the individual crystalline forms are different, the substances are said to be isodimorphous.

Since then chemically analogous elements can, in this way, often replace one another without alteration of the crystalline form, the property of isomorphism has in some cases been made use of in order to fix the value of atomic weights. The atomic weights of chromium and iron for example were at one time taken at twice their present value, ferric oxide being written as FeO_3 and the green oxide of chromium as CrO_3. But the higher (acidic) oxide of chromium forms salts, the chromates, which were found to be isomorphous with the sulphates, and since, for independent reasons, sulphuric anhydride was regarded as SO_3, the higher oxide of chromium required the formula CrO_3. The green oxide must therefore be Cr_2O_3, and since this is isomorphous with ferric oxide, the latter is Fe_2O_3; for this reason therefore the atomic weights of the two metals were halved.

As an example in more recent times, when the law of isomorphism was instrumental in fixing the true value of the atomic weight of an element, the case of gallium may be mentioned. The equivalent weight was found by de Boisbaudran (1875) to be 23·33 so that its atomic weight must be $n \times 23{\cdot}33$. But gallium sulphate with ammonium sulphate forms a double salt which is isomorphous with ammonium aluminium alum

$$(NH_4)\,Al\,(SO_4)_2\,12H_2O.$$

Hence the value of n is 3 and the atomic weight 70. In other words 70 parts of gallium replace 27 parts of aluminium in the chemically similar salt without alteration of crystalline form.

Although in a very considerable number of instances identity of crystalline form is associated with similarity of chemical composition it must not be supposed that this is invariably the case. Sodium nitrate for example is isomorphous, in this sense, with calcium carbonate (as calcite). Here although the empirical formula weights are similar there is no chemical analogy. Barium permanganate $Ba(MnO_4)_2$ is, according to Mitscherlich, isomorphous with anhydrous sodium sulphate Na_2SO_4, and Marignac found that potassium titanifluoride $K_2TiF_6 . H_2O$ is isomorphous with niobium oxyfluoride $K_2NbOF_5 . H_2O$ and with tungsten oxyfluoride $K_2WO_2F_4 . H_2O$. Wyrouboff found that lithium silicotungstate was

isomorphous with the corresponding calcium and barium salts and considered that this circumstance favoured the view that lithium is a bivalent metal with an atomic weight of 14. [*Bull. Soc. franc. min.* 1896 (19) 219.]

32. III. Method based on the molecular hypothesis.

According to the conceptions of 'atom' and 'molecule,' which have been briefly indicated in the previous sections, it is evident that a molecule of an element or of any of its compounds cannot contain less than one atom, since the atom is, by hypothesis, indivisible. If for example we determine the molecular weight M of any one compound of a given element by any of the methods previously described and then, by analysis, find the weight W of the element which is contained in M parts by weight of the compound, it is evident that the atomic weight of the element cannot be represented by a number greater than W, in terms of the units chosen. We may now continue these operations with a large number of other compounds of the same element and the smallest value of W which is ever found is evidently the maximum atomic weight. Or 'the maximum atomic weight of an element is the least weight of it which is ever found in one molecular weight of any of its compounds*.' If however we perform these operations with a sufficiently large number of different compounds it is probable that one at any rate of these compounds will contain only a single atom of the element in its molecule; if this is the case W will not only represent the maximum, but also the actual value of the atomic weight. In our experiment on page 12 we found the density of carbon dioxide to be about 22; the molecular weight is therefore about 44. An accurate experiment according to the method described on page 60 shews that the ratio of carbon to oxygen is as 3 to 8. From these results it follows that the molecular weight is exactly 44† and that in 44 parts by weight of carbon dioxide there are 12 parts of carbon. Therefore the atomic weight of carbon is not greater than 12. In a similar way it can be shewn that in 46 parts of ethyl alcohol there are 24 parts of carbon; in 74 parts of ethyl ether 48 parts of carbon, and so on. But in the many thousands of carbon compounds

* If it should happen that the higher values obtained were not multiples by a whole number of this least value, it would of course be necessary to take the G.C.M. of the values as the maximum atomic weight; no such case is known at present.

† If O = 16.

which have been investigated, less than 12 parts of carbon has never been found in the molecular weight of any one. We therefore conclude that the atomic weight of carbon *is* 12, and this conclusion is found to be borne out by a variety of other considerations. But yet, strictly speaking, the method only gives us the maximum value. A compound *might* be discovered in one molecular weight of which there would, for example, be only six parts by weight of carbon, although such a result is in the highest degree improbable. [Such a discovery was in fact actually announced about 20 years ago, by Wanklyn, but was not substantiated.]

33. IV. Application of the periodic classification.

The general chemical character of an element, of known atomic weight, is in the majority of cases very clearly indicated by the position it occupies in the Periodic Table. Conversely, if we first ascertain the general chemical characters of an element whose atomic weight is not known we can, with a fair degree of certainty, assign to it an appropriate position in the table, and so obtain an approximation to its atomic weight. The subject will be more fully considered in a future section, in which the Periodic law is discussed; for the present it will be sufficient to refer to a few well-known instances in which the correct value of the atomic weight has been arrived at from considerations of the kind here mentioned.

Beryllium ($E = 4{\cdot}55$) was, owing to certain general resemblances with aluminium, regarded as a trivalent element with the atomic weight 13·65. Placed in the numerical order of atomic weights the element would then fall between carbon and nitrogen, where it is obviously out of place. But regarding it as bivalent, with the atomic weight 9·1, it falls, as the first member of the second group, amongst elements with which it has more marked chemical analogy. Subsequent determinations of the vapour densities of its chloride and bromide, and of its specific heat at a sufficiently high temperature, entirely confirmed the value 9·1 as the true atomic weight. Further confirmation was afterwards obtained by determination of the vapour densities of certain volatile organic derivatives of beryllium, e.g. the so-called basic acetate

$Be_4O(OAc)_6$ (Urbain and Lacombe) and of the acetylacetone derivative $Be(C_5H_7O_2)_2$ (Combes).

Indium ($E = 38{\cdot}33$) was originally looked upon as a bivalent element with the atomic weight of about 76. But in this case it would fall, in the periodic classification, between arsenic and selenium. But indium closely resembles elements of the third group in its general chemical and physical characters, and from these it is clear that the element appropriately falls in the horizontal line, or series, between cadmium (112·4) and tin (119). In this case therefore indium must be tervalent with the atomic weight 115. This number is now well established by determination of the specific heat, by the molecular weight of the chlorides, InCl, $InCl_2$ and $InCl_3$, and by the isomorphism of its ammonium, caesium and rubidium double sulphates with the ordinary alums.

The atomic weight of uranium ($E = 39{\cdot}75$) was, until 1872, taken as about 120, the highest oxide being looked upon as a sesquioxide U_2O_3 analogous to ferric oxide. But Mendelejeff pointed out the general resemblance of uranium to chromium, molybdenum and tungsten, and drew attention to the well-marked acidic character of its highest oxide. For these and other reasons he proposed to double the value then assigned to the atomic weight and to place uranium as the last member of the sixth group. The correctness of this suggestion has since been entirely borne out by determinations of the specific heat of the metal and of the molecular weights of its tetrachloride and tetrabromide.

34. V. Relation of the atomic weight of an element to its density in the gaseous state.

The weights of equal volumes of hydrogen, oxygen, nitrogen, chlorine, bromine, iodine and sulphur stand to one another in the ratio of their atomic weights; in other words, the densities of these elements specified in grams per 11·2 litres at 0° C. and 760 mm. pressure are numerically equal to their atomic weights.

At one time it was supposed that this relationship was a general one, and that the molecular weight was necessarily twice the atomic weight; if this were so, the atomic weight of an element could be found at once by a determination of its gaseous density. The statement will indeed be found in some of the older

books that 'the atomic weight of an element is that weight of it which fills the same space as is filled by one part by weight of hydrogen measured at the same temperature and pressure.' Phosphorus and arsenic vapours however appeared to be notable exceptions, and later investigations shew that the exceptions are numerous, and that the relationship above mentioned often depends upon the temperature at which the density is determined. The tables given below indicate, broadly, some of the relationships which have been found to exist between the atomic weights and the densities in the gaseous state.

In brief explanation of the terms employed it may be mentioned that

The *atomic weight* of an element is taken as the least weight ever found in a molecule of any of its compounds, or is determined by the various other methods above described.

The *density* is here (approximately) expressed in grams per 11·2 litres calculated at 0° and 760 mm.

The term *atomicity* is used to denote the number of atoms in the molecule (or practically speaking, the number of times the molecular weight contains the atomic weight).

The *atomic volume* refers here to the atomic weight divided by the density as above defined, and the *molecular weight* is numerically equal to the weight in grams of 22·4 litres measured (or calculated) at 0° and 760 mm., that is, twice the density.

The values are, for the sake of simplicity, given in round numbers.

	Atomic weight	Density	Atomic volume	Molecular weight	Atomicity
Hydrogen	1	1	1	2	2
Nitrogen	14	14	1	28	2
Oxygen	16	16	1	32	2

A similar relationship (Atomic weight = Density) is found in Fluorine, Chlorine, Bromine, Iodine, Thallium, Sulphur, Selenium and Tellurium. In the cases of the last three elements however the relation only holds at very high temperatures*. With Iodine,

* According to von Wartenberg [*Zeit. Anorg. Chem.* 1907 (56) 320] the vapours of Bismuth, Antimony, Thallium, Selenium, Tellurium and Lead, are all monatomic at about 2000°. The value obtained for sulphur at this temperature was between that required for S and S_2.

on the other hand, this relation no longer holds at high temperatures. The influence of temperature on the densities of Fluorine and of Thallium has not been studied.

Phosphorus	31	62	$\frac{1}{2}$	124
Arsenic	75	150	$\frac{1}{2}$	300

The densities of these two elements become smaller at very high temperatures; at 1700° for example the density of Phosphorus is about 45 and that of Arsenic about 78.

Mercury	200	100	2	200	1
Zinc	65	32·5	2	65	1
Cadmium	112	56	2	112	1

Silver vapour at about 2000° has a density of about 54—56 and is therefore also monatomic (von Wartenberg). This relationship (Atomic weight = Density × 2) appears to hold also in the cases of Potassium and Sodium. [A considerable number of metals when examined by the freezing point method, using certain other metals as solvent, appear to exist as monatomic molecules, and similar results are in many cases obtained by the vapour pressure method using mercury as solvent.]

The density of Antimony vapour at 1572° is about 154 and at 1640° about 140, corresponding therefore to values between Sb_2 and Sb_3. The density of Bismuth vapour at 1700° is about 158, being therefore intermediate between the values required for Bi and Bi_2.

Iodine molecules, although diatomic at low temperatures, dissociate gradually at higher temperatures, eventually becoming monatomic. The density is, for example, 125·5 at 600°, 98·3 at 1030°, 75·3 at 1390° and 64·8 at 1500°. Bromine also appears to dissociate in a similar way.

Sulphur vapour above 860° has a density of 32, i.e. is diatomic. But at lower temperatures the density becomes greater. At about 500° it approximates to the value required for S_6 or S_7 and at somewhat lower temperatures to S_8 or S_9 (Biltz). In boiling carbon tetrachloride or carbon disulphide values such as S_8 or S_9 have also been obtained (Beckmann, Oddo, etc.).

Oxygen in the state of Ozone has a density of 24 (Soret, Ladenburg) corresponding to the triatomic state O_3.

Helium, Neon, Argon, Krypton and Xenon all have densities which are probably half of their atomic weights, i.e. they are monatomic.

The relationship between the atomic weight of an element and its density in the gaseous state, may be expressed as follows:

$$\text{atomic weight} = \frac{\text{molecular weight}}{\text{atomicity}} = \frac{\text{density} \times 2}{\text{atomicity}}.$$

From this it is evident that the density of an element alone is not sufficient to fix the true value of the atomic weight, since two unknown quantities are involved in the relation—namely the atomic weight and the atomicity. [It appears necessary to emphasise this point which, although obvious, is sometimes misunderstood.]

Now it happens that, by making certain assumptions, it is possible in some cases to deduce the probable value of the atomicity from a knowledge of the specific heat of the gas at constant volume. In practice it is customary to determine the specific heat of gases at constant pressure and from this result to calculate the value at constant volume, since the direct determination at constant volume presents obvious difficulties. [Compare Joly, *Phil. Trans.* 1891 (182) 73.] Or the ratio of the two values may be calculated from the velocity of sound in the gas. A complete theoretical treatment of this subject is by no means simple; for our present purpose it will be sufficient to indicate the general principle of the calculation by the following elementary outline.

Consider one molecular weight in grams (or one 'mole') of any gas. Its volume at 0° and 760 mm. is 22400 c.c., and when heated from 0° to 1° will increase in volume by $\frac{22400}{273}$ = about 82 c.c. The work done, measured in gram centimetre units, will therefore be $82 \times 13{\cdot}6 \times 76$ = about 84800, or in thermal measure $\frac{84800}{42640}$ = about 2.

The molecular heat at constant pressure is therefore always two units higher than that at constant volume, as it exceeds that at constant volume by the thermal equivalent of the work done in expanding the gas.

In fact, the difference between the specific molecular heats at constant pressure and constant volume is numerically equal to the gas constant R in the relation $PV = RT$. (RT also being expressed in thermal units. See (**6**).)

On the kinetic theory, the total energy of the molecule at $t°$ is represented by the heat required to raise its temperature from absolute zero to $t°$, and this is increased by $\frac{1}{273}$rd of its amount when heated from 0° to 1°.

The molecular specific heat of a gas at constant volume, i.e. the quantity of heat necessary to raise the temperature of one molecular weight of the gas from 0 to 1°, will, in terms of this theory, be $\frac{Mv^2}{2}\frac{1}{273}$, assuming that all the heat supplied goes to increase the kinetic energy of the molecule.

And since $$PV = \frac{Mv^2}{3},$$

it follows that $$\frac{Mv^2}{2}\frac{1}{273} = \frac{PV}{273}\cdot\frac{3}{2}.$$

But, as previously shewn, $\frac{PV}{273}$ is, in thermal measure, equal to about 2 cal. and, consequently, the molecular specific heat at constant volume (C_v) = about 3 cal.

At constant pressure the value (C_p) is two units more and therefore $\frac{C_p}{C_v} = \frac{5}{3} = 1{\cdot}\dot{6}$.

The molecular specific heats at constant pressure of many diatomic gases (O_2, H_2, N_2, NO, CO, HCl) are found by experiment to be about 6·8, the value at constant volume being therefore 4·8 and the ratio $\frac{C_p}{C_v} = 1{\cdot}41$. But for gases whose molecules contain more than two atoms the numerical value of this ratio becomes smaller. For hydrogen sulphide, for example, $C_p = 8{\cdot}27$ and $\frac{C_p}{C_v} = 1{\cdot}3$, and in the case of methane $C_p = 9{\cdot}49$ and $\frac{C_p}{C_v} = 1{\cdot}27$.

Now in the case of mercury vapour, Kundt and Warburg found that $\frac{C_p}{C_v} = 1{\cdot}67$, and we have already seen that the molecular weight of mercury deduced from its vapour density is identical with its atomic weight. These observations are explained by supposing that in the case of monatomic molecules the heat supplied is all employed in increasing the kinetic (translatory) energy of the molecule, i.e. in raising its temperature; whereas in polyatomic molecules a certain amount of the heat is consumed in performing *intra*-molecular work, increasing, perhaps, the speed of rotation of the atoms or separating them further apart. If we denote the latter part of the energy by x, we shall have $\frac{C_p}{C_v} = \frac{5+x}{3+x}$, the ratio therefore becoming smaller as the value of x increases

By determination of the ratio $\frac{C_p}{C_v}$ we therefore have a method which, if the foregoing assumptions are accepted, enables us in certain cases to ascertain whether the molecules of a gas are monatomic or not. Beyond this it would probably not be safe to go, since abnormalities may present themselves. [The values of $\frac{C_p}{C_v}$ for chlorine and bromine, for example, are abnormally low.]

This method has been used in the determination of the atomic weights of the non-valent elements, helium, neon, argon, krypton and xenon, which all give the ratio $\frac{C_p}{C_v} = 1{\cdot}67$. In these cases it is obviously impossible to determine the equivalent weights, since the elements named form no compounds and the atomic weights cannot therefore be arrived at in the ordinary manner. But the densities of these elements have been determined and since, on the above reasoning, they are monatomic, it follows that their atomic weights must be equal to twice the density.

The ratio $\frac{C_p}{C_v}$ can be determined indirectly from the velocity of sound in the gas, since this velocity $= \sqrt{\frac{P}{D}K}$ where $K = \frac{C_p}{C_v}$. By comparing the velocity (V_1) of sound in the gas to be investigated,

the density of which is D_1, with that (V_2) in another gas, say carbon dioxide, of density D_2 at the same temperature, we obtain the relation

$$\frac{V_1}{V_2} = \sqrt{\frac{K_1 D_2}{K_2 D_1}},$$

from which the value of K_1 can be determined, since D_1, D_2 and K_2 are already known. Since the pressure varies as the density, it is evident that the pressures need not be identical.

CHAPTER VIII.

SPECIFIC VOLUME

35. THE term specific volume is generally understood to mean the reciprocal of specific gravity. In chemistry however it is the custom to multiply this value by the formula weight, so that

$$\text{specific volume} = \frac{\text{formula weight}}{\text{specific gravity}}.$$

The formula may refer to that of an atom, molecule or group, the term specific volume including the particular cases of

$$\text{atomic volume} \left(= \frac{\text{atomic weight}}{\text{specific gravity}} \right)$$

and

$$\text{molecular volume} \left(= \frac{\text{molecular weight}}{\text{specific gravity}} \right).$$

If the specific gravity is taken in reference to water at 4° the value is numerically equal to the density In this case specific volume $= \frac{\text{formula weight}}{\text{density}}$, that is to say, the specific volume represents the volume in cubic centimetres which is filled by the formula weight in grams. [It must be observed however that the results of many observers have been calculated from the specific gravity referred to water at 0°.]

In the case of gases the specific volume is expressed by the formula weight calculated on the basis H = 1, divided by the specific gravity referred to hydrogen. Or by the formula weight on the basis O = 16, divided by the specific gravity referred to that of oxygen as 16. Instead of the specific gravities we may, as stated in (**5**), employ the densities in grams per 11110 c.c.

or per 11200 c.c. respectively, these volumes being calculated at 0° and 760 mm.

In these terms it is evident that the molecular volume always = 2, if the gas laws are obeyed.

The atomic volumes of gases will not necessarily be equal. They are, however, simply related as was previously explained (**34**), the value for oxygen, hydrogen, nitrogen, chlorine, etc. being 1, phosphorus and arsenic ½, mercury 2, and so on.

The relation between the specific volumes of elements or compounds in the liquid or solid state is by no means so simple, but certain highly interesting and important generalisations have been found. Here it is usual to refer the specific gravity to water at 4° (or at 0°) as above indicated.

36. In comparing the values of the specific volumes of liquids the question of temperature is an important one, since, unlike gases, different liquids may have very different coefficients of expansion. It would not appear probable therefore that much regularity should be obtained if comparison is made at any one arbitrary temperature. Theoretically it might be best to choose temperatures which are equal fractions of the critical temperatures, but the latter are known only for comparatively few substances.

As a matter of fact, Kopp obtained relationships of a fairly definite character by determining the specific volumes of liquids at temperatures at which their vapour pressures are equal to the standard atmospheric pressure, i.e. at their boiling points. It does not follow that this is a strictly comparable condition from a theoretical point of view; it merely happens that certain regularities are obtained if these temperatures are chosen. [Guldberg however states that the boiling point (absolute scale) is nearly always about two-thirds of the critical temperature. *Zeit. Physikal. Chem.* 1890 (5) 374*.]

Kopp found that in a homologous series of similar compounds (e.g. the alcohols of the $C_nH_{2n+1}.OH$ series) an increase of CH_2 corresponds to an increase of specific volume of 22 units. Further, the replacement in a compound of one carbon atom by two hydrogen atoms causes no change in the specific volume. It follows therefore that (V) C = 11 and (V) H = 5·5†. Oxygen is

* See also Kurbatoff, *J. Russ. Phys. Chem. Soc.* 1908 (40) 813.

† The symbol (V) is used to denote 'the specific volume of.'

found to have different values according to the way in which it is combined. The specific volume of water is 18·8; therefore that of oxygen when combined as OH is, by subtraction, 7·8. But the replacement of two atoms of hydrogen by oxygen when the latter is doubly linked to carbon (i.e. by 'carbonyl' oxygen) is attended with a slight increase of specific volume. The probable value of (*V*) O when the oxygen is linked in this manner is 12·2

Therefore a compound of the chemical formula $C_wH_xO'_yO''_z$ (where O' represents the singly linked and O'' the doubly linked oxygen) should have a specific volume of $11w + 5{\cdot}5x + 7{\cdot}8y + 12{\cdot}2z$. This relation is found to hold good in a large number of cases. It must be noticed however that the mode of linkage of carbon also affects the result. Kopp considered that isomeric compounds of the same chemical type have nearly the same specific volumes. But this does not by any means always hold. The difference between the volumes, for example, of ethylene and ethylidene compounds considerably exceeds the limit of error allowed by Kopp. Doubly linked carbon appears always to 'occupy' a larger volume than when singly linked.

Kopp also found that, in many cases, liquid elements or groups have the same volume in the free state as when in combination. The calculated values agree well, for example, in the cases of Br, Cl, NO_2 and CN, with those obtained by observing the specific volumes of these elements or groups in the free state.

The above conclusions are arrived at on the assumption that the specific volume is an additive property. One assumes that the volume of one constituent remains constant and that of the other constituent is obtained by subtraction. Although interesting and useful results have been obtained in this way the assumption is obviously unjustifiable. An illustration of this fact may be observed in the interesting determinations of Thorpe and of Ramsay on the specific volume of phosphorus oxychloride. The former, by subtracting (*V*) PCl_3 from (*V*) $POCl_3$ obtained the value 7·8 for oxygen. Ramsay however subtracted the volumes found for liquid phosphorus and liquid chlorine from that of $POCl_3$, and obtained about 12·2 for oxygen*.

This method of subtraction may, in fact, sometimes lead even

* Compare Prideaux, *Trans. Chem. Soc.* 1907, 1711 and 1909, 445.

to negative values for the atomic volume. Thus (V) KCl = 37·4 and (V) K = 45·2, so that (V) Cl, by subtraction, would be − 7·8!

Certain regular relationships have also been observed in the specific volumes of substances in the solid state. Here the choice of a suitable temperature of comparison is of less importance, since the expansion coefficients are small. There is, however, the additional difficulty that the same solid may exist in more than one crystalline form, each having a different specific volume; strict comparison can therefore only be made when the substances crystallise in the same form.

After the discovery of the laws of combination by volume of gaseous substances (3), many attempts were made to find some such simple relations in the case of solids and liquids. Royer and Dumas at first considered that the atomic volumes of the elements formed an arithmetical series, and Herapath (1824) attempted to shew that the volume of oxygen in a metallic oxide bears a simple ratio to that of the metal. Ammermüller (1840) concluded that the specific volumes of compounds containing the same elements in different proportions are simply related, and shewed, for example, that the specific volume of Cu_2O is the same as that of 2CuO. The atomic volume of oxygen therefore appeared to be twice as great in cuprous oxide. Schröder also observed several remarkable regularities in the volumes of solid compounds. He shewed, for instance, that by subtracting the volume of the metal from the oxides of lead, zinc, copper, mercury and cadmium he obtained a constant value for the volume of the oxygen. He assumed therefore that a metal retains its primitive volume. Kopp found similar relationships in the salts of heavy metals, but he shewed that in the case of the alkali and alkaline earth metals such a conclusion is not possible, since the specific volumes of the salts are often smaller than those of the metals contained in them.

Schiff pointed out that the molecular volumes of many isomorphous salts are practically identical.

[e.g. (V) $M'M'''(SO_4)_2 12H_2O$ = about 277.

(V) $M_2'M''(SO_4)_2 . 6H_2O = 207$.

(V) $M''SO_4 . 7H_2O = 146$.]

Playfair and Joule shewed that in certain highly hydrated

salts, such as $Na_2CO_3 10H_2O$ and $Na_2HPO_4 . 12H_2O$, the specific volume is exactly equal to that of the water contained taken as ice. In certain other less hydrated salts, such as $Na_2B_4O_7 . 5H_2O$, the volume is equal to that of the water, taken as ice, together with that of the base in the free state. If the method of subtraction were applied in these cases, the salt in the first case and the acid in the second case, would 'occupy' no volume.

Thorpe and Watts [*Trans. Chem. Soc.* 1880, 102] determined the specific volume of the water of crystallisation in various hydrates of the same salt. They shewed that each additional molecule of water appears to occupy an increasing volume, e.g. that the contraction occurring in the combination of the first molecule of water is greater than that in the combination of the second molecule, and so on. Thus the difference in volume between the first and second hydrates of $MgSO_4$ is 13·3, between the second and third 14·5, between the third and fourth 15·4, and between the sixth and seventh 16·2. These observations are of much interest in connection with the fact, first noticed by Graham, that far more heat is evolved in the combination of the first molecule of water with the salt, than with any of the remaining molecules. This connection between contraction, heat evolved in combination and stability of the resulting compound is very often noticed. [Deville attempted to formulate a 'law' that the heat evolved in the formation of a solid compound is equal to that which is necessary to convert the volume of the compound into the sum of the volumes of its constituents in the free state. Although this appeared to hold good in a few cases it is evidently not general; the heat evolved is generally less than that representing the work necessary to effect the change of volume. [*Comptes Rend.* (50) 354.]

The most far-reaching generalisation which has yet been obtained from a study of the atomic volumes in the solid state is the periodic relationship observed by Lothar Meyer. His well-known curve is obtained by plotting the atomic volumes of the solid* elements as ordinates and the atomic weights as abscissæ.

* The values given in the usual tables for the atomic volumes of chlorine, bromine, argon, krypton and xenon are those of the liquids at some stated temperature.

A complete study of this curve is best made in connection with the Periodic classification; at the present stage it will be sufficient to draw attention to one or two of the leading features.

Chemically similar elements often have the same, or nearly the same, atomic volume. e.g. (*V*) Cl, Br and I = about 26. (*V*) Mn, Fe, Ni and Co = 7. (*V*) Ru, Rh, Pd, Os, Ir and Pt = 9. (*V*) Au and Ag = 10. But in other cases the volumes increase with increasing atomic weight, e.g. the volumes of Li, Na, K, Rb and Cs are in the ratio of 1 : 2 : 4 : 5 : 6.

The volumes of oxygen in the highest salt-forming oxides, obtained by subtracting the volume of the element in the free state, are negative in the alkali metals, become nearly zero in oxides of the 'indifferent' elements of group IV, and positive in the acidic oxides of groups VI and VII. The exact position of several other elements, such as phosphorus, arsenic, silicon and tin, will also depend on the particular modification considered. Elements of pronounced chemical activity, e.g. the alkali metals and halogens, occupy high positions, that is, they have relatively large atomic volumes, whereas 'indifferent' elements, like carbon, boron and silicon, are situated at the minima of the curve.

It will be observed that the alkali metals occupy the maxima, these increasing as above indicated. In many cases, but not always, negative elements are situated on the ascending portions of the curve and positive elements on the descending portions.

Periodic relationships of a similar kind are to be observed also with regard to such properties as volatility, melting point, refractivity, malleability, etc.

Determination of the specific volume of a liquid at its boiling point.

The most accurate method consists in ascertaining (1) the specific gravity of the liquid at some convenient temperature t, (2) the boiling point t_1 of the liquid, and (3) the expansion between t and t_1. [Compare Thorpe, *Trans. Chem. Soc.* 1880, 141 and 1893, 262.]

But the direct method of Ramsay is very much more simple and is capable of yielding excellent results. [*Trans. Chem. Soc.*

1879, 466.] The bulb *A* is made of thin glass (preferably lead glass) and has a capacity of about 10 c.c. Its capacity is first accurately determined by filling it with distilled water at a known temperature and weighing. Its volume at 0° is then easily calculated It is then emptied (by suspending it with the open end downwards and heating) and washed out first with alcohol and then with the liquid to be examined; it is then filled (or nearly filled) with the latter It is then suspended as shewn in the sketch and the liquid (the same as that under investigation) in the flask is heated to vigorous boiling. The liquid in the bulb expands and soon begins to drop over from the capillary neck (*b*). When this expansion ceases the flame is removed and the bulb cooled, dried outside and weighed.

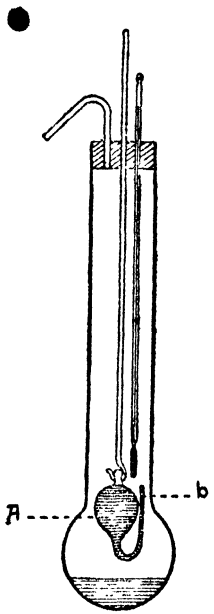


Fig. 18.

Ramsay calculates the specific gravity of the liquid referred to water at 0°, as follows:

$$\text{sp. gr.} = \frac{W_1}{1 + (0{\cdot}00015 \times TW)},$$

where W_1 is the weight of liquid and W is the weight of water filling the bulb at 0°. The coefficient 0·00015 was empirically determined by making blank experiments with pure water and was found to be the same for nearly all the bulbs employed.

Schiff [*Ber.* 1881 (14) 2761] modifies this method by using, in place of the bulb, an accurately graduated dilatometer, in the form of a flask, with a long neck, holding about 7 or 8 c.c. This is suspended in the boiling flask as before and the position of the liquid read off on the graduated neck when, as is assumed, the liquid has acquired the temperature of the surrounding vapour. It is then removed, cooled and weighed. The specific gravity at $t°$ referred to water at 4° is calculated as follows:

$$\text{sp. gr.} = \frac{P}{V_t[1 + K(t-4)]},$$

where P = the corrected weight of the liquid in the flask, V_t is the

apparent volume of the liquid at $t°$ and K is the coefficient of expansion of the glass.

37. Refraction equivalent.

The index of refraction (n) of a substance, for light of a particular wave length, changes with the temperature and with the state of aggregation. Gladstone and Dale however, in 1858, shewed that the quantity $\frac{n-1}{d}$ (where d is the density) was constant for a given liquid compound and was nearly independent of the temperature. These authors termed the expression the 'specific refractive energy' of the substance, but it is now referred to as the specific refractivity or specific refraction. As in the case of specific volume, however, it is usual to multiply this quantity by the formula weight in order to obtain chemically comparable results.

The expressions 'molecular refractivity' and 'atomic refractivity' are used for the value $\frac{n-1}{d}M$, where M is the molecular or atomic weight. [Or we may write $n-1 \,.\, V$ where V is the molecular or atomic volume.]

A different formula was subsequently deduced independently by L. Lorenz and by H. Lorentz, from theoretical considerations, namely $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$; this appears in many cases to give better results and has the advantage moreover that the value holds both for the liquid and gaseous states.

The molecular or atomic refractivities will in this case be

$$\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} \quad \text{or} \quad \frac{n^2-1}{n^2+2} \cdot V.$$

The atomic refractivity is, like the atomic volume, to some extent an additive property, so that it is possible to calculate the molecular refractivity from the sum of the atomic refractivities. But here again the value to be assigned to a given polyvalent atom depends to a considerable extent on the mode of combination. Thus, for sodium light, the value of $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$ is 2·501 for singly linked carbon; for the carbon double linkage, the value is 1·707. Oxygen when linked as in hydroxyl has the value

1·521, whereas for oxygen in the carbonyl group the value is 2·287; hydrogen has the value 1·051. So that the molecular refractivity of a compound $C_wH_xO_y'O_z''$, where the carbon is singly linked and O′ and O″ stand for hydroxylic and carbonyl linked oxygen respectively, should be given by the sum

$$w \,.\, 2{\cdot}501 + x\ 1{\cdot}051 + y\ 1{\cdot}521 + z\ 2{\cdot}287.$$

Thus the observed value for acetone is 16·09, the formula $CO(CH_3)_2$ requiring 16·10.

It is evident that this property affords a valuable means of throwing light on constitution. It has been employed by Bruhl, for example, in distinguishing between the keto and enol forms of tantomeric substances like aceto acetic ester—

$$CH_3 \,.\, CO \,.\, CH_2 \,.\, COO\,Et \text{ and } CH_3C(OH) : CH \,.\, COO\,Et.$$

The molecular refractivity of benzene corresponds to the sum of the refractivities of six hydrogen atoms with three carbon atoms singly linked and three doubly linked as in ethylene. Paraldehyde $C_6H_{12}O_3$, although obtained by polymerisation of acetaldehyde, $CH_3 \,.\, CHO$, has a molecular refractivity corresponding to six singly linked carbon atoms, twelve hydrogen atoms and three oxygen atoms linked as in hydroxyl, i.e. it no longer contains carbonyl oxygen.

The *molecular dispersion* of a compound, i.e. the difference between the values of the molecular refractivity referred to two different lines in the spectrum (e.g. the blue and red hydrogen lines H_α and H_γ) is also nearly independent of the temperature. This value is also of much service in determining constitution, being still more dependent on the mode of atomic linking.

38. Magnetic rotation.

The fact, discovered by Faraday, that transparent substances, when placed in a magnetic field, have the power of rotating the plane of polarisation, has been applied by Sir W. Perkin to the study of constitution. The rotation is proportional to the thickness of the substance through which the light passes and to the intensity of the magnetic field; it depends also on the temperature and the nature of the substance. The specific rotation of a liquid at a given temperature is defined as the ratio of the rotations given by the substance and by water. Thus if α is the angle of rotation of

the liquid, l the length of the column and d the density and a', l', d' the corresponding values for water, the specific rotation is $\frac{al'd'}{a'ld}$. This quantity multiplied by the molecular weight of the substance and divided by that of water is called the molecular (magnetic) rotatory power.

Perkin shews that a difference of CH_2 in a homologous series of similarly constituted compounds corresponds to a nearly constant difference in the magnetic rotation (= about 1·02). But constitution here makes a very marked difference, propyl alcohol for example, having a value different from isopropyl alcohol. Perkin derives many important conclusions from the application of this method to the study of the constitution of organic compounds. A full account of his method of working and of many of his results will be found in *Trans. Chem. Soc.* 1896, 1025.

CHAPTER IX.

VALENCY.

39. It was previously mentioned that the atomic weight and the equivalent weight of an element are simply related, the ratio $\frac{\text{atomic weight}}{\text{equivalent weight}} = n$, being usually a small whole number. The value of this ratio, that is, the number of times the atomic weight contains the equivalent weight, is often spoken of as the valency or valence (first definition). This simple definition has certain advantages in that the value can be actually determined by measurement, and is independent of all hypotheses except such as may have been employed in fixing the value of the atomic weight. (See **32**.) According to this definition, a normally constituted compound of the x valent atom A with the y valent atom B will have the composition A_yB_x or some multiple of this formula. And conversely, if the compound is known to have this empirical formula A_yB_x the ratio of the valencies of A and B must be as x to y.

According to Faraday's law, equivalent weights of different elements convey equal quantities of electricity when their compounds are electrolysed. If unit charge is conveyed by one equivalent weight it is evident that the atomic weight will convey n unit charges, n being the valency as above defined. This would hold equally well if, for some reason, the wrong value had been assigned to n in fixing the atomic weight. If, for example, the older atomic weight of beryllium 13·65 were adopted, one atom would convey three unit charges, whereas with the present value 9·1, one atom conveys two unit charges.

This practical definition of valency, which is based on composition only and is independent of any hypothesis of atom-linkage, is of course limited in its application. Moreover, if applied in a literal manner it will in some cases necessitate fractional values for the valency. In propane C_3H_8, for example, the value of carbon would be $\frac{12}{4{\cdot}5}$, and in the oxide Fe_3O_4 (if this is regarded as a 'true' compound) the valency of iron would be $\frac{56}{21}$. (One assumes here that the equivalent weight of oxygen is 8 and that the equivalent weight of the carbon or the iron is deduced from analysis of the compound in question.)

A difficulty is experienced also in the case of hydrogen dioxide. If the equivalent weight of oxygen is 8, then from the composition of the compound, the equivalent weight of hydrogen is 0·5 and its valency is 2; whereas, if the equivalent weight of hydrogen is 1, that of oxygen is 16 and the valency of oxygen is 1.

The conception of valency as a term denoting the saturation capacity of a given atom, that is, the number of other atoms, of whatsoever kind, with which it can unite, is due in the first instance to Frankland (1848). Employed in this sense the term has, in a general way, the widest possible application. But the attempt to frame a strict definition of the term, when used in this way, is a matter of considerable difficulty. The subject is one of fundamental importance, and requires the most careful study*. It will only be possible here to mention some of the best known theories on the subject and to point out a few of the difficulties met with.

The elements hydrogen, chlorine, bromine, iodine and fluorine exist in the gaseous state (under ordinary conditions at any rate) as diatomic molecules. The groups methyl, ethyl, propyl, etc., when isolated, also exist in the 'paired' condition, that is, as ethane, butane, hexane, etc. The compounds which these different elements or groups form when they unite with one another, also consist of 'pairs.' The molecules then of these elements themselves, or of the compounds which they form with one another, are

* The student is recommended to make a careful abstract of the information given on this subject in the various text books. A useful historical summary of the matter is given by Scheiber, *Zeit. angewandte Chemie*, 1907 (41) 1767.

never found to contain more than two atoms in the molecule, and a similar remark applies to the groups mentioned.

[One or two exceptions to this statement must be noticed. Iodine pentafluoride IF_5 is known and appears to exist in the gaseous condition (Moissan). Iodine trichloride cannot be vaporised unchanged. Hydrogen fluoride has the single formula HF at 100 (Gore), but Mallet, from the vapour density at 30°, obtained values corresponding to H_2F_2. Thorpe and Hambly, however, shewed that the molecule is still more complex at lower temperatures, and that the value depends also on the pressure. Cryoscopic determination indicates that in solution the acid is bimolecular (Abegg).]

If then we regard these elements as standard univalent atoms, we may define the valency of any given atom as the number of these univalent atoms which one atom of it can combine with to form a molecule (second definition). [The number so obtained must of course be identical with that given by the first definition if the equivalent weight is determined from the composition of the compound in question; if not, the two values are not necessarily identical, as will be seen below.]

It is evident that this second definition of valency is very limited. In the first place, it can only be employed to determine the valency of the given atom when in combination with these univalent atoms. And secondly, it is not applicable, without further hypothesis, when more than one atom of the given element is present in a molecule. When there are two atoms of the given element united, in a molecule, with only univalent atoms, it is natural to assume that the two polyvalent atoms are combined with one another. Ferric chloride, for example, was formerly considered to have the double formula Fe_2Cl_6. If the two iron atoms are linked together each would in this sense be quadrivalent:

$$Cl_3Fe—FeCl_3.$$

But in this case we are defining the valency by the total number of atoms linked, not restricting ourselves to univalent atoms only. Much confusion arose at one time owing to this want of precision in the definitions. By the first definition, the valency of iron is here 3, whereas by the second definition, it is 4.

The discrepancy is removed in this instance if we adopt the single formula $FeCl_3$, which is justified by the more recent determinations of the vapour density at higher temperatures. Very similar remarks apply to the cases of several other metallic chlorides which, at low temperatures, have more complex formulae but exist in the simplest form at higher temperatures*.

By taking the simplest formulae then we can, as a rule, reconcile the first and second definitions without further hypothesis, and it is remarkable that among inorganic compounds there are very few instances in which there are sufficient grounds for adopting more complex formulae. But in the case of carbon compounds this is no longer possible, since we have to deal with an enormous number of compounds whose molecules contain more than one atom of carbon, the formulae of which are firmly established on various grounds. Whenever, then, we have more than one polyvalent atom in a molecule it becomes impossible to directly deduce the valency of the polyvalent atoms, unless we make conjectures as to how they are linked. In ethane, ethylene and acetylene, it is the custom to consider that the carbon is uniformly quadrivalent, but this is obviously not indicated by the formulae C_2H_6, C_2H_4 and C_2H_2 unless we make assumptions as to how the carbon atoms are joined together. In carbon monoxide again, if the equivalent weight of oxygen is 8 the valency of carbon will, by the first definition, be 2. If, however, we wish to define valency strictly as atom-linking capability, and to consider that carbon is still quadrivalent, we must either suppose that two of the carbon valencies saturate one another, or else that oxygen is quadrivalent. If, on the other hand, we regard valency as merely indicating the number of atoms actually linked in the compound under consideration, the carbon and oxygen would each be univalent.

It has very generally been the custom, up to the present time, to assign to each atom a fixed maximum valency and, in compounds in which the atom appears to exert a lower valency, to assume multiple linkages. Such symbols as $:C=C:$ or $\cdot C\equiv C\cdot$ are extremely useful as denoting the degree of so-called unsaturation, i.e. the capacity for further combination. But there is some danger in regarding such formulae as true representations of atom

Compare page 99.

linking, and in many cases difference of opinion may exist as to the mode of linkage. Carbon monoxide, for example, might be represented as $<C=O$, $C\equiv O$, or $<C=O>$.

[An attempt is sometimes made to define a 'saturated' compound as one which cannot unite by addition and can only react by substitution; whereas an 'unsaturated' compound can combine by direct addition. This distinction serves well to illustrate, for example, the behaviour of paraffins C_nH_{2n+2} and olefines C_nH_{2n}, or acetylenes C_nH_{2n-2}, towards chlorine or bromine. But the restriction serves satisfactorily only as regards the behaviour of compounds towards univalent atoms. Carbon dioxide and potassium hydroxide are sometimes looked upon as saturated—yet they combine to form potassium hydrogen carbonate. Similar remarks apply to many salts which combine directly with water.]

In assigning a maximum valency to each element different standards have been adopted from time to time. We may, for example, (I) deduce the equivalent weight from the composition of the highest oxide, considering the equivalent weight of oxygen as fixed and equal to 8 (or 7·94). The valency is then obtained according to the first definition. Thus, the maximum valency of an element whose highest oxide is represented by the formula M_xO_y will be $\frac{2y}{x}$. According to this method we may have valencies as high as *eight*.

On the other hand, we might (II) determine the valency of an element from the highest compound which it forms with *hydrogen* or with *methyl*, *ethyl*, *propyl*, etc. In this case the maximum valency in no case exceeds *four*.

Or we may measure the value (III) by the highest *halogen* compounds, in which case the maximum valency seldom exceeds *six*. It is to be noticed however that even here there are comparatively few valencies exceeding four; those at present known are included in the following compounds:

OsF_8. WCl_6. SF_6 SeF_6. TeF_6. WF_6. MoF_6. UF_6 $NbCl_5$. $TaCl_5$. $MoCl_5$. WCl_5. PF_5. AsF_5. SbF_5. IF_5.

PCl_5, $SbCl_5$ and UCl_5 are unstable in the gaseous state.

In the relationships between the valencies of elements taken in series according to the periodic classification, it is interesting

to notice the remarkable difference which will obtain, according to whether we determine the maximum valency by the oxygen standard (I)* or the hydrogen (or methyl, ethyl, etc.) standard (II). In the series, for example:

Ne . Na . Mg . Al . Si . P . S . Cl . A,

the corresponding valencies by (I) will be 0 . 1 . 2 . 3 . 4 . 5 . 6 . 7 . 0, whereas by (II) they will be 0 . 1 . 2 . 3 . 4 . 3 . 2 . 1 . 0.

Mendelejeff was the first to point out that in many cases the sum of the valencies, determined by (I) and (II) is, for a given element, equal to *eight*. This is at once noticeable, for example, in the following compounds. ClH and Cl_2O_7; SH_2 and SO_3; PH_3 and P_2O_5; SiH_4 and SiO_2.

[Unfortunately there are a large number of elements in which this remarkable relation does not hold. If the rule were universal, the alkali metals, for example, should be capable of exhibiting the valency 7, the calcium group 6, and so on. Brauner attempted to indicate such valencies by compounds such as

$NaOH . 3H_2O = NaH_3(OH)_4$ and $Ca(OH)_2 . 2H_2O = CaH_2(OH)_4$, etc.]

It will be noticed that in the majority of cases in which an element exhibits more than one valency, there is a difference of two units (or multiples of two units) between the values (e.g. PCl_3 and PCl_5; SH_2, SO_2 and SO_3). This regularity was so constantly observed that at one time it was supposed to be a universal rule, and was termed the 'law of even numbers.' It was expressed by saying that the atoms are uniformly 'artiad' (even valent) or 'perissad' (odd valent); or by the statement that 'the sum of the valencies of all the atoms in any molecule is always an even number.' It was supposed that when an atom exhibited a lower valency, two free valencies became latent and satisfied one another. Nitric oxide afforded a very annoying exception, and every effort was made to justify a doubling of its formula, but without success.

So many other 'exceptions' have now been brought to light

* It must be admitted that Mendelejeff's choice of the highest salt-forming oxide is sometimes rather arbitrary and that the more recent isolation of such compounds as the perborates, percarbonates and persulphates is not in harmony with his views, unless a special constitution is assumed for these compounds.

that the so-called 'law' has to be adandoned (e.g. $InCl_3$, $InCl_2$ and InCl; $GaCl_3$ and $GaCl_2$; $FeCl_3$ and $FeCl_2$; ClO_2 and Cl_2O, etc.).

Notwithstanding these many exceptions, however, the coincidence is a remarkable one, and must not be lost sight of in attempting to frame a consistent theory of valency.

40. *Maximum valency and 'Molecular' compounds.* The constitution of a very large proportion of the chemical compounds which are known can be clearly represented on the assumption that each atom has a definite and fixed maximum valency. This is more particularly evident, as was first pointed out by Kekulé, in the case of carbon compounds. If we represent carbon as quadrivalent, oxygen bivalent, and hydrogen as univalent, we can construct graphic or constitutional formulae for some thousands of compounds which will give, in a practical sense, a complete account of their chemical behaviour. When we come to consider the constitutional representation of isomeric compounds (i.e. those which have the same composition and molecular weight but different properties) we are at once struck by the fact that, in a vast number of cases, the number of isomers which can actually be isolated is equal to the number of different ways in which the symbols can be arranged. [Note, for example, the following: C_2H_6O can be written in two ways, and only two compounds having this formula are known. $C_5H_{11}(OH)$ can be arranged in eight different ways (leaving the OH group intact) and eight amyl alcohols are known.]

Until about the year 1874 there were some notable examples of isomeric compounds which appeared to afford exceptions to this statement, since the number of isomers actually isolated exceeded the number of ways in which the formulae could be written. Well known illustrations are the lactic or tartaric acids and the hexoses. These difficulties were entirely cleared away by the method of representing formulae in space of three dimensions, proposed by van 't Hoff and by Le Bel. Similar difficulties as regards certain unsaturated compounds (e.g. fumaric and maleic acids) were overcome, although perhaps in a less conclusive manner, by Wislicenus' extension of the hypothesis of van 't Hoff and Le Bel.

As regards carbon then, the assignment of a fixed maximum valency appears to be entirely appropriate and satisfactory. [Bi-

valent carbon appears to be present in carbon monoxide, unless oxygen is quadrivalent; also perhaps, according to Nef, in acetylidene compounds and in fulminic acid, etc. The existence of trivalent carbon has been suggested by Gomberg, in the compound triphenylmethyl, but its existence in the unimolecular state has not been confirmed.]

But when the attempt is made to extend this assignment to other elements, it frequently happens that serious difficulties are encountered. We should naturally, for example, fix the maximum valency of silicon as four, on the strength of the composition of its highest chloride, bromide, oxide, etc. and generally, of its close relationship to carbon. Yet we obtain a well marked crystalline chemical compound K_2SiF_6. In other words, silicon tetrafluoride, presumably a 'saturated' compound, combines further with two molecules of potassium fluoride—the latter also being usually regarded as saturated.

Similar remarks apply to the combination of salts with 'water of crystallisation,' and to the formation of double salts, racemic compounds, 'associated' liquids or vapours, etc.

In order to evade these difficulties Kekulé developed the idea of 'molecular compounds' as distinct from atomic compounds. In the latter the atoms were supposed to be linked by means of their true valencies, whilst the former were associated or held together somehow by something distinct from valency. Combination of the 'molecular' kind was supposed to be much weaker than that due to true atomic linking; and it is a fact that in nearly all cases in which refuge has to be taken in this molecular compound hypothesis, the compounds in question are very easily dissociable. But after all, this strength or weakness is only a question of degree, and one often finds a compound represented as 'molecular' which is, in reality, less easily dissociable than another which is represented as atomic.

The question whether ammonium chloride was to be regarded as an atomic compound of pentavalent nitrogen or as a molecular compound of hydrochloric acid and ammonia, the nitrogen in this case being trivalent, was the subject of a long controversy. The ingenious experiment of L. Meyer and Lecco, 1874, appeared to afford strong support to the former hypothesis. They shewed

that the compound obtained from NR_3 and R'I was identical with that from NR_2R' and RI which could scarcely be the case if nitrogen were trivalent. Much more conclusive however is the existence of optically active nitrogen compounds $NR_1R_2R_3R_4I$. [Le Bel, 1891, Pope and Peachey, 1899.]

In order to account for the possibility of a compound which is apparently saturated being able to enter into further combination, the idea of 'residual affinity' or residual valency has been suggested. Each atom might have, in addition to its principal valency, certain extra or additional valencies, which are usually latent, but which can be called into play when required. Ideas of this kind were originally made use of by Berzelius to explain the composition of salts, etc. on the dualistic type. The mere statement of the possibility of such residual valency is of little if any assistance; it practically amounts to the assumption that any atom may have any valency. The idea has however been brought into a more substantial and definite form in connection with the more recent developments of the theory of valency.

That the valency of an atom is intimately connected with the electric charge which it carries when in the ionic condition, is evident from Faraday's law. In the case of non-electrolytes, however, the connection is not apparent. Berzelius, who represented acids, salts and bases by the dualistic formulae, considered that each atom might be regarded as having a positive and a negative pole, but that one of these poles is usually stronger than the other. When atoms are in combination, the opposite poles of two atoms neutralise one another, more or less, according to the magnitude of the negative and positive charges and, if complete neutralisation is not effected, the resulting compound will itself be positive or negative. That is, the compound will have a resultant positive or negative polarity and may therefore undergo further combination. In potassium oxide the positive charge on the potassium was considered to be greater than the negative charge on the oxygen, so that the compound had still a resultant positive charge. Sulphur trioxide had a resultant negative charge, since the sulphur atom had a predominating negative charge as well as a positive charge, and the latter was neutralised by the oxygen. The union of potassium oxide and sulphur trioxide gave

potassium sulphate, but it was supposed that even here the charges did not quite neutralise one another, since the salt was able to undergo yet further combination, e.g. with aluminium sulphate. Helmholtz in later years considerably developed this idea of the connection between combining capability and electric charge; he was inclined to consider that all chemical compounds are electrolytes and that the electric forces are the only ones, or at any rate the principal ones, which 'hold the atoms together.'

It must be particularly noticed however that the number of such bindings, i.e. the valency, is entirely distinct from the 'combining force' as it is sometimes called, or the work necessary to decompose the compound. Much confusion arose at one time owing to the want of distinction in this sense. A double bond, for example, was regarded as representing a 'firmer' linking than a single bond, whereas experiment shews the contrary to be the case (compare, for example, the preferential disruption of unsaturated compounds, on oxidation, at the double linkage). Thomsen emphasised this point in his well-known determinations of the heats of formation of the single, double and triple linkage in hydrocarbons and, although some of his assumptions were perhaps open to objection, the results are of much interest. He found, for example, that the thermal value of the combination C – C was about equal to that of C = C, each corresponding to the development of about 14,000 or 15,000 heat units, whereas the thermal value of C ≡ C was negative.

41. It will be evident, from what has been said, that considerable difference of opinion exists as to the precise meaning which is to be attached to the term valency, some regarding it as a fixed inherent property of the atom and others, as a variable quantity which depends on the nature of the atoms in combination and on the temperature, etc. For this reason difficulties are at once encountered in attempting to give a hard and fast definition of the term.

In recent years many interesting theories and speculations have been advanced with the object of throwing light on the nature of valency, and some of these promise to be of far-reaching importance. Abegg [*Chem. Centr.* 1903 (1) 1203, *Zeit. anorg.*

Chem. 1904 (39) 330, etc.] supposes that each atom is possessed of valencies of two kinds which he calls 'normal' and 'contra-' valencies. The normal valencies are the stronger and are positive in the metals and negative in the non-metals. The number of contra-valencies is always greater than, or equal to, the number of normal valencies, and the sum of the two is always equal to eight. [Compare Mendelejeff's observation (**39**).] Thus chlorine has a normal (negative) valency of 1 and a contra-valency (positive) of 7. Silver has a normal (positive) valency of 1 and, it is supposed, a contra-valency (negative) of 7. In the first seven groups of the periodic system then we shall have

	I	II	III	IV	V	VI	VII
Normal valency	+1	+2	+3	±4	−3	−2	−1
Contra-valency	−7	−6	−5	±4	+5	+6	+7

The elements of the eighth group have no normal valency, but eight contra-valencies.

The higher the maximum normal valency of an element the greater is the tendency of the valencies to become latent and further, the negative contra-valencies of the metals are less active than the positive contra-valencies of the non-metals. The higher the atomic weight of an element, in a given group, the greater becomes the activity of the contra-valencies; thus in iodine the seven contra-valencies are more manifest than in bromine or chlorine.

In any binary compound only one kind of valency in each atom is satisfied, the remainder therefore being available for the formation of 'molecular compounds.'

Associated molecules and other 'molecular' compounds owe their formation to latent valencies, and it is therefore to be expected that such compounds will be of more common occurrence when atoms are present which have a high number of disposable valencies (e.g. the 6th and 7th groups in the periodic classification). In illustration of this the author refers to the association of NO_2, P_2O_3, HF, $FeCl_3$, $SnCl_2$, etc., and to H_2O hydroxy-acids and alcohols. [Compare (**24**).]

In NO_2, for example, three out of the four normal valencies of the two atoms of oxygen are satisfied by three valencies of the

nitrogen, and the 4th normal (negative) valency of the oxygen is then able to link another molecule of NO_2 through the positive contra-valencies of the oxygen in the latter.

Morozoff also regards every element as possessing eight valencies, of which some are negative and others positive. The number of positive valencies increases, in a series of the periodic classification, from 1 to 8. But as the number increases the 'strength' decreases. Thus, starting with univalent lithium, the positive valencies reach the maximum of 8 in argon, and are here so weak as to be unrecognisable. The negative valencies of course increase in the opposite direction.

Werner* considers that atoms can be connected to one another by chemical affinity even though they are not directly linked. In compounds such as $CoCl_3.6NH_3$ and $CoCl_3.6H_2O$ the ammonia or water molecules form a sort of envelope round the cobalt atom and prevent the direct linkage of the chlorine atom with it. Atoms or groups which are thus indirectly 'bound' usually shew much greater capability of entering into reactions than those which are directly bound. In aqueous solutions, for example, these indirectly bound parts act as ions, and those directly bound do not. In solutions of $CoCl_3.6NH_3$, for example, all the chlorine is ionic. In a freshly prepared solution of $CoCl_3.5NH_3$ two-thirds of the chlorine can be precipitated by silver nitrate, the third atom remaining as a complex ion, and in $PtCl_4.4NH_3$ one-half of the chlorine is ionic. Hence the formulae may provisionally be written

$$[Co(NH_3)_6]Cl_3,\ [CoCl(NH_3)_5]Cl_2 \text{ and } [PtCl_2(NH_3)_4]Cl_2.$$

Regarding the compounds as constituted in this way, it is remarkable that in a very large number of cases the maximum number of atoms, groups or molecules which are directly bound to the central atom is *six*. In a few cases it is four. Werner regards this maximum number or 'co-ordination number' as a fundamental property of the elementary atom. In this way it becomes possible to account for the many cases of isomerism which have been observed in the 'ammine' compounds. In elements with the co-ordination number 6 the symmetrical space position of the groups is represented by the solid angles of an

* See for example *Ber.* 1907 (40) 15.

octahedron. Two different modifications, for example, of the compound $Co(NO_2)_3.4NH_3$ exist. In both, only one of the NO_2 groups is ionic, so that they are to be represented as $[Co(NO_2)_2(NH_3)_4]NO_2$, and the difference can be accounted for by the relative positions of the two directly bound NO_2 groups—that is to say, whether they occupy the consecutive or symmetrical position in the space formula.

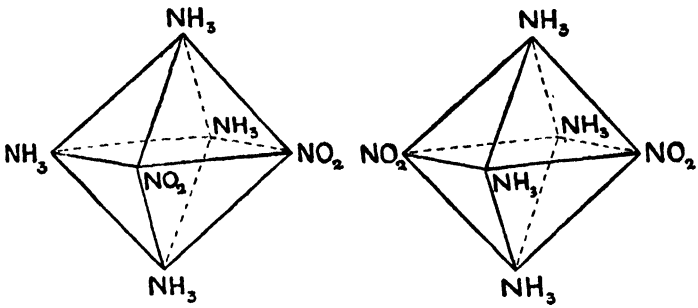


Fig. 19.

Some further examples of the frequent occurrence of the group MA_6 are given as follows, the behaviour as regards ionisation being indicated by the brackets. It will be noticed that the valency of the group MA_6 is always equal to the algebraical difference between the 'normal' valency of the metal and the number of negative elements or groups directly attached to the metal. Taking, for example, the normal valency of platinum as 4, the valency of the group $[PtCl_3(NH_3)_3]$ will be $+1$ and that of the group $[PtCl_5NH_3]$ will be -1.

$[CoCl_3 3NH_3]$ neutral. $CoCl_3.4NH_3 = [CoCl_2(NH_3)_4]Cl$.
$CoCl_3.4NH_3.H_2O = [CoCl(NH_3)_4.H_2O]Cl_2$.
$CoCl_3 4NH_3.2H_2O = [Co(NH_3)_4.2H_2O]Cl_3$.
$PtCl_4.6NH_3 = [Pt(NH_3)_6]Cl_4$. $PtCl_4 3NH_3 = [PtCl_3(NH_3)_3]Cl$.
$PtCl_4.2NH_3$ neutral. $PtCl_4.KCl.NH_3 = K[PtCl_5NH_3]$.
$PtCl_4.2KCl = K_2[PtCl_6]$.

It is well known that two modifications of hydrated chromium chloride, $CrCl_3.6H_2O$, exist, namely, the green and violet forms. The aqueous solution of the violet form contains all the chlorine in the ionic condition whereas in solutions of the green modification,

only one atom of chlorine is ionic. Hence Werner represents the violet form as $[Cr(H_2O)_6]Cl_3$ and the green form as

$$[CrCl_2(H_2O)_4]Cl + 2H_2O.$$

A large number of salts crystallising with $6H_2O$ may be similarly represented; e.g. $NiSO_4 . 6H_2O = [Ni(H_2O)_6]SO_4$.

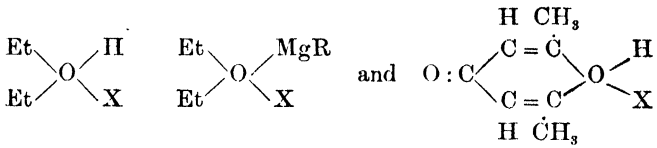
Thomson [*Phil. Mag.* 1904 (VI) 7, 237] regards the atom as consisting of a large number of negative corpuscles in a sphere of uniform positive electrification. The corpuscles are supposed to move in concentric shells and are subject to their mutual repulsion and to the attraction of the positive charge. In the special case in which the corpuscles are arranged in circles round the centre of the atom, it can be shewn that the stability of the outer ring increases with the number of corpuscles in the inner rings. If the outer ring is not very stable, one corpuscle may easily be removed and the residual system now has unit positive charge, i.e. it constitutes a univalent positive ion. Or, again starting with the neutral system, two corpuscles may be lost, although less easily than one, leaving a divalent positive ion. This recalls the fact that the positive character of the univalent metals, such as potassium, is more pronounced than that of the corresponding divalent metals, such as calcium. Similarly, when the number of corpuscles in the inner rings becomes relatively large, the stability of the outer ring is so great that it becomes possible for one or more corpuscles to be added or attached to it; in this way we obtain univalent, divalent, etc. anions.

According to this hypothesis then, the valency of an atom depends on the number of corpuscles which can be transferred to or from it by the action of other atoms. A 'bond of union' in a constitutional formula indicates that a corpuscle from one atom has been transferred from one atom to the other, the atom which has lost the corpuscle acquiring a unit positive charge and that which has received the corpuscle acquiring a unit negative charge.

This remarkable hypothesis is, from a chemist's standpoint, of particular importance in its application to the periodic classification of the elements and will be again referred to in that connection.

When molecules combine together to form 'addition compounds' the operation may often be regarded as the simultaneous

linking of a negative and a positive element, or group. Thus the combination of water with salts may be looked upon as the linking of OH and H. Ether combines with halide acids, HX, or with magnesium alkyl halides RMgX, to give well marked addition compounds, and dimethyl pyrone combines with acids in a similar way giving substances which behave as salts. In these cases the oxygen is usually represented as quadrivalent; it is therefore assumed that the oxygen in the parent substance has two latent valencies and that on combination these link the negative and positive elements respectively, thus:



Associated' oxygen compounds (e.g. acetic acid near its boiling point) may be regarded as linked in this way by the extra oxygen valencies. Helmholtz assumed that unsaturated carbon compounds, which can combine by addition, contain an electrical double linking, that is that one of the latent 'affinities' has a positive and the other a negative charge. A similar view is taken by Arrhenius with regard to the latent valencies in ammonia. On bringing electrically neutral HCl into sufficiently close approximation to NH_3 the electrical double linkage of the nitrogen, and the single linkage of HCl, become broken; the positively charged hydrogen and negatively charged chlorine then neutralise the negative and positive charges, respectively, on the nitrogen.

[It appears less easy to apply a like explanation to the linking of two atoms of the same kind, e.g. Cl_2 to PCl_3, unless it be assumed that in the chlorine molecule the two atoms have one a positive charge and the other a negative charge. This view, that the atoms in the molecule of an element may be oppositely charged, is supported by the fact that at high temperatures the conductivity of a gaseous element, such as iodine is considerable, indicating the presence of both positive and negative ions.]

Abegg (*loc. cit.*) considers that in ammonia the hydrogen atoms are linked by the normal (negative) valencies of the nitrogen and that another hydrogen atom may become attached by the com-

paratively feeble contra-valencies (positive in the nitrogen and negative in the hydrogen). The resulting positively charged ammonium then links the negative chlorine (a positive contra-valency of nitrogen linking the normal valency of chlorine).

Werner supposes that in ammonium chloride, one atom of hydrogen is differentiated from the other three. This atom of hydrogen plays the same part as the metal in the 'ammine' compounds mentioned above, the ammonia being linked to it by means of a subsidiary valency:

$$Cl(H \ldots NH_3).$$

On this view, acids, although monobasic, should be capable of combining with more than one molecule of ammonia and the author mentions a large number of examples which may be considered as illustrations of this property. Troost, for example, obtained the compounds $2NH_3.HBr$ and $2NH_3.HI$, the individual character of which was afterwards recognised by Roozeboom. Substituted ammonias, such as hydroxylamine and amides, also exhibit this property. [See Werner, *Ber.* 1903, 147.]

Instead of stating such explanations in terms of pre-existent electrical charges on the atom one may regard a positive valency as signifying the ability to part with an electron and a negative valency as the ability to receive an electron. The nitrogen atom then carries five electrons and, when combined with hydrogen as ammonia, has received three more, making the total equal to eight, which is the maximum possible. One cannot expect therefore to isolate NH_4. But the nitrogen atom in ammonia, carrying eight electrons, may give up one of these to the chlorine atom (converting it into a chlorine ion) and is then capable of taking up another electron from the hydrogen atom thus giving rise to the ammonium ion. (Compare Ramsay, *Trans. Chem. Soc.*, 1908, 785; also Friend, *ibid.* 1006.)

42. Interesting relationships between valency and volume have been observed by Barlow and Pope [*Trans. Chem. Soc.* 1906, 1675 and 1907, 112] and by Traube [see, for example, *Ber.* 1907, 130 and 723]. It would be impossible here to attempt to give any useful abstract of the theories of these authors; the original

papers should be consulted. It may be mentioned that the first-named authors assume that the chemical atom occupies in a compound a certain space or 'sphere of influence' and that in crystals the structure is determined by the arrangement of these spheres in such a way as to present the closest possible packing of the assemblage. The volumes of these spheres of influence, in a compound, are directly proportional to the fundamental valencies of the atoms.

Le Bas [*Trans. Chem. Soc.* 1907, 754] shews that if the molecular volumes of many compounds (e.g. higher hydrocarbons) are compared at their melting points, the values obtained when divided by the number of valencies present = about 2·970. This then may be regarded as the unit valency volume or valency 'stere.' The mean difference in the molecular volumes for a difference of CH_2 is found to be 17·83. Since in this group the number of valencies is six, the calculated value is $6 \times 2{\cdot}970 = 17{\cdot}82$. It is further shewn that in the higher normal paraffins, this relation holds not only at the melting points but at equal intervals above them. Traube shews that the atomic refractivities (for the red hydrogen line) of carbon, nitrogen, oxygen and hydrogen, in a large number of organic compounds, are in the ratio of 4 : 3 : 2 : 1, i.e. of their valencies on the hydrogen standard. The refractivity unit of valency, or refractivity stere, has an average value of 0·787. Compounds therefore in which there are the same number of valencies present, should have the same molecular refractivity, and this is found to hold in many cases. For example, the molecular refractions of *n*-pentane C_5H_{12} (32 valencies) and of valeric aldehyde $C_4H_9.CHO$ (32 valencies) are found to be 25·32 and 25·31.

43. Oxidation and Reduction.

The term oxidation was originally employed only in the sense of 'addition of oxygen,' as for example in the conversion of a metal into an oxide or of a lower oxide into a higher oxide. Reduction was the converse process. The terms are still employed in this sense but are extended also to include many other operations in which oxygen does not necessarily take part. Thus we speak of the oxidation of ferrous compounds to ferric compounds

no matter whether they are oxides, sulphates, chlorides, etc. [The statement that ferrous chloride is 'oxidised' to ferric chloride is intelligible if we regard each salt as derived from a corresponding oxide, ferrous salts corresponding to FeO and ferric salts to Fe_2O_3.]

Similarly, we say that aldehydes are 'reduced' to alcohols, although the process consists, not in withdrawal of oxygen, but in addition of hydrogen. A rough definition of the terms, which will include the types of change here referred to, might be made by saying that an oxidising process is one by which a negative element, or group, is added to an element or compound or by which a positive element, or group, is removed. Generally, when a compound is regarded as made up of a positive part and a negative part, the effect of oxidation is to increase the ratio of negative to positive; whilst reduction increases the ratio of positive to negative.

It is sometimes stated that an oxidising agent is a 'valency-increasing' agent, but evidently this is only true in certain cases. When ferrous salts are oxidised to ferric salts it is true that the valency of the metal is increased from 2 to 3. But on the other hand, when potassium ferrocyanide is oxidised to the ferricyanide the valency of the acidic radicle is *decreased*, that of the metal being unchanged,

$$2K_4(FeC_6N_6)^{IV} + Cl_2 = 2K_3(FeC_6N_6)^{III} + 2KCl.$$

Again, when potassium iodide is oxidised to potassium iodate the valency of the iodine is increased; but when oxidised in such a way that iodine is liberated, it cannot be said, in terms of the usual definitions, that there has been any 'increasing of valency.'

The general conception of the terms oxidation and reduction is much simplified, in the case of substances in solution, by reference to the hypothesis of ionisation [Chapter XV]. According to this view the operations may be looked upon as due to the transfer of electric charges. Thus the 'oxidation' of ferrous chloride in aqueous solution to ferric chloride by means of free chlorine is to be regarded as consisting in the assumption of one positive charge by each divalent iron ion whereby it becomes

trivalent, the 'neutral' chlorine at the same time becoming ionic, i.e. each atom assuming a negative charge.

$$2Fe^{\cdot\cdot} + 4Cl' + Cl_2 = 2Fe^{\cdot\cdot\cdot} + 6Cl'.$$

In most cases it may be said that an oxidation process is accompanied by a corresponding reduction process; in the change

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$

for example, the tin salt is 'oxidised' and the iron salt 'reduced.'

The terms oxidising agent and reducing agent are to some extent only relative. Thus nitrous acid acts as an oxidising agent towards hydrogen iodide but as a reducing agent towards potassium permanganate. The same remark applies to hydrogen dioxide although its reducing actions belong to a different type. (See page 189.)

But one often speaks of a given substance as an oxidising agent or a reducing agent in a general way in reference to its more usual behaviour, and for the purpose of this rough classification the following tests may be suggested.

(*a*) The liberation of iodine from hydriodic acid.

This is probably the most general and the most delicate reaction for the recognition of oxidising property. The substance to be examined is mixed with excess of a solution of potassium iodide and dilute sulphuric acid, the liberated iodine being identified by shaking with carbon disulphide, or by means of starch. (It is advisable always to make a 'blank' test with the reagents employed since the iodide may contain iodate.)

(*b*) The conversion of ferrous to ferric salts.

A solution of ferrous sulphate and dilute sulphuric acid is employed and the mixture heated. The change of valency of the iron is indicated by application of the usual tests. (Since the ferrous salt employed is almost sure to contain some ferric salt it is generally best to rely upon the colour of the precipitate produced by alkalis rather than upon the ferrocyanide, ferricyanide or sulphocyanate tests.)

Many oxidising agents also (*c*) liberate chlorine when heated with concentrated hydrochloric acid, (*d*) cause separation of sulphur

from a solution of hydrogen sulphide, (*e*) convert chromic salts to chromates, in alkaline solution, and (*f*) convert ferrocyanides into ferricyanides, etc.

Reducing agents are recognised by (*a*) the decolorisation of a solution of potassium permanganate, acidified with dilute sulphuric acid; (*b*) the conversion, in acid solution, of orange bichromates to solutions of green chromic salts; (*c*) the precipitation of red cuprous oxide from Fehling's solution, either in the cold or on heating; (*d*) the separation of metallic silver (as mirror or otherwise) from ammoniacal silver nitrate solution; (*e*) the conversion of ferric salts to ferrous salts; and (*f*) the production of a dark blue precipitate (or coloration) when added to a mixture of a ferricyanide and a ferric salt.

The terms 'strong' and 'weak' as applied to oxidising or reducing agents are often used somewhat vaguely in reference either to the *nature* or the *amount* of oxidising or reducing capability. As regards the first meaning, atmospheric oxygen for example at the ordinary temperature will oxidise phosphorus but will not oxidise alcohol; nitric acid will do both, and is therefore said to be 'stronger.' Similarly, sulphurous acid will reduce ferric salts or chromates but will not reduce aldehydes to alcohols; sodium amalgam will act as a reducer in all these cases.

A more precise classification of the relative strength of oxidising and reducing agents, in this sense, is based on the measurement of the electromotive force of oxidation and reduction elements. Bancroft [*Zeit. Physikal. Chem.* 1892 (10) 394] carried out experiments of this kind in the following manner. Solutions of the oxidising agent and the reducing agent were contained in two tubes connected electrolytically with each other by means of side tubes and an inverted syphon containing a solution of sodium chloride, or by means of mercury. Electrodes of platinum, cut from the same piece of foil, were immersed in the two solutions and the electromotive force between them measured in the usual way. The electromotive force of such cells is an additive property, i.e. it is made up of two terms, one depending on the nature of the oxidising agent and the other on the nature of the reducing agent. In this way he was able to draw up a list representing the relative behaviour of various substances as

oxidising and reducing agents. Measured in this way a solution of stannous chloride in caustic potash was the strongest reducing agent of the substances examined, the strongest oxidising agent being potassium permanganate in dilute sulphuric acid.

There are many instances in which an oxidising agent by itself appears to be incapable of effecting the oxidation of a given substance, but becomes able to do so when a suitable catalyst is added. Thus many aliphatic hydroxy-acids, polyhydric alcohols and sugars appear to be unaffected by a dilute solution of hydrogen dioxide; but in the presence of a mere trace of ferrous iron, rapid oxidation takes place. According to the prevailing view, the difference is a question of time only. In absence of the catalyst it is supposed that the oxidation does really proceed, but so slowly that its progress cannot be detected; the catalyst then merely hastens the speed of the reaction.

In addition to catalytic influences of this kind, the capability of a given agent to bring about some specified oxidation process may depend also in many cases on the temperature or concentrations, or on the presence of some substance capable of combining with the products of oxidation. Hydrogen dioxide for example will oxidise chromic salts to chromates (potentially, Cr_2O_3 to $2CrO_3$) if alkalis are present; whereas in presence of acids it will bring about the converse change.

The *amount* of oxidising capability which a given agent possesses will in many cases depend on the conditions. One atomic proportion of chlorine, bromine or iodine has one 'unit of oxidising capability' (i.e. it can oxidise one atomic proportion of hydrogen or its equivalent) under various conditions. One double formula-weight of potassium permanganate, $K_2Mn_2O_8$, has ten such units if excess of free acid is present, since in this case salts corresponding to the oxides K_2O and $2MnO$ are formed; but in neutral or alkaline solution the oxidising capability is less, since oxides of the type $xMnO.yMnO_2$ are then precipitated or, as an initial stage, potassium manganate $K_2O.MnO_3$ is formed. Nitric acid, HNO_3, when it oxidises ferrous to ferric salts, has three units ($H_2O.2NO.3O$) whereas in its reduction to ammonia (e.g. by a copper-zinc couple) it may be said to possess eight units,

$$HNO_3 + 8H = NH_3 + 3H_2O.$$

44. The term '*autoxidation*' has been applied to certain processes of oxidation by atmospheric oxygen which take place spontaneously at ordinary temperatures. It is frequently noticed that such changes may induce the oxidation of other substances present which are not otherwise capable of spontaneous oxidation; while therefore one portion of the oxygen oxidises the 'autoxidiser,' or easily oxidisable substance, another portion of the oxygen appears to be 'rendered active,' and according to Schönbein, and others, the quantity rendered active is equal to that consumed in oxidising the autoxidiser. In some cases the 'active oxygen,' in the form of ozone or hydrogen dioxide, may be actually demonstrated. Schönbein, Brodie and others supposed that the ordinary oxygen was first transformed into two parts each assuming electric charges of opposite sign; these two parts were then called ozone and antozone. Hoppe-Seyler and Baumann on the other hand supposed that nascent hydrogen appropriates one atom of oxygen form the oxygen molecule leaving the other atom as active oxygen. Traube [*Ber.* 1893, 1471] regards such oxidations as being due to the oxygen or hydroxyl in the molecule of water. Thus the spontaneous oxidation of zinc by water and air is represented as

$$Zn + \begin{matrix} OHH \\ OHH \end{matrix} + \begin{matrix} O \\ \ddot{O} \end{matrix} = Zn(OH)_2 + \begin{matrix} H.O \\ H.\dot{O}. \end{matrix}$$

The water therefore, and not the oxygen molecule, is dissociated and the resulting hydrogen dioxide is to be regarded as hydrogenised (or reduced) oxygen, not as oxidised water.

Practical Work.

It is not possible to suggest experiments bearing directly upon the theory of valency which would be suitable for the purpose of a demonstration. In connection with this subject, students are directed to construct cardboard models illustrating the arrangement of atoms in space. They also make experiments on oxidation and reduction as follows:

Unknown substances (*A*, *B*, *C*, *D*, etc.) are given for examination by general reactions, such as those suggested in the lecture, with the object of ascertaining the behaviour of each as an oxidising agent or a reducing agent.

CHAPTER X.

CHEMICAL CHANGE.

45. No hard and fast line of demarcation can be drawn between chemical and physical changes, and it is perhaps better to regard the distinction as one of convenience in classification rather than of reality. The difference is well illustrated in a broad and general way by reference to the familiar examples usually given in the text books. On heating a platinum wire or on vaporising a liquid, changes of properties occur but, on cooling, the original properties are restored. When on the other hand an iron wire is strongly heated in air or when potassium chlorate is heated, new substances make their appearance and these are persistent. Chemical changes then are said to be of a lasting or permanent character, whereas physical changes are temporary. But obvious difficulties arise if this criterion is pushed too far. Phosphorus pentachloride when sufficiently heated breaks up to a considerable extent, giving new substances, but on cooling the original substance is reproduced, yet the change is classified as chemical. There is here the important difference, however, that the new constituents may be separated, in part, at any rate (for example, by diffusion), at the high temperature. But the distinction is less obvious when one considers the reversible transformation of the allotropic modifications of an element or the dissociation of nitrogen tetroxide, changes which are usually regarded as chemical. When two or more substances undergo chemical interaction, or when a substance breaks up into two or more new ones, there is the important characteristic, which distinguishes such action from physical change, that the quantities which react, or are produced, stand to one another in some simple ratio of the formula weights.

The distinction between the two classes is sometimes expressed by saying that in a chemical change the composition of the molecules is altered, whereas, in a physical change the composition remains the same; but even this distinction may be open to objection in some cases. (See **25.**)

The simpler types of chemical change are usually classified under the following heads:

I. The direct union of two or more simpler molecules to form one more complex molecule. (*Direct synthesis.*)

Examples: $PCl_3 + Cl_2 = PCl_5$, $2NH_3 + CO_2 = CO(NH_2)ONH_4$, $3HCNO = H_3C_3N_3O_3$. [In the latter case where the molecules are of the same kind the change is termed polymerisation. See page 48.]

II. The resolution of more complex into simpler molecules. It is often the custom to differentiate changes of this type according as they are reversible, in the practical sense, or not. In the first case (*a*) the process is called *dissociation*, and in the second case (*b*), simply *decomposition*.

Examples: (*a*) $PCl_5 \rightleftarrows PCl_3 + Cl_2$, $CaCO_3 \rightleftarrows CaO + CO_2$.
(*b*) $NH_4NO_3 = N_2O + 2H_2O$, $2KClO_3 = 2KCl + 3O_2$.

III. Single replacement or displacement.

Examples: $Ag_2SO_4 + Cu = CuSO_4 + 2Ag$,
$CuSO_4 + Zn = ZnSO_4 + Cu$.

IV. Double decomposition or double displacement. This change is of the type $AB + CD = AD + CB$.

Examples: $NaCl + AgNO_3 = AgCl + NaNO_3$,
$C_2H_5(OH) + CH_3COOH \rightleftarrows CH_3COO(C_2H_5) + H(OH)$.

V. Rearrangement of the atoms in a molecule. This class includes isomeric and tautomeric changes.

Examples: The change of maleic into fumaric acid; the transformation of ammonium cyanate into urea; the changes from the enol to the keto form of acetoacetic ester, and the reverse operations.

It is usually the custom to classify all cases of the direct formation of compounds from their elements as examples of

changes of the first type, whether the molecules are more complex or not. Similarly, the resolution of a compound into its free elements is regarded as a change of the second type. But strictly speaking when in such changes there is no difference of molecular complexity—as regards the number of atoms in a molecule—it is perhaps more accurate to regard the changes as double decompositions. One speaks for example of the synthesis of, or the dissociation of, hydrogen iodide; but these changes might be formulated as

$$HH + II = HI + HI \text{ and } HI + HI = HH + II.$$

[Chemical changes are also classified, according to the number of molecules supposed to take part in the change, as monomolecular, bimolecular, and so on. ' Also as 'exothermic' and 'endothermic' according as they are accompanied by evolution or absorption of heat.]

46. 'Reversible' reactions.

From a theoretical point of view it might be considered that all chemical changes could be reversed, to some extent at any rate, if appropriate conditions could be obtained. But actually in practice one finds a considerable number of changes in which it has not so far been possible to demonstrate the reversibility. The expression 'irreversible chemical change' is generally used in this practical sense (e.g. the breaking down of unstable substances such as explosives). If a chemical process is to any extent reversible without alteration of conditions, it follows that the final result when equilibrium is attained must be a limited change. The double decomposition of *AB* and *CD* for example, will give rise to a system containing the four constituents *AB*, *CD*, *AD* and *CB*, the proportion of each depending on the various circumstances and conditions which will be described below.

If one of the four constituents is removed, or is rendered inert as regards the change in question, equilibrium is destroyed and further change proceeds in the direction of producing more of the substance removed, and this process may be continued until the change has, in a practical sense, gone to completion. Before discussing the theoretical aspect of the matter it will be advisable

to refer to a few well-known experimental illustrations of changes in which the reversibility can be demonstrated.

One type of such reactions which has been studied in a very complete manner is the behaviour of alcohols towards acids. The general reaction may, in its simplest form, be formulated as follows:

$$ROH + HX \rightleftharpoons RX + HOH.$$

The change in the forward direction is termed *esterification*, and the reverse change is an example of *hydrolysis*.

By acting, for example, on ethyl alcohol with acetic acid a certain amount of ethyl acetate and water are formed and conversely, water acts upon ethyl acetate with production of ethyl alcohol and acetic acid. But at the ordinary temperature both of these reactions are extremely slow so that equilibrium is not attained until a very long time has elapsed. Raising the temperature very greatly hastens the action either way, and by heating the mixtures, say to 200°, the equilibrium state will be reached after a few hours. But the two changes in question can easily be demonstrated in a qualitative way if one arranges the conditions so that one of the products is removed or is rendered inert. The forward action will therefore be favoured if one adds a dehydrating agent to take up the water as fast as it is formed, whereas the converse change can be demonstrated by the addition of alkali. In the latter case it might be imagined that the acetic acid is neutralised as fast as formed, or it may be regarded as the action of the alkali in place of water, $RX + MOH = MX + ROH$. The action of an alkali on an ester to produce an alcohol and a metallic salt of the acid is termed *saponification*; the term originating from the circumstance that the formation of soaps from fats or oils is a reaction of this nature. [In terms of the ionic hypothesis the change is to be regarded as due to hydroxyl ions, and is represented as $RX + OH' = ROH + X'$.]

The action of hydrogen sulphide on solutions of metallic salts affords many interesting examples of reversible changes. A solution of antimony chloride for example gives an orange precipitate of antimony sulphide when a current of hydrogen

sulphide is passed, provided there is not too much free acid present.

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 + 6HCl.$$

The change is practically completed in the forward direction when hydrogen sulphide in excess is passed through the cold or warm dilute solution. If, however, antimony sulphide is boiled with strong hydrochloric acid the reverse change takes place and is practically completed if the hydrogen sulphide is allowed to escape. The usual elementary explanation, apart from the hypothesis of ionisation, is to consider that in either case all four substances first exist in the solution in a state of equilibrium. If the solution is dilute, antimony sulphide separates, being nearly insoluble in dilute acids, and is therefore to a large extent removed from the 'sphere of action'; this causes a disturbance of the equilibrium with consequent formation of a further quantity of antimony sulphide from the products remaining. Similarly, when the strongly acid solution is boiled hydrogen sulphide is removed owing to its greater volatility. The complete explanation, however, is of a more complex character and will be discussed in a future section.

A solution of calcium chloride yields a white precipitate with ammonium carbonate; yet if calcium carbonate is boiled with a strong solution of ammonium chloride in excess, it will dissolve and ammonium carbonate will escape.

$$CaCl_2 + (NH_4)_2CO_3 \rightleftarrows CaCO_3 + 2NH_4Cl.$$

It is important to bear this in mind in the ordinary course of analysis, since traces of calcium might be overlooked if great excess of ammonium chloride is present.

When a little iodine is suspended in water and the mixture is subjected to a current of hydrogen sulphide, sulphur is precipitated and a solution of hydriodic acid is obtained. On the other hand, if powdered sulphur is digested with a very strong solution of hydriodic acid, iodine is liberated and hydrogen sulphide is formed. If water is absent, iodine and hydrogen sulphide do not perceptibly react*; this is easily shewn by passing the dry gas into a solution of iodine in carbon disulphide. If only a relatively

* According to Pollitzen [*Zeit. Anorg. Chem.* 1909 [64] ii. 121] dry hydrogen sulphide does react, to an appreciable extent, with solid iodine at the ordinary temperature.

small proportion of water is present the action stops short of completion. [This action is of interest as an illustration of a change occurring spontaneously only when the thermal effect is positive—a condition which at one time was regarded as essential. See page 163.]

A current of steam passed over iron filings heated to redness (best in an iron tube) gives rise to an oxide of iron ($x\text{FeO} . y\text{Fe}_2\text{O}_3$) and hydrogen; whereas if hydrogen is passed over this (or other) oxide of iron, metallic iron is produced and water is formed. The exact composition of the resulting oxide is uncertain and appears to be variable with the conditions: the change is often represented as

$$3\text{Fe} + 4\text{H}_2\text{O} \rightleftarrows \text{Fe}_3\text{O}_4 + 4\text{H}_2.$$

The simple qualitative explanation is generally stated in the form that the hydrogen in the first case, or the water vapour in the second case, is removed from the sphere of action by the current of gas. If the operation, either way, is conducted in a closed vessel, without removal of the products, all four substances remain in equilibrium, the proportions depending on the conditions which will be referred to below. Experiment shews that for each temperature a definite ratio exists between the pressure of the water vapour and of the hydrogen, which is independent of the quantities of the solids, iron and oxide of iron, provided both are present.

Iodine and bromine in presence of water are converted by sulphur dioxide into hydriodic and hydrobromic acids respectively; the change is complete, in a practical sense, only in extremely dilute solutions. On the other hand, strong sulphuric acid decomposes hydriodic or hydrobromic acids with liberation of the halogen and production of sulphur dioxide

$$2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \rightleftarrows \text{H}_2\text{SO}_4 + 2\text{HI}.$$

47. Dissociation.

This term was originally restricted to reversible decompositions in which one or more of the products were gaseous and which was also of an endothermic character. No such limitations are now

implied; the term is used to denote any change of a reversible character in which more complex molecules are resolved into simpler ones or in which compounds are resolved into their free elements or, in the case of electrolytes, into their ions. When one of the products of dissociation is gaseous, the pressure produced by this product is found to have a definite and constant maximum pressure for a given temperature which, within certain limits, is entirely independent of the quantities of the reacting substances. This maximum pressure is sometimes called the 'tension of dissociation' of the substance, or better, the dissociation pressure, at the given temperature. This is often expressed by saying that "the tension of dissociation is a function of the temperature only and is independent of the mass" (Deville's law).

Familiar illustrations of dissociation phenomena are afforded by the following changes:

Calcium carbonate. Debray heated Iceland spar in a closed vessel connected with a manometer, an air pump and a tube for the introduction of carbon dioxide. He observed that decomposition began at about 440°, the transparent crystals becoming, at this temperature, opaque. Above this the pressure of the carbon dioxide reached a maximum for a given temperature, being 85 mm. at 860° and 520 mm. at 1040°. More exact measurements by le Chatelier (1886) gave

$t°$.....	547	610	625	740	745	810	812	865
p mm....	27	46	56	255	289	678	753	1333

Somewhat different numbers have been obtained by later observers If, at a constant temperature, carbon dioxide is removed by means of the air pump, the pressure momentarily falls; but further dissociation then occurs and eventually the original pressure is re-established. If this process be continued until the final pressure falls below the limiting value, the carbonate is entirely decomposed. The system now contains only lime and carbon dioxide, and the pressure of the latter will depend on the quantity present, i.e. it is no longer constant for a given temperature. Conversely, if when

* Compare Zavrieff, *C. R.* 1907 (55) 195 and Rissenfeld *Jour. Chim. Phys.* 1909 (7) 561.

the original equilibrium pressure has been established at a certain temperature, more carbon dioxide is introduced, the pressure, for the time being, rises; but on standing, falls to its original value, further combination occurring. But if the introduction of carbon dioxide be continued until the final pressure, after standing, exceeds the limiting value, all the lime will be converted into calcium carbonate. Beyond this point the pressure of the carbon dioxide will increase as more is introduced, that is to say, the pressure is no longer a function of the temperature only but depends on the quantity of gas present. [Observe that the pressure is constant for a given temperature only when lime calcium carbonate and carbon dioxide are *all three* present.]

In reference to the above experiments it may be mentioned that Raoult found that quicklime and carbon dioxide combine with incandescence at 550°. He considers that a compound having the composition $2CaO . CO_2$ is here formed and that this can slowly take up more carbon dioxide, giving $4CaO . 3CO_2$. He also states that the amount of carbon dioxide absorbed depends on the previous history of the lime; less is absorbed if the lime has been strongly heated. It is generally stated that under a sufficiently high pressure of carbon dioxide, calcium carbonate may be fused at a high temperature (Hall, le Chatelier and others); but Boeke [*Zeit. anorg. Chem.* 1906 (50) 244] states that no fusion occurs even at 1400—1500° under a pressure of carbon dioxide of 30 atmospheres. Barium carbonate when heated in the air does not dissociate until a temperature of about 1400° is reached, because its tension of dissociation at lower temperatures is less than the pressure of carbon dioxide present in the air. If the air is freed from carbon dioxide, the carbonate dissociates at a much lower temperature.

Barium dioxide dissociates into barium monoxide and oxygen, and the behaviour is quite analogous to that of calcium carbonate. If the barium monoxide is heated in air (previously freed from carbon dioxide) to about 500° it absorbs oxygen, giving the dioxide; the latter heated to a bright red heat gives up this oxygen again, regenerating the monoxide. This indicates that

the dissociation pressure of the oxygen from the dioxide at 500° is less than the oxygen pressure in the air (about $\frac{1}{5}$ of 760 mm.). If, however, the pressure of the air is reduced until its oxygen pressure is less than the dissociation pressure of the barium dioxide, at the given temperature, the dioxide will decompose. The process can therefore be reversed by alteration of pressure alone and this fact is taken advantage of in the manufacture of oxygen from the air.

Hydrated salts behave similarly, shewing a definite 'tension of dissociation' for a given temperature. If at a constant temperature, some of the water vapour be removed, further dissociation will occur and the original pressure (P) will be regained as in the previous examples. If this process be continued so as to keep the water vapour pressure less than (P) at the given temperature, the hydrate will be entirely decomposed. But if a lower hydrate can be formed the pressure will again become constant at the given temperature, this lower pressure (P') now representing the dissociation pressure of the lower hydrate. If, however, no lower hydrate is capable of existence, the pressure will no longer be constant but will depend on the quantity of water vapour removed or introduced. Observe that here again the pressure is only constant for the given temperature, and independent of the quantities, when there are simultaneously present (1) the vapour, (2) the hydrate and (3) the anhydrous salt or lower hydrate. If additional water vapour be continuously pumped into the apparatus until all the salt is converted into the higher hydrate, the pressure will rise above P and will no longer be a function of the temperature only.

Sodium bicarbonate. The reversible decomposition of this salt into normal carbonate, carbon dioxide and water is, in effect, similar to the examples mentioned above, the gaseous product giving a definite dissociation pressure at a given temperature. Note, however, that here the gaseous product consists of a mixture of two different substances but that the proportion in which they exist is necessarily constant—i.e. the relative concentration is fixed by the chemical relationship,

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2.$$

48. In illustration of dissociation in gaseous systems the following well-known examples may be referred to in addition to those mentioned in Chapters III. and VII. The methods used in following such changes experimentally are generally of two kinds. The first method consists in heating the gas to the required temperature and then suddenly reducing the reaction velocity by cooling, or by removal of a catalyst. In applying this method it is assumed that the change of composition during the cooling, etc. may be neglected. The second method is to estimate quantitatively some property of the gaseous mixture, such as density or colour, which varies with the degree of dissociation.

Hydrogen iodide. The dissociation of this gas is easily demonstrated, in a qualitative way, as a lecture experiment, by heating it in a glass bulb over a flame; the production of free iodine is indicated by the colour. On the other hand, if a sealed tube filled with hydrogen and containing a little iodine is heated to about the temperature of boiling sulphur a considerable quantity of hydrogen iodide is produced. (The change is much facilitated, however, if the gaseous mixture is passed over platinised asbestos in the manner illustrated in the lecture.)

The conditions influencing this change were studied in the first instance by Hautefeuille in 1867, and afterwards, in a more elaborate manner, by Lemoine [*Ann. Chim. Phys.* 1877, 145] and by Bodenstein and Meyer [*Ber.* 1893, 1146, *Zeit. Physikal. Chem.* 1897 (22) 1, etc.]. The experiments were made by heating hydrogen iodide, or mixtures of hydrogen and iodine, in glass globes to various temperatures, and for various times, and then suddenly cooling and analysing the resulting products. (By absorbing in water, measuring residual hydrogen and estimating iodine or hydriodic acid, or both, by titration.) Some of the principal results arrived at may be summarised as follows:

(*a*) No changes could be observed at the ordinary temperature, but as the temperature was raised the rate of change increased very rapidly; equilibrium was reached at 265° only after some months, whereas at 350° the time required was a matter of days and at 444°, of hours.

(*b*) The same degree or percentage of dissociation is reached at a given temperature, when equilibrium is attained, whether one starts with hydrogen iodide or an equivalent mixture of hydrogen and iodine.

(*c*) The percentage of dissociation at a given temperature is at its maximum when the hydrogen and iodine are present in equivalent quantities; addition of excess of either one or the other diminished the dissociation.

(*d*) The final state of equilibrium is independent of the total pressure of the mixture, i.e. of the external pressure. [Some of the earlier experiments appeared to indicate that the dissociation was slightly increased by increased pressure, but this was probably due to errors caused by the action of hydrogen iodide on the glass vessels (Bodenstein, *loc. cit.* 1897).]

(*e*) The *rate* of change, either way, is however increased by increasing the external pressure. Porous substances, such as spongy platinum, act similarly to increased pressure, that is to say, they accelerate the changes but do not shift the final equilibrium.

(*f*) The rate of dissociation appears to follow the law for a bimolecular reaction. (See page 132.)

(*g*) Hydrogen iodide is decomposed slowly, but practically completely, by sunlight; here, however, the rate of change follows the law for a unimolecular reaction.

(*h*) The percentage of dissociation, when equilibrium is attained, appears to diminish as the temperature rises until it reaches a minimum at about 320°, after which the dissociation becomes greater as the temperature rises. The heat of formation of hydrogen iodide at ordinary temperatures is negative and we would expect therefore that the dissociation should diminish with rising temperature according to the principle of van 't Hoff and le Chatelier. (See page 159.) At about 320° the heat of formation should be about zero and at higher temperatures it should be positive. If the experimental observation is correct therefore one would say that hydrogen iodide is endothermic below about 320° and exothermic above that temperature.

The mean numbers obtained by Bodenstein were as follows:

Temperature	Degree of dissociation
290°	0·1637
310	0·1669
320	0·1601
340	0·1706
350	0·1763
394	0·1957
448	0·2143
518	0·2363

Certain other compounds shew a similar behaviour; the combination of hydrogen with sulphur for example increases with rising temperature up to 358°; above this temperature hydrogen sulphide dissociates, the amount of dissociation increasing with the temperature. The combination of hydrogen and selenium shews a similar maximum at 520°. Silicon hexachloride exhibits an opposite behaviour, the dissociation into silicon tetrachloride and silicon increasing with rising temperature between 350° and 800°; above 1000° however combination again takes place.

Water. The complete synthesis of water from its elements has been illustrated in a quantitative manner in the earlier demonstrations. (Page 63.) The dissociation of water vapour into oxygen and hydrogen was shewn in the lecture by passing a rapid current of steam over an incandescent platinum spiral. A portion of the dissociated gas is swept away by the current of steam, thus escaping recombination, and may be collected over water. Deville demonstrated the dissociation of water vapour by passing it through a porous porcelain tube heated to 1100—1300°. The porous tube was enclosed in a glazed porcelain tube through which a current of carbon dioxide passed. A portion of the water vapour dissociated; the resulting hydrogen was, in part, removed from the sphere of action by diffusion and was swept forward by the current of carbon dioxide so that it could be collected and identified. Grove also shewed that notable quantities of oxy-hydrogen were produced when a lump of platinum was heated to incandescence and suddenly plunged into water.

Nernst and his pupils have recently studied the change quantitatively by the following ingenious device of Loevenstein [*Zeit.*

Physikal. Chem. 54, 715]. An exhausted platinum bulb, connected with a manometer, was placed in the gas to be examined, which was heated to the required temperature. Hydrogen diffused through the platinum and its pressure was indicated by the manometer; after a short time this pressure became constant and indicated the partial pressure of the hydrogen in the gaseous mixture surrounding the bulb. By a similar method they also studied the dissociation of hydrogen chloride and hydrogen sulphide. Langmuir [*Journ. Am. Chem. Soc.* 1906, 1357] has made experiments in the same direction by passing the gases over a heated platinum wire, collecting the resulting product over mercury and analysing the mixture.

The results of these, and of many other, experiments shew that at sufficiently high temperatures there is a definite dissociation pressure at a given temperature. Langmuir estimates the percentage of dissociation as 0·000028 at 1000°, 0·0197 at 1500°, 0·504 at 2000°, 3·38 at 2500° and 11·1 at 3000°.

The effect of adding an excess of hydrogen or of oxygen, at constant volume, is to diminish the dissociation at a given temperature: increase of total pressure has a similar effect. The mixture, after equilibrium is attained, will have the same percentage of dissociation whether one starts with water vapour or with an equivalent mixture of oxygen and hydrogen. The rate at which the equilibrium state is arrived at depends however on the temperature (also on the presence of catalysts). The mixture of oxygen and hydrogen is to be regarded as in a state of 'false equilibrium' at the ordinary temperature and the reaction velocity is then so small that no perceptible change can be detected after many years.

The heat evolved by this small amount of combination is altogether too minute to appreciably raise the temperature of the gas since the heat is dissipated by conduction, etc. so that the reaction velocity remains unchanged. But if by any external means the temperature is raised to a certain point the combination will proceed with such rapidity that the temperature, and consequently the reaction velocity, will continue to rise and an explosive combination will be the result. The exact temperature at which this effect can be initiated—the 'ignition point'—is

somewhat doubtful since it appears to depend on conditions such as the pressure and nature of the vessel. Mallard and le Chatelier for example estimated the ignition point of oxy-hydrogen as between 500° and 600°. V. Meyer however found that when the gases were passed through a heated tube, combination did not occur at 650° but did at 730°. The temperature of ignition is lower if the gases are confined in a closed tube*.

If oxygen and hydrogen in equivalent proportions were caused to combine in a closed vessel under such conditions that none of the resulting heat escaped, it is evident that the combination could not be complete. If all the heat were concentrated in the products and if it be imagined that complete combination occurred, the resulting temperature would be far above that at which considerable dissociation has been shewn to exist. Combination would only occur until the temperature of the mixture was such that a further rise would cause dissociation.

Nitrogen tetroxide. 'Peroxide of nitrogen' exists at low temperatures as a colourless (or almost colourless) crystalline solid; this melts at $-12°$ to a yellow liquid, which becomes somewhat darker in colour as the temperature rises, and boils at about 22°. The vapour produced at this temperature is orange coloured and the colour is intensified with rising temperature, becoming orange red and eventually reddish brown. The maximum intensity is reached at about 140°. If the temperature is raised above 180° the colour begins again to diminish until about 600° when the product is quite colourless. These changes are explained by the two reversible reactions,

$$N_2O_4 \rightleftarrows 2NO_2 \quad \text{and} \quad 2NO_2 \rightleftarrows 2NO + O_2.$$

Ramsay determined the molecular weight of 'peroxide of nitrogen' in solution by the cryoscopic method, using glacial acetic acid as solvent, and obtained concordant results agreeing almost exactly with the formula N_2O_4. Only slight differences were observed with varying dilution. Cundall however [*Trans. Chem. Soc.* 1888, 621 and 1891, 1076] afterwards found that in chloroform solution the dissociation increases with the dilution as in the case of the gas (see below).

* Compare Dixon and Coward, *Trans. Chem. Soc.* 1909, 514.

The density of gaseous 'peroxide of nitrogen' was first determined at various temperatures by Deville and Troost. The following are some of the results obtained at a pressure of one atmosphere:

Temperature	26·7	35·4	39·8	49·6	60·2	80·6
Density (0 = 16) ...	38·29	36·49	35·54	32·80	30·05	26·01
Temperature	100·1	121·5	135·0	154·0	183·2	
Density (0 = 16) ...	24·27	23·40	23·12	22·79	22·72	

The density of nitrogen tetroxide, N_2O_4, would be 46 and that of the dioxide, NO_2, is 23. Hence at about 140° the dissociation into the simpler molecules appears to be complete. At lower temperatures the percentage of dissociation can be calculated from the density in the manner previously indicated (page 21). Thus if x is the percentage of the NO_2 molecules and d is the observed density,

$$\frac{x}{23} + \frac{100-x}{46} = \frac{100}{d}; \text{ whence } x = \frac{100\,(46-d)}{d}.$$

The degree of dissociation of nitrogen tetroxide (like that of phosphorus pentachloride but unlike that of hydrogen iodide) at a constant temperature, is altered by pressure, being less as the pressure is greater. Thus E. and L. Natanson in 1885 found that the density at 49·7° is 24·03 under a pressure of 26·8 mm., 27·36 under 182·69 mm. and 30·98 under 497·75 mm.

With regard to the further dissociation of nitrogen dioxide into nitric oxide and oxygen, Richardson [*Trans. Chem. Soc.* 1887, 397] shewed that the gas becomes almost colourless when heated to about 500° and on cooling regains its original colour. The density changes in a corresponding manner and the following are some of the numbers which he obtained:

Temperature	130	184·1	279·2	448·2	619·5
Density.....	23·26	22·35	21·59	19·20	15·30

The calculated density of a mixture of $2NO + O_2$ is $\frac{92}{6} = 15{\cdot}33$.

Here again the dissociation is diminished by increased pressure; Richardson shewed for example that no diminution in the colour-intensity was perceptible when the gas was heated to 500° under very great pressure.

Practical Work.

The qualitative study of some reversible reactions.

1. *Esterification.* A mixture of equal volumes of absolute alcohol and concentrated sulphuric acid is heated in a distilling flask connected with a condenser. The temperature is maintained at about 130—135° and a mixture is now very gradually run in (from a tap funnel) consisting of equal volumes of absolute alcohol and glacial acetic acid. (Run in, say, 100 c.c. of the second mixture to 50 c.c. of the first.) The liquid which distils over is the impure ester; it contains some alcohol, acetic acid, ether, etc. In order to purify it, it is shaken in a separating funnel first with a strong solution of sodium carbonate and afterwards with a very concentrated solution of calcium chloride (1 : 1). The separated ester is then allowed to stand over solid calcium chloride for some hours, and is then distilled; the portion boiling at 72—78° is the nearly pure ester.

2. *Saponification.* The ester is heated with a solution of caustic alkali, in sufficient excess, in a flask fitted with an upright condenser. Take say, 20 c.c. of the ester and 3 times its volume of an aqueous solution of caustic potash (1 in 3). Boil the mixture gently for about an hour, or until the odour of the ester is no longer perceptible. Distil off the resulting alcohol, dehydrate it by means of solid potassium carbonate and identify by the usual tests. The solution of potassium acetate which remains in the flask is neutralised, evaporated to dryness on a water bath, mixed with concentrated sulphuric acid and distilled at about 130°. The acetic acid which distils over is identified as usual.

Experiments of a similar kind may be made on the saponification of mutton fat or olive oil, etc.

3. *The action of acids on certain metallic sulphides.*

Prepare a solution of antimony trichloride containing sufficient hydrochloric acid to prevent the precipitation of the oxychloride. Pass hydrogen sulphide; collect and wash the resulting orange precipitate and allow it to drain on filter paper. Now dissolve

this precipitate in cold concentrated hydrochloric acid and divide the resulting solution into two parts. Boil one part for a few minutes and then cool it. To both parts now add much water; observe the separation of the white oxychloride in the part which has been boiled and of the orange sulphide in the other.

[Observations are also made on the behaviour of hydrogen sulphide towards solutions of zinc, manganese, iron, nickel, etc. in solutions which are (*a*) neutral, (*b*) alkaline, (*c*) acidified with acetic acid and (*d*) acidified with hydrochloric acid.]

The interactions of (*a*) *iodine, hydrogen sulphide and water*, (*b*) *hydrogen iodide and sulphur*, (*c*) *iodine, sulphur dioxide and water*, (*d*) *calcium chloride and ammonium carbonate and* (*e*) *steam on iron filings*, are studied in the manner indicated in the lecture.

CHAPTER XI.

CHEMICAL CHANGE (*continued*).

49. In studying the possibility, probability, extent, rate, etc. of chemical changes, a variety of circumstances have to be taken into consideration. Such, for example, as the temperature, pressure and concentration of the reacting system, the presence of catalytic agents and the so-called specific 'affinities' of the reacting substances. A brief outline will here be given of some of these circumstances or conditions which are of particular importance.

Law of Mass action.

Most of the leading chemists of the 18th century appear to have inclined to the opinion that a chemical change depended only on chemical 'affinity'—a term employed in a vague sense to imply generally a specific tendency to enter into reaction. Bergman for example (1775) considered that a chemical change acts exclusively in one direction, and proceeds to completion. $AB + C$ will give $AC + B$ if the affinity of A for C is greater than that of A for B. He supposed however that the order of the affinities might in certain cases be reversed, e.g. by alteration of temperature, or according as the change took place in the 'dry' or 'wet' way. Berthollet (1801) appears to have been the first definitely to suggest that the relative quantities of the reacting substances have to be taken into consideration as well as their affinities. "Toute substance qui tend à entrer en combinaison, agit en raison de son affinité et de sa quantité." He employed the word mass to mean, apparently, the product of quantity and affinity. In the neutralisation of a base by different acids, for example, he considered that the smaller the quantity of acid required to effect the neutralisa-

tion, the greater the affinity. He regarded all normal chemical changes as being of a limited or incomplete character; a completed reaction being due to changes in the state of aggregation, etc. He supposed however that combination in fixed proportions was not necessary and that the composition of compounds could be continuously varied within certain limits.

Williamson in 1851, from a study of etherification, came to the conclusion that the equilibrium arrived at in a chemical change is not a statical one but that a continuous balanced interchange of constituents is taking place.

Wenzel (1777) from observations on the dissolution of metals by acids came to the conclusion that the rate at which the action proceeds is proportional to the concentration of the acid; but the first accurate quantitative measurements in this direction were made by Wilhelmy, in 1850, who studied the rate of inversion of cane sugar in presence of acids. He shewed conclusively that the rate of change at any moment is directly proportional to the concentration of the cane sugar present at the time.

Berthelot and Pean de St Gilles in 1862 measured the rate of esterification of acids by alcohols and found that, initially, the rate was proportional to the product of the concentrations of the alcohol and the acid.

Guldberg and Waage (1867) gave a more precise and accurate meaning to Berthollet's conceptions and expressed the law of mass action in a mathematical form. Berthollet had regarded chemical change as being proportional to the quantity of the reacting substance without reference to chemical equivalence or concentration; whereas Guldberg and Waage introduced the idea of 'active mass' meaning thereby the number of molecules (or of equivalents) in unit volume. Chemical change then was proportional to the product of the active masses of the substances and a constant; the latter was called the 'coefficient of affinity' and expressed numerically the 'force' or 'tendency' which induced the change to take place in a certain direction. Since however the idea of this chemical 'force' is obviously vague and difficult to define, it was afterwards considered preferable, as emphasised by van 't Hoff, to regard these coefficients as velocity constants. According to

this idea chemical equilibrium results when the velocities of the forward and reverse change become equal. The term 'velocity' is here perhaps somewhat unfortunate, but it is still very generally employed in this connection.

In developing the law of mass action then, it will be seen that two different methods of observation have been employed; these are often referred to as the 'statical' and 'dynamical' methods. For the application of the first method a reversible chemical change is allowed to come to a state of equilibrium, under given conditions, and the quantities of the reacting substances are then estimated, for example by chemical analysis or by the determination of some characteristic physical property. In the second method a series of determinations of the concentration are made at definite intervals of time in order to study the rate at which the change proceeds. It is evident that so-called irreversible reactions are the best suited for studying the law by the second method since, in a reversible change, the forward reaction becomes more and more impeded by the reverse change as the action proceeds.

The law of mass action has been verified experimentally in a very large number of cases; it may be deduced theoretically from kinetic considerations, as was done by Guldberg and Waage, or it may be arrived at by thermodynamics. [See, for example, Nernst, *Theoretical Chemistry*, page 647.]

50. For the purpose of explaining the law in its most general form, one may define the *active mass* of a substance as the number of molecules of it present in unit volume, i.e. as the molecular concentration. (Practically, for example, moles per litre.) By the *rate of chemical change* or *reaction velocity* is understood the quantity of substance changed in unit time, i.e. $\frac{\text{quantity changed}}{\text{time}}$. But since the rate is continually changing it becomes necessary to specify the rate at a particular instant. If at the time t the infinitely small quantity dx is transformed in the infinitely small time interval dt, the rate of change at the time $= \frac{dx}{dt}$. Another

way of stating the matter is to take dC as the infinitely small diminution in concentration in the time dt; in this case, the rate is $-\frac{dC}{dt}$. [Since as time increases, x increases but C decreases.]

The law of mass action then states that the rate of change is proportional to the product of the active masses of the reacting substances.

If a single substance only (i.e. one molecular species) undergoes change and if only one molecule of it takes part in the change,

$$-\frac{dC}{dt} = kC,$$

where C is the active mass present at the time; k is a constant depending on the nature of the substance and the temperature (but independent of the concentration) and is called the *velocity constant.* (k therefore represents the reaction velocity when the reacting substance has unit concentration.)

If n molecules of the substance take part in the change,

$$-\frac{dC}{dt} = kC^n,$$

that is to say, the rate is proportional to the nth power of the molecular concentration.

Similarly, when two different molecular species A and B interact, and one molecule only of each is concerned in the change,

$$-\frac{dC}{dt} = kC_1C_2,$$

where C_1 and C_2 are the active masses respectively of A and B; and so on with any number of reacting substances. If n_1 molecules of A interact with n_2 molecules of B,

$$-\frac{dC}{dt} = kC_1^{n_1}C_2^{n_2}.$$

In a reversible or 'balanced' action the system will come to a state of equilibrium, at a given temperature, when the velocities of the forward and reverse changes are equal. In a reversible double decomposition of the type $AB + CD \rightleftarrows AD + CB$, for example, let the active masses of the four substances be denoted by C_1, C_2, C_3 and C_4, then the system will come to equilibrium when

$$kC_1C_2 = k_1C_3C_4,$$

k and k_1 being the velocity constants for the forward and reverse changes respectively. Or generally, if n_1 molecules of AB react with n_2 molecules of CD to give n_3 molecules of AD and n_4 molecules of CB

$$kC_1^{n_1}C_2^{n_2} = k_1C_3^{n_3}C_4^{n_4}.$$

A reaction is said to be of the first, second, third, etc. order according to the value of the sum of the exponents in the expression $kC_1^{n_1}C_2^{n_2}\ldots\ldots$ Theoretically then a reaction in which only one molecule takes part is a reaction of the first order, where two molecules take part it is of the second order and so on, whether the molecular species are the same or different. The terms 'unimolecular,' 'bimolecular' or 'termolecular' reaction are often used as synonymous with reaction of the first, second or third order, and it would appear that we have here a simple method for ascertaining the number of molecules which take part in a chemical change. It is true that in a considerable number of cases this theoretical conclusion is borne out by experiment, but, it must be confessed, there are other cases, probably more numerous, where the order of the reaction observed does not agree with the number of molecules taking part according to the generally accepted chemical equation. It is in fact very rarely that the measurement of reaction velocity indicates an order higher than the first or second; reactions of the third, fourth, etc. order are seldom met with. In those cases where the observed order is of a lower value than the number of molecules indicated by the chemical equation, it is the custom to make the assumption, which is not at all improbable, that the change takes place in stages, that these may proceed at very different rates and that the velocity actually measured is that of the slower change. In certain cases the abnormality' is otherwise explained. Examples of such cases will be given below.

In order to determine the order of a reaction various methods may be employed. The most usual method is to determine the concentration of the reacting substance at a series of different time intervals and to ascertain which of the various formulae give the nearest approach to constancy for the value of k. Thus, taking for example, a change in which only *one* molecule of a substance takes part in the change, if A is the original concentra-

tion at the start ($t = 0$) and x is the amount changed at the time t,

$$\frac{dx}{dt} = k(A - x);$$

whence, by integration,

$$k = \frac{1}{t} \log_e \frac{A}{A - x}.$$

[In practice if one is only seeking for constancy in the value of k, ordinary logarithms may be employed in place of $\log_e$.]

If *two* molecules take part in the change (i.e. two molecules of the same substance or one molecule each of two different substances taken in equivalent proportions)

$$\frac{dx}{dt} = k(A - x)^2,$$

whence

$$k = \frac{1}{t} \cdot \frac{x}{A(A - x)}.$$

If three molecules (of the same substance or of two or three different substances taken in equivalent proportions) take part in the change,

$$\frac{dx}{dt} = k(A - x)^3,$$

and

$$k = \frac{1}{t} \frac{x(2A - x)}{2A^2(A - x)^2}$$

and so on.

Instead of proceeding in the above manner (that is, in observing the rate when the volume is kept constant) one may start with different initial concentrations and observe the influence of change of volume on the velocity of the reaction. When the volume is V_1 let the rate observed be U_1; in a second experiment let the volume be V_2 and the observed rate be U_2. Then, if the reaction is one of the first order $U_1 : U_2 = V_2 : V_1$. But if the reaction is of the second order $U_1 : U_2 = V_2^2 : V_1^2$ and so on, since the concentrations are inversely as the volumes.

A different method again, which is applicable, for example, when three different substances take part in the change, consists in making the concentration of two of the substances (A) and (B) very large as compared with the other (C), so that the active

masses of (A) and (B) become practically constant and the number of molecules of (C) may be deduced from the simpler relation

$$-\frac{dC}{dt} = kC^n.$$

The rate of chemical change is greatly influenced by temperature; hence the necessity of keeping the temperature absolutely constant during the determinations. It is also influenced by the presence of contact substances or catalysts, and, in the case of reactions taking place in solution, by the nature of the solvent. Change of pressure also has an influence even in liquids and solids; in the case of gases the influence of pressure is obvious, since the concentration is altered correspondingly.

According to Röntgen and to Rothmund [*Zeit. Physikal. Chem.* 1896 (20) 168] the rate of inversion of cane sugar is increased by about 1 per cent. for an increase of pressure of 100 atmospheres.

The influence of temperature on reaction velocity has an important bearing on a large number of chemical problems and many changes which were at one time regarded as changes of equilibrium state with temperature can be shewn to be the result of alteration in reaction velocity. A rise of 10°, at ordinary temperatures, is usually found to increase the velocity of most reactions to about double or treble the original value; the rate of increase generally falls off, however, at higher temperatures. Compare Trautz and Volkmann, *Zeit. Physikal. Chem.* 1908 (64) 53. As an example of the influence of the solvent on the velocity of a reaction taking place in solution, Menschutkin's experiments may be referred to, in which he studied the rate of formation of tetraethylammonium iodide from triethylamine and ethyl iodide in various indifferent solvents. Taking the rate of decomposition in hexane as 1, the rates in benzene, bromobenzene, acetone and benzyl alcohol were as 38·2 : 150 : 337·7 : 742 respectively.

51. A few examples will now be given of chemical changes which have been studied by (1) the 'dynamical' or rate method and (2) the statical or equilibrium method.

Inversion of Cane Sugar.

The rate of 'inversion' of cane sugar in dilute aqueous solution, was first quantitatively studied, as above mentioned, by Wilhelmy.

In this change one molecule of cane sugar reacts with one molecule of water, giving one molecule each of dextrose and laevulose; since cane sugar is dextrorotatory and the resulting mixture ('invert sugar') is laevorotatory, the change can be readily followed by means of the polarimeter. At ordinary temperatures this change takes place so slowly that its progress is quite inappreciable; at 100°, however, it becomes noticeable after a few hours. But if a small quantity of a dilute acid (or of certain enzymes) be added as catalyst the rate is greatly increased and can be conveniently measured at, say, 25°. Experiment shews that the reaction is here one of the *first* order. It is true that two molecules actually taken part in the change as represented in the chemical equation, but the quantity of water is relatively so very large that its active mass may be regarded as constant. The active mass of the catalyst is also constant since it is, apparently, unchanged in the process. [The statement that the rate is proportional to the molecular concentration is not strictly true since, in strong solutions, one must take into account the space occupied by the sugar molecules. Thus it is found that the coefficient k increases considerably as the concentration of the sugar increases, instead of remaining constant. Cohen [*Zeit. Physikal. Chem.* 1897 (23) 442] considers that this is because the effective volume of reaction is reduced and hence the number of collisions between the acid (hydrogen ions) and sugar is increased. According to Arrhenius it is preferable to say that the rate is proportional to the osmotic pressure.]

Similar remarks apply to the *hydrolysis of methyl acetate* in dilute aqueous solution using acids as catalysts, which can easily be followed by simple titration with barium hydroxide.

The *decomposition of dibromosuccinic* acid into bromomaleic acid and hydrobromic acid in aqueous solution at 100° can also be examined by titration, since the degree of acidity increases as the reaction proceeds:

$$C_2H_2Br_2(COOH)_2 = C_2HBr(COOH)_2 + HBr.$$

Here again the action is found by experiment to be of the first order and, from the chemical equation, it is a unimolecular change.

The rate of *decomposition of ammonium nitrite*,

$$NH_4NO_2 = 2H_2O + N_2,$$

in aqueous solution, at temperatures of about 60—70°, can be followed by measurement of the gas evolved. The change takes place slowly at first owing apparently to the retention of the gas by the liquid (Harcourt) but afterwards proceeds regularly as a reaction of the first order. The decomposition is impeded or stopped by ammonia, amines, hydrazines or oximes, but is temporarily accelerated by certain amides [Veley, *Trans. Chem. Soc.* 1903, 736].

The interaction of hydrogen dioxide and hydriodic acid was first studied in an exhaustive manner by Harcourt and Esson in 1864. According to the chemical equation

$$H_2O_2 + 2HI = 2H_2O + I_2$$

the action should be termolecular. But by the simple device of adding known constant amounts of sodium thiosulphate as soon as the free iodine made its appearance, and having a sufficient excess of free acid present, they were able to keep the active mass of the hydriodic acid constant

$$(I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI)$$

consequently the concentration of the hydrogen dioxide only is continually diminished. The change is to some extent complicated by secondary reactions, but they were able to shew that, within wide limits of temperature and concentration, the amount of change at any moment is proportional to the amount of changing substance. [For detailed account see Harcourt and Esson, *Phil. Trans.* 1895 (186) 817.]

If the reaction is allowed to take place in the ordinary way, so that the concentration of the hydrogen iodide diminishes as well as that of the hydrogen dioxide, the change is found to be of the *second* order [Noyes and Scott, *Zeit. Physikal. Chem.* 1895 (18) 131], whereas the chemical equation indicates a reaction of the third order, as above stated. The authors mentioned consider it probable therefore that the change proceeds in stages, hypoiodous acid being an intermediate product,

$$HI + H_2O_2 = HIO + H_2O \text{ and } HI + HIO = H_2O + I_2.$$

It is supposed that the first change takes a measureable time and that the other is instantaneous.

The decomposition of arsenic trihydride. This change has been studied by heating the gas to a suitable temperature in a closed vessel connected with a manometer and observing the increase of pressure when the volume is kept constant (van 't Hoff and Kooy). In this decomposition two volumes of arsenic trihydride yields three volumes of hydrogen, at constant pressure, and the volume of the solid arsenic may be neglected. If therefore the volume is kept constant, the pressure will rise in the ratio of 2 : 3. The result of experiments in this direction shews that the reaction is one of the *first* order. This fact does not correspond therefore with the ordinary chemical equation

$$4AsH_3 = As_4 + 6H_2,$$

which should be a reaction of the fourth order. This discrepancy was at first explained away by assuming that the change took place in stages and that only the initial change $AsH_3 = As + 3H$ was slow enough to be measured. But a more probable explanation is that the decomposition only takes place on the surface of the vessel and that the rate is therefore proportional to that of the adsorption of the gas by the solid, which again, would be approximately proportional to the pressure.

According to Cohen [*Zeit. Physikal. Chem.* 1896 (20) 303 and 1898 (25) 483] the value of k does not become constant until the walls of the vessel are completely covered with arsenic. Admixture of the gas with nitrogen or hydrogen had no effect on the rate of decomposition.

[The experiments were made at a temperature of 310° (boiling diphenylamine); at this temperature the rate is measureable in hours and the slow rate at this temperature is considered by van 't Hoff to indicate that the molecules are not all in the same condition, otherwise they would be decomposed simultaneously or not at all.]

Many other gaseous chemical changes which according to the ordinary chemical equations should be polymolecular, are found experimentally to be of the first order and the results may be explained in a manner similar to that suggested in the foregoing

example. One may account in a similar way for the very irregular and diverse results which have been obtained by various observers in studying the rate of *combination of oxygen and hydrogen.*

Van 't Hoff for example heated the oxy-hydrogen mixture in glass bulbs to 440° for many hours and determined the rate of combination and Meyer, Krause and Askenasy made similar measurements at 518°. But in both cases abnormal results were obtained. "Disturbances occurred which completely mask the normal course of the reaction." Different results were obtained even with two different glass bulbs carefully cleaned in the same way and under similar conditions. Bodenstein, later, used porcelain vessels and obtained somewhat more regular results and concluded that the reaction was one of the third order although it is admitted that, at the temperatures employed, the rate is nearly proportional to the porcelain surface. Storch [*loc. cit.* 1896, 191] obtained results with the moist gases indicating a reaction of the ninth and with the dry gases, of the twelfth order! Bone and Wheeler, by a greatly improved method, have studied the rate of combination of these gases under various conditions and with a variety of different catalysts. They shew that the catalysing power of a new surface increases up to a steady maximum when successive charges of oxy-hydrogen are circulated over it and, after the surface has acquired its 'normal' degree of activity, the change is always of the 'monomolecular' type. [*Phil. Trans.* 1906 (206) 1.]

The decomposition of hydrogen dioxide in presence of catalysts (such as colloidal platinum) or under the influence of sunlight or of radium, is a reaction of the first order, whereas according to the usual equation, $2H_2O_2 = H_2O_2 + O_2$, it should be of the second order. According to Nernst however [*Zeit. electrochem.* 1905 (11) 710] the decomposition is of the second order when a current of air containing a known quantity of hydrogen dioxide is passed through a hot glass tube.

Perman and Greaves found that the rate of *decomposition of ozone* in glass vessels is approximately of the second order, but in contact with a porous substance (such as clay-pipe stems) it is of the first order. They consider that the decomposition takes

place mainly if not entirely at the surfaces and that the pressure measurements give no indication of the number of reacting molecules. (See page 185.)

Amongst normal reactions of the second order one may refer to the *saponification of ethyl acetate by caustic soda.* Here the change is practically irreversible. The action of acetic acid on alcohol is also found to be of the second order, but as the change proceeds the forward action is opposed by the reverse change, so that the velocity actually measured is the difference between the two opposing velocities $k_1C_1C_2 - k_2C_3C_4$.

The polymerisation of cyanic acid to cyamelide is found to be a reaction of the third order and is sometimes represented as $3HCNO = C_3H_3N_3O_3$ although the molecular weight of cyamelide is not known. Cyanic acid polymerises above 150° to cyanuric acid $H_3C_3N_3O_3$ but below that temperature to cyamelide, $H_xC_xN_xO_x$. The rate of the last mentioned change can be conveniently measured at ordinary temperatures. The reaction between *ferric chloride and stannous chloride* $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$ was found by Noyes to be of the third order; but some difference of opinion has existed with regard to this point; Kahlenberg [*Jour. Am. Chem. Soc.* 1894, 314] found the change to be of the second order. Noyes points out, however, that the rate is increased more by ferric chloride than by stannous chloride, in equivalent quantity, when these are added in excess; this fact is intelligible if two molecules of ferric chloride react with one of stannous chloride. (Compare page 152.)

Schenck [*Ber.* 1902, 351] studied the rate of transformation of ordinary *vitreous phosphorus into red phosphorus* at temperatures of 172° and 184°, using phosphorus tribromide as solvent. He found the reaction to be of the *second* order and concluded that since the vitreous phosphorus is usually regarded as having the molecular formula P_4 (see page 73) the initial change at any rate must consist of the conversion of P_4 into P_8. But it does not follow that red phosphorus has the latter formula; he suggests that P_8 is a very labile form quickly changing to a more highly polymerised modification. This result attracted considerable attention at the time and some chemists were inclined to draw general conclusions from it with regard to the nature of allotropic changes. But

the same author [*loc. cit.* 1903, 4207] has since repeated his experiments and the change is now found to be of the *first* order. Phosphorus iodide was employed as catalyst in the earlier experiments and it would appear that the red phosphorus in separating tended to carry down the phosphorus iodide and so remove it from the solution.

The few examples mentioned above will be sufficient to shew that it is necessary to use much caution in drawing conclusions, from the observed order of a reaction, as to the number of molecules which take part in a change. There has been, it must be confessed, rather a tendency to accept the evidence afforded by such experiments as conclusive when the result indicated was in accordance with that required by theory and to explain the result away when it was found not to be of the order expected.

Practical Work.

The study of Reaction Velocities in certain chemical changes.

I. *The decomposition of hydrogen dioxide.*

This change proceeds extremely slowly at ordinary temperatures. [A strong solution of the pure substance (e.g. Merck's '100 volume' solution) if kept in the dark will lose 1 per cent. or less in the course of a year.] In order to accelerate the change suitably for measurement in a short time one must therefore either raise the temperature or make use of a catalyst. A most convenient substance for this purpose is Bredig's colloidal platinum, the preparation of which was illustrated in the lecture.

Prepare a solution of pure hydrogen dioxide of about 0·06 molar strength (e.g. about 7 c.c. of Merck's '100 volume' solution in a litre of water). Place 50 c.c., or 100 c.c., of this solution in a flask (best coated with paraffin), keep it in the thermostat at some constant temperature—say 25°—and add 2 c.c. of the colloidal platinum solution. Now withdraw 5 c.c. of the mixture, mix it with excess of dilute sulphuric acid and titrate with a dilute solution of potassium permanganate of convenient strength—say about $\frac{N}{20}$. (For our present purpose it is unnecessary to know the

exact strength of the permanganate.) Let C_1 be the number of c.cs. of permanganate required. Take as the time observation (t_1) the mean time between the beginning and end of the titration. Repeat the observations, using 5 c.c. of the hydrogen dioxide mixture each time, at intervals of, say, five minutes, and thus get the values of C_1, C_2, C_3... corresponding to the times t_1, t_2, t_3.... Make about eight or ten of these observations and calculate the values of K according to the formula for a reaction of the first and of the second order*. If the reaction is of the first order,

$$K = \frac{1}{t_2 - t_1} \cdot \log \frac{C_1}{C_2} = \frac{1}{t_3 - t_2} \cdot \log \frac{C_2}{C_3} = \frac{1}{t_n - t_m} \cdot \log \frac{C_m}{C_n}.$$

[Since one is only ascertaining the constancy of K, ordinary logarithms may be employed.]

If it is of the second order,

$$K = \frac{1}{t_2 - t_1} \cdot \frac{C_1 - C_2}{C_1 \times C_2} = \frac{1}{t_3 - t_2} \cdot \frac{C_2 - C_3}{C_2 \times C_3} = \frac{1}{t_n - t_m} \cdot \frac{C_m - C_n}{C_m \times C_n}.$$

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* If the reaction is of the first order, $-\frac{dC}{dt} = KC$ and, by integration,

$$-\log_e C = Kt + \text{a constant.}$$

If now C_1 and C_2 are the concentrations at the times t_1 and t_2 we shall have

$$-\log_e C_1 = Kt_1 + \text{a constant}$$

and

$$-\log_e C_2 = Kt_2 + \text{a constant.}$$

Hence by subtraction, $-\log_e C_2 + \log_e C_1 = K(t_2 - t_1)$ and $K = \frac{1}{t_2 - t_1} \cdot \log_e \frac{C_1}{C_2}$.

If the reaction is of the second order and only one kind of substance is concerned in the change (or if, as in the second example, two different substances react in equal molecular proportions)

$$-\frac{dC}{dt} = KC^2$$

and, by integration,

$$\frac{1}{C} = Kt + \text{a constant.}$$

Taking C_1 and C_2 as the concentrations (of the one substance in the first case or *either* of the two substances in the second case) at the times t_1 and t_2 respectively we have

$$\frac{1}{C_1} = Kt_1 + \text{a constant}$$

and

$$\frac{1}{C_2} = Kt_2 + \text{a constant;}$$

so that

$$\frac{1}{C_2} - \frac{1}{C_1} = K(t_2 - t_1) \text{ or } K = \frac{1}{t_2 - t_1} \frac{C_1 - C_2}{C_1 \times C_2}.$$

Note that it is not necessary to take the first, or any particular, reading; any two observations should give equal values for K. Instead of taking constant intervals of five minutes, the intervals may be increased as the change proceeds.

The experiments may afterwards be modified in various ways. A series of observations may be made, for example, at some other temperature, say 20° or 30°, and the influence on the value of K noted*. Similarly instructive experiments may be carried out by ascertaining the effect of 'poisons' (HCN, $HgCl_2$, etc.) of electrolytes such as Na_2HPO_4, or of varying proportions of the catalyst. [See page 197.]

II. *The saponification of ethyl acetate.*

A dilute solution of ethyl acetate is mixed with an equivalent quantity of caustic soda and kept at a constant temperature as in the previous experiment. [The flasks employed, preferably of Jena glass, should be 'steamed' for about half an hour before use, otherwise notable quantities of alkali may be derived from the glass.] Measured volumes of the mixture are then withdrawn at definite intervals and are introduced at once into a measured excess of dilute nitric acid. In this way the saponification is suddenly arrested at the given time. The excess of nitric acid remaining is then determined by titration with pure sodium hydroxide (free from carbonate) using phenol phthalein as indicator.

Since the sodium hydroxide and ethyl acetate react in equal molecular proportions, the concentration of the sodium hydroxide found by the titration is a measure of that of the ethyl acetate which remains unchanged.

Prepare solutions of pure ethyl acetate and of sodium hydroxide (free from carbonate) of $\frac{1}{20}$ molar strength (e.g. 0·444 gram ethyl acetate in 100 c.c. and $\frac{N}{20}$ sodium hydroxide). The two solutions are kept in (steamed) flasks in the thermostat until they have attained the temperature of the bath. Equal volumes (say 50 c.c.) of each solution are withdrawn and mixed together; the mixture is then well shaken and again kept at the constant tem-

* The influence of concentration on the order of the reaction should also be studied. Compare Dyer and Dale, *Proc. Chem. Soc.*, 1913, 55.

perature. After two or three minutes a measured volume (say, 5 c.c. or 10 c.c.) of the mixture is withdrawn by means of a pipette and immediately run into a (steamed) flask containing 10 c.c. of $\frac{N}{20}$ nitric acid. [It is advisable to have ready about ten flasks into each of which 10 c.c. of the nitric acid has been measured.] The time of observation is taken as the mean of that at which the first and last drop of the mixture leaves the pipette. The excess of nitric acid remaining is then determined by titration, best with $\frac{N}{40}$ sodium hydroxide. The observations are repeated at stated intervals, beginning say with three minutes. It is evident that the amount of sodium hydroxide required in the titration will continually increase as the time increases; the alkali in the original mixture is continually diminishing so that the amount of nitric acid used to neutralize it will correspondingly decrease. The concentrations C_1, C_2, etc. of the sodium hydroxide, and therefore of the ethyl acetate, in the mixture taken at the times t_1, t_2 etc. are therefore found by subtracting the volumes V_1, V_2, etc. of nitric acid found in excess, from 10 c.c. The value of the constant K is then calculated in the manner indicated above.

Experiments of this kind on the rate of saponification have many important applications; they may be employed for example in comparing the relative strengths of bases. [See Chap. XX.]

III. *Harcourt and Esson's experiment.*

In order to obtain the most accurate results by this method a large number of minute details have to be taken into consideration; the rate of change is influenced, for example, by the amount of free acid, and to some extent by the nature and quantity of the salts used. But the experiment even if carried out in an approximate manner, suitable for a demonstration, will be found to be highly instructive. For this purpose solutions of potassium iodide, sulphuric acid, hydrogen dioxide and starch are prepared of suitable strengths and the quantities employed are so adjusted that the times of observation are not inconveniently long or short. Take, for example, 20 c.c. of dilute sulphuric acid, say 1 in 6, and dissolve in it a few crystals of potassium iodide. Dilute

the mixture considerably (say to 200 or 300 c.c.) and add a few drops of the starch as indicator. Measure out into test tubes, 10 or 12 quantities of 5 c.c. each, of $\frac{N}{20}$ sodium thiosulphate. Now add 20 c.c. of hydrogen dioxide solution, of about 0·3 per cent. strength, to the mixture of iodide and acid and, as soon as the blue colour is observed, throw in one of the measured quantities of thiosulphate and shake. The blue colour will be immediately discharged but will reappear after a certain interval of time. The instant that the reappearance of the colour is observed the time is noted and a second quantity of the thiosulphate is added. The intervals of time required for the reappearance of the blue colour will continually increase since the active mass of the hydrogen dioxide is continually diminishing. If the solutions employed are of known strength, the concentration of the hydrogen dioxide at the given time can be found from the total quantity of thiosulphate which has been added.

IV. *The hydration of ammonium carbamate.*

When ammonium carbamate is dissolved in water, it is slowly converted into ammonium carbonate; the change, however, is limited and reversible,

$$CO\begin{matrix}\diagup NH_2\\ \diagdown O(NH_4)\end{matrix} + H_2O \rightleftarrows CO\begin{matrix}\diagup O(NH_4)\\ \diagdown O(NH_4)\end{matrix}.$$

It happens that the progress of this change can be easily followed by measurement of the volume of nitrogen which is evolved when the mixture is treated with excess of sodium hypochlorite in presence of sodium hydroxide. For, under these circumstances, the nitrogen of the (NH_4) group is liberated in the free state, whereas the NH_2 group is not attacked.

$$2CO(NH_2).ONH_4 + 3NaClO + 2NaOH$$
$$= 2CO(NH_2)ONa + 3NaCl + 5H_2O + N_2.$$

A weighed quantity of the carbamate is dissolved in water, the solution kept at a constant temperature; measured volumes are then withdrawn at stated intervals and examined by treatment with the reagents mentioned.

Since the hydration is a reversible process, the rate measured represents the difference between the forward and reverse action,

but the latter is relatively small. The change is of interest as an example of a reaction in solution in which one of the acting substances is the solvent itself. It will be instructive therefore to ascertain the effect, on the rate of change, when the solution is diluted. This effect may be illustrated as follows:

Dissolve ammonium carbamate in cold water. (Say, about 6 grams in 100 c.c.) Dilute a portion of the solution to 2 or 3 times its volume, allow both solutions to stand at the same temperature for 20 minutes and then determine the nitrogen evolved from equivalent amounts of the two solutions by the hypochlorite method. Take, for example, 5 c.c. of the strong solution and 10 or 15 c.c. of the diluted solution.

CHAPTER XII.

CHEMICAL CHANGE (*continued*).

52. Equilibrium. In studying the law of mass action we have so far confined ourselves to the consideration of the rate of change. Some examples may now be given of the application of the law to the study of reversible systems in which equilibrium has been established. In making experiments in this direction conditions have to be chosen such that the equilibrium condition is attained in a conveniently short period of time; that is to say it is frequently necessary to accelerate the rate of change either by working at temperatures higher than the ordinary temperature or by the use of catalysts.

A type of reversible change which is extremely well suited for experiments of this nature is afforded by the process of *esterification*, to which reference has already been made. The alcohol and acid, or the ester and water, are heated to a suitable temperature in sealed vessels until equilibrium is attained. (This point must be ascertained by repeated analyses under the same conditions, of similar mixtures, until constancy of composition is reached.) If known quantities of the two substances are taken to start with, it is evident that the estimation of any one constituent, alcohol, acid, ester or water, will be sufficient to define the system. The free acid is naturally the most easy to determine; fortunately, it generally happens that this determination may be made by simple titration with baryta water, since the amount of action of this reagent on the ester is, as a rule, negligible under the experimental conditions.

Let p molecules of alcohol be mixed with q molecules of a monobasic acid and produce p' molecules of ester and q' molecules

of water, and let V be the volume of the reacting mixture. Then the active masses of the four substances are $\frac{p}{V}, \frac{q}{V}, \frac{p'}{V}$ and respectively.

When equilibrium is attained we shall have therefore the relation,

$$\frac{p}{V} \cdot \frac{q}{V} \cdot k = \frac{p'}{V} \cdot \frac{q'}{V} k'.$$

It appears therefore that the final state of equilibrium should be independent of the volume of the reacting mixture, since the V's cancel. Experiment shews that this is the case. The state of equilibrium will evidently be independent of the initial state of the system, i.e. it will be the same whether we start from alcohol and acid or ester and water. It is also evident that if to the system in equilibrium we introduce an additional quantity of one of the constituents, the equilibrium will be shifted. If, for example, we increase the proportion of alcohol, the product on the left hand side of the equation becomes too large for equilibrium and change must proceed in the direction of further esterification.

By analysis of the equilibrium mixture we can, as above indicated, determine the values of p, q, p' and q'; we cannot directly determine either k or k' but we can obtain their ratio. Thus, making use of the much quoted example, let us start with a mixture of the four constituents which has not reached the equilibrium state. Suppose, for example, that esterification is still proceeding. Let the quantities *started with* be p, q, p' and q' molecular proportions as before. Then, when equilibrium is attained, a further quantity x of alcohol will be esterified, an equivalent quantity x of acid being used in the process so that

$$(p - x)(q - x) k = (p' + x)(q' + x) k'.$$

If we start with one molecular proportion each of alcohol and

$$p = 1,\ q = 1,\ p' = 0 \text{ and } q' = 0, \text{ so that } (1 - x)^2 k = x^2 k'$$

and

$$\frac{k}{k'} = \frac{x^2}{(1 - x)^2}.$$

In the case of ethyl alcohol and acetic acid experiment shews that $x = \frac{2}{3}$ and consequently $\frac{k}{k'} = 4$. Knowing this value, we are

in a position to predict the composition of the equilibrium mixture which will result when other known proportions of the constituents are allowed to interact. If, for example, one molecule of ethyl alcohol and two molecules of acetic acid are taken to start with, we shall have

$$\frac{x^2}{(1-x)(2-x)} = 4,$$

whence $x = 0{\cdot}845$, a number which agrees fairly well with that found by experiment (0·858).

In the experiments here quoted [Berthelot and Péan Saint Gilles *loc. cit.*] it was found that the degree of esterification, when equilibrium was attained was, within wide limits, practically the same at different temperatures (10° to 220°). [The *rate* at which the change proceeds is of course enormously influenced by temperature, as above mentioned; thus the time required for the system to come to equilibrium at 10° is measured by years, whereas at 200° about 24 hours is sufficient.]

The equilibrium in the system $2HI \rightleftarrows H_2 + I_2$ may be formulated in a similar way. If one molecular proportion of hydriodic acid is taken and a fraction x (molecular proportion) of it undergoes dissociation, there will be formed $\frac{x}{2}$ molecular proportions of hydrogen and $\frac{x}{2}$ molecular proportions of iodine, so that, if V is the volume of the reacting mixture, the acting mass of the hydriodic acid will be $\frac{1-x}{V}$ and that of the hydrogen and iodine will each be $\frac{x}{2V}$ and when equilibrium is attained

$$\frac{(1-x)^2}{V^2}K = \left(\frac{x}{2V}\right)^2 \quad \left[K = \frac{k}{k'}\right].$$

Or one may consider a fraction $(1-2x)$ of the hydriodic acid left undissociated, in which case

$$\frac{(1-2x)^2}{V^2}K = \frac{x^2}{V^2}.$$

This relation shews at a glance that the degree of dissociation is independent of the volume, and therefore of the pressure, as found experimentally. The addition of more hydrogen or more

iodine to the equilibrium mixture will evidently make the right-hand side of the equation too large and consequently the equilibrium will be shifted in the direction of further combination, i.e. less dissociation, at the given temperature.

In these two examples we have been concerned with chemical changes of the type $AB + CD = AD + CB$, or 'double decompositions'; we will now consider a case of dissociation in the stricter sense, that is the reversible resolution of a more complex into two or more simpler molecules. Take for example the familiar instance of the dissociation of phosphorus pentachloride

$$PCl_5 \rightleftarrows PCl_3 + Cl_2;$$

let one molecular proportion of it be taken and a fraction x (molecular proportions) undergo dissociation. Then, when equilibrium is reached,

$$\frac{1-x}{V} K = \frac{x}{V} \cdot \frac{x}{V}.$$

From this it is evident that increase of volume will increase the degree of dissociation, since the volumes no longer cancel. In order to ascertain the effect of adding an excess of one or other product of dissociation we may proceed in the following simple way, which was first suggested by Bancroft.

To the equilibrium mixture add an excess of chlorine (or of phosphorus trichloride) at the *same partial pressure* as it is contained in the mixture, that is, let V volumes of it contain x molecules.

If the added volume is nV the total volume of the mixture will now be $V + nV$. The result will then be

$$\frac{1-x}{V+nV} K = \frac{x}{V+nV} \cdot \frac{x+nx}{V+nV}$$

or

$$\frac{1-x}{(n+1)V} K = \frac{x}{(n+1)V} \cdot \frac{(n+1)x}{(n+1)V}.$$

Since here the $(n+1)$ factor cancels, it is evident that the addition of the excess of chlorine (or trichloride) under the stated conditions, has no influence on the degree of dissociation. If the chlorine added has a pressure greater than its partial pressure in the original mixture, the dissociation will be diminished since x

will increase more than V, and conversely. In Wurtz's experiment (page 21) the trichloride was added at *constant volume* hence the dissociation was thereby diminished.

In the hydrogen iodide equilibrium we should have, in the first instance,

$$\frac{1-2x}{(n+1)V}\cdot\frac{1-2x}{(n+1)V} \text{ and } \frac{x}{(n+1)V}\cdot\frac{(n+1)x}{(n+1)V}$$

as the active masses of the hydrogen iodide and the hydrogen iodine mixture, respectively. The right hand side of the equation is now too large for equilibrium and it follows therefore that the addition of hydrogen, or of iodine, will diminish the dissociation notwithstanding the increase of total volume.

The effect of dilution on equilibrium in a system in which the *diluting agent is one of the acting substances* may be illustrated in a similar way. Only a few such cases have been practically investigated, but the question is evidently well worth attention and the following examples may be referred to.

A calculation on the foregoing lines might be made to investigate the effect of dilution on the degree of hydration of a substance in aqueous solution. Take for example a non-electrolyte A which forms a dissociable hydrate in simple molecular proportion,

$$A + H_2O \rightleftarrows A.H_2O$$

and suppose for simplicity that the concentration of the water in the solution is practically the same as in the water itself and that no expansion or contraction occurs on dilution. The case will then be analagous to that of the dissociation of phosphorus pentachloride and, on dilution,

$$\frac{x}{(n+1)V}\cdot\frac{(n+1)x}{(n+1)V} K = \frac{1-x}{(n+1)V}.$$

The conditions named may be regarded as being nearly fulfilled if the solution is sufficiently dilute; one may say therefore that in a dilute solution the active mass of water is constant and the ratio $\frac{1-x}{x}$ is constant; under such conditions therefore, dilution makes no difference in the degree of hydration.

An example closely analogous to this was investigated by Nernst and Hohmann [*Zeit. Physikal. Chem.* 1893 (11) 352]. It

has been shewn that the esters produced by the action of acids on tertiary amyl alcohol undergo decomposition when heated (in presence of a sufficient excess of acid) into amylene (trimethylethylene) and the free acid. For example,

$$CCl_3COO(C_5H_{11}) \rightleftarrows CCl_3COOH + C_5H_{10}.$$

In order to determine the state of equilibrium in such systems the acid was heated to 100°, in sealed tubes, with varying proportions of amylene for a sufficiently long time and the mixture was then analysed by titration. The authors found that the quantity of ester produced from one molecule of the acid was nearly the same when it was heated with amounts of amylene varying from 4 to 14 molecules.

[According to Konowaloff, *Journ. Russ. Phys. Chem. Soc.* 1907 (39) 825, the equilibrium is of a more complicated character.]

A change which at first sight appeared to be of the same order was investigated by the present writer in 1885 [*Proc. Roy. Soc.* (241) 386]. It was mentioned above (page 144) that the change of ammonium carbamate into ammonium carbonate in aqueous solution is reversible and limited and it appeared therefore to be of interest to study the conditions of equilibrium of the system at various temperatures and at different dilutions. A simple method of determining the progress of the change was afforded by the action of sodium hypochlorite, to which reference has already been made. The results of the experiments shewed that the equilibrium state is arrived at in the course of two or three hours and that the hydration proceeds further at higher temperatures. It was also found that, at constant temperature, the degree of hydration increases as the solution is more dilute. For example

Mols. of carbamate	Mols. of water	Degree of hydration
1	200	0·748
1	300	0·796
1	400	0·844
1	500	0·916

No great accuracy could be expected from the method employed but the results are sufficient to shew that the change proceeds further on dilution, although water is the diluting agent. This

result did not then appear to be in agreement with the law of mass action since it was supposed that the change was of the simple type $A + B \rightleftarrows AB$. But the result is easily accounted for on the hypothesis of ionisation which, at the time mentioned, was unknown.

In the *hydrolysis of salts*, if we consider the simplest type, we have a change of the 'double' decomposition order:

$$MX + H.OH \rightleftarrows HX + M.OH$$

whence $K = \dfrac{x^2}{(1-x)(n-x)}$, since V cancels.

But in a dilute solution we may regard the active mass of water as constant, so that the change is then of the type

$$K = \frac{x^2}{(1-x)V}.$$

From this we see that if the degree of hydrolysis is small, x, varies approximately as the square root of the dilution. The same result is arrived at if we regard the change in terms of the ionic dissociation hypothesis.

In the system $PCl_5 \rightleftarrows PCl_3 + Cl_2$ it is evident that the addition of excess of either the trichloride or chlorine, in equivalent proportion, at constant volume, will diminish the degree of dissociation of the trichloride to the same extent. If however a compound dissociates into two simpler compounds and these latter are produced in unequal molecular ratio, the effect of adding excess of one or other product will not be the same. Thus it was shewn by Naumann and Horstmann that the *dissociation of ammonium carbamate*,

$$CO(NH_2)ONH_4 \rightleftarrows 2NH_3 + CO_2,$$

at a given temperature, is diminished by the addition of excess of either ammonia or carbon dioxide, but that ammonia has a greater effect than carbon dioxide. These experiments were made at constant volume; but it is interesting to ascertain what the result would be if the gases, respectively, were added at the same partial pressure and the volume allowed to increase.

In the original system obtained by heating ammonium carbamate itself to a given temperature, we shall have

$$\frac{1-x}{V} K = \frac{2x}{V} \cdot \frac{2x}{V} \cdot \frac{x}{V}.$$

If now we add say, an equal volume of ammonia at the same partial pressure (i.e. V volumes contain $2x$ molecules) the result will be

$$\frac{1-x}{2V}K = \frac{4x}{2V}\cdot\frac{4x}{2V}\cdot\frac{x}{2V},$$

that is, the equilibrium will not be affected; whereas if an equal volume of carbon dioxide were added, at its same partial pressure, instead of ammonia, the initial active masses would be

$$\frac{1-x}{2V}K \text{ and } \frac{2x}{2V}\cdot\frac{2x}{2V}\cdot\frac{2x}{2V},$$

so that the degree of dissociation would be *increased.*

In the foregoing examples we have confined ourselves to the application of the law of mass action to the equilibrium in homogeneous systems. For the purpose of extending the law to *heterogeneous systems* in which solids are in equilibrium with gases or liquids, one may suppose that all solids are in reality volatile, but that the vapour pressure of the so-called ' non volatile ' solids are so small as to be imperceptible by ordinary methods of observation. In the case of the system $CaCO_3 \rightleftarrows CaO + CO_2$, for example, it is assumed that vapours of $CaCO_3$ and of CaO are actually present in the space above the solids and that the law of mass action may be applied to the equilibrium between these vapours and carbon dioxide. But since there are always appreciable quantities of the solids present when the system is in equilibrium, and the actual quantities of the vapours of these solids are almost infinitely small, it follows that one may regard their active masses as constant, that is, the value of these active masses may be included in the constant K. In the equilibrium here mentioned we shall have

$$kC = k'C'P,$$

where C, C' and P represent the active masses of the chalk, lime and carbon dioxide respectively. But since C and C' are constant,

$$\frac{kC}{k'C'} = P$$

that is, the pressure of the carbon dioxide is constant for a given temperature and independent of the quantities of chalk and lime, so long as appreciable quantities of these are present.

Again, in the system

$$\text{steam} + \text{iron} \rightleftarrows \text{oxide of iron} + \text{hydrogen}$$

the active masses of the iron and oxide of iron are constant, so that, at a given temperature the ratio of the pressure of the water vapour (P_1) and of the hydrogen (P_2) should be constant. This will be the case no matter what is the composition of the resulting oxide of iron, since the number of molecules of hydrogen found is equal to that of the water consumed. Hence if the oxide were Fe_3O_4 we should have $\frac{P_1^4}{P_2^4} = K$, whereas if the oxide were Fe_4O_5 the relation would be $\frac{P_1^5}{P_2^5} = K$, and so on.

Deville in 1870 determined the value of this ratio at given temperatures; he kept the water vapour pressure constant in each experiment and determined the pressure of the resulting hydrogen. Using different pressures of water vapour, he found that at a given temperature the ratio was approximately constant; its value at 440°, for example, was about 0·178.

Pruener [*Zeit. Physikal. Chem.* 1904 (47) 385] has extended these observations and finds for the ratio the mean values

0·69 at 900°, 0·78 at 1025° and 0·86 at 1150°.

The equilibrium between a volatile solid and its vapour when the latter undergoes dissociation, is well illustrated by reference to the behaviour of the ammonium salts of volatile acids (such as the ammonium halides or carbamate). If the solid salt is heated, to a suitable temperature, in a closed vessel, it will be found that, as long as any of the salt remains, there is a constant (total) vapour pressure for a given temperature. The solid will then be in equilibrium with its own vapour (i.e. the undissociated compound) and the latter will also be in equilibrium with its products of dissociation.

In the cases of ammonium chloride, bromide, iodide, cyanide and hydrosulphide, the equilibrium, as regards the vapour phase, will be regulated by the relation

$$kP = k'p^2$$

where P is the partial pressure of the vapour of the undissociated

compound and p is the partial pressure of each of the products of dissociation, since they are produced in equal molecular proportions.

But since, in the cases mentioned, the dissociation is very nearly complete, the total pressure measured, P_0 is practically equal to the sum of the partial pressures of the products of dissociation, i.e. $p = \frac{P_0}{2}$

Consequently, in the gaseous phase,

$$kP = k' \frac{P_0^2}{4},$$

and since at any given temperature the vapour pressure P of the undissociated compound must be constant, the product $\frac{P_0^2}{4}$ must also be constant.

Addition of one or other product of dissociation at constant volume will of course diminish the degree of dissociation and, in the cases mentioned, either product will diminish it to the same extent. The result will therefore be that the dissociation pressure is diminished although the pressure of the undissociated compound and the product of the partial pressures of the dissociated products, remain constant.

The experimental results hitherto obtained agree remarkably well with the theory here indicated. Compare, for example, Isambert's experiments with ammonium hydrosulphide and with ammonium carbamate [*C. R.* 1881 (93) 731 and 1883 (97) 1212]. Abegg and Johnson [*Zeit. Physikal. Chem.* 1908 (61) 455 and (62) 194, 678] have recently made observations with ammonium chloride which, unless some further assumption is made, appear to offer a remarkable exception. They find that this substance, when vaporised, exerts the same pressure whether it has been perfectly dried or not. Ammonium chloride in its ordinary state, when vaporised, undergoes almost complete dissociation, whereas when exceptionally well dried it vaporises unchanged. Hence one would expect, on the reasoning outlined above, that the vapour pressure of the perfectly dried substance should be extremely small since, whether dry or not, the solid is in equilibrium with its own undissociated vapour. Yet the experiments quoted shew that the vapour pressure of the dry substance is, at a given temperature, as great as the sum of the partial pressures of the dissociation products of the undried substance. For criticisms and possible explanations see van Laar, *Zeit. Physikal. Chem.* 1908 (62) 194; Abegg, *ibid.* 607; Wegscheider, *ibid.* (65) 97, etc.

Practical Work.

It is not easy to provide simple and accurate experiments, suitable for demonstration purposes, by which the law of mass action may be illustrated in systems which have come to a state of equilibrium. In many of the examples mentioned above the time taken to reach the equilibrium state would be inconveniently long at the ordinary temperature, and the temperature necessary to accelerate the change sufficiently would be inconveniently high. If it is desired, for example, to demonstrate the final state of equilibrium in the esterification of ethyl alcohol by acetic acid weighed quantities of the substances must be heated in sealed tubes to a temperature of 155° in order that the final state may be reached in about 48 hours.

The following experiments are instructive as qualitative illustrations of the influence of concentration on the final equilibrium, although accurate quantitative results must not be expected.

1. The fact that the change

$$FeCl_3 + 3KCNS \rightleftarrows Fe(CNS)_3 + 3KCl$$

is limited is easily shewn by the fact that when aqueous solutions of the substances are mixed, in the proportions represented in the equation, the red colour obtained is not the maximum. If the volume of the mixture is kept constant it can easily be shewn that, taking a given weight of one constituent, the intensity of the colour increases as increasing proportions of the other constituent are added.

Standard solutions of the two substances are given which contain the two substances in *equivalent* proportions (e.g. $\frac{N}{20}$ solutions of each), 10 c.c. of each solution are mixed together in a 'Nessler' cylinder and the mixture diluted to a convenient volume, so that the colour is not too intense; 10 c.c. of one solution is then mixed with 20, 40, 60...c.c. of the other and each mixture is made up to the same volume. The cylinders containing the various mixtures are then placed on a sheet of white paper and the colour intensities compared. Similar experiments are then made by taking quantities of 10 c.c. of the second substance and

adding varying excess of the first. No direct quantitative conclusions can be arrived at from these results alone, since the effects are complicated by ionisation. [The red colour is supposed to be due to non-ionised $Fe(CNS)_3$; it is clearly not due to the simple Fe''' or (CNS) ions. It might be due to a complex anion such as $[Fe(CNS)_6]$. Rosenheim and Cohn, however [*Zeit. Anorg. Chem.* 1901 (27) 280], state that this complex, which is violet in alcohol solution, is decomposed by water giving red ferric thiocyanate.

2. Experiments may be made on the equilibrium state which is reached in the system ammonium carbamate—water at a given temperature, when the proportions are varied.

Dissolve about 5 grams of ammonium carbamate in 100 c.c. of water. Dilute 25 c.c. of this solution up to 50 c.c. and another 25 c.c. of it to 250 c.c. Allow the three solutions to stand for some hours and determine the nitrogen evolved when a suitable volume of each solution is acted upon by sodium hypochlorite and sodium hydroxide. Take, for example, 5 c.c. of the first solution, 10 c.c. of the second and 50 c.c. of the third.

Examine each solution after a longer interval, say 48 hours, in order to ascertain whether equilibrium had been established.

As a result of such experiments, it will be found that after equilibrium is established, the hydration has proceeded further in the more dilute solution.

CHAPTER XIII.

CHEMICAL CHANGE (*continued.*)

Influence of temperature.

53. Considerable difficulty was at one time experienced in accounting for the different results which may be obtained by alteration of temperature in chemical systems. Raising the temperature caused increased dissociation in the majority of reactions studied, but on the other hand the opposite effect was often observed, for example, in the combination of iodine and hydrogen. The fact that oxygen and hydrogen in combining evolve a large amount of heat and yet do not combine unless the temperature of the mixture is sufficiently raised, was explained by supposing that the molecules of the elementary gases had first to be dissociated into free atoms before they were able to combine. Much of the difficulty which has existed in attempting to give a general explanation of the influence of temperature on chemical change has, in fact, been due to a confusion between the reaction velocity and the final distribution, in reversible systems, when equilibrium is attained.

As regards reaction velocity, the influence of temperature is, as has previously been mentioned, generally very great; in nearly all cases the effect of raising the temperature is to increase the reaction velocity. But as regards the final state of equilibrium, the effect may be to displace the point of equilibrium either way, or, in a few instances the effect may be practically zero. In a reversible chemical system both the forward and the reverse reactions will be accelerated by rise of temperature; but, in general the increase is different for the two, so that the point of

equilibrium will be shifted. When it is found that the point of equilibrium is not altered by changing temperature it must be assumed that the forward and reverse action are equally influenced.

The *direction* in which the equilibrium state will be shifted by change of temperature can be predicted at once, if the sign of the thermal value of the change is known, by the application of the *rule of le Chatelier* (otherwise known as "the principle of resistance of reaction to action" or "the principle of least action"). This rule, which is a deduction from thermodynamic reasoning, states, in effect, that if a system which is in equilibrium be subjected to a constraint (i.e. to an alteration of one of the conditions upon which the equilibrium depends, such as temperature, pressure or concentration) a change will take place in the system which is in opposition to the constraint. The effects of change of pressure and of temperature in the system, ice $\rightleftarrows$ water, afford familiar examples. Here the result of increasing the pressure, at constant temperature, or of increasing the temperature, at constant pressure, is to bring about melting of ice—a change which is attended by diminution of volume and absorption of heat. Van 't Hoff's "principle of mobile equilibrium" is an application of this rule to the case in which the imposed constraint is an alteration of temperature. If a system, at constant volume, is in equilibrium at a certain temperature and the temperature is then *raised* the change (if any) which takes place in the system will be of an endothermic character, i.e. one in which heat is *absorbed*—and *vice versa*. In the reversible systems $CaCO_3 \rightleftarrows CaO + CO_2$, $N_2O_4 \rightleftarrows 2NO_2$ and most other processes of dissociation, the forward change is attended with absorption of heat; raising the temperature therefore shifts the equilibrium in the direction of further *dissociation*. But the synthetical formation of cyanogen, nitric oxide, carbon disulphide or acetylene from their elements is attended with absorption of heat; here then raising temperature favours the *formation* of the compound. In the system $3O_2 \rightleftarrows 2O_3$ the forward change is accompanied by absorption of heat; i.e. ozone is an 'endothermic compound' so that the proportion of ozone in the mixture should be greater the higher the temperature. This actually appears to be the case, although the experimental evidence of different authors is

somewhat contradictory. Clement, for example [*Ann. Physik.* 1904 (14) 334], passed a rapid stream of oxygen over the electrolytic glow body of a Nernst lamp and was unable to detect any ozone. But F. Fischer and Brachmar [*Ber.* 1906 (39) 940] state that they have definitely proved the production of ozone at high temperatures. The oxygen was heated in various ways—for example, by combustion of hydrogen, etc., by an electrically heated platinum wire and by means of a Nernst filament—and in all cases ozone was produced. In order to detect the ozone, the products are suddenly cooled by liquid air or liquid oxygen; it is probable that the failure of previous observers has been due to the very great rate at which ozone decomposes, at high temperatures, as the temperature is lowered. If then the production of ozone is favoured by rise of temperature it would appear, at first sight, difficult to explain the ordinary lecture experiment in which ozonised oxygen is passed through a heated tube; the result of this experiment, it will be remembered, is that ozone can no longer be detected in the mixture. The probable explanation appears to be that the equilibrium mixture $3O_2 \rightleftarrows 2O_3$ at ordinary temperatures contains a proportion of ozone which is quite inappreciable by tests. The mixture taken, containing say 4 or 5 per cent. of ozone, is already in the process of slow decomposition tending to reach the normal equilibrium proportion, and the effect of heating the gas has been to hasten the reaction velocity with which this normal condition is arrived at.

Similar explanations can be applied in other cases (e.g. $2H_2O_2 = 2H_2O + O_2$) in which decomposition of an endothermic compound is brought about by raising the temperature.

If the thermal value of a reaction is zero, the point of equilibrium will not be shifted by alteration of temperature, other conditions being constant. Compare the esterification equilibrium mentioned on page 148.

The *influence of pressure* in shifting the point of equilibrium in gaseous systems has already been referred to; by application of the law of mass action it is generally easy to predict what the influence will be qualitatively and quantitatively at constant temperature. The direction in which the point of equilibrium will be shifted by alteration of pressure can also be determined by

the application of le Chatelier's rule. The lowering of the melting point of ice by increased pressure has already been referred to. Monoclinic sulphur again (s.g. 1·96), near the transition point, is converted into rhombic sulphur (s.g. 2·06) by increase of pressure.

The *quantitative* relationships between the point of equilibrium, thermal change, temperature, and pressure can only be completely studied by means of the application of the laws of thermodynamics. Considerable progress is now being made in this direction, but the actual results are not at present numerous owing to the lack of experimental data.

Combining the thermodynamic relation for a cycle consisting of evaporation at T and condensation at $T-dT$

$$VdP = Q\frac{dT}{T}$$

with the gas equation $PV = RT$ we obtain the formula

$$\frac{dP}{PdT} = \frac{Q}{RT^2} \quad \text{or} \quad \frac{d\log_e P}{dT} = \frac{Q}{RT^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1).$$

In the latter form, the equation is found convenient in a large number of physical and chemical calculations. As a simple illustration one may refer to the calculation of the molecular latent heat of vaporisation of a liquid from the vapour pressures at two temperatures.

Taking two pressures P_1 and P_2 at absolute temperatures T_1 and T_2 (which are sufficiently close together that Q may be regarded as constant) we obtain, by integration of the above formula

$$\log_e P_2 - \log_e P_1 = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

Taking $R = 2$ and using ordinary logarithms,

$$Q = \frac{2 \times 2{\cdot}303\,(T_1 \times T_2)}{T_2 - T_1} \cdot \log \frac{P_2}{P_1}.$$

Similarly, it has been shewn by van't Hoff that the influence of temperature on the equilibrium constant K for dilute systems (e.g. the value of $\frac{k}{k'}$ in the mass action formula) at constant volume, may be expressed by a similar relation, namely

$$\frac{d\log_e K}{dT} = -\frac{Q}{RT^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2),$$

where Q is now the molecular heat of reaction at T, at constant volume so that none of the heat is used up in work against external pressure.

Note that the negative sign is here introduced in order that Q may denote the heat of the *forward* change. Thus, for example, if this equation is

employed in reference to the dissociation of a compound, Q represents the thermal change accompanying dissociation, whereas in the first equation (1) Q refers to the thermal value of the *combination* of the dissociation-products.

If for small differences of temperature Q is assumed to be constant, this equation may be employed to calculate the displacement of equilibrium with temperature or, conversely, from the observed displacement to calculate the thermal value of the change, at *constant volume.*

[When dealing with greater temperature differences it has to be remembered that, in reality, Q is a function of the temperature and the form of this function is not exactly known; empirical formulae of the form

$$\frac{d\log K}{dT} = \frac{A}{T^2} + \frac{B}{T} + C$$

are employed to express this relation.]

Van 't Hoff's 'principle of mobile equilibrium' follows at once from this equation. If K_1 and K_2 are the values of the equilibrium constants at T_1 and T_2 respectively and Q is regarded as constant, we obtain by integration

$$\log_e K_1 - \log_e K_2 = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

If T_2 is greater than T_1, Q must have the same sign as $(\log_e K_1 - \log_e K_2)$. Hence if Q is positive, K_1 will be greater than K_2, i.e. with increase of temperature, the value of K_1 will increase relatively to K_2—and conversely.

Consider now a reversible reaction of the type $AB + CD \rightleftarrows AD + CB$, in which the concentrations of the reacting substances are c_1, c_2, c_3 and c_4 respectively. Then according to the law of mass action $kc_1c_2 = k'c_3c_4$ and

$$K\left(=\frac{k}{k'}\right) = \frac{c_3c_4}{c_1c_2}.$$

[That is to say, the greater the value of K, the more will the reaction proceed in the forward direction.]

If now Q represents the heat evolved or absorbed in the completed forward reaction at constant volume, it follows from the above formula that when Q is *positive*, increase of temperature will diminish K, that is, the change will proceed in the *reverse* direction, whereas if Q is *negative*, increase of temperature will favour the *forward* change.

The formula can be extended so as to apply to a phase which is in equilibrium with another constant phase, e.g. to the change of solubility with temperature. In this case it is only the concentration c of the solute which changes, so that c is a constant in the equilibrium between the phases at each temperature and varies only with T. It can be shewn that, in such cases, the formula applies if we make $K = c$.*

If Q represents the heat of solution of one gram molecule of the substance (non-electrolyte) and c_1 and c_2 are the solubilities at T_1 and T_2 respectively, we have

$$\log c_1 - \log c_2 = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

* The unit in which c is measured is immaterial, since c enters as a logarithm.

so that if the substance dissolves with absorption of heat (i.e. if Q is negative) and T_2 is greater than T_1, $\log c_2$ must be greater than $\log c_1$, i.e. the solubility will be greater at the higher temperature.

The formula (2) may thus be applied to a large number of chemical phenomena, such as dissociation, ionisation, etc. The value of Q thus obtained will differ however from that calculated by the first formula (1). The molecular latent heat, for example, obtained in (1) represents the heat necessary to vaporise one gram molecule of the liquid plus the heat equivalent of the work done in expansion of the gaseous product against P, and it therefore exceeds the value which would be obtained by (2), with opposite sign, by $2T$ calories. [See 6.]

54. Exothermic and endothermic reactions.

It is of course a matter of common experience that a large majority of spontaneous chemical changes are exothermic, i.e. take place with evolution of heat, and it was at one time supposed that heat evolution was a necessary accompaniment of all such chemical changes. Many endothermic compounds are notably unstable at ordinary temperatures, and, if a series of similarly constituted compounds is compared, it often happens that the stability is greater as the heat of formation is larger. [Compare, for example, the halogen acids or the hydrates of copper sulphate.] Berthelot, in fact, laid it down as a fundamental rule (inappropriately called the 'law of maximum work') that every chemical change accomplished without addition of external energy, tends towards the formation of that compound, or that system, the production of which is attended with the maximum heat evolution. Thomsen likewise thought that every simple and complex change of a 'purely chemical' kind is accompanied by evolution of heat. A large number of thermochemical data were collected which appeared to bear out these generalisations.

Amongst these one may refer again to the experiment mentioned on page 115, from which it appeared that dry hydrogen sulphide and iodine do not react*; in the presence of a little water, however, the change proceeds reversibly and is only apparently completed if a relatively large amount of water is present. The thermal data determined by experiment were as follows:

$$H_2, S\,(gas) = +4600. \qquad H, I\,(gas) = -6200,$$

so that if

$$H_2S + I_2 = 2HI + S$$

* See footnote *loc. cit.*

the thermal effect would be $-(4600+12400)=-17000$; the change therefore would be endothermic. But when gaseous hydrogen iodide is dissolved in water heat is evolved, the quantity of heat diminishing as the solution becomes stronger. For a 1 per cent. solution of the acid at 15°, HI, xAq $= +19400$. Consequently if H_2S and I_2 are brought together in presence of water sufficient to form a 1 per cent. solution of the resulting hydriodic acid, the total thermal effect will be positive, namely $+38800-17000$.

But as the solution of hydriodic acid increases in strength the thermal value of the change HI, xAq diminishes, and when a certain concentration is reached this positive thermal effect will just balance the negative thermal value of the hypothetical reaction $H_2S + I_2 = 2HI + S$, and the reaction will then cease. The experimental results therefore appear to agree well with the theory put forward. [It must be observed that no notice is taken of the thermal value of the changes concerned in the production of solid sulphur molecules from gaseous sulphur atoms or the dissolution of solid iodine, etc.] The objection is often raised that the explanation is based on the fact that HI, $x H_2O$ is positive, whereas no HI is originally present. But this objection is generally disposed of by saying that there is no necessity to imagine that the change actually occurs in stages; all that is required is to shew that the system

$$\underset{\text{(gas)}}{H_2S} + \underset{\text{(solid)}}{I_2} + x\text{Aq} \text{ passes into the system } \underset{\text{(solution)}}{2HI\,.\,x\text{Aq}} + \underset{\text{(solid)}}{S}$$

with positive thermal effect if x is sufficiently large.

But although such a large number of experimental facts can be quoted in support of Berthelot's rule it is evident that there are also many notable exceptions. Amongst these one may refer to the spontaneous formation of endothermic compounds, such as acetylene, nitric oxide or ozone, at high temperatures, the action of sodium sulphate on hydrochloric acid in aqueous solution, or the spontaneous decomposition of phosphonium chloride, all of which changes take place with absorption of heat. Moreover if the rule were universal it would be impossible to explain why exothermic changes should ever be limited and reversible. Thus ammonia

and hydrogen chloride combine together with evolution of heat and conversely ammonium chloride dissociates with absorption of heat. Yet at the same constant temperature one may bring about either the combination or the dissociation by suitably altering the volume of the containing vessel, which involves gain or loss of work.

As a matter of fact there is no theoretical reason to suppose that Berthelot's rule should be true under all conditions. It was subsequently abandoned both by Berthelot and by Thomsen. The last named author in referring to the numerous anomalies makes a remark which, at the present time, is well worth considering; he says, "instead of making useless speculations as to the cause of these anomalies I choose rather the more difficult, but by far the more certain method, namely, by means of a comprehensive experimental investigation to collect new and reliable material."

All the same, notwithstanding its shortcomings from a theoretical, and to some extent from a practical, point of view, Berthelot's original statement does happen to serve very well as a rough and ready indication of the *probable* course of a chemical change at ordinary temperatures. A simple way of accounting for this circumstance is to consider, with van 't Hoff, that the ordinary temperature is relatively a low temperature, being only 273 degrees above absolute zero, and that therefore in a reactive chemical system, in accordance with the principle mentioned, the equilibrium will change in such a direction that heat is evolved.

It may be shewn by thermodynamical reasoning that Berthelot's rule would be true at absolute zero. At this temperature then only exothermic reactions could occur and they would be complete.

In accordance with the principles of thermodynamics, for every chemical reaction connecting a definite initial with a definite final state of the system, there is a certain definite maximum amount of work obtainable by means of the reaction, at a given temperature, which cannot be exceeded however the reaction is performed—namely, the amount of work which will be done if the reaction proceeds in a reversible manner. This amount of work performed, at constant temperature, is the decrease in the free or available energy (A) of the system, which is a definite quantity determined by its state.

The heat developed and conducted away from the system when the

change takes place without doing work on outside bodies, is the decrease of the total energy (E); the total energy is also a definite quantity determined by the state of the system. If the change of state takes place with expansion against pressure, or with performance of work of any other kind, the heat evolved will be diminished from the above amount by the external work which the system performs. Thus, when one-gram atom of zinc dissolves in dilute sulphuric acid, say at 20°, the heat developed is 34200 gram calories; but the reaction gives rise to one gram molecule of hydrogen, the production of which at 20° and 760 mm. involves expenditure of work represented by $2T$ calories (see page 12)—in this case $(2 \times 293) = 586$ calories. The diminution of total energy in the system is therefore 34786 gram calories. Again, when one gram molecule of hydrogen combines with oxygen to produce liquid water at 20° the heat evolved is 68400 calories; but for every gram molecule of hydrogen so combined there is a condensation of 1·5 gram molecules of the gases, and this implies performance of work *on* the system, which adds to its energy, represented by $1{\cdot}5 \times 2T$—in this case $(1{\cdot}5 \times 2 \times 293) = 879$ calories. The diminution of total energy is therefore represented by 67521 gram calories; this would be the heat evolved if the combination took place in a closed vessel.

In a reaction from one definite state of a system to another, the decrement (U) of total energy is equal to the work (W) expended on external bodies together with the heat (H) emitted. If the process is reversible, taking any given system, it can be undone at a different temperature; thus it admits of a Carnot's cycle, giving after some reductions

$$\frac{-H}{T} = \frac{dW}{dT},$$

where, as above, $U = H + W$. Hence $W - U = T\frac{dW}{dT}$. Here W is the decrement of available energy (A) and U is the decrement of total energy (E). Thus we may write

$$A - E = T\frac{dA}{dT},$$

which is the most general expression (Kelvin, Gibbs, Helmholtz) of Carnot's principle.

According to this principle, transformation at constant temperature can proceed spontaneously only in the direction in which the available energy (A) diminishes. A different rule, introduced mainly by Berthelot, used the criterion that the direction of reaction is that in which heat is emitted, when the change is performed without work, and this would make the total energy E diminish. The rule of Berthelot, though in many cases useful as a rough indication, can be exact only in circumstances in which A and E are equivalent. In general this tends to be the case universally at very low temperatures of reaction, and would be exactly true at the absolute zero, where $T = 0$. It is also true in special systems for which $\frac{dA}{dT} = 0$, that is, in which the available energy does not alter with temperature; as the available energy determines the equilibrium, it is thus

true for systems in which chemical equilibrium is not affected by change of temperature. For example, in a Daniell's cell the electromotive force measures the available energy (or work that can be done) per electrochemical equivalent of reaction; it has long been known to be determinable from the change of total energy (E); and the reason is (Gibbs, Helmholtz), that in this cell, the electromotive force does not change sensibly with temperature.

[For the above method of stating this theory, the author is indebted to Professor Larmor.]

55. We thus no longer regard the evolution of heat as a criterion of chemical 'affinity.' The necessary condition of a spontaneous chemical change is that work shall be lost, i.e. that the free energy of the system shall diminish. If we could always measure the change of free energy, when the reaction took place reversibly and isothermally, we should be able to give a definite and scientific meaning to the term affinity..

Chemical changes then may take place spontaneously, that is without access of external energy, with either development or absorption of heat. It is to be observed, however, that if the change is exothermic, and precautions are not taken to remove the heat as fast as it is generated, the temperature will mount up and the reaction velocity will consequently be increased. Thus it happens that the rate of a chemical change under such conditions gives no necessary indication as to 'affinity.' Many substances which react upon one another energetically at ordinary temperatures are found to have no apparent action at the temperature of liquid air (e.g. fluorine and iodine). This, however, does not shew that fluorine has no 'affinity' for this element at the temperature mentioned, it is merely due, no doubt, to the very great retardation of the reaction-velocity.

Many different meanings have, from time to time, been attached to the term 'affinity.' The word has sometimes been used as if it were synonymous with valency, whereas others employ it, in a vague, general way, to mean a 'tendency to combine or react.' In attempting to give a more precise signification to the term, it has been the custom to regard the velocity constants in the mass-action formula as 'affinity' constants. But, unless the conditions are precisely the same and the temperature undergoes no change, it is obvious that reaction velocity alone is no true measure of the tendency to react. The velocity is enormously influenced, not only by temperature, but also by the nature of the medium and by catalysts, etc.

More appropriately, one may regard chemical affinity as the intensity-factor of chemical energy or as the 'driving force' of chemical change. In the latter sense, van 't Hoff expresses the relation,

$$\text{reaction velocity} = \frac{\text{driving force}}{\text{resistance}};$$

in this way, if we could find a definite measure of chemical resistance, reaction velocity could be employed to deduce 'affinity.'

On the whole however, until some more general agreement is arrived at, it will be better to discontinue the use of the word altogether.

CHAPTER XIV.

CATALYSIS.

56. THE student is of course already familiar with a large number of instances in which chemical changes are greatly influenced or modified by the presence of a minute quantity of a foreign substance—foreign, that is, in the sense that its presence is not included in the chemical equation used to represent the change, and it is itself found to be unaltered in chemical composition and in quantity at the end of the reaction. The foreign substance which behaves in this way is called a 'catalyst,' 'catalytic agent' or 'catalyser.' The modification thus brought about in a chemical change consists, in the majority of cases, in mere acceleration of the rate of change; as examples of this one may refer to (1) the much discussed influence of manganese dioxide in accelerating the decomposition of potassium chlorate, (2) the dissociation of hydrogen iodide, or the combination of hydrogen and iodine, in presence of spongy platinum, (3) the inversion of cane sugar in presence of acids and (4) the decomposition of hydrogen dioxide in presence of spongy platinum.

In certain other cases the influence of the catalyst is exerted in a negative direction. The rate of oxidation of certain substances (e.g. sodium sulphite or phosphorus) by atmospheric oxygen, is found to be greatly retarded by the introduction of small quantities of various organic substances. The hydrolysis of esters again may be accelerated by some salts and retarded by others. Most of the cases of so-called negative catalysis, however, are those in which the accelerative effect of a positive catalyst is diminished by the addition of another substance, e.g. the 'poisoning' of colloidal platinum (see page 187).

In all the above mentioned examples it can be shewn *experimentally* that the change in question does actually take place when the catalyst is absent, the only observed difference being the greatly increased rate of change when the catalyst is present.

But there are a great many other instances of catalysis which from the experimental standpoint *appear* to be actually initiated or caused by the presence of the catalyst. The following may be referred to as examples:—(1) Hydrogen and oxygen, carbon monoxide and oxygen, hydrogen chloride and ammonia, hydrogen chloride and sodium are all entirely without action if the substances are perfectly dry. (A mixture of dry oxygen and hydrogen, for example, may be heated to the fusing point of silver without combination taking place.) Similarly dry ammonium chloride may be vaporised without dissociation if perfectly dry. But all these changes take place, at suitable temperatures, in presence of a trace of moisture. (2) The influence of spongy platinum in bringing about the reaction between oxygen and hydrogen, or nitric oxide and hydrogen, at temperatures where otherwise the mixture shews no sign of reaction, is of course well known. (3) Many organic hydroxy-compounds shew no sign of oxidation by hydrogen dioxide unless a trace of ferrous iron is present. (4) The conversion of triethylsilicon-orthoformate $H.Si(OEt)_3$ into ethylorthosilicate $Si(OEt)_4$ and silicon hydride, only appears to take place if sodium is present. In all these cases experiment fails to detect any change in absence of the catalyst. But it is considered improbable that the catalyst should be able actually to initiate the change, and it is now the very generally (but not quite universally) accepted view that, as Ostwald first insisted, in the cases just mentioned we have systems which are actually in the course of change before the introduction of the catalyst, but that the reaction velocity is so slight that the change cannot be experimentally recognised. Ostwald compares the action of the catalyst to that of oil used to remove friction in a machine which is actually in motion; the oil diminishes the friction and allows the machine to work faster. Some have considered that the analogy might be stretched to the case of a machine actually stopped by friction and set in motion again by the application of the oil. Instances have been recorded in which a chemical change, which

is limited and reversible, appears to come to a stop at a point short of true equilibrium; examples of such cases are the systems

$$2AgCl + H_2 \rightleftarrows 2Ag + 2HCl \text{ and } H_2Se \rightleftarrows H_2 + Se.$$

In these systems it is stated that the final state of distribution is different according as it is approached from one side or the other. It is still a matter of dispute, however, whether this experimentally reached limit is really final, i.e. whether the change is not still actually in progress at an extremely slow rate. In such cases, whether the action is actually stopped, or the reaction-velocity enormously reduced, at a point short of the true equilibrium state, one might compare the result to our machine working with friction and in this case it might be expected that true equilibrium should be obtained if a suitable catalyst were introduced.

The prevailing opinion is that the only function performed by the catalyst is that of altering reaction velocity, and the essential characteristics of a catalytic action are now generally summarised as follows:

(*a*) The catalyst is incapable of initiating a reaction, it only alters the reaction velocity of a change which is actually proceeding before the catalyst is introduced.

(*b*) It must have the same chemical composition and quantity before and after the action, although in some cases its physical properties may be altered. [It will be noticed in the examples given below that this condition is not always insisted upon.] [On the principle of energy (*a*) would be a consequence of (*b*).]

(*c*) The quantity of the catalyst present need bear no relation whatever to the quantity of substance which undergoes the accelerated change; a minute trace of the catalyst is usually sufficient. Quantities of the order of a millionth of a milligram are often sufficient to produce a marked acceleration. As a rule, the increase of reaction velocity is proportional to the quantity of catalyst present; the order of the reaction, however, is generally unaltered by its presence; but there are many exceptions to these statements.

(*d*) A catalyst exerts no influence on the final equilibrium; in reversible changes therefore, the velocities of the forward and

reverse changes must be influenced to the same extent, i.e. both velocity constants must be altered in the same ratio. Thus the presence of spongy platinum, at the same temperature, accelerates both the dissociation of hydrogen iodide and the combination of iodine and hydrogen, and the final state of equilibrium reached is the same as that obtained when the catalyst is absent.

It must be remembered that the conditions here laid down are somewhat arbitrary, and the precise meaning to be attached to the term 'catalytic action' is to some extent a matter of opinion.

There are many instances in which the addition of a foreign substance, or the expenditure of the most minute amount of energy, as heat, light, etc., may be sufficient to set in motion a chemical change resulting in the evolution of a relatively enormous quantity of heat, or energy in some other form. (e.g. the union of oxygen and hydrogen, hydrogen and chlorine or the crystallisation of supersaturated solutions.) Such 'trigger actions' or 'catch actions'—which have sometimes been compared to 'the power of a fly at the end of a lever to open a floodgate'—are usually to be regarded as distinct from true catalytic actions. In the former the quantity of foreign substance, etc., is practically immaterial, whereas in the latter, the reaction velocity is dependent on the quantity of catalyst present. But it is questionable whether a hard and fast line can be drawn between the two classes.

Examples of catalytic actions are met with in changes of such widely different types that it is convenient to employ some method of classification in dealing with them. Opinions differ, however, as to the best mode of classification, and it is doubtful whether any of the proposed systems are satisfactory. The term 'contact action' is often used in reference to changes in gaseous systems which are accelerated by the presence of a solid. Noyes and Sammet (*Journ. Am. Chem. Soc.* 1902, 498) include, as the important types of catalyst, (*a*) carriers, (*b*) absorbent contact agents, (*c*) electrolytic contact agents, (*d*) water, (*e*) dissolved electrolytes, (*f*) enzymes, (*g*) inorganic colloids. Ostwald classifies catalytic actions under the heads (*a*) crystallisation from supersaturated solutions (page 310), (*b*) catalysis in homogeneous

systems, (*c*) catalysis in heterogeneous systems, (*d*) enzyme actions. Examples illustrating these various classes will be referred to below.

57. Notwithstanding the enormous mass of experimental evidence which has accumulated, no satisfactory and consistent theory has yet been put forward to account for all of the phenomena of catalysis, though the formal possibility of such actions is clear from the point of view of thermodynamics in general. Various so-called 'explanations' have been offered for particular cases, or for certain types, of catalytic change, but they amount, in general, to little more than a re-statement of the case in a different form; in many instances these explanations are the merest conjectures.

It will be noticed that in most of the so-called 'chemical' explanations the occurrence of an intermediate stage is assumed to take place. [The term 'carrier action' has been used to mean a catalytic action in which the catalyst combines with one of the reacting substances to form an intermediate compound.] There is no objection to this form of explanation if it can be shewn that the occurrence of the intermediate stage is possible. Often, however, it has been the custom to consider a catalytic process to be 'explained' if one conjectured the intermediate formation of some unknown compound whose existence is improbable, e.g. the occurrence of some spontaneous change which would involve gain of free energy to the system. As instances of catalytic actions in which the intermediate stage hypothesis appears to be justifiable, one may refer to the following well-known experiments (*a*), (*b*) and (*c*), although it must be admitted that even in these cases alternative explanations are quite possible.

(*a*) When air is passed over heated copper the metal becomes oxidised, and nitrogen (with argon, etc.) passes on and may be collected. Also when ammonia is passed over heated oxide of copper, the oxide is reduced to metal, free nitrogen and water being formed. But now if air saturated with ammonia is passed over heated metallic copper the metal remains bright and free nitrogen is obtained both from the air and the ammonia. Disregarding the first two experiments one may consider the

third experiment as the oxidation of ammonia by air with copper as a 'contact agent' or catalyst. But, taking the first two experiments into consideration, it is not at all unreasonable to suppose that the copper actually undergoes a series of successive oxidations and reductions:

$$O_2 + 2Cu = 2CuO \text{ and } 3CuO + 2NH_3 = 3Cu + 3H_2O + N_2.$$

(*b*) In the 'lead chamber process' again, the net result obtained may be regarded as the oxidation of sulphur dioxide in presence of water to sulphuric acid, with nitric oxide as catalyst. But we can experimentally carry out the same oxidation in stages, starting with nitric oxide and obtaining it again at the end of the operations:

(1) $2NO + O_2 = 2NO_2$. (2) $NO_2 + SO_2 + H_2O = H_2SO_4 + NO$,

so that a given quantity of nitric oxide ought theoretically to be able to bring about the oxidation, in this way, of an unlimited quantity of sulphur dioxide.

(*c*) When a solution of sodium carbamate is mixed with excess of sodium hypobromite, in presence of sodium hydroxide, the nitrogen is evolved rapidly and quantitatively:

$$2CO(NH_2)ONa + 3NaBrO + 2NaOH = 2Na_2CO_3 + 3NaBr + 3H_2O + N_2,$$

whereas if sodium hypochlorite is substituted for the hypobromite there is practically no action at first. (A very slow decomposition then takes place owing to the action of water on the carbamate giving rise to ammonia.) If now one starts with a mixture of sodium carbamate and excess of hypochlorite the addition of a very small quantity of sodium *bromide* will cause the rapid evolution of nitrogen*. Hence it would appear natural to assume the intermediate stage

$$NaClO + NaBr = NaBrO + NaCl.$$

Liebig explained catalysis by saying that "a body in the act of combination or decomposition enables another body with which it is in contact to enter into the same state," and that "the influence

* Fenton, *Proc. Cambridge Philosophical Soc.* 1886, 375.

exerted by one compound upon the other is exactly similar to that which a body in the act of combustion exercises upon a combustible body in its vicinity; with this difference only, that the causes which determine the participation and duration of these conditions are different." Many catalytic actions are now explained in such a way; it is usual to say that 'a fast' (primary) reaction may carry a slow (secondary) reaction along with it.' Catalytic reactions which are explained in this way are sometimes called coupled reactions or induced reactions.

In the primary reaction the substance A is supposed to react rapidly with the catalyst C, and in the secondary reaction the substance A reacts slowly with the substance B. The names 'actor,' 'acceptor' and 'inductor' are suggested for A, B and C respectively. Thus in the oxidation of certain organic substances by means of hydrogen dioxide in presence of ferrous iron, which will be referred to below, the hydrogen dioxide is the actor, the organic substance the acceptor, and the ferrous iron the inductor.

[For many other illustrations see Schilow, *Zeit. Physikal. Chem.* 1903 (42) 641.]

These and other so-called explanations of catalysis will best be understood by reference to a few well-known examples. The suggested explanations are given in each case for what they are worth; in many instances they are unsatisfactory, and in no case must they be regarded as final.

(*d*) *Decomposition of potassium chlorate. Catalyst—manganese dioxide.* Potassium chlorate, when heated, melts at about 359°; between about 370 and 400° the evolution of oxygen takes place, perceptibly but slowly. If the heating be continued at this temperature the evolution of oxygen eventually ceases and a mixture of chloride and perchlorate remains. But if a small quantity of manganese dioxide is mixed with the chlorate, evolution of gas begins at about 200° and the salt is rapidly decomposed into potassium chloride and oxygen, perchlorate not being obtained*. Oxides of copper, iron, cobalt, nickel and lead produce

* Frankland and Dingwall shewed that when potassium chlorate is heated with powdered glass to 444° it decomposes according to the relation

$$KClO_3 = KClO_4 + KCl + O_2,$$

whereas when heated alone only about half as much oxygen is liberated. They

a similar effect. [It is stated that magnesium oxide, zinc oxide or silica produce scarcely any effect; this statement should be tested in the practical demonstration.]

The suggested explanations of this action are of various kinds. Mercer and others considered that the catalyst acts by exerting a feeble chemical attraction on one of the constituents of the compound in question. The manganese dioxide was supposed to have an attraction for an additional quantity of oxygen; a very unstable higher oxide of manganese was therefore first formed, thus facilitating the decomposition of the chlorate, and then almost immediately decomposed. This idea appeared to be supported by the fact that the most efficient catalysts, in this reaction, were oxides of those metals which can form many oxides. Veley found that barium sulphate acted energetically in this way; Sodeau, however, states that its influence is small compared to that of the oxides mentioned above, and he explains its action by assuming a small amount of double decomposition, barium chlorate being less stable than potassium chlorate.

Another similar suggestion was that potassium chlorate when heated alone gives potassium chloride and 'nascent ozone,' and that the latter oxidises a second molecule of the chlorate to perchlorate; if, however, manganese dioxide is present the ozone oxidises this instead, producing an unstable higher oxide.

McLeod considered that the changes which take place may be of the following kind:

$$(a)\quad 2MnO_2 + 2KClO_3 = 2KMnO_4 + Cl_2 + O_2,$$

$$(b)\quad 2KMnO_4 = K_2MnO_4 + MnO_2 + O_2,$$

$$(c)\quad K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2.$$

This would account for the fact that the oxygen obtained in this way very often contains traces of chlorine (thought at one time to be ozone), and also for the pink colour which is usually observed in the residue. (It was suggested that this colour might be due to ferrate, but McLeod shewed that iron-free manganese dioxide gave a similar result.)

also found that when potassium perchlorate is heated alone it gives in the first place, some chlorate; but in presence of manganese dioxide this is not the case.

An explanation of quite a different kind, and which, at first sight, appears to be much more satisfactory, is the purely physical one. It is suggested that the molten chlorate may be regarded as a supersaturated solution of oxygen in the chloride, and that the addition of the catalyst promotes the rapid or explosive evolution of the gas in the same manner as porous bodies are known to bring about the explosive ebullition of superheated liquids. Sodeau, however, finds that the ease of decomposition of potassium chlorate is not appreciably altered by reducing the pressure to 1 mm., and this fact hardly appears to be consistent with the theory suggested. It is difficult, moreover, on this theory, to account for the very varying efficiency of different metallic oxides as catalysts. Platinum black is said to have a facilitating action, but Sodeau suggests that at the temperature at which its activity is apparent, there may be an alternate formation and decomposition of a platinum oxide.

(*e*) *Decomposition of oxalic acid by nitric acid. Catalyst—a manganous salt.* Nitric acid if sufficiently concentrated will readily oxidise oxalic acid (to carbon dioxide and water) when the mixture is warmed. But with a more dilute solution of the acid the oxidation only proceeds very slowly; the addition of a small quantity of a manganous salt, however, brings about a rapid action. Mercer observed this and shewed that starch could be entirely oxidised to carbon dioxide, if a manganous salt is present, under conditions which would otherwise give rise to oxalic acid.

The explanation given was that the manganous salt by tending to pass into the manganic state, endeavours to deprive the nitric acid of its oxygen and so 'aids the oxalic acid to decompose the nitric acid.' But the oxalic acid, having a stronger attraction for oxygen than has the manganous salt, immediately appropriates the oxygen. Another view was that the nitric acid oxidises the manganous salt to a manganic salt, and the latter then oxidises the oxalic acid. It is difficult to see that this explanation makes the phenomenon more intelligible; there is no experimental evidence that manganous salts are oxidised to the manganic state by nitric acid.

(*f*) *The decomposition of bleaching powder* with a *cobalt salt*

as catalyst is similarly explained by supposing that a higher oxide of cobalt first formed, is decomposed and re-formed alternately.

If we consider the bleaching powder solution to contain calcium, chloride, hypochlorite and hydroxide, the essential changes might be represented, on the above hypothesis, as

(1) $CoCl_2 + Ca(OH)_2 = Co(OH)_2 + CaCl_2$.

(2) $4Co(OH)_2 + Ca(ClO)_2 + 2H_2O = 4Co(OH)_3 + CaCl_2$,

and $4Co(OH)_3 = 4Co(OH)_2 + 2H_2O + O_2$.

(*g*) *The catalytic effect of dilute acids* in bringing about various changes (such as the inversion of cane sugar, the hydrolysis of esters or the decomposition of diazo compounds) has already been referred to. Such actions are now usually considered to be due to hydrogen ions; if this is admitted, one still has to enquire why and how these ions behave as catalysts and no very satisfactory theory has been suggested. The view that such actions are due to hydrogen ions is favoured by the fact that in many cases the effects are roughly proportional to the concentration of hydrogen ions (as measured by the various methods to be described below, see **77**), i.e. to the 'strengths' of the acids. Consequently one would expect that the addition of the salt of the same acid, by lowering the concentration of free hydrogen ions, would diminish the capability of the acid used. Although this is sometimes the case, the effect is often in the opposite direction and additional conjectures have, in this event, to be made; it has been suggested, for example, that the salt added may 'stimulate the activity' of the hydrogen ions, and so on. Another view is that the increased activity which is obtained by the addition of a salt may be due to the 'concentrating effect' produced by the combination of the salt with water, or that diminished activity may be due to the combination of the salt with ester, etc. [Compare Armstrong, *Proc. Roy. Soc.* 1908 (81) 102; Cole, *Jour. of Physiology*, 1903 (30) 202.]

According to Kastle and others the hydrogen ions first react with the substance undergoing change, forming an unstable addition product which subsequently resolves itself into the final products. [Compare Acree, *Am. Chem. Journ.* 1907, 258 and 1908, 145; Fitzgerald and Lapworth, *Journ. Chem. Soc.* 1908, 2163, and Dawson and Powis, *ibid.* 1913, 2135].

The influence of enzymes in bringing about the hydrolytic decomposition of polysaccharides, glucosides, certain esters, is comparable in nearly all respects with the action of dilute acids. Yet it is well known that enzymes usually have a selective action; maltase for example will bring about the hydrolytic decomposition of maltose or of α methylglucoside, but not of cane sugar or of β methylglucoside. It appears somewhat difficult to reconcile this selective action with the hypothesis that the effects mentioned are due to hydrogen ions. Since most acids can effect the hydrolytic decomposition of cane sugar, one might perhaps expect that most enzymes should behave likewise; yet only one (invertase) is known to have this property. According to the theory of catalysis commonly accepted, a dilute aqueous solution of cane sugar is, even at the ordinary temperature, slowly undergoing hydrolytic decomposition into dextrose and laevulose, although the rate of change is so slow that no physical or chemical test can give any indication of it. A mere trace of acid will accelerate the change sufficiently to make it recognisable and on increasing the concentration of the acid the rate will increase nearly in proportion to this concentration. This is explained by saying that the concentration of hydrogen ions in pure water is altogether insufficient to produce a recognisable effect. But the effect of adding a minute proportion of acid in causing the previously inappreciable change to become appreciable, is considered to be quite of a different order to the subsequent increase of reaction velocity with increasing concentration of (supposed) hydrogen ions. For these, and other reasons, Armstrong considers that hydrogen ions are not the effective cause of the hydrolytic changes referred to. [See, for example, 'The Nature of Chemical Change,' Armstrong, *British Association Report*, 1908.]

(*h*) *The Friedel and Crafts reaction. Catalyst—anhydrous aluminium chloride.* A considerable number of instances are met with in which two or more organic substances appear, under ordinary circumstances, to have no action upon one another and yet react energetically if anhydrous aluminium chloride is present. The best known examples are those in which aromatic hydrocarbons are caused to react with various halogen compounds.

For example, in presence of aluminium chloride, benzene reacts with methyl chloride to give toluene

$$(C_6H_6 + CH_3Cl = C_6H_5 . CH_3 + HCl),$$

and with acetyl chloride to give acetophenone

$$(C_6H_6 + CH_3COCl = C_6H_5COCH_3 + HCl).$$

This catalyst may also bring about other types of change; it may, for example, act as a condensing agent, or it can bring about a 'disruptive' change, e.g. toluene in presence of hydrogen chloride yields benzene and methyl chloride.

The catalytic influence of aluminium chloride is generally explained by assuming the formation of intermediate compounds, and this view is supported by the fact that the reagent is known to have a tendency to form additive compounds. Thus crystalline compounds of aluminium chloride with benzene or toluene, with acid chlorides and with ketones, etc., have been isolated.

Friedel and Crafts explained the action of benzene on ethyl chloride as follows:

$$Al_2Cl_6 + C_6H_6 = Al_2Cl_5 . C_6H_5 + HCl$$

and

$$Al_2Cl_5 . C_6H_5 + C_2H_5Cl = Al_2Cl_6 + C_6H_5 . C_2H_5.$$

It must be observed that the action of aluminium chloride differs from that of most other catalysts in that a minute quantity of it is not sufficient to bring about the interaction of large quantities of the substances concerned; also in that the catalyst is generally withdrawn from the system, as the change proceeds, by the fact of its combining with one of the products of the change. [See Wallace Walker, *Trans. Chem. Soc.* 1903, 1091. Also Heller and Schülke, *Ber.* 1908, 3627.]

(*i*) *Deacon's process for the manufacture of chlorine. Catalyst—cupric salts, etc.* A mixture of oxygen (or air) and hydrogen chloride may be heated to 370—400° without apparent action. If, however, the mixture, at the same temperature, is passed over pieces of brick or pumice-stone which have been saturated with a solution of copper sulphate and subsequently dried, the gases interact with production of chlorine and water.

This action is usually explained in a 'chemical' way by assuming the occurrence of intermediate stages. Cupric chloride

on heating yields cuprous chloride and free chlorine; hence it has been assumed that changes of the following kind occur:

(1) $CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$,

(2) $2CuCl_2 = 2CuCl + Cl_2$,

(3) $4CuCl + O_2 = 2(CuCl_2 . CuO)$,

and (4) $CuCl_2 . CuO + 2HCl = 2CuCl_2 + H_2O$.

[It has also been suggested that the only function of the copper salt is that of a dehydrating agent, i.e. that it facilitates the change by absorbing the water formed.]

The change can, however, be accelerated in other ways—for example, by platinic chloride at 500°.

Probably it is better to regard the porous material, with the copper salt, as a 'contact agent' which accelerates the attainment of the equilibrium state, either way, in the change

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2.$$

In terms of the law of mass action we shall have

$$kC_1C_2^4 = k'C_3^2C_4^2,$$

where C_1, C_2, C_3 and C_4 are the concentrations (or partial pressures) of the oxygen, hydrogen chloride, water and chlorine respectively. von Falckenstein [*Zeit. Electrochem.* 1906, 763] finds practically the same value for $\frac{k}{k'}$ when starting from oxygen and hydrogen chloride or from chlorine and water.

(*j*) *The oxidation of certain organic compounds by hydrogen dioxide. Catalyst—ferrous iron.* A considerable number of organic compounds (more particularly hydroxy-compounds) appear to be unaffected by hydrogen dioxide in aqueous solution; but if the merest trace of a ferrous salt has been previously added the dioxide will bring about a rapid oxidation. In most of the changes referred to there appears to be no change whatever in absence of the ferrous salt; but in accordance with the prevailing view one must, as previously stated, consider that it is only a question of time. [Even if this is the case the time question is all-important here, since the initial products of oxidation are often highly unstable and might be entirely lost in a prolonged operation.]

These changes are of much interest owing to their obvious bearing upon many natural processes in which the presence of iron appears to be essential, and the method of regulated oxidation offers a means of preparing certain products which cannot be obtained in any other way, or which can only be prepared otherwise with great difficulty. No metal other than iron is found to produce the effects mentioned, and it appears probable that the ferrous condition is essential. There are, it is true, some cases in which ferric salts appear to be active—for example, in the oxidation of phenol and of gluconic acid—but these compounds are powerful reducing agents, and it is highly probable that reduction to the ferrous state takes place in the first instance.

[In certain cases, it appears that the so-called 'peroxidases' may produce effects analogous to that of ferrous iron.]

The following are some of the oxidations by this method which may be easily demonstrated:

Tartaric acid to dihydroxymaleic acid. Malic acid to oxalacetic acid. Lactic acid to pyruvic acid. Glycol to glycollic aldehyde. Glycerol to glyceric aldehyde. Erythritol to tetrose. Mannitol to mannose.

[In the case of tartaric acid the product has the property of giving an intense blue-violet colour with ferric salts in presence of alkalis. It is a crystalline substance which, when warmed in aqueous solution, yields glycollic aldehyde

$$\begin{matrix}\mathrm{COOH}\\ \dot{\mathrm{C}}.\mathrm{OH}\\ \dot{\mathrm{C}}.\mathrm{OH}\\ \mathrm{COOH}\end{matrix} = \begin{matrix}\mathrm{CH_2}.\mathrm{OH}\\ \dot{\mathrm{C}}\mathrm{HO}\end{matrix} + 2\mathrm{CO_2},$$

and when oxidised by bromine is converted into dihydroxytartaric acid $\mathrm{COOH}.\mathrm{C(OH)_2}.\mathrm{COOH}$.]

The initial type of change produced may be regarded as the replacement of H by OH; thus the initial product in the case of tartaric acid may be trihydroxysuccinic acid. Many of the resulting products when heated lose carbon dioxide, and the process is therefore available for the 'degradation' of certain

classes of compounds; e.g. tartaric acid, the dibasic acid corresponding to tetrose, is converted, in this way, into diose; gluconic acid, corresponding to hexose, similarly treated, yields a pentose.

Many of these oxidations in presence of iron can be brought about by means of air and sunlight instead of by the direct addition of hydrogen dioxide.

The peculiar function of the iron in these reactions is yet unexplained. The general character of the type of change may be referred to that in which a fast reaction 'carries along with it' a slow reaction. But this statement offers no explanation why other easily oxidisable substances should not act as well as ferrous salts. A similar objection may be made to the suggestion that the iron merely brings about the catalytic decomposition of the hydrogen dioxide. Manchot [*Liebig's Annalen*, 1902 (325) 93] considers that a peroxide of iron such as FeO_2 or Fe_2O_5 is first produced.

Another view is that the initial change consists in the replacement of two atoms of hydrogen in the acceptor by divalent iron, that on addition of the oxidising agent the iron becomes trivalent and can consequently no longer be 'held in combination.' If so the replacement probably occurs either in the alcoholic hydroxyl or in the non-hydroxylic hydrogen, since the effects are as well marked in polyhydric alcohols as in acids. In tartaric acid the result might be represented as

$$\begin{array}{c} \mathrm{COOH} \\ \mathrm{H.\dot{C}.OH} \\ \mathrm{H.\dot{C}.OH} \\ \mathrm{\dot{C}OOH} \end{array} \longrightarrow \begin{array}{c} \mathrm{COOH} \\ \mathrm{Fe}\langle\ \mathrm{\dot{C}.OH} \\ \mathrm{\dot{C}.OH} \\ \mathrm{\dot{C}OOH} \end{array} \longrightarrow \begin{array}{c} \mathrm{COOH} \\ \mathrm{\dot{C}.OH} \\ \mathrm{\ddot{C}.OH} \\ \mathrm{\dot{C}OOH} \end{array}.$$

but in this case one would expect the fumaroid instead of the maleinoid modification.

(*k*) *Contact actions.* In a very large number of instances the rate of chemical change is considerably modified by mere contact with a solid substance, and, as a rule, the influence of the solid is more marked as the surface presented is greater. Solids of a porous character usually have, therefore, a greater efficiency.

As familiar examples of contact actions in which spongy platinum is used, one may refer to the following:

The ignition of a mixture of oxygen and hydrogen by contact with spongy platinum at ordinary temperatures; at more elevated temperatures, the interaction of nitric oxide and hydrogen to give ammonia and water; of ammonia and oxygen to give nitrous acid, oxides of nitrogen, etc.; of sulphur dioxide and oxygen to give sulphur trioxide; the acceleration of the combination of hydrogen and iodine or hydrogen and bromine, and the dissociation of hydriodic acid.

Many substances which are, apparently, quite unaltered by atmospheric oxygen under ordinary conditions are rapidly oxidised if 'platinum black is present, for example, the oxidation of methyl alcohol to formaldehyde. Metallic opper will often bring about similar changes, and will also favour the oxidation of ammonia, and of amines, in aqueous solution by atmospheric oxygen; in this way ammonia yields nitrous acid, methylamine yields formaldehyde, and ethylamine yields acetaldehyde.

Rhodium black will cause the decomposition of formic acid into hydrogen and carbon dioxide, and in presence of alkalis, of alcohol into hydrogen and an acetate. Platinum black will also bring about the hydrolytic decomposition of glucosides, such as amygdalin and salicin, and also of starch. [Neilson, *Am. Journ. of Physiol.* 1905, 148, 412.]

The finely divided state of the metal is by no means always essential; a heated platinum wire, for example, will accelerate many changes in a remarkable way. It was shewn, for instance, by Erman in 1818 that a platinum spiral heated only to 50° will bring about the ignition of hydrogen in air. Compare also the oxidation of ammonia by atmospheric oxygen in contact with a heated platinum coil; nitrous acid is formed (which unites with more ammonia to give white fumes of ammonium nitrite) and the heat generated by the change is sufficient to keep the wire red hot.

Sabatier and Senderens [*Ann. Chem. Phys.* 1905 (4) 319] have made an exhaustive study of the remarkable efficiency of finely divided nickel (also cobalt, copper, etc.) as a catalyst in bringing about various combinations and condensations in organic substances. Aldehydes, ketones, nitriles, oximes and many unsaturated

hydrocarbons, can in this way be directly hydrogenised; the vapours being mixed with free hydrogen and passed over the nickel, heated to about 250°. Many compounds, when subjected alone to the action of nickel, undergo resolution into simpler molecules, e.g. primary or secondary alcohols give free hydrogen and the corresponding aldehyde or ketone; in other cases condensation may occur, with or without the addition of hydrogen. A mixture of acetylene and hydrogen when subjected for some time to the action of reduced nickel at 200° yields a liquid having all the physical and chemical properties of ordinary petroleum.

The efficiency of these contact agents is often greatly interfered with by the presence of certain foreign gases. Nearly a century ago Turner observed that the activity of spongy platinum, in bringing about the combination of oxygen and hydrogen, is diminished by the presence of hydrogen sulphide, ammonia, etc. A similar 'poisoning' of the catalyst has been observed in numerous other cases (e.g. in colloidal platinum, see page 187). In the 'contact process' for the oxidation of sulphur dioxide it was found that the platinum soon lost its activity and became practically useless. This was shewn later to be due to the 'poisoning' effects of impurities—especially arsenic (also phosphorus and mercury, etc.)—in the materials used. It is very difficult to get rid of the last traces of arsenic, since in the fumes of sulphur dioxide there are always present particles of unburnt sulphur containing arsenic, and it is only by ensuring more complete combustion, washing, etc., that the impurity can be removed. When these precautions are taken the contact substance can be maintained in an efficient condition. [Compare Knietsch, *Ber.* 1901, 4069.]

The chemical changes in gaseous systems are influenced not only by the introduction of these contact substances but also by the walls of the containing vessel; in many cases, if not always, the chemical change appears to be confined to the layer of gases in immediate contact with the surface of the vessel. This circumstance probably accounts, as previously suggested (page 138), for the very variable and abnormal results which have often been obtained in measuring the velocity of reaction in gases. The rates of decomposition of the hydrides of arsenic

and phosphorus, for example, are shewn to be different according as the experiments are carried out in new vessels or those which have been previously used.

Bone and Wheeler [*Phil. Trans.* 1906 (206) 1] shew that the catalysing power of a new surface usually increases up to a steady maximum when successive charges of oxy-hydrogen are circulated over it; after this steady state is attained the rate of combination is always directly proportional to the pressure, i.e. the reaction is of the *first* order.

Warburg [*Sitz. k. Acad. Wiss. Berlin,* 1901 (48) 1126] found that the rate of decomposition of ozone at ordinary temperatures was a reaction of the first order. This result he attributed to the disturbing influence of the glass vessel and he considered that, in absence of such disturbances, the reaction was of the second order. Perman and Greaves have also studied this decomposition in glass vessels and shew that the rate depends on the extent of surface, although it could not be shewn to be proportional to the surface. With a large surface a much better velocity constant (for a reaction of the second order) was obtained (page 138). They considered the possibility, suggested by Nernst, that the decomposition might take place instantaneously at the surface of the glass and that the rate actually measured would simply be the rate of diffusion of the gas towards the surface; but in this case the rate should vary as the square root of the absolute temperature, and this is not found to be the case in the present instance. [See also Clarke and Chapman, *Trans. Chem. Soc.* 1908, 1638.]

The explanations which have been offered with regard to the nature of these contact actions are of various kinds. Doberciner (1835) considered that, in the case of the combination of oxygen and hydrogen, the metal acted as a carrier of oxygen to the hydrogen. Faraday and others attributed the effect to the power of the metal to occlude both oxygen and hydrogen on its surface. The molecules of the two gases being brought into closer approximation the reaction velocity would be increased. Another way of regarding the matter is to say that the condensation or occlusion of the gas, or gases, is attended with evolution of heat and this, in exothermic changes such as the combination of oxygen and

hydrogen, is sufficient to start the reaction. Thomson considers that the effects in many cases may be due to the influence of surface tension; in very thin films this influence might be sufficient to modify completely the conditions of chemical equilibrium.

Others have suggested that the results are due to the formation of intermediate compounds. Unstable oxide, or peroxide, of platinum has been supposed to be first formed and then reduced by the hydrogen; or unstable hydrides of platinum may be first produced and then react with the oxygen. Bone and Wheeler (*loc. cit.*) consider that in most cases the hydrogen plays an all-important part, being rendered 'active' by its association with the surface of the contact agent. The hydrogen is, as a rule, merely occluded or condensed on the surface, but in the case of silver there is evidence of a more intimate association, such as the formation of an unstable hydride.

(*l*) *Action of water.*

The fact that perfectly dry substances often do not interact but do so when water is present, appears to have been recognised in a superficial manner by Bergmann (1780) and more especially by Mrs Fulhame (1794). [See Mellor, *Journ. Phys. Chem.* 1903, 557.] But the matter was first clearly established by experiment in 1880, when Dixon shewed that a perfectly dry mixture of carbon monoxide and oxygen cannot be exploded even by the electric spark; the merest trace of moisture, however, is sufficient to enable the change to take place. Numerous other instances of the same fact were afterwards discovered by Baker who extended the observations to dissociating as well as to reacting systems.

Amongst the various explanations which have been suggested one may refer to the following:

In the case of the union of carbon monoxide and oxygen it was suggested that carbon monoxide reacts with water yielding carbon dioxide and nascent hydrogen, and that the latter then combines with the free oxygen to re-form water; these stages were actually demonstrated by Dixon. Traube considered that the oxygen of the water oxidises the carbon monoxide and the hydrogen unites with the free oxygen to give hydrogen dioxide; the latter

then oxidises a further quantity of carbon monoxide. The production of hydrogen dioxide has been detected in this reaction, but Dixon considers that it is only a bye-product and plays no important part. The last named author also shewed that traces of hydrogen sulphide, formic acid, ethylene, ammonia, etc., instead of water, will enable the dry gases to explode.

The catalytic action of water has also been referred to its high ionising power, since there appears to be an evident connection between the above-mentioned facts and the circumstance that perfectly dry, pure acids, etc., are often non-conductors. Baker has observed that water may actually be formed when partially dry hydrogen and oxygen are heated and yet no explosion occurs. Armstrong explains this by supposing that the water so formed is too pure; he regards chemical combination as 'reversed electrolysis' and assumes that, in order that chemical change may occur, a conducting system is necessary. When two pure substances come together they may associate together to form a complex, but in order that chemical interaction may take place a third substance must be present and one of the three must be of the nature of an electrolyte. [See, for example, *Journ. Chem. Soc.* Presidential Address 1895, 1122, and 1903, 1088.]

(*m*) *Decomposition of hydrogen dioxide. Catalysts, colloidal platinum, etc.* The fact has long been known that hydrogen dioxide undergoes rapid decomposition when brought into contact with certain metals such as platinum, gold or silver, especially if these metals are in a finely divided condition. Schönbein observed that organic ferments, or enzymes, such as yeast, diastase or emulsin, produce a similar effect, and suspected that the activities of these substances and that of platinum, etc., must 'have their foundation in similar causes.'

This decomposition can be studied in a most efficient manner by employing as catalyst the colloidal solutions of platinum (gold, palladium, etc.) prepared by Bredig's method; an example of the application of this method to the study of reaction velocity has already been discussed (page 140). In order to prepare this solution two short platinum wires, about 2 mm. in diameter, are attached to stout copper wires connected with the terminals of a direct

circuit (about 70 volts) and a suitable resistance to yield a current of about 5 ampères. The wires are inserted in glass tubes, to serve as insulating handles, which cover them to within about 1 cm. of the ends. The ends of the wires are then brought together under the surface of very pure water ('conductivity water') contained in a glass dish surrounded by ice. The moment the wires touch they are separated about 1 or 2 mm. apart so that an arc is formed. They are repeatedly touched and pulled apart in this way for about 10 minutes, and the resulting dark-coloured 'sol' is filtered from the coarser particles which have separated.

The activity of this solution as a catalyst in the decomposition of hydrogen dioxide is so great that a quantity of it containing $\frac{1}{3000000}$ of a milligram of platinum has an appreciable effect. The rate of decomposition of the dioxide increases as the concentration of the platinum is greater, but solutions of equal concentration do not necessarily give the same result; the activity depends not only on the temperature but also on the way in which the solution has been prepared and the time it has been kept, etc.

The activity of the platinum is often greatly decreased by the addition of electrolytes, presumably because the colloidal solution is precipitated or 'salted out.' Most remarkable, however, is the behaviour of certain substances, such as hydrocyanic acid, mercuric chloride, iodine, or hydrogen sulphide, which paralyse or 'intoxicate' the platinum; a solution containing about 0·001 milligram of hydrogen cyanide per litre will diminish the rate of catalytic decomposition to about half its value. The paralysing effect is more evident when the hydrogen cyanide, etc., is added to the platinum solution before the addition of the hydrogen dioxide. After a time the effect of these poisons passes off and the platinum 'recovers.'

In these properties the behaviour of colloidal platinum shews a remarkable resemblance to that of organic ferments or enzymes[1]. Points of difference sometimes insisted upon are that in many enzyme actions the products of the change diminish the activity of the enzyme and that these actions are limited, whereas the

[1] The subject of enzyme-action, although closely allied to catalysis, cannot appropriately be considered here. The student is advised to read 'The Nature of Enzyme Action' by Bayliss (Monographs of Biochemistry).

decomposition of hydrogen dioxide in contact with the platinum is completed. Since, however, the products in the latter case are only water and oxygen, there does not seem to be any necessity to assume that they would inhibit the action of the catalyst or that the reverse action is likely to occur.

(*n*) *Brodie's oxide of silver experiment*

The mutual decomposition of hydrogen dioxide and silver oxide, often referred to as Brodie's experiment, may from one point of view be regarded as a catalytic action. On pouring an aqueous solution of hydrogen dioxide on to silver oxide, at the ordinary temperature, oxygen is evolved not only from the dioxide but also from the silver oxide. Brodie found that there was a quantitative relation between the amounts of the two substances decomposed, which is expressed by the equation

$$H_2O_2 + Ag_2O = 2Ag + H_2O + O_2.$$

[Berthelot, however, shewed that the result depends somewhat on the conditions and that, if the peroxide is not in excess, the residue consists of the oxide Ag_4O_3 and not metallic silver.]

In order to explain this remarkable change, in which a substance known to be a powerful oxidising agent actually reduced a metallic oxide, Brodie supposed that the particles of the same element may have an attraction for each other and that the extra atom of oxygen in hydrogen dioxide was positive in its relation to the oxygen in the silver oxide and these two atoms of oxygen therefore attract one another. To illustrate this, the equation was written

$$H_2\overset{-}{O}\overset{+}{O} + \overset{-}{O}Ag_2 = H_2O + \overset{+}{O}\overset{-}{O} + Ag_2.$$

Others explain it by saying that the silver oxide brings about the catalytic decomposition of the hydrogen dioxide, in the same way that platinum does, and that the heat of decomposition of the dioxide is more than sufficient to effect the decomposition of the silver oxide. (H_2O, $O = -23059$ and Ag_2, $O = +5900$.) It is true that under the conditions of the experiment the temperature of the mixture is not raised to that point at which silver oxide is known to be rapidly decomposed (about 300°) but, as

Liveing puts it, "the energy parted with by the decomposing molecules of hydrogen dioxide will be communicated most rapidly and at the highest potential to the molecules of silver oxide with which they are in contact[1]."

Hydrogen dioxide brings about, in a similar way, the reduction of potassium permanganate, potassium bichromate, calcium hypochlorite and many other oxygen-giving compounds, and explanations similar to the above are usually given for these changes also. According to Brodie's view the oxygen liberated comes from both of the reacting substances; Traube, however, regarding hydrogen dioxide as a hydrogenised molecule of oxygen, considers that the free oxygen comes from the hydrogen dioxide and its hydrogen then reacts with the oxygen of the silver oxide, etc., producing water.

58. Autocatalysis.

It happens in certain cases that one of the products of a slowly proceeding reaction may act as a catalyst in the reaction itself. The slow hydrolysis of an ester by water alone, for example, yields the alcohol and the acid and acids, as above mentioned, catalytically accelerate the hydrolysis; in this case the amount of the catalyst increases as the reaction proceeds. In other cases one of the constituents originally present may act as a catalyst in the reaction and may be continuously removed as the reaction proceeds. Such phenomena have been more particularly studied in the formation of lactones from hydroxy-acids, and in the converse change. Lactone formation is known to be accelerated by the addition of foreign acids and the influence of these is proportional to their strengths or 'affinities,' i.e. to the concentration of hydrogen ions. But the hydroxy-acids themselves, although weak, are to some extent ionised in solution and the spontaneous lactone formation, which occurs in absence of foreign acid, is accelerated by the hydrogen ions of the hydroxy-acid itself and these are continually disappearing as the change proceeds. This at any rate is the explanation in terms of the ionic hypothesis, and support is given to this explanation by the experiments of Ostwald. He shewed

[1] *Chemical equilibrium the result of the dissipation of energy*, page 76.

that the rate of lactone formation, in the case of γ hydroxy valeric acid,

$$\begin{matrix} CH_3 & CH.CH_2.CH_2.CO \\ & \dot{O}H \qquad\quad \dot{O}H \end{matrix} \rightleftarrows \begin{matrix} CH_3.CH.CH_2.CH_2.CO \\ \qquad\quad \llcorner\!\!\!

grounds. In the first place it is contended that one has no evidence whatever that, in these changes, the hydrogen or oxygen ever have a separate existence, whether as atoms or molecules. The zinc, acid and arsenious oxide may all co-act, forming perhaps an unstable intermediate compound which then resolves itself into the more stable system, namely arsenic trihydride, zinc salt and water. Or, if for the sake of argument one admits that these elements are first produced, there is no need to consider that they act in the form of isolated atoms; they may be produced as molecules in the usual way and the greater activity may be ascribed to the energy run down in the action which produced them. That is to say, 'nascent' hydrogen = molecules of hydrogen + the energy of the reaction. When on the other hand the hydrogen is prepared separately, this energy has been dissipated as heat, etc.

Liveing considers (*loc. cit.* page 54) that the change

$$Zn + 2HCl + Aq = ZnCl_2 + H + H + Aq$$

would probably be an endothermic one, since the positive thermal value of the change $Zn + 2HCl + Aq = ZnCl_2 + H_2 + Aq$ is probably due to the value of H, H, which has been estimated at + 128000 heat units. If therefore we admit that the thermal value of a reaction gives a rough indication as to the *probability* of its spontaneous occurrences (at relatively low temperatures, see **54**), the first mentioned change, in which free hydrogen atoms are produced, is unlikely to occur. So far then, if one admits the validity of the foregoing objections, it would appear that the 'nascent' hypothesis is not only unnecessary but improbable. The question assumes a different aspect, however, if stated in terms of the theory of ionic dissociation. The action of zinc on hydrochloric acid will then be represented as $Zn + 2\dot{H} + 2Cl' = \ddot{Z}n + 2Cl' + H_2$, i.e. as the transfer of two positive charges from the hydrogen to the zinc; in this sense one might regard 'nascent' hydrogen as representing the condition of the element at the instant when its ions give up their electric charges.

The influence of light upon chemical change will be considered in a future section.

Practical Work.

The examples of catalysis which have been discussed in the lecture are practically examined as far as time allows. A few points of practical detail may be given as follows:

[The experiments (*a*), (*b*) and (*i*) were illustrated in the lecture.]

(*c*) Ammonium carbamate (prepared by union of dry ammonia and carbon dioxide) is dissolved in a solution of caustic soda and sodium hypochlorite, both in excess, and shaken until the evolution of nitrogen practically ceases. A few drops of a solution of sodium (or potassium) bromide is then added and the mixture allowed to stand for about a minute, when a fresh evolution of gas takes place. It is of interest also to repeat this experiment with varying proportions of the bromide; equal volumes of the original sodium carbamate and hypochlorite mixture are placed in small wide-mouthed bottles connected with delivery tubes as in Fig. 13 *a*, page 56, the bromide solution being contained in the small tube. The solutions are then mixed and the gas volumes read off at stated intervals.

(*d*) Small quantities of dry powdered potassium chlorate, alone and mixed with the various metallic oxides, etc., mentioned, are heated in hard glass tubes and the results are compared.

(*e*) Dissolve say, 2 grams of oxalic acid in 20 c.c. of water and add 2 c.c. of nitric acid (sp_A gr. about 1·3). On heating this mixture to about 80 or 90° scarcely any change is observed, but if a very small quantity of a manganous salt is added, a brisk evolution of carbon dioxide takes place.

(*f*) Bleaching powder is stirred into a paste with water, further diluted with water, and the nearly clear liquid poured off. On boiling the latter solution alone no perceptible evolution of oxygen is observed, but on the addition of a drop of cobaltous nitrate or chloride a black precipitate appears and oxygen is given off.

(*g*) Experiments illustrating the catalytic effect of acids in accelerating the hydrolysis of esters will be made in a future demonstration. The effect of alkalis has already been studied (page 142).

The 'inversion' of cane sugar may be illustrated by heating a dilute solution (say 1 in 50) of cane sugar with about 5 drops of strong hydrochloric acid in the water bath for about half an hour. The solution is then made just alkaline with sodium carbonate and (1) tested with Fehling's solution (2) made just acid with acetic acid and heated with a few drops of phenylhydrazine acetate. The original cane sugar solution before heating is similarly tested and the results compared.

The hydrolytic decomposition of starch may be similarly demonstrated. In this case it is interesting to compare the action of dilute acids with that of ptyalin.

(*h*) Friedel and Crafts' reaction may be illustrated by studying the behaviour of aluminium chloride towards a mixture of benzene and acetyl chloride. An experiment is first made on a very small scale to shew that these substances do not react in absence of the aluminium chloride. The latter must be quite anhydrous.

Take say 15 grams of benzene and about 25 grams of aluminium chloride in a distilling flask and add, drop by drop, from a tap funnel, 17 grams of acetyl chloride. Observe the rapid effervescence with evolution of hydrogen chloride. If it is desired to isolate the product, the flask should be provided with an upright condenser and the mixture should be allowed to stand for an hour after the operation. It is then treated with ice-cold water, mixed with a little benzene and separated in a separating funnel. The lighter layer is then washed with dilute caustic soda and with water, dried over calcium chloride and distilled, collecting the portion which comes over at 195—200°; this distillate on standing and cooling solidifies to a crystalline mass.

(*j*) Typical examples of the catalytic influence of ferrous salts on the oxidation of organic substances may be demonstrated most easily in the cases of tartaric acid and glycerol.

Tartaric acid. A solution of tartaric acid is treated with a few drops of ferrous sulphate and then with two or three drops of hydrogen dioxide; the mixture becomes hot and on addition of excess of caustic soda, gives a deep violet colour. [This colour is due to the interaction of the resulting dihydroxymaleic acid with a

ferric salt; it is intensified if a drop or two of ferric chloride is subsequently added.] Observe that if a ferric salt is originally used, instead of a ferrous salt, the effect is not produced; a negative result is usually obtained also if the oxidising agent is added before the ferrous salt.

[If it is desired to isolate the dihydroxymaleic acid, special precautions must be taken. See *Trans. Chem. Soc.* 1894, 899.]

To illustrate the production of the same substance by means of atmospheric oxygen in presence of sunlight, proceed as follows. To a fairly strong solution of Rochelle salt add a few drops of ferrous sulphate solution and divide the mixture into two parts. Expose one part in an open dish to air and sunlight for about 15 minutes, keeping the other part (either exposed to air or not) in a dark cupboard. Now test both parts by adding excess of caustic soda (and a drop of ferric chloride if necessary).

Glycerol. An aqueous solution of glycerol is oxidised by hydrogen dioxide in presence of a ferrous salt; the resulting product (glyceraldehyde, with possibly some dihydroxy acetone) is identified by conversion into glycerosazone.

Take, for example, 10 grams glycerol diluted with an equal volume of water and dissolve in it about 1 gram of ferrous sulphate. Add gradually about 45 c.c. of hydrogen dioxide (20 volume) not allowing the temperature to rise above about 50 or 60°. After the mixture has stood for half an hour, test (with chromic acid and ether or titanic acid) to ascertain whether all the hydrogen dioxide has disappeared. When this is the case, add a slight excess of phenylhydrazine acetate and allow to stand until a bulky crystalline precipitate has accumulated. The precipitate is collected, washed, allowed to dry and crystallised first from 50 per cent. alcohol and then from benzene. The crystals of glycerosazone melt at 130—131°.

(*k*) The following experiments illustrating well-known examples of contact have been shewn in the lecture:

The combination of hydrogen and oxygen, hydrogen and bromine, sulphur dioxide and oxygen and the interaction of hydrogen and nitric oxide, in contact with spongy platinum. The behaviour of a mixture of air and ammonia when passed over

heated copper. These experiments may be repeated, if desired, in the demonstration, students fitting up the necessary apparatus. In addition, the following experiments may be made:

A small quantity of strong ammonia is poured into a large flask and a platinum coil, heated to redness, is quickly introduced above the liquid. After the action has proceeded for some minutes the wire is withdrawn and the flask shaken so as to cause the fumes to dissolve in the liquid. The solution is then just acidified with dilute sulphuric acid and tested for nitrous acid by means of the usual tests (ferrous sulphate; potassium iodide; potassium permanganate, etc.). Note that if the action proceeds rapidly oxides of nitrogen eventually make their appearance; in some cases an explosion occurs.

A few drops of an aqueous solution of methyl alcohol are introduced into a wide test tube and a coil of copper wire (which has previously been oxidised on the surface) is heated to redness and plunged partly into the liquid; it is then withdrawn, heated to redness and again introduced, the operations being repeated four or five times. The solution is then tested for formaldehyde by any of the delicate colour reactions (such as resorcinol and sulphuric acid; sodium nitroprusside, phenylhydrazine hydrochloride and caustic soda).

(*l*) The influence of moisture on the interaction of gases is easily illustrated in the case of a mixture of sulphur dioxide and hydrogen sulphide. These gases when dry do not react, but in presence of water a separation of sulphur immediately takes place and a solution containing pentathionic acid (and perhaps hexathionic acid) is obtained

$$5H_2S + 5SO_2 = H_2S_5O_6 + 4H_2O + 5S.$$

The gases are prepared in the ordinary way; the hydrogen sulphide is dried by passing it through a calcium chloride tower and the sulphur dioxide by strong sulphuric acid. The two gases are passed together into a large flask or stoppered bottle in which has been placed a thin sealed glass tube containing water; large excess of sulphur dioxide should be avoided. In order to start the action, the tube is broken by shaking.

An experiment illustrating the influence of water in bringing

about the interaction of iodine and hydrogen sulphide has already been referred to (page 115).

(*m*) The influence of negative catalysts on the efficiency of colloidal platinum in the decomposition of hydrogen dioxide may be illustrated by making comparative measurements of the rate of evolution of gas when equal volumes of a solution of hydrogen dioxide are treated with the same quantity of colloidal platinum solution, alone and in presence of small quantities of the substances mentioned (e.g. mercuric chloride, iodine, hydrocyanic acid and hydrogen sulphide). Any convenient form of apparatus may be employed such as that represented in Fig. 13 *a*, page 56.

(*n*) The action is investigated of hydrogen dioxide on the following substances: silver oxide, potassium permanganate in presence of dilute sulphuric acid, bleaching powder. In each case the nature of the evolved gas and of the residual products should be ascertained as far as possible by qualitative tests.

CHAPTER XV.

ELECTROLYTIC DISSOCIATION.

60. THE laws of osmotic pressure have already been referred to in Chapter IV. It was shewn that the osmotic pressure is proportional to the concentration and, with every degree of probability, to the absolute temperature, so that the gas equation $PV = RT$ may be applied to substances in solution, P in this case denoting the osmotic pressure. Further, as shewn by van 't Hoff, the constant R has in this case the same value as for substances in the gaseous state. But although these laws hold so remarkably well for dilute solutions of non-electrolytes, such as cane sugar or urea, it was soon noticed that considerable deviations occur in the case of most salts, acids and bases, the deviations in the last-named cases being greater as the acids or bases are stronger. In order to bring such substances into harmony with the general laws of osmotic pressure, van 't Hoff introduced a factor, which he denoted by the symbol (i), representing the number of times that the observed osmotic pressure is greater than that calculated by the formula given above. Thus if p_1 is the observed value of the osmotic pressure and p_2 is that calculated from the above formula, $i = \frac{p_1}{p_2}$

Instead of the osmotic pressure one may take effects which are proportional to it, such as the depression of the freezing point or rise of the boiling point. For example, the observed depression of the freezing point produced by dissolving 0·682 gram of sodium chloride in 100 grams of water was 0·424, and the value calculated from Raoult's equation is $\frac{18{\cdot}6 \times 0{\cdot}682}{58{\cdot}5} = 0{\cdot}2168$; hence $i = \frac{0{\cdot}4240}{0{\cdot}2168} = 1{\cdot}95$.

Introducing this factor, the general equation becomes $PV = iRT$.

A remarkably complete explanation of this apparently anomalous behaviour of electrolytes was offered by Arrhenius in 1887, that is shortly after the publication of van 't Hoff's theory of solutions. Just as the so-called 'abnormally' low values of the vapour densities of ammonium chloride, phosphorus pentachloride, etc., had been explained in a most conclusive manner by the theory of dissociation, so, according to Arrhenius, these abnormally high values of the osmotic pressure of aqueous solutions of salts, acids and bases can be accounted for if one supposes that the molecules of these substances, when dissolved, become more or less split up into parts, each part then behaving as an independent individual. Arrhenius was led to this view not only by reference to the abnormalities mentioned but also by the results of his extended studies on the conductivity of electrolytes. Planck, in the same year, also pointed out that the observed abnormalities of freezing point, etc., could only be brought into harmony with thermodynamic laws by assuming that the molecules of the substances in solution undergo dissociation to some extent. The idea of the free existing parts of a salt, or ions, in solution, had been foreshadowed by Clausius who shewed, from kinetic considerations, that in a solution of an electrolyte a certain minute fraction of its dissolved molecules must "at any instant be broken up into their constituent atoms" On electrolysis, therefore, the electromotive force influences the motions of these constituents during their freedom but it does not, as was previously imagined, produce the disruption of the molecules. The constituent parts of the molecules with which we are concerned, the positive and negative ions, were, to some extent, pre-existent in the solution before the electromotive force was applied. When the current passes these ions, carrying opposite charges, which were at first moving in all directions, are now directed towards the anode and cathode respectively, and on reaching these electrodes give up their electric charges.

Upon this hypothesis it is possible to account for many facts which were inconsistent with the older views of the nature of electrolysis. [For example, the fact that the smallest possible electromotive force is able to bring about electrolysis, if non-polar-

isable electrodes are employed; that substances usually regarded as containing their elements most firmly 'bound together,' such as sodium chloride or hydrochloric acid, are the best conductors, and that pure liquids are usually non-conductors.]

The conception then, that a minute fraction of the molecules of an electrolyte might exist in solution at any moment in the ionised condition, was of assistance in affording a qualitative explanation of many apparent difficulties; the great advance upon this conception due to Arrhenius, consisted in its quantitative aspect. He was able to shew that the deviations from the laws of osmotic pressure and the conductivities were quantitatively related and he pointed out how, from these phenomena, the degree of electrolytic dissociation or 'ionisation' could be calculated. As a result it is found that the proportion of dissociated molecules is by no means necessarily very minute and that in dilute solutions (of strong acids and bases and many salts) the dissociation may be almost complete.

The term ion was employed by Faraday 'to express those bodies which can pass to the electrodes' whether as primary or secondary products; thus the hydrogen, caustic potash and oxygen, obtained on electrolysing potassium sulphate, would all be classed as ions. The word is now used in reference to the electrically charged atoms, or groups of atoms, into which the molecule of the electrolyte is dissociated when dissolved and by which, on electrolysing, the current is conveyed. (The conductivity of gases, particularly after they have been subjected to certain influences,—radium, Röntgen rays, ultra-violet rays, etc.—is explained also by supposing that the current is conveyed by charged particles; one speaks therefore of 'gaseous ions' and the ionisation of gases.)

These charged atoms or groups are supposed then to exist in the solution 'free' as regards their independent movement; the necessary restriction is that the total number of unit positive charges carried by the kations must at any moment be equal to the number of negative charges carried by the anions. As regards conformity to the laws of osmotic pressure and of mass action the effect of these ions is just like that of the undissociated molecule.

Further evidence in support of the theory is afforded by the

additive properties of salt solutions; such properties as specific gravity, colour, refractivity or conductivity, of dilute solutions of salts, can be numerically expressed as the sum of the properties of the anions and the kations. Thus the specific gravities of equivalent solutions of many metallic chlorides differ by an amount depending on the nature of the metal, and these differences are found to be the same if for chlorides we substitute equivalent solutions of, say, nitrates or bromides of the same metals. Similarly the differences in the specific gravity of equivalent solutions of chlorides, bromides, nitrates, etc., differ by amounts independent of the nature of the metal. Thus Ostwald shewed that if two different bases A and B are neutralised by various different acids, the change in volume on neutralisation of A differs from that observed on neutralisation of B by the same amount for all acids; i.e. it is independent of the nature of the acid.

This additive character is also well illustrated if we study the colours of dilute solutions of salts derived from a coloured acid and a colourless base, or *vice versa*. Thus Ostwald examined the absorption spectra of the permanganates of a large number of metals, whose chlorides, sulphates, etc., are colourless, and he came to the conclusion that the spectra were the same in all cases. Salts of fluorescein, eosin, rosaniline, etc., shewed similar results.

The properties, then, of a dilute solution of a salt are, in general, the additive properties of its ions and most of the ordinary tests applied in qualitative analysis are regarded as tests for the respective ions. Silver nitrate for example will indicate the presence of chlorine ions in solutions of chlorides but it gives no indication with solutions of chlorates, perchlorates or chloral, because, in these, chlorine ions are not present.

The theory of ionic dissociation met with violent opposition at first and is still bitterly 'resented' by certain chemists of undoubted reputation. It may be of interest here to draw attention to some of the objections and adverse criticisms which have been made with regard to the theory and the way in which they have been met by its supporters. We shall then deal with the more important applications of the theory and shall endeavour to shew that, as a working hypothesis, it gives qualitative and quantitative explanations of a large number of chemical phenomena which can

otherwise only be accounted for in a vague and unsatisfactory way. Beyond this there is no necessity to go. Whatever may be our own individual convictions it is best to content ourselves for the present with a careful summing up of the evidence and not to attempt a final judgment. The practice of making use of 'ions' for the purpose of a working hypothesis in no way implies the necessity of having faith in their actual existence.

61. Objections and criticisms.

(*a*) One of the earliest objections raised against the theory of electrolytic dissociation was based upon a misconception with regard to the postulated character of the ions. Bearing in mind the well-known violent action of metallic sodium on water and also the poisonous and corrosive action of free chlorine, it was considered absurd to suppose that these substances could exist *as such* in an aqueous solution of common salt. But in terms of the theory they do not so exist; by the sodium ion and the chlorine ion we understand the sodium or chlorine atom plus an enormous electric charge, positive and negative respectively. The properties of these charged atoms are entirely distinct from those of the neutral molecules of sodium and chlorine as we know them in the isolated condition.

(*b*) Similarly it was contended that chlorine and sodium combine with very great 'affinity' and how therefore could the mere action of solution succeed in overcoming this affinity and separating them apart? In fact it very often happens that those compounds which are formed from their free elements with the greatest evolution of heat are the ones which are found to be most ionised when dissolved. But the theory does not say that the compound is separated into the original constituents, but into charged atoms. Even so, whence comes the energy necessary to pull apart these charged atoms? According to Larmor, "we are tempted to conclude that internal potential energy is released owing to the ions falling into relations of closer affinity with the solvent and that the process is nearly a self-contained interchange of energy, reversible as regards each molecule separately,—being a steady static drawing apart of the ions unaccompanied by the

generation of violent subsidiary electronic motions whose energy would escape into the general store of heat."

(*c*) An attempt was made in the first instance to shew that in order to account for the deviations from the laws of osmotic pressure (abnormal freezing points, etc.), the hypothesis of ionisation was unnecessary. It was suggested for example that sodium chloride might, to a large extent, undergo hydrolysis in aqueous solution, one molecule of solute thus giving rise to two molecules—$NaCl + HOH = NaOH + HCl$—and hence producing an approximate doubling of the osmotic pressure. But in this case it would not be possible to explain why heat should be evolved when dilute solutions of caustic soda and hydrochloric acid are mixed together. Again, it would not be possible to account in a similar way for the deviations in the case of strong acids or bases.

(*d*) If the deviations from the laws of osmotic pressure are to be explained by ionisation, and comparison is made with the explanation of 'abnormal' vapour densities by gaseous dissociation, one should be able, in the former case as in the latter, to effect a partial separation of the dissociated constituents by diffusion. The chlorine ion is, in terms of the ionisation hypothesis, more mobile than the sodium ion; hence if a solution of sodium chloride was covered with a layer of pure water, the chlorine should accumulate in the upper layer. But it must be remembered that the ions carry enormous, equal and opposite, electric charges and diffusion to any extent is therefore impossible owing to electrostatic attraction. It can however be demonstrated that *some* separation is thus effected in the first instance, since it can be shewn that, in the experiment mentioned, the lower layer becomes positively charged and the upper layer negatively charged, and if the two layers are joined by a wire (terminating in unpolarisable electrodes), a current can be detected.

(*e*) It has also been suggested that the deviations from the laws of osmotic pressure might be explained by assuming that the solute molecules combine with water molecules to form hydrates and the ratio of the number of solute molecules to the free water molecules is thereby increased; in other words the water molecules

which are combined with the solute can no longer be regarded as solvent molecules and the 'effective' concentration is consequently increased. Although the formation of hydrates is possible, and even probable, it is clear that this circumstance alone could not, without further assumptions, afford a satisfactory explanation. Thus in order to account for the approximate doubling of the osmotic pressure in a solution of sodium chloride of, say, $\frac{1}{1000}$ molar strength (i.e. $\frac{1}{1000}$ molecule of sodium chloride to about 55 molecules of water), each molecule of salt would have to 'put out of action' about 27000 molecules of water in order to reach the 'effective' concentration required to account for the result.

(*f*) The fact that, in a large class of electrolytes, the law of mass action expresses with remarkable accuracy the influence of dilution on the degree of ionisation, is regarded as affording powerful evidence in favour of the theory of electrolytic dissociation. Conversely the fact that the law does not hold for 'strong' electrolytes (see page 210) is not yet thoroughly explained and is used by the opponents as an argument against the theory.

(*g*) Kahlenberg [*Journ. Physical Chem.* 1902, 1 and 54] has described a large number of experiments, the results of which appear to be in opposition to the requirements of the theory. He shews for example that certain salts or acids may react instantaneously with one another although dissolved in some solvent in which ionisation does not occur. Thus the oleates of copper, nickel or cobalt dissolve in dry benzene giving non-conducting solutions; hydrogen chloride, stannic chloride, phosphorus trichloride, etc., do likewise. Yet on mixing dry benzene solutions of, say, copper oleate and hydrogen chloride, double decomposition immediately takes place with precipitation of cupric chloride Oleates of copper, nickel or cobalt likewise react with hydrogen sulphide and ammonia or pyridine with hydrogen chloride, when dissolved in dry benzene. These facts are to be regarded as antagonistic to the somewhat common opinion that all instantaneous reactions in solution must of necessity be ionic reactions, but they need not for that reason be incompatible with the theory of ionic dissociation. It has been suggested that the solutions mentioned do really contain some ions of the reacting substances,

but that their quantity is too small even to be detected by the conductivity method. In this case " we may conclude that very great reaction velocities may be reached even with quantities of ions so small as to be beyond detection " (Abegg).

Kahlenberg also finds that abnormally low molecular weights are sometimes found in solutions in which no ions can be present. Diphenylamine and silver nitrate for example both give abnormally low molecular weights, by the boiling point method, when dissolved in acetonitrile. Yet, in this solvent, silver nitrate is a fairly good electrolyte and diphenylamine a non-electrolyte. He also states [*loc. cit.* 1906, 141] that when dissolved in pyridine, lithium chloride, which in this solvent is a good electrolyte, gives a lower osmotic pressure than cane sugar, although the latter is a non-electrolyte.

(*h*) Armstrong [*Proc. Roy. Soc.* 1908 (545) 80, *B. A. Report,* 1908] considers that the effects usually ascribed to ionisation can best be explained by making certain assumptions as to the existence of molecular complexes in solution. Water itself is supposed to be a complex mixture of active and inactive molecules. The simple molecule H_2O is termed 'hydrone' or 'monad hydrone,' and the complex $H_2O\langle^{H}_{OH}$ is called 'hydronol'; both of these are active. The inactive molecules are the closed systems formed by association, such as $H_2O = OH_2$ (dihydrone),

$$\begin{matrix} H_2O{-}OH_2 \\ \diagdown\diagup \\ OH_2 \end{matrix} \text{ (trihydrone), and } \begin{matrix} H_2O{-}OH_2 \\ |\quad| \\ H_2O{-}OH_2 \end{matrix} \text{ (tetrahydrone).}$$

When a substance such as hydrogen chloride is dissolved in water, it becomes partly 'hydronated' and partly 'hydrolated' and partly 'hydrolysed,' forming compounds such as $HCl = OH_2$ and $HCl\langle^{H}_{OH}$ or $H_2O\langle^{H}_{Cl}$. The two latter are regarded as effective molecules whilst the former being a closed system is, as such, inactive. Compounds such as alcohol become hydronated and hydrolated but not hydrolysed. In order that a conducting solution may be obtained it is necessary that rearrangement shall

take place both in solvent and solute, conduction being dependent, in some way, on the interaction of molecules of two such types as $H_2O\langle^{H}_{Cl}$ and $^{HO}_{H}\rangle ClH$. "The occurrence of electrolysis in such solutions is dependent on influences which these composite molecules exert, reciprocally, on one another whilst under the influence of the electric strain." The apparent increase in the electrolytic activity of a dissolved substance on dilution is considered to be due to an increase in the proportion of effective or active composite molecules. In a dilute solution there is probably a greater proportion of hydrolated molecules of the solute, $HX\langle^{H}_{OH}$ and these, in some way, are connected with superior activity as electrical conductors. In concentrated solutions there is a larger proportion of hydrolysed molecules of the solute $H_2O\langle^{H}_{X}$ and to these the author ascribes greater hydrolytic activity.

The author draws attention to several circumstances which appear to be out of harmony with the hypothesis of ionisation and suggests alternative explanations on lines similar to those above indicated.

62. Degree of ionisation.

An electrolyte when dissolved in water will, according to the theory, become electrolytically dissociated, or ionised, to a certain extent; this extent will depend upon the nature of the substance (and of the solvent), the degree of dilution and, to a small extent, on the temperature.

Suppose that one molecule of the electrolyte when completely ionised yields n ions. Dissolve now one gram molecular weight of it in a limited quantity of water and let m be the fraction of it which becomes ionised, or the 'degree of ionisation.' The solution will then contain (in gram formula weights) $(1 - m)$ non-ionised molecules and nm ions. The total number of individuals (molecules and ions) will therefore be $(1 - m) + nm$. The value of m may be found by two distinct methods.

If one gram molecule of the substance were dissolved in the given quantity of solvent without ionisation it would produce the 'normal' osmotic pressure P_1; but if it ionises to the extent mentioned, the actual osmotic pressure observed, P_2, will be $(1 - m + nm)$ times as great, or $\frac{P_2}{P_1} = \frac{1 + (n-1)m}{1}$. But this ratio $\frac{P_2}{P_1}$ is what was defined above as the value of van 't Hoff's coefficient i so that $i = 1 + (n-1)m$ and $m = \frac{i-1}{n-1}$.

Practically, therefore, the first method of ascertaining the degree of ionisation in a given solution of an electrolyte consists in finding the freezing point depression, boiling point elevation (or other property directly dependent on the osmotic pressure) and dividing the result by the value calculated on the assumption that no ionisation took place. In this way we obtain the value of i and so calculate m as above.

The second method of finding m depends upon the determination of the electric conductivity. The molecular conductivity of a solution of an electrolyte is its specific conductivity divided by its molecular concentration, or, the specific conductivity multiplied by the volume of the solution which contains one molecular weight of the electrolyte. The molecular conductivity is found to be dependent on the temperature and also on the dilution. In the case of strong acids and bases, and most salts, the increase of molecular conductivity with dilution is small, but with weak acids or bases it is considerable. In both cases it approximates to a limit at a sufficiently great dilution and this limit may actually be observed in the case of strong electrolytes (e.g. KCl or $BaCl_2$). But with weak electrolytes the dilution at which the limit would be attained is too great for practical measurement.

Kohlrausch in 1876 shewed that the equivalent conductivities of many neutral salts are additively composed of two values, one depending on the nature of the metal and the other on the nature of the acid radicle. This holds good, however, only if the dilution is such that the limit has been reached at which the equivalent conductivity no longer increases with dilution, or at which the salts are ionised to the same extent. The conductivity depends

on the number of ions and the speed with which they move, the current being conveyed only by the ions and not at all by the non-ionised molecules. In an aqueous solution of an electrolyte at a given temperature, the molecular conductivity λ at a given dilution v is proportional to the number of free ions and this number is again proportional to the degree of ionisation m. We may therefore write $\lambda_v = \kappa m$, where κ is a numerical factor. But at very great dilution, where the limit is reached, the ionisation would become complete, so that $m = 1$. If therefore λ_∞ represents the molecular conductivity at this great (or infinitely great) dilution, $\lambda_\infty = \kappa$ and consequently $m = \frac{\lambda_v}{\lambda_\infty}$.

The same thing may be stated in a somewhat different way, as follows. If, at a given difference of potential between the electrodes, we electrolyse a solution of a binary electrolyte, the two ions are driven towards the respective electrodes and the speed with which each ion travels will depend on the charge it carries and on the frictional resistance offered by the liquid. The amount of this resistance depends on the nature of the ion, i.e. it is different for different ions and they therefore generally move at different rates. [The force necessary to drive one gram equivalent of an ion against this resistance at the rate of 1 centimetre per second is sometimes called the 'resistance-friction,' and the rate, in centimetres per second, at which the gram equivalent of an ion is transported under a potential gradient of one volt per centimetre, is called the 'mobility' of the ion.]

If we take numbers U and V proportional to the speed of the two ions respectively, we may, choosing appropriate units, write $\lambda_\infty = U + V$ for the molecular conductivity at infinite dilution and $\lambda_v = m(U + V)$ for that at the given dilution v, and consequently $m = \frac{\lambda_v}{\lambda_\infty}$.

It is assumed here that the change in molecular conductivity depends only on the change in the number of ions, i.e. that U and V remain practically the same at the different dilutions. Since the solutions are extremely dilute it appears not unreasonable to assume that the frictional resistance of the solutions is practically that of pure water.

Practically, therefore, in order to find the degree of ionisation

by this method it is necessary to know the molecular conductivity of the solution at the given dilution v and also that at a dilution great enough to ensure that the electrolyte is completely ionised. The latter value may be practically determined in the case of the strong electrolytes referred to; the limit is sometimes approximately reached in such cases at a dilution of one gram molecule in about 1000 to 2000 litres. But in the case of weak acids or bases, which are only slightly ionised at such dilutions, the direct determination is impossible since, at the enormous dilution necessary, the conductivity would be so low as to make the comparative experiments worthless on account of experimental error. The values of λ at infinite dilution may however be calculated indirectly, for example, by determining the conductivities of salts, or strong acids or bases, which contain ions in common with the weak electrolytes to be investigated. Thus if we wish to find the molecular conductivity of, say, acetic acid at infinite dilution we can observe the molecular conductivities of potassium acetate, potassium chloride and hydrochloric acid at dilutions where the ionisation is complete and so obtain the desired value by subtraction. Thus denoting the speeds U and V of the respective ions by the chemical symbol of the elements, we have

$$[K + (CH_3CO_2)] + [H + Cl] - [K + Cl] = [H + (CH_3CO_2)].$$

Theoretically then, we should obtain the same value for m by the two methods, that is to say, we should expect that in a sufficiently dilute solution,

$$\frac{i-1}{n-1} = \frac{\lambda_v}{\lambda_\infty}.$$

[Although it is evident from the nature of the experimental methods that much greater accuracy is to be expected from the second method.]

Experiments by Arrhenius and others shewed, in the first instance, a fairly good agreement in the results obtained by the two methods, a fact which has sometimes been emphasised as a strong argument in favour of the theory of electrolytic dissociation.

The question has since been submitted to a critical examination by Whetham, Griffiths, Jones and others, and a very close agreement has been observed in the case of potassium chloride at certain

dilutions. In many other cases however there are very considerable discrepancies, more particularly, as might be expected, if the solutions are not extremely dilute. [Compare for example, Whetham, *Phil. Trans.* 1900 (194) 321.]

Electrolytes may be broadly classified as 'strong' or 'weak' according to the extent to which they become ionised at moderate dilution.

Thus, most salts and the stronger acids and bases, become very considerably ionised even in fairly concentrated solutions, such for example as are employed in analysis. In solutions of molar strength (one gram molecular weight per litre) potassium chloride for instance is ionised to the extent of about 75 per cent. and hydrochloric acid of about 80 per cent. Generally the salts of univalent metals with monobasic acids are, at moderate dilution, highly ionised, whereas for salts of bivalent metals with monobasic acids, or of univalent metals with dibasic acids, the degree of ionisation is lower and is still less for salts of bivalent metals with dibasic acids.

On the other hand, most organic carboxylic acids, phenols, primary, secondary and tertiary amines and ammonia (these being regarded, in solution, as hydroxides), hydrosulphuric, hydrofluoric, hydrocyanic, boric and carbonic acids are ionised only to a very small extent even at great dilutions.

Thus in a solution of $\frac{1}{8}$ molar strength (one molar weight in 8 litres) acetic acid is ionised only to the extent of about 2 per cent. and in a $\frac{1}{1000}$ molar solution to about 12 per cent.

Most salts as above stated are usually highly ionised even at moderate dilution and this is true whether the acids and bases from which they are derived are strong or weak; there are some notable exceptions, however, such as mercuric or cadmium halides, and mercuric cyanide, which are very slightly ionised.

63. Influence of dilution.

According to the theory of electrolytic dissociation one would expect that the law of mass action should be applicable to the equilibrium between an electrolyte and its ions, in just the same way as, in ordinary dissociation, it applies to the equilibrium

between the more complex molecule and the simpler molecules into which it is resolved. By means of this law we ought then to be able at once to calculate the influence of dilution on the degree of ionisation, and, in the case of weak electrolytes, the results so calculated do agree, on the whole, remarkably well with the values found by experiment. Taking for example the case of a weak binary electrolyte such as acetic acid, let one molar weight of it be dissolved in V litres of water, at a given temperature, and let the degree of ionisation obtained be m. Then in the system $HA \rightleftarrows \dot{H} + A'$ we shall have the active masses $\frac{1-m}{V}$ of the non-ionised acid and $\frac{x}{V}$ of each ion so that, for equilibrium,

$$k\frac{1-m}{V} = k_1 \frac{m}{V}\cdot\frac{m}{V} \quad \text{or} \quad \frac{k}{k_1} = K = \frac{m^2}{(1-m)V}.$$

This relation is known as Ostwald's dilution law and the value of K is called the dissociation constant. In the case of very weak electrolytes, where the degree of ionisation is very small and varies only slowly with dilution, $1-m$ differs very little from 1, so that in this case $\frac{m^2}{V}$ is practically constant; in other words, the degree of ionisation is proportional to the square root of the dilution.

If the electrolyte dissociates into three ions instead of two we shall have the relation

$$\frac{1-m}{V}k = \frac{m^3}{V^3}k_1 \quad \text{or} \quad K = \frac{m^3}{(1-m)V^2},$$

and so on. Polybasic acids usually ionise in stages, so that the form of the relationship changes when the dilution is sufficiently increased.

Solutions of weak polybasic acids, at moderate dilutions, are found to obey the simple law of dilution, shewing that they give rise to two ions; thus a weak dibasic acid H_2A first ionises as $\dot{H} + (HA)'$. As the acids are stronger, or as the dilution is considerably increased, the $(HA)'$ ions further ionise into $\dot{H} + A''$ so that the equilibrium becomes more complicated.

The fact that such excellent results have been obtained by the application of the law of mass action in the calculation of the

equilibrium of weak electrolytes and their ions is, as above stated, regarded as powerful evidence in favour of the theory of electrolytic dissociation. Conversely it may be said that the law of mass action has been experimentally tested in this way far more widely and accurately than by any other method.

Unfortunately however it happens that, for strong electrolytes, the above method of calculation is no longer applicable. Whereas for weak electrolytes the value of k is found to be practically independent of dilution one finds in the case of salts, or strong acids or bases, very considerable deviations. Thus in the case of potassium chloride the value of k, calculated by the above formula, varies from 0·6 in a $\frac{1}{10}$ molar solution ($m = 0{\cdot}873$) to 0·16 in a $\frac{1}{1000}$ molar solution ($m = 0{\cdot}994$).

Various empirical formulae have been suggested in order to connect the degree of ionisation with the dilution in the case of strong electrolytes such as

$$K = \frac{m^2}{\sqrt{V}(1-m)} \quad \text{or} \quad K = \frac{m^{\frac{3}{2}}}{(1-m)V^{\frac{1}{2}}},$$

but no completely satisfactory theoretical explanation appears to have been found. It has been suggested that the presence of the ions of the strong electrolyte may increase the ionising power of the solvent, or that the methods employed (osmotic effects and conductivity, as above) do not give the correct values for m owing to (*a*) a mutual action between the ions, (*b*) to a combination between ions and non-ionised molecules to form complex ions, or (*c*) to a combination of the ions with the solvent. In the case of weak electrolytes where the ions are few, such disturbances are negligible. Abegg and Labendzinski [*Zeit. electrochem.* 1904 (10) 77] for example, describe experiments indicating the formation of complex ions, in the strong solution, which break up into simple ions as the dilution increases.

64. Influence of temperature.

In order to ascertain the influence of temperature on the degree of electrolytic dissociation it is evidently not sufficient merely to compare the molecular conductivities of the solution at different temperatures. For the conductivity depends, as above indicated,

not only on the degree of ionisation but also on the frictional resistance of the solution to the passage of the ions and this latter property also varies with the temperature. If by any means we can determine the heat of ionisation of the electrolyte in question it is possible to calculate the influence of temperature on the degree of ionisation by the thermodynamic formula referred to on page 161.

Thus if m_1 and m_2 are the degrees of ionisation of a binary electrolyte at the absolute temperatures T_1 and T_2, and V represents the volume of the solution containing one gram molecular weight of the electrolyte, we have, by the law of mass action,

$$K_1 = \frac{m_1^2}{(1-m_1)V} \text{ and } K_2 = \frac{m_2^2}{(1-m_2)V}$$

(neglecting any slight change in the volume V), and consequently,

$$\log_e \frac{K_1}{K_2} = \log_e \frac{m_1^2(1-m_2)}{m_2^2(1-m_1)} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

where Q represents the heat of ionisation.

The heat of ionisation has been calculated in various ways. For example, one may ascertain the deviation from the 'constant' heat of neutralisation (see page 288) or from the law of thermo-neutrality (see page 278). Thus suppose two strongly ionised salts AB and CD are mixed in dilute aqueous solution there should be no thermal effect if the salts AD and CB are also highly ionised. But if strongly ionised AB and CD produce highly ionised AD and practically non-ionised CB the thermal effect observed would represent the heat of formation of CB from its ions (i.e. the heat of ionisation with opposite sign). By making determinations of this kind at different temperatures one may calculate the change in the degree of ionisation with temperature.

Arrhenius proceeded in the opposite way and succeeded in calculating the heat of ionisation of certain electrolytes from the rate of change of conductivity with temperature. But he selected electrolytes in which the degree of ionisation decreased so markedly with rising temperature that the simultaneous increase of ionic mobility with temperature was comparatively insignificant.

By the above methods it has been found that the heat of ionisation is usually small and may be either positive or negative; in the majority of cases it is positive, i.e. the dissociation of an

electrolyte is usually attended with evolution of heat. According to the principle of le Chatelier therefore, the degree of ionisation should generally be less as the temperature is higher. [This can be seen at once from the formula given above, since if T_2 is higher than T_1 and Q is positive, k_1 must be greater than k_2 and consequently m_1 is greater than m_2.]

65. Influence of the solvent.

In the foregoing generalisations with regard to the theory of electrolytic dissociation we have confined ourselves to the results obtained from the study of the properties of aqueous solutions. Although the theory has been developed principally from observations in which water is used as solvent, increasing attention is now being paid to the behaviour of non-aqueous solutions. That different solvents may possess very different 'ionising power' is at once evident if we compare the osmotic effects, such as freezing point depression or boiling point elevation, produced when electrolytes are dissolved in them. In methyl alcohol, for example, the bromides and iodides of potassium are dissociated to about 50 per cent., and in ethyl alcohol to about 20—25 per cent., in solutions of $\frac{1}{500}$ to $\frac{1}{1000}$ molar strength. Similar conclusions may be arrived at from conductivity measurements, but, for reasons above indicated, it is only in a few cases that the degree of ionisation can be directly calculated. Since the degree of ionisation is usually small it is not possible directly to determine λ_∞, so that the mobilities have to be arrived at independently.

Results obtained by one or other of the above-mentioned methods indicate that the hydrocarbons, ethers, esters and aldehydes have generally little if any ionising power. Alcohols and ketones, formic acid, pyridine, liquid ammonia and liquid sulphur dioxide have ionising powers which are more or less considerable. In a series of homologous compounds this property is most marked in the lowest member, and diminishes as the compounds become more complex. In methyl alcohol, for instance, it is about one-half or two-thirds that of water, and in ethyl alcohol about one-third or less.

The ionising power of water appears to be greater than that of any other liquid yet examined, although that of hydrogen

dioxide and of liquid hydrogen cyanide are not far removed. It has even been considered by some that the value is greater in the last-named substances than in water, but for many reasons the results are very uncertain. The molecular conductivity of potassium iodide in liquid hydrogen cyanide at 0° is said to be about four times as great as in water, but, for the reasons indicated above, it does not follow from this alone that the ionising power is greater.

It is remarkable that liquid hydrogen sulphide appears to have little or no ionising power; it is stated by Skilling [*Am. Chem. Journ.* 1901, 383] that a solution of potassium chloride in this liquid is a non-conductor. From the analogy of hydrogen sulphide with water this result was unexpected, but it may probably be accounted for by the considerations referred to below.

With regard to the connection between the ionising power and other physical or chemical properties in different solvents, certain important, though approximate, generalisations have been made. It is found, for example, that in a large number of liquids the order of the relative ionising powers is the same as that of the dielectric constants. Thus the dielectric constants (at ordinary temperatures) of some of the liquids above referred to are as follows:

Hydrogen cyanide 95. Hydrogen dioxide 92·8. Water 81. Formic acid 57. Methyl alcohol 32·5. Ethyl alcohol 22. Sulphur dioxide 14·8. Ether 4·4. Benzene 2·3.

This apparent connection has been explained by supposing that the electric forces holding the ions together in the molecule may become weakened when the electrolyte is surrounded by a medium whose dielectric constant is large. There are some exceptions to this parallelism between dielectric constant and ionising power. The measurements made by Matthews [*Journ. Physical Chem.* 1905, 641] appear to indicate in fact that the exceptions are more numerous than the agreements; in any case it cannot be shewn that the two properties are proportional. But there are no doubt other circumstances which must be taken into consideration. It appears, for example, that there is an undoubted relationship between the ionising power of liquids and their tendency to exist in the state of associated molecules;

water, formic acid and alcohols, for example, all shew this tendency (see **24**). Benzonitrile and propionitrile afford a further instance of this; the former is a non-associated liquid, whereas the latter exists to a large extent as associated molecules, and it has been shewn by Schlundt that silver nitrate dissolved in these solvents is much more ionised in propionitrile. It is suggested that this connection may be due to a tendency of the ions to associate themselves with molecules of the solvent.

The formation of associated molecules is evidently connected with the presence of unsaturated valencies (see page 99) and, regarding oxygen as quadrivalent, this might account for the fact that so many oxygen-containing compounds exhibit ionising capability.

Archibald and McIntosh [*Proc. Roy. Soc.* 1904, 454] shew that many organic substances dissolve in liquid hydrogen halides forming conducting solutions, and in these cases the molecular conductivity enormously diminishes with increasing dilution. In order to explain these results the authors consider that the dissolved substance combines with the solvent and the resulting compound undergoes ionisation.

66. Combination of ions with the solvent.

The 'hydrate theory' is often spoken of as an alternative to the theory of electrolytic dissociation, and mention has been made above to the views of some authors who attempt to account for all the phenomena which are commonly ascribed to ionisation by reference to the formation of chemical compounds of the solute and solvent. But the two theories are by no means incompatible, and there is in fact a considerable amount of evidence in favour of the view that both the undissociated molecules and the ions may be present in solution in combination with the solvent. Deviations from the law of mass action in strong solutions might, as before mentioned, be accounted for if it be supposed that the proportion of 'effective' solvent is lowered when a portion of it is appropriated by combination with the ions.

Kohlrausch [*Proc. Roy. Soc.* 1903 (71) 338] from experiments on the temperature coefficient of conductivity, comes to the conclusion that electrolytic resistance must be considered as a resistance of the solvent, and suggests the hypothesis that each

ion is enveloped with an atmosphere of solvent which moves along with it; the resistance increases with the extent of this atmosphere, the extent depending on the nature of the ion. H. C. Jones and his colleagues from an extensive series of cryoscopic and conductivity measurements, come to a somewhat similar conclusion. They shew that the higher the temperature the less complex are the hydrates formed by the ions in aqueous solution and that this circumstance accounts, in part, for the large increase of conductivity with rise of temperature. [See for example Jones and West, *Amer. Chem. Journ.* 1905, 357.]

Lowry [*Trans. Faraday Soc.* 1905, 197] considers that in an aqueous solution of an electrolyte both the non-ionised molecules and the ions are hydrated, but that the latter are more highly hydrated than the non-ionised molecules in their highest degree of hydration. Consequently it will only be at great dilution that complete ionisation is possible.

Compare also Callendar, *Proc. Roy. Soc.* 1908, 490.

Lobry de Bruyn shewed that when silver nitrate is dissolved in aqueous methyl alcohol and the solution is electrolysed, there is no variation of the proportion of water to alcohol round the two electrodes. If the ions had been hydrated to a different extent the proportion should have been different. It would appear therefore either that both ions are equally hydrated or that they are not hydrated at all. Morgan and Kanolt, however, performed similar experiments using a mixture of pyridine and water as solvent and found a greater concentration of pyridine round the kathode, a result which appears to indicate that combination occurs between the silver ions and pyridine. With ethyl alcohol and water they obtained indications of a certain amount of hydration of the silver ion. [*Journ. Am. Chem. Soc.* 1906, 572.] Further experiments in this direction have recently been published by many others; see for example Washburn, *ibid.* 1909, 323.

Practical Work.

Determine the freezing-point depressions in solutions of potassium chloride at different concentrations (say about $\frac{1}{20}$ molar and $\frac{1}{10}$ molar). From the results, calculate the values of i and the degrees of ionisation.

CHAPTER XVI.

ELECTROLYTIC DISSOCIATION *(continued)*.

Applications of the hypothesis.

It may be of interest here to mention some of the well-known applications of the hypothesis of electrolytic dissociation to commonly occurring chemical changes which take place in aqueous solutions. The student is advised to consider each of these applications side by side with the older explanations which are independent of the hypothesis of ionisation. Very often it will appear that, qualitatively, the two methods merely express the same thing in a different form; in other cases either one or other method may appear preferable. But from a quantitative point of view, it must be admitted that the ionic explanations are far more generally applicable and thus they often give a complete and systematic explanation of experimental results where the older method fails.

67. Solubility of electrolytes.

A given solid substance will be in equilibrium with its aqueous solution at a given temperature when the concentration of the substance in solution has a certain constant and definite maximum value c (see page 307). In the case of a non-ionisable substance this concentration is the solubility, as determined in the ordinary way. If, however, the solid in question is a compound which undergoes partial ionisation when dissolved, it is evident that the concentration of the non-ionised portion will be diminished by this ionisation and more solid must therefore

dissolve in order to restore the concentration (of the non-ionised substance) to c. If therefore we determine the concentration of the resulting solution, in the usual manner, the result obtained—the 'apparent solubility'—will be greater than that representing the true solubility of the undecomposed compound. It follows then that if by any means we can diminish the degree of ionisation of the compound, the actual amount of the given solid which has to go into solution in order that equilibrium may be reached, i.e. the true solubility, will be less than before. If therefore a saturated solution of the electrolyte is first prepared and then, by any means, the degree of ionisation is lessened, some of the non-ionised substance must go out of solution (i.e. be precipitated) or else the solution must remain supersaturated. Conversely, if the degree of ionisation is increased, more solid must dissolve to make up for the part lost by ionisation.

If we consider, for the sake of simplicity, the case of a binary electrolyte, the equilibrium in solution, assuming that under the circumstances the law of mass action is obeyed is, as before stated, represented by the relation

$$\frac{1-m}{V}K = \frac{m^2}{V^2},$$

since the two ions are produced in equivalent quantities. This relation is often conveniently abbreviated into the form

$$ab = kc,$$

in which a and b represent the concentrations of the two ions $\left(\frac{m}{V}\right)$ and c is the concentration of the non-ionised part $\left(\frac{1-m}{V}\right)$. In the case quoted $a = b$, but in many of the applications to be considered this equality no longer exists. We may, for example, increase either a or b by adding a strongly ionised electrolyte which contains the ion referred to, provided, of course, the volume is kept constant. Thus if we have a slightly ionised compound HX in equilibrium with its two ions $H + X'$ and we add (without material increase of volume) the highly ionised salt MX, it is

evident that the concentration of the X′ ion will be increased; consequently that of the Ḣ ion will decrease, with production of a further quantity of the non-ionised compound HX. If the degree of ionisation of HX is very small, $(1 - m)$ is nearly equal to unity, so that in this case a varies almost inversely as b, i.e. the Ḣ ion is 'suppressed' almost in proportion to the increased concentration of the X′ ion.

Returning now to the example of a solution of an electrolyte AB in contact with its own solid, we see that if excess of the solid is shaken up with pure water, at a given temperature, until a normally saturated solution is obtained we get the maximum concentration c of the non-ionised compound, i.e. the solid is in equilibrium with its own solution; at the same time there is a further equilibrium established between the non-ionised compound in solution and its ions. If now we add to the solution a highly ionised compound which contains one of the ions A or B in common with the original substance AB, the degree of ionisation of the latter will be diminished and precipitation, or supersaturation, will occur. [Compare the vaporisation of ammonium salts, page 154.]

Familiar examples of this phenomenon are afforded by the well-known experiment of passing hydrochloric acid gas into a nearly saturated solution of common salt, in which case a separation of solid salt occurs. A strong aqueous solution of the acid will produce a similar effect, although to a lesser degree since the total volume is thereby increased. Addition of strong hydrochloric acid to a strong solution of barium chloride, or of strong nitric acid to barium nitrate, will shew similar results. The 'salting out' of soaps is another familiar example. Theoretically in the case of a binary electrolyte the increase of concentration of either ion, A or B, should produce the same result, other things being equal. This may be illustrated practically, for example, in the case of silver acetate; a nearly saturated solution of this salt will give a precipitate with concentrated solutions of either silver nitrate or sodium acetate.

The foregoing principles explain clearly the fact so well established in qualitative and quantitative analysis, that in

order to get the most complete precipitation it is nearly always necessary to add an excess of the precipitant.

Solubility product. Assuming that the law of mass action is obeyed the equilibrium between a binary electrolyte and its ions will, as above stated, be represented by the relation $ab = kc$. If the electrolyte splits up into more than two ions the relation will be of the form $a^m b^n = kc$. It follows therefore that for a given concentration of the non-ionised part (c) the product of the concentrations of the ions (ab or $a^m b^n$) must be constant. But if the solid electrolyte is present, the value of c is constant for a given temperature, i.e. the true solubility of the electrolyte is constant; and consequently the product of the ionic concentrations must also be constant. Equilibrium will therefore be established between a solid electrolyte and its aqueous solution at a given temperature when the product ab (or $a^m b^n$) is constant and the value of this product under these circumstances is called the 'solubility product.' The solubility product as thus defined has a fixed value at a given temperature; if it is exceeded precipitation or supersaturation will occur, whereas if it is not reached a further dissolution of solid takes place. [It must be noticed that certain authors do not use the term strictly in this sense and refer to the solubility product merely as the variable product of the ionic concentrations.]

This diminution of solubility by the addition of a common ion can be considered quantitatively in the following way[1]. Let s_1 be the apparent solubility, say in gram equivalents per c.c., of the electrolyte AB in pure water at the given temperature, and m_1 the degree of ionisation at the concentration of the saturated solution. Then in 1 c.c. of the solution there will be $s_1(1-m_1)$ gram equivalents of the non-ionised substance and $s_1 m_1$ gram equivalents of the ionised portion (i.e. $s_1 m_1$ of each ion). Now add another electrolyte (without change of volume) which contains one of the ions in common, and let the added concentration of this ion be represented by c. The result will be that the solubility of AB will be diminished; let the required new solubility be s_2 and the degree of ionisation m_2. The concentration of the non-ionised substance will now be $s_2(1-m_2)$ and that of the ions will be $s_2 m_2 + c$ and $s_2 m_2$ respectively. But since the solubility of the non-ionised portion must be the same in both cases

$$s_1(1-m_1) = s_2(1-m_2).$$

[1] Compare Nernst's *Theoretical Chemistry*, 537.

By the law of mass action we have, as the equilibrium in solution, in the first case

$$s_1(1-m_1)K=(s_1m_1)^2,$$

and in the second case

$$s_2(1-m_2)K=(s_2m_2)(s_2m_2+c),$$

and hence

$$(s_1m_1)^2=(s_2m_2)(s_2m_2+c).$$

From this relation, if we know the degrees of ionisation m_1 and m_2 and also the concentration of the added ion, we can, from a determination of the solubility in pure water (s_1), calculate the diminished solubility s_2 due to the added ion. This theoretical 'law of solubility' has been experimentally tested by Nernst and by Noyes and the results obtained appear, on the whole, to be satisfactory. Perfect agreement in all cases is not to be expected, since, as above mentioned, salts and other strong electrolytes do not conform to the law of mass action as applied to the ionic equilibrium in solution. Stieglitz [*Journ. Amer. Chem. Soc.* 1908, 946] has recalculated the results of a large number of experimental data on the solubilities of silver salts, etc., and he comes to the conclusion that the law of solubility referred to must be regarded only as an approximate empirical principle.

Armstrong and his colleagues [*Proc. Roy. Soc.* 1907 (79).564] regard the precipitation of a nearly saturated solution of a chloride by hydrochloric acid as due to the dehydrating effect of the latter; they shew that the same kind of influence is exerted by alcohol as by hydrogen chloride, although the latter is more active.

Whilst the apparent solubility of an electrolyte is diminished by the addition of another strongly ionised electrolyte containing a common ion, the reverse is usually the case when the added ions are both different to those of the original electrolyte. Thus the solubility of silver bromate is diminished by the addition of silver nitrate or of potassium bromate, but is increased by the addition of potassium nitrate. In the latter case, the double decomposition $AgBrO_3 + KNO_3 = AgNO_3 + KBrO_3$ takes place to a certain extent; the concentration of silver bromate in solution is therefore lowered and more solid must dissolve.

68. The action of salts on acids and bases.

The change which takes place when the salt of a weak acid acts upon a stronger acid has generally been interpreted as consisting in the seizure of the base by the stronger acid and consequent expulsion of the weaker acid, the stronger acid having a greater 'affinity' for the base. The hypothesis of ionisation

accounts for the change in quite a different way, attributing the result mainly to the combination of hydrogen ions of the stronger acid with the anions of the weaker acid. Thus, if a strong acid HX_1 reacts in aqueous solution with the salt, MX_2, of a weak acid, the principal change is represented as

$$\dot{M} + X_2' + \dot{H} + X_1' = \dot{M} + X_1' + HX_2.$$

The properties which we describe as *acid* are, in aqueous solution, supposed to be due to hydrogen ions, and the greater the concentration of these the stronger or more pronounced will be the acid properties of the solution. It follows therefore that the addition of the salt of a weak acid should have the effect of diminishing the acidic properties of a solution of the acid itself or of a stronger acid. Representing the concentrations of X_2', $\dot{H}$, and HX_2 by the symbols a, b and c respectively, the equilibrium will be represented by $ab = kc$, shewing that increase of a will result in diminution of b and, if the acid is very weak (i.e. if k is very small), the diminution of b will be nearly proportional to the increase of a, as before indicated. By adding the salt of the weak acid we increase the concentration of a and so 'suppress' the hydrogen ions.

Quite in a similar way, one may explain the action of the salt of a weak base in 'suppressing' the basic properties of a solution of the base itself or of a stronger base. These *basic* properties are ascribed to hydroxyl ions and are therefore more pronounced as the concentration of these ions is greater. At a given dilution then and taking one equivalent of each base, the base which is more ionised is the stronger.

Ammonium hydroxide is a much weaker base than sodium hydroxide; this may be expressed by saying that in the relation $K = \frac{m^2}{(1-m)V}$ (or, at a given dilution, $ab = kc$) the constant for ammonium hydroxide is much smaller than for sodium hydroxide. The addition of an ammonium salt (which at moderate dilutions is highly ionised) to an aqueous solution of ammonia, will have the effect of diminishing the concentration of OH' and consequently of lessening the basic character of the solution. If we represent the equilibrium in the ammonia solution by $NH_4OH \rightleftarrows \dot{N}H_4 + OH'$

and the respective concentrations by c, a and b it is evident, as in the previous example, that increase of concentration of the ammonium ions (a) will result in a decrease of the concentration of hydroxyl (b).

This theory of the suppression of hydrogen ions, or of hydroxyl ions, by the addition of salts of weak acids, or bases, respectively, has many useful applications in explaining various well-established chemical facts. Many of these applications will be referred to in future sections.

The following simple colour reactions are often mentioned as illustrations of the phenomena in question, and although it will be seen that, in these particular cases, the ionic explanation offers little, if any, advantage over the older views, the experiments are well worth investigation.

To a dilute solution of acetic acid a drop or two of methyl-orange indicator is added; the change of colour from yellow to orange indicates a certain degree of acidity. If a few crystals (or a strong solution) of sodium acetate is now added, the colour is changed back to yellow. Or, if a dilute solution of hydrochloric acid is used instead of acetic acid, the pink colour of the indicator, which shews a greater concentration of hydrogen ions than before, will become orange or yellow on addition of sufficient sodium acetate.

Similarly, if a dilute solution of ammonia is mixed with a few drops of phenol-phthalein indicator the pink colour, indicating an appreciable concentration of hydroxyl ions, will be discharged on addition of sufficient ammonium chloride.

Since however both sodium acetate and ammonium chloride are considerably hydrolysed when dissolved in water (into strong base and weak acid, strong acid and weak base respectively) the results mentioned can, so far, be easily accounted for without reference to ions.

69. Isohydric solutions.

If we mix a dilute solution of an acid HX_1 with another pure acid in such a way that the volume is not materially altered, the concentration of the hydrogen ions will be increased and the

equilibrium between the acid HX_1 and its ions will be shifted. If C is the concentration of the non-ionised portion of HX_1 and c_1 that of each of its ions, the original equilibrium is represented by the relation $kC = c_1^2$. On now adding the second acid, the concentration of the ions of this being c_2, the concentration of the non-ionised part of HX_1 will become C_0 and the relation at equilibrium will be $kC_0 = c_1 \times (c_1 + c_2)$, shewing therefore that C_0 will become greater than the original concentration C, and the concentration of the anion X_1 will be less than c_1.

If however we mix the solution of HX_1 with a solution of the second acid HX_2 so that the total volume is increased, there may or may not result a change in the degree of ionisation of the two acids. It was first pointed out by Arrhenius, that if the concentrations of two acids before mixing are so adjusted that each contains the same concentration of hydrogen ions there will be no change in the degree of ionisation of either acid when the solutions are mixed. The same is true of other electrolytes containing an ion in common. Such solutions he termed *isohydric*.

Suppose that v_1 volumes of HX_1 are mixed with v_2 volumes of HX_2. Then, if we represent the equilibrium in the two solutions before mixing as $k_1C_1 = c_2^2$ and $k_2C_3 = c_4^2$ respectively, we shall have, after mixing, the concentrations $C_1\left(\frac{v_1}{v_1+v_2}\right)$ and $C_3\left(\frac{v_2}{v_1+v_2}\right)$ for the non-ionised parts of the acids; for the two anions X_1 and X_2 the concentrations will be $c_2\left(\frac{v_1}{v_1+v_2}\right)$ and $c_4\left(\frac{v_2}{v_1+v_2}\right)$, and for the hydrogen ions $\frac{c_2v_1+c_4v_2}{v_1+v_2}$. The equilibrium in the mixture of the two solutions will therefore be represented, as regards the first acid, HX_1, by

$$k_1C_1\left(\frac{v_1}{v_1+v_2}\right) = c_2\left(\frac{v_1}{v_1+v_2}\right) \times \frac{c_2v_1+c_4v_2}{v_1+v_2},$$

and as regards the second acid, HX_2,

$$k_2C_3\left(\frac{v_2}{v_1+v_2}\right) = c_4\left(\frac{v_2}{v_1+v_2}\right) \times \frac{c_2v_1+c_4v_2}{v_1+v_2}$$

If we make $c_2 = c_4$ the last two equations become

$$k_1C_1 = c_2^2 \text{ and } k_2C_3 = c_4^2,$$

as in the solutions before mixing. Hence if the concentration of the hydrogen ions was the same in the two original solutions the degrees of ionisation will be the same after the solutions are mixed.

This result may be expressed in words by saying that, although after mixing, each acid is contained in a larger volume than before, the concen-

tration of the hydrogen ions remains unaffected whilst the effect of dilution on the ratio of the concentrations $\frac{\text{anions}}{\text{non-ionised molecules}}$, cancels out.

If two salts AB and CD, having no common ion, are mixed together in solution, it might at first sight appear that the degree of ionisation of each would be unaffected. As a matter of fact, however, one must assume that in all cases there is a certain amount of double decomposition. Hence we shall have the four reactions $AB \rightleftarrows A+B$, $CD \rightleftarrows C+D$, $AD \rightleftarrows A+D$ and $CB \rightleftarrows C+B$ taking place side by side. It can readily be shewn, by a calculation on similar lines, that if the four salts AB, CD, AD and CB are present in the quantities W_1, W_2, W_3, and W_4 respectively, these must, when equilibrium is attained, be the relation $W_1m_1 \times W_2m_2 = W_3m_3 \times W_4m_4$, the degrees of dissociation being m_1, m_2, m_3 and m_4 respectively. Since binary salts of this type are generally largely ionised at moderate dilutions, and are mostly ionised to the same extent, there will not as a rule be a very material alteration of the degree of ionisation on mixing their solutions. But if one of the four electrolytes happens to be only slightly ionised, the alteration may be very considerable, e.g. in the case of sodium acetate and hydrochloric acid referred to above.

70. Examples of the application of the hypothesis to analytical operations.

The dissolution of a sparingly soluble salt of a weak acid by a stronger acid has generally been attributed to the combination of the base with the stronger acid, to form a soluble salt, and explusion of the weak acid. According to the hypothesis of ionisation the essential change consists in the combination of the hydrogen ions of the strong acid with the anions of the weak acid; by this process, the concentration of the anions being lowered, the product of the concentrations of the metallic ions and anions will fall below the value of the solubility product and more salt will consequently go into solution. In such a way one may account for solubility of calcium oxalate or calcium sulphate in hydrochloric acid and for the different solvent effects of acids on metallic sulphides. If the salts are equally soluble in water the solvent action of the strong acid is more marked as the acid of the salt is weaker. In analysis one takes advantage of the fact that the sulphides of lead, mercury, copper, bismuth, cadmium, antimony, arsenic and tin are practically insoluble in dilute hydrochloric acid. Stronger hydrochloric acid may redissolve some of the precipitates —e.g. cadmium, antimony and tin. The sulphides of iron and zinc dissolve readily in dilute hydrochloric acid but only slightly in

acetic acid, whereas manganous sulphide, although nearly insoluble in water, dissolves easily in acetic acid. In each case one supposes that the sulphide, although apparently insoluble in water, does really dissolve, but to an extent which is inappreciable. On keeping any of the above-mentioned sulphides in contact with water therefore, there will be equilibrium between the solid and its non-ionised part in aqueous solution, at the given temperature, and further, as before indicated, equilibrium between the non-ionised sulphide in solution and the ions. For example, in the case of sulphides of divalent metals we shall have in solution the equilibrium $MS \rightleftarrows \dot{M} + S''$ (or in some cases $M(SH)_2 \rightleftarrows \dot{M} + 2(SH)'$), any cause therefore which tends to lower the concentration of the S'' (or $(HS)'$) ions may have the effect of bringing the product of the concentrations $\dot{M} \times S''$ below the value of the solubility product, causing therefore the solution to become unsaturated and more solid to dissolve. By addition of a strong acid we introduce hydrogen ions and these combine with S'' or $(HS)'$ ions until equilibrium is reached as regards the reaction $2\dot{H} + S'' \rightleftarrows H_2S$ (or $\dot{H} + (SH)' \rightleftarrows H_2S$). But hydrogen sulphide is an extremely weak acid so that a comparatively small concentration of $\dot{H}$ is sufficient to convert nearly all the S'' into non-ionised H_2S; if excess of the strong acid is added, this combination is all the more complete since the degree of ionisation of the H_2S is thereby diminished in the manner referred to above. The greater the concentration of the added hydrogen ions, the more will the ionisation of H_2S be retrograded and consequently, the more will the concentration of the S'' ions be decreased.

Similarly, when hydrogen sulphide is passed into a solution of a metallic chloride, the solution will contain the ions of the metal and chlorine together with non-ionised H_2S and comparatively few ions of H and S. If now the product of the concentrations of the $\dot{M}$ and S ions present reaches the value of the solubility product of the metallic sulphide, the solution will become saturated and any further increase in the value will cause precipitation or super-saturation. The greater the solubility of the given metallic sulphide in water the greater is the value of the solubility product, and hence for a given concentration of the metallic ions, the greater is the concentration of S'' necessary in order that $\dot{M} \times S''$

shall reach the solubility product value. The addition of an acid, by increasing the concentration of $\dot{H}$ ions will suppress the S'' ions and hence lower the value of $\dot{M} \times S''$, whereas if, by any means, we lower the concentration of $\dot{H}$, the concentration of S'' will increase. When hydrogen sulphide is passed into dilute solutions of chlorides of mercury, lead, copper, etc., the concentrations of $\dot{M}$ and S'' are more than sufficient to reach the value of the small solubility product, and this is still the case even if hydrochloric acid is added, although by this means the concentration of S'' is lowered. But with chlorides of zinc, iron, or manganese, even though no acid is added, the concentration of $\dot{M} \times S''$ is not sufficient, since the solubility products of the sulphides of these metals is greater. If acetates are substituted for chlorides, however, zinc and ferrous sulphides may be to a considerable extent precipitated; here the anion of the weak acid appropriates some of the $\dot{H}$ ions to form molecules of the acid, and hence the concentration of S'' is greater than it was when chlorides were employed. Manganous sulphide being more soluble requires a greater concentration of S'', other things being equal, and this concentration is not reached even though the manganous salt of a weak acid is used. But if ammonium sulphide or sodium sulphide, which are highly ionised in solution, be substituted for the slightly ionised hydrogen sulphide, the concentration of S'' is sufficient to bring about practically complete precipitation of manganous sulphide. A difficulty is encountered when trying to apply this form of explanation to the precipitation of the sulphides of nickel and cobalt; these are not precipitated by hydrogen sulphide in presence of dilute hydrochloric acid and yet, when obtained by precipitation in alkaline or acetic acid solutions, they are practically insoluble in dilute hydrochloric acid. Some attempt to account for this by supposing that when first precipitated the sulphides are in a more soluble hydrated form and that they readily lose water and pass into less hydrated and less soluble modifications. Thiel and Ohl [*Zeit. Anorg. Chem.* 1909 (61) 396] consider that the less soluble forms may be polymeric modifications.

Reference may be made here to the well-known experiment suggested by Crum-Brown, which is often considered to afford strong evidence in support of the hypothesis of ionisation. Ferrous

sulphide will be precipitated to some extent if hydrogen sulphide is passed into a solution of ferrous acetate, but if a sufficient amount of acetic acid is added, the precipitation may be prevented. If to such a mixture—namely, ferrous acetate, hydrogen sulphide and a sufficiency of acetic acid to prevent precipitation—a strong solution of sodium acetate is added, the black precipitate of ferrous sulphide almost immediately separates. This result is perfectly intelligible in terms of the general explanations given above, since the addition of sodium acetate lowers the concentration of $\dot{H}$ and so has the effect of increasing the concentration of S''. The fact that ferrous sulphide is not precipitated when hydrogen sulphide is passed into a solution of a ferrous salt acidified with hydrochloric acid but is precipitated if an excess of sodium acetate is also added, was generally explained by saying that ferrous sulphide is soluble in strong acids but nearly insoluble in acetic acid. But some further hypothesis will then be necessary to account for the facts illustrated in the above experiment. Some have attempted to ascribe the effect of the sodium acetate in this case to dehydration; the salt is supposed to combine with part of the water and so increase the effective concentration of the solution; if this is the case one would expect various other salts to produce a similar result. The student is recommended to make experiments in this direction.

Other cases of precipitation can be dealt with in a way quite similar to that which has been indicated for the precipitation of sulphides. A solution of calcium chloride gives no precipitate with ammonia, but with sodium hydroxide a precipitate of calcium hydroxide is obtained, provided the solutions are not too dilute. For a given concentration of calcium ions therefore, ammonia in solution, will never yield a sufficient concentration of hydroxyl ions for the product of the concentrations $\ddot{C}a \times (OH)'^2$ to reach the value of the solubility product of calcium hydroxide. With the stronger base sodium hydroxide, however, the hydroxyl concentration is sufficient, when solutions of ordinary laboratory strength are employed. With chlorides of iron, chromium, aluminium, and many other metals, whose hydroxides are less soluble in water than calcium hydroxide, ammonia does precipitate the hydroxides; the solubility products are in these cases smaller, so that with the usual concentration of metal ions, the small concentration of

hydroxyl yielded by the ammonium hydroxide suffices to effect a more or less complete precipitation. Magnesium hydroxide is rather less soluble than calcium hydroxide and, in solutions of ordinary strength, is precipitated to a considerable extent on addition of ammonia. If, however, ammonium chloride is first added, as in the usual process of analysis, ammonia gives no precipitate with magnesium salts. Formerly it was considered a sufficient explanation to say that the ammonium chloride formed a stable double salt with the magnesium chloride and that this was not decomposed by ammonia. According to current views, however, this would offer no explanation, since experience shews that dilute solutions of double salts give the reactions of both constituent metals. In terms of the ionic hypothesis, this effect of ammonium chloride is due to the 'suppression' of the hydroxyl ions by the increased concentration of ammonium, in the manner previously indicated.

71. Formation of complex ions.

From what has been already said, it is evident that in order to bring about the precipitation of a sparingly soluble electrolyte from an aqueous solution, the necessary condition is that the product of the concentrations of its anion and kation shall, at the given temperature, reach a certain minimum value. Precipitation may therefore be prevented by any cause which sufficiently lowers the concentration of either anion or kation or of both. A very commonly occurring circumstance which tends to produce this effect is the formation of a complex anion or kation at the expense of one of the simpler ions, whereby the concentration of the latter is lowered. Thus the addition of sodium hydroxide to a zinc or aluminium salt produces in the first instance a precipitate of the hydroxide, but a further quantity of the reagent will redissolve the precipitate. This is explained by the formation of complex anions such as $(ZnO_2)''$ and $(AlO_2)'$ from the simple kations $\ddot{Z}n$ and $\ddot{\ddot{A}}l$ whereby the concentrations of the latter become too small to give, with the hydroxyl concentrations, products which reach the solubility value. Similarly one explains the redissolving of the precipitate produced when potassium cyanide is added to silver nitrate; the silver ions

being withdrawn owing to the formation of the complex anions $[Ag(CN)_2]'$. When potassium cyanide is added to a solution of a ferrous salt the brown precipitate first produced is immediately dissolved in excess of the reagent giving the complex anions $[Fe(CN)_6]''''$. [The brown precipitate was first regarded as ferrous cyanide, but it appears to have the composition $KFe_2(CN)_5$.] The solution so obtained gives none of the reactions for ferrous ions so that the latter appear to have been entirely appropriated in forming the complex ions. In the case of cadmium salts a somewhat similar result is brought about, but in this case even after excess of potassium cyanide has been added it is possible to detect the presence of the simple cadmium kations (e.g. by means of H_2S).

[These last two examples offer an illustration of the varying degree with which the change of a simple double salt into complex single salt may proceed in different cases. Compare **82**.]

Ammonia precipitates the hydroxides (or basic salts) of silver, copper, cadmium, zinc, nickel, or cobalt, but excess of ammonia redissolves the precipitates. In these cases the effect is due to the formation of complex *kations*. These appear to be of the general type $[M.xNH_3]$ and the valency of the ion is that of the metal contained in it and is independent of the value of x (compare page 100). Thus silver gives $[Ag(NH_3)_2]$ which is univalent, copper gives $[Cu(NH_3)_4]$ which is bivalent, and so on. Here again we have evidence that *some* of the simple kations still exist in solution, since although most of the ionic reactions fail, the solutions still give precipitates with hydrogen sulphide.

These considerations may be applied to explain the solubility of silver chloride in potassium cyanide or in ammonia. In sodium thiosulphate solution also silver chloride dissolves, owing to the formation of the complex anion $[AgS_2O_3]'$. The solubility of silver chloride in hydrochloric acid is similarly explained; if complex ions were not formed one would expect silver chloride to be less soluble in hydrochloric acid than in pure water. The solubility of gold in aqua regia is explained by the removal of the simple Äu kations to form the complex anions $[AuCl_4]'$. The greater solubility of mercuric chloride in hydrochloric acid than in pure water is attributed to the formation of complex anions such as $[HgCl_3]'$ or

$(HgCl_4)''$, and the solubility of mercuric iodide in potassium iodide is similarly accounted for.

The fact that lead sulphate easily dissolves in a solution of ammonium acetate was generally explained, in a similar way, by supposing the formation of complex anions or kations. The experiments of Noyes, however, shew that in this case the effect is due to the remarkably small degree of ionisation of lead acetate. Very few $\ddot{P}b$ ions are sufficient, with the SO_4 ions, to reach the small solubility product of lead sulphate; but the addition of ammonium acetate necessitates a further equilibrium between the acetate ions and lead kations. In this equilibrium the lead kations are largely appropriated to form the slightly ionised lead acetate, the more so, when the acetate ions are in excess.

72. The colours of salt solutions.

According to the hypothesis of electrolytic dissociation, the colour of a dilute aqueous solution of a strong electrolyte is due, additively, to the colours of its anion and kation, and it may often happen that the colour of the non-ionised compound is entirely different from that of its dilute solution. Amongst commonly occurring ions the following colours may be mentioned.

Cu'' blue, Fe'' green, Cr''' green, Ni'' green, Co'' red or pink, Mn'' pale pink, $(CrO_4)''$ yellow, $(Cr_2O_7)''$ orange, $(MnO_4)'$ purple-red, $(MnO_4)''$ green, $(FeO_4)''$ violet-red, $(FeC_6N_6)''''$ yellow. Ions of the following give colourless solutions. Li, Na, K, Ca, Sr, Ba, Cu', Pb, Bi, Cd, Fe''', Al''', Mg'', (SO_4), Cl, Br, I, (CN), (CNS), NO_3, NO_2, (PO_4), (ClO), (ClO_3), (ClO_4) and several others.

The following well-known experiments, amongst others, appear to lend support to the foregoing interpretation of the colours of solutions of electrolytes.

1. Solid cupric chloride, which exists in the anhydrous form as a dark brown powder, when treated with a small quantity of water yields a green solution, but, on further dilution, the solution becomes blue. It is supposed that non-ionised cupric chloride in solution is yellow and that this colour together with the blue colour of the cupric ions, which arise from the partial ionisation of the salt, produce the sensation of green (the colours not being

pure). On diluting the solution, further ionisation takes place, the yellow non-ionised molecules giving a further quantity of blue ions. If this explanation is correct one would expect that any cause tending to diminish the degree of ionisation of the salt might, at suitable concentrations, turn the blue colour back to green. Such an effect is, in fact, easily produced if a concentrated solution of hydrochloric acid or ammonium chloride is added to the (not too dilute) blue solution. Here the increased concentration of chlorine ions due to the addition of the strongly ionised chloride has the effect of 'suppressing' the cupric ions, i.e. of diminishing the degree of ionisation of the cupric chloride. Mercuric chloride is, as previously stated, only very slightly ionised in aqueous solution and consequently the addition of this salt does not restore the green colour. The colour changes, in solutions of the cupric salts of weak acids, are more complicated; in the case of cupric acetate for example, the variation of colour on dilution appears to be largely due to the change $CuA_2 = CuA + A'$. [See Sidgwick and Tizard, *Trans. Chem. Soc.* 1908, 187.]

2. Cobaltous chloride dissolves in water giving a pink or red solution; hence it is assumed that cobaltous ions give this colour. If now strong hydrochloric acid is added the solution becomes blue. This is explained by Ostwald in a manner similar to that given in the previous example, non-ionised cobaltous chloride being blue. The same effect is produced by heating the solution, and this is accounted for by supposing that the degree of ionisation is decreased by increasing temperature—a result frequently observed in other cases (see page 213). But this simple explanation of the colour changes is here insufficient to account for all the facts. It can be shewn, for example, that the red solution also turns blue on addition of calcium chloride but that zinc chloride has the opposite effect, i.e. turns the blue solution red. Donnan and Bassett [*Trans. Chem. Soc.* 1902, 939] suggest that when the cobalt atom is in close association with chlorine atoms the system gives rise to a blue colour and that the blue colour of the solutions mentioned above is due to the existence of complex anions such as $(CoCl_3)$ or $(CoCl_4)$. Zinc shews considerable tendency to form complex ions; cobalt has also this tendency, but calcium has not.

Hence in the experiments referred to one may suppose that the addition of calcium chloride results in the formation of the salt $Ca(CoCl_4)$, which yields the blue ions $(CoCl_4)$. But on addition of zinc chloride, it is supposed that the complex salt $Co(ZnCl_4)$ is produced, the zinc having a greater tendency than cobalt to enter the complex group, and this salt yields colourless $(ZnCl_4)$ and red Co″ ions. Many other explanations have from time to time been offered of these colour changes, the effects being ascribed variously to hydration and dehydration, isomerism, etc. [Compare Benrath, *Zeit. Anorgan. Chem.* 1907, 328.]

3. Cobaltous chloride in sufficiently strong solution gives with ammonium thiocyanate a deep blue colour, but, on diluting the solution, the blue colour disappears and gives place to the slight red colour due to the solution of cobaltous ions. If now the solution is shaken with ether (or better, a mixture of amyl alcohol and ether), the blue colour re-appears in the latter solvent layer. From this solution complex single salts such as $(NH_4)_2[Co(CNS)_4]$ can be isolated and it is supposed that the blue colour is due to this compound or, more probably, to its complex anion. The latter may be sufficiently stable in the strong aqueous solution or in the slightly ionising organic solvent, but in the more dilute aqueous solution it breaks up giving simple cobaltous ions

$$[Co(CNS)_4]'' \rightleftarrows \dot{C}o + 4(CNS)'.$$

4. Reference has already been made to the nature of the blood-red colour produced when ferric salts are mixed with thiocyanates, the colour being in this case variously ascribed to the non-ionised ferric thiocyanate, to a complex ion, or to an oxidation product such as peroxythiocyanic acid $H_3C_3O_3N_3S_3$ [Tarugi, *Gazzetta*, 1904 (ii) 326].

The colour of a concentrated aqueous solution of ferric chloride is brownish red, becoming on dilution yellow and then colourless. It is generally considered that the brownish red colour is due to colloidal ferric hydroxide produced by hydrolysis. Hydrochloric acid changes this colour to deep yellow and this may perhaps be due to complex anions such as $(FeCl_4)'$. Since the colour disappears at moderate dilution, it is assumed that the simple ferric ion is colourless. The deep blue colour of

ammoniacal cupric solutions is usually ascribed to the complex kation $[Cu(NH_3)_4]$, and that of Fehling's solution to a complex anion such as $[C_{12}H_9Cu_4O_{19}]'''$ (Masson and Steele).

5. The fact that chromic chloride and chromic sulphate may give rise to both green and violet solutions has been explained in a variety of different ways. Some have considered that the difference is due to hydration and dehydration or to ordinary isomerism, and others have sought to shew that the green salt is a basic compound, being formed from the violet salt by hydrolysis. A more probable explanation, however, is found by application of the ionic hypothesis according to which the violet salts are to be regarded as normal salts of trivalent chromium, yielding therefore the simple $\ddot{C}r$ ion which is violet; whereas the green salts contain complex ions such as $(CrCl_2)$ and $[Cr(SO_4)_3]$. This view is supported by experiments on the electric conductivities and reactions of the salts. Thus silver nitrate precipitates all the chlorine from the violet solution of chromic chloride, whereas from the green solution only $\frac{1}{3}$ of the chlorine is precipitated. (Compare also page 101.) The division between the two classes is not very sharp, and it is probable that equilibrium exists in solution between the two forms. Thus, in the case of the sulphates we might have the reversible change

$$Cr_2(SO_4)_3 + 3H_2SO_4 \rightleftarrows 2H_3[Cr(SO_4)_3],$$

analogous to that which usually occurs between simple double salts and complex single salts.

The difference between a chromate and a bichromate in solution was formerly regarded as merely that between a normal and an acid salt, potassium bichromate, for example, being looked upon as the acid chromate *minus* water, $2KHCrO_4 - H_2O = K_2Cr_2O_7$. But since there is such a marked difference between the colours of their aqueous solutions, Ostwald was led to regard them as salts of two different acids, the anion of the chromates $(CrO_4)''$ being yellow and that of the bichromates $(Cr_2O_7)''$, orange or red. It is supposed that the ion CrO_4 is unstable in presence of acids,

$$2(CrO_4)'' + 2\dot{H} = (Cr_2O_7)'' + H_2O,$$

whereas alkalis effect the converse change

$$(Cr_2O_7)'' + 2OH' = 2(CrO_4)'' + H_2O.$$

Chromic anhydride dissolves in water giving an orange solution which appears therefore to indicate the formation of bichromic acid rather than chromic acid as formerly supposed. This view is strongly supported by cryoscopic and electric conductivity measurements.

Thus the molecular depression of the freezing point of chromium trioxide (calculated as CrO_3) dissolved in water was found to be about 26·8, and since the resulting acid is strong (as shewn by the comparatively slight increase of equivalent conductivity with dilution) one may assume that it was, at the dilution employed, nearly completely ionised. Therefore the value of $\frac{i-1}{n-1}$ should be about unity (see page 206). If the acid were H_2CrO_4 we should have $i=\frac{26{\cdot}8}{18{\cdot}7}$ = about 1·5 and $n=3$, which gives m = about 0·25; whereas if the acid is $H_2Cr_2O_7$, $i=\frac{53{\cdot}6}{18{\cdot}7}$ = about 3, $n=3$ and $\frac{i-1}{n-1}$ = about 1.

Compare Abegg and Cox, *Zeit. Physikal. Chem.* 1904 (48) 725 and Spitalski, *Zeit. Anorg. Chem.* 1907 (54) 265.

Practical Work.

The various examples given in the foregoing pages in illustration of the applications of the hypothesis of electrolytic dissociation are, whenever possible, studied experimentally. For example:

1. The influence of a common ion in reducing the degree of acidity or of alkalinity (page 224).

2. (*a*) The precipitation of sodium chloride and of barium chloride by hydrochloric acid, (*b*) of silver acetate by sodium acetate and by silver nitrate (page 220), (*c*) the effects of passing hydrogen sulphide into solutions of various metallic salts in presence of varying concentration of hydrogen ions, (*d*) Crum Brown's experiment (page 228), (*e*) the precipitation of magnesium salts by ammonia (page 229).

3. The formation of certain complex ions e.g. $[Fe(CN)_6]$, $[Cd(CN)_4]$, $[Ag(NH_3)_x]$, $[Cu(NH_3)_x]$, $[AgS_2O_3]$, $[HgCl_4]$, $[HgI_4]$, etc. (page 230).

4. (*a*) The colour changes on dissolving cupric chloride and the results of adding sodium chloride, mercuric chloride, etc., to the solution. (*b*) The colour changes of cobaltous chloride and of ammonium cobaltous thiocyanate (page 234) and (*c*) chromate and bichromate (page 235).

CHAPTER XVII.

ACIDS.

73. In discussing the properties, reactions and relationships of acids, salts and bases it has now become the general custom to regard the subject exclusively from the point of view of electrolytic dissociation. This is easily accounted for when one takes into consideration the remarkably simple and comprehensive interpretation which the theory offers of the various phenomena in question and the exact quantitative results which can, in most cases, be obtained by its application. Nevertheless the student is recommended to adopt, for the present, an impartial attitude, and, while making full use of the ionic explanation as a working hypothesis, to make a practice of giving due consideration to the older or alternative views.

Although no difficulty is ever experienced in conveying a general idea of the essential characters of acids, salts and bases, it will generally be found that attempts to frame hard and fast definitions of the terms have been more or less unsuccessful. This may be due in great part to the practice which seemed to prevail of regarding the distinction between the three classes as absolute rather than relative; one finds no difficulty now in believing that one and the same substance may be both an acid and a base, or that, from one point of view, both acids and bases may be regarded as salts. The dualistic or binary theory of salts, originated by Lavoisier and systematically developed by Berzelius, represented these substances as compounds of an acid and a base. Acids were looked upon as oxides of non-metals or of negative radicles, whilst bases were oxides of metals or positive radicles. Sulphuric acid and nitric acid, as we know them, were regarded

as hydrates of the true acids. Berzelius considered that every compound body could be separated into two constituents, one of which is positively and the other negatively electrified. The base 'potash' for example, then written KO, was compounded of the positively electrified potassium with negatively electrified oxygen, but the positive 'polarity' of potassium is greater than the negative polarity of oxygen, so that the oxide has a resultant positive polarity or charge. Sulphuric acid (SO_3) for similar reasons had a resultant negative polarity and in the salt potassium sulphate ($KO.SO_3$), these opposite polarities nearly (but not quite) neutralised one another. Electrolysis was supposed to overcome the attraction between these opposite charges, and the result, in this case, was regarded as the separation of the salt into acid and base. The combination between acid and base was therefore due to electrical attraction, but the amount of this attraction was different for different acids and bases, since some were more strongly charged than others. It is evident that such a view is entirely inconsistent with Faraday's law, according to which the same quantity of electricity will, on electrolysis, cause the decomposition of equivalent quantities of different salts. The inconsistency was demonstrated in a more definite form by Daniell (1840), who shewed that the same current passing for the same time through dilute sulphuric acid and sodium sulphate gave the same quantity of hydrogen at the kathode in each case; yet in the latter solution the salt must, according to Berzelius, have been simultaneously decomposed into acid and base. Berzelius himself recognised these difficulties but preferred to explain them by calling in question the validity of Faraday's law. Another obvious difficulty attaching to the dualistic method is the fact that the commonest of all salts, sodium chloride, cannot be represented at all on this type. Similarly the halogen acids, hydrosulphuric acids, etc., will be excluded from the category of acids since they contain no oxygen.

Davy observed that the so-called iodic 'acid' (I_2O_5) did not exhibit its acid properties until water was present, and similar observations were afterwards made with other supposed acids (e.g. carbon dioxide which even to this date is still sometimes called carbonic acid!). It is evident that this circumstance alone

would be wholly insufficient as an argument against the older view, since hydrochloric acid itself behaves in the same way. The representation of acids as hydrogen compounds was more particularly due to Liebig and to Graham who first clearly indicated the character of polybasic acids, the properties of which would find no simple interpretation in terms of the older view. Salts were then looked upon as compounds in which the hydrogen of an acid has been replaced by a metal.

Dumas in 1837 shewed that chlorine can replace part of the hydrogen in acetic acid yielding a monobasic acid resembling acetic acid itself, a fact which shewed that individual atoms could be substituted for one another independently of their electrochemical character. Salts, acids and bases were then regarded from the 'unitary' standpoint, i.e. as single individuals in which parts could be replaced by other elements or groups. At the present time we have in one sense gone back to a dualistic conception of these compounds, but instead of regarding a salt as a positive compound united to a negative compound, i.e. of an acid and a base, we represent it as a single compound capable of easy resolution into oppositely charged atoms or groups.

Although for theoretical reasons it has become the custom to abandon the dualistic method in its original form, the student will find it advantageous to translate the customary modern formulae for salts, acids and bases on the dualistic plan and to compare the nature of the information conveyed by each type of formula. It will in certain cases be seen that the practical chemical facts are more clearly indicated by the old formulae than by the new. The composition of the various sodium silicates, for example, on the dualistic type would be expressed as $m\mathrm{Na_2O}.n\mathrm{SiO_2}$ and that of the silicic acids as $m\mathrm{H_2O}.n\mathrm{SiO_2}$; whereas according to the modern type one is obliged to regard the salts as derivations of a large number of entirely distinct acids, such as $\mathrm{O:Si(OH)_2}$, $\mathrm{Si(OH)_4}$,

$$\mathrm{OH.Si.O.Si.OH}, \qquad \mathrm{(OH)_3Si.O.Si(OH)_3}, \text{ etc.}$$
$$\ddot{\mathrm{O}} \quad \ddot{\mathrm{O}}$$

In translating formulae in this way it is of course often necessary to take a multiple of the usual formula, but it may be questioned, in

many instances, whether one multiple is not as much justified as the other. (See page 50.) Thus sodium bicarbonate would become $Na_2O.H_2O.2CO_2$, ammonium magnesium phosphate would be $2MgO.(NH_4)_2O.P_2O_5$, and bismuth nitrate $Bi_2O_3.3N_2O_5$.

74. Definitions. It may be of some interest here to consider briefly a few of the definitions which, from time to time, have been proposed for the term 'acid.' For example, (*a*) A salt of hydrogen, (*b*) A compound of hydrogen with an electronegative element or group, (*c*) A compound of hydrogen in which the hydrogen can be replaced, wholly or in part, by a metal, (*d*) A substance which yields water by its action on caustic alkalis, (*e*) A compound of hydrogen which can exchange its hydrogen, whole or part, for a metal when the latter is presented to it in the form of a hydroxide, (*f*) A compound which can yield free hydrogen ions when dissolved in water.

The first two definitions are objectionable in that they imply a previous knowledge of the terms used, a knowledge which can scarcely be gained without reference to acids themselves. The third definition is obviously faulty; ammonia, for example, would have to be included as an acid according to this definition. The fourth definition, although ingenious, is evidently liable to misinterpretation; silver nitrate, for example, when acted upon by caustic alkalis under ordinary conditions yields, to a large extent, silver oxide and water. The fifth definition certainly gives a fairly complete account of what is generally understood to be the essential function of an acid, although it omits to convey the idea of reversibility. (Thus a very weak acid would only conform to the necessary conditions at a sufficient concentration, etc.) This definition might be briefly symbolised thus:

$$H_nR + nM.OH \rightleftarrows M_nR + nH.OH,$$

in which n represents the basicity of the acid (see **76**).

[Evidently, in these terms, one must include such substances as zinc, hydroxide and aluminium hydroxide as acids; at one time this was objected to and it was proposed to restrict the term to those hydrogen compounds which can behave in the manner indicated 'even in the presence of much water,' thus excluding

the metallic hydroxides mentioned. Obviously such a restriction would be quite arbitrary and unnecessary.]

The sixth definition has already been considered in the preceding chapter.

75. Recognition.

From a purely practical point of view it is the custom to test for acidic character by reference to the following well-known reactions or properties.

1. *Sour taste.* This rough and ready means of identifying acidic properties is of course the most ancient; the recognition of 'acids' as a distinct class of substances, as the name implies, owes its origin to the observation of this property. For acids which are not too weak and which have no other specific taste which might obscure the 'sourness,' the test certainly does afford useful information. According to the ionic hypothesis, the taste of a very dilute aqueous solution of an electrolyte must be due to the sum of the 'tastes' of its ions, and Kahlenberg found that the sour taste of hydrochloric acid could be detected even at a dilution of about $\frac{1}{800}$ normal strength, a dilution at which sodium chloride is altogether tasteless. Consequently it might appear reasonable to ascribe the sour taste to hydrogen ions. Nitric, hydriodic and sulphuric acids also give indications of sourness at the dilution mentioned. Richards [*Am. Chem. J.* 1848 (20) 121] found that solutions of acetic or tartaric acids are less sour than those of mineral acids of corresponding concentration, and that the acid taste of hydrochloric acid is diminished by the addition of sodium acetate; he was even able to observe the end point within 0·5 per cent. in the neutralisation of decinormal solutions of acid and alkali by the sense of taste. But attempts to trace a quantitative relationship between the concentration of hydrogen ions and sour taste have not been successful. Thus Kahlenberg found that the taste was perceptible in $\frac{1}{200}$ normal acetic acid although the concentration of hydrogen ions is here only about a quarter as great as that in the limit solution of hydrochloric acid ($\frac{1}{800}$ normal). With acid sodium salts again the taste is perceptible at dilutions where the concentrations of hydrogen ions is far below this limit, and the author considers that the ionic explanation of this property

is unsatisfactory [*J. Physical Chem.* 1900 (4) 33]. Experiments of Höber and Kiesow on the taste of various sodium and potassium salts, indicate that the taste of the solutions is due to the anion [*Zeit. Physikal. Chem.* 1898 (27) 601].

2. *Action on carbonates or on hydrosulphides.* The well-known methods of recognising acidic character by ascertaining whether carbon dioxide is evolved from a carbonate, of hydrogen sulphide from a soluble hydrosulphide, are of course reliable and convenient in the case of the stronger acids; with very weak acids, however, the tests may fail. Thus hydrocyanic acid and boric acid do not under ordinary conditions evolve carbon dioxide from sodium carbonate; carbon dioxide will in fact liberate some weak acids from solutions of their salts, e.g. cyanides, phenolates and silicates can be decomposed in this way. The changes must be regarded as limited and reversible; whether carbon dioxide is evolved or not will depend on the relative 'strengths' or 'affinities' of the acids mentioned and carbonic acid, and on the conditions of the experiment.

3. *Liberation of iodine from a mixture of an iodide and iodate.* Since free hydriodic and iodic acids immediately react to produce free iodine and water, the mixture of the two salts is often used as a test for the presence of acidic character in a solution. The reaction is sufficiently delicate to detect carbonic acid, hence when using potassium iodide as a test for an oxidising agent (e.g. ozone) it is important to ensure that the reagent is free from iodate. Boric acid gives only a very slight indication with this test; on the addition of glycerol however, a copious liberation of iodine occurs.

4 *Catalysis of esters, etc.* Mention has already been made of the remarkable accelerating influence which acids exert on the rate of hydrolysis of esters. Methyl acetate is particularly suitable for this purpose and, by a careful study of the rate of its hydrolysis in aqueous solution, one can detect the most minute concentration of 'acid,' or, in terms of the hypothesis of electrolytic dissociation, of hydrogen ions. Similar information may be gained by observations on the rate of decomposition of diazo-compounds and of the hydrolytic decomposition of polysaccharides, such as cane sugar. The reactions here referred to are not

to be regarded as specific tests for acidic character, since the changes are capable of being accelerated by other agents. They afford, however, most delicate methods of detecting the presence of hydrogen ions, and estimating their concentration, provided these other agents (alkalis, contact substances, etc.) are known to be absent.

The test of 'acidity' by means of *colour 'indicators'* will be referred to below.

76. Basicity of Acids.

The usual definition of the basicity of an acid as 'the number of atoms of hydrogen, contained in one molecule of the acid, which are capable of being replaced by metals, or positive radicles, to form salts,' does not present any particular difficulty when applied to the strongest acids. In other cases, however, the application of this definition may lead to different results according to the conditions under which the replacement is investigated and to the strict interpretation given to the term 'salt.'

Thus in the case of orthophosphoric acid, if we deduce the basicity from the composition of the metallic derivatives of the acid which can actually be isolated in the solid state, we shall conclude that the acid is tribasic. We can, for instance, easily isolate NaH_2PO_4, Na_2HPO_4 and Ag_3PO_4, etc But a study of its behaviour in aqueous solution leads to the conclusion that the acid generally appears to be dibasic or monobasic, according to the conditions of dilution and relative concentrations of the reacting substances. Acetic acid, again, yields two distinct potassium salts (see page 2), whereas its behaviour in solution is that of a monobasic acid; oxalic acid, which is undoubtedly dibasic in solution, may yield the salts KHC_2O_4, $K_2C_2O_4$ and $KH_3(C_2O_4)_2$, as well-marked crystalline compounds. Malonic acid is regarded as a dibasic acid, yet it can form the compound $CHNa(COOEt)_2$.

Evidently therefore there is a want of precision in the common conception of the term 'basicity.' If, as is sometimes the custom, we refer the term (*a*) only to the behaviour of acids in solution, it becomes necessary to define the conditions; whereas, if (*b*) we deduce the value from all the metallic derivatives actually obtainable under any circumstances, we shall have to regard acetic

acid as dibasic, oxalic acid as tetrabasic and malonic acid as tribasic, etc. The basicity of an acid is sometimes deduced from the composition of its esters, instead of its metallic salts. There is an advantage here in that the molecular weight of the ester can usually be easily determined. The result may, however, be different from that obtained from a study of the behaviour of the acid in solution; phosphorous acid for example would, from the composition of its ethyl ester, be tribasic.

Methods of determination. (A) The oldest and best known method of determining the basicity of an acid consists in ascertaining the number of different salts, or esters, which the acid can be made to yield by fractional replacements of its hydrogen with monovalent metals, or alkyl groups. The results therefore indicate the basicity according to the second view (*b*), and may be quite different from those obtained by investigating the properties of the acid in aqueous solution. Since, however, the method is still extensively used, it may be well to illustrate its practical application by a few well-known examples.

(1) A solution of the acid is exactly neutralised with a suitable metallic carbonate or hydroxide. [No definite rule can be given as to which is best and it is advisable to make experiments with different ones, e.g. potassium, sodium or ammonium, carbonate or hydroxide, in order to ascertain which gives the best crystalline product.]

(2) A solution of the acid is divided into two equal parts; one part is then exactly neutralised, as before, and the other part is added to it. In this way the acid is just half neutralised. The process may, if desired, be repeated by dividing another solution into three parts, neutralising one part and adding the other two, and so on.

The various solutions so prepared are then carefully concentrated, preferably in a water bath, and allowed to crystallise. The resulting crystals are carefully examined under the microscope, recrystallised from a little hot water and their properties examined (e.g. their solubilities, the behaviour of their aqueous solutions towards various indicators, and the reactions with reagents such as silver nitrate, sodium carbonate, etc.). In the case

of well-defined strong acids, it is evident that a monobasic acid would yield the same result in each case, i.e. the salt obtained would be the same no matter what proportion of acid and alkali were employed. With polybasic acids, however, the results will be different; an acid which is n basic should yield n different salts.

With weaker acids various difficulties may arise; the neutralisation point may be ill-defined or may be different with different indicators and the salts obtained may undergo partial change on recrystallisation. Instead of relying on colour indicators one may of course start with a known quantity of the acid and, if its composition is known, add the quantities of alkali calculated to replace the whole, one-half, one-third, etc., of its hydrogen.

Amongst the various methods which are employed for determining the basicities of acids in solution, the following may be mentioned.

(B) If the molecular weight of the acid is known the basicity, in solution, can be found by simple titration, provided, of course, that the end point given by the indicator represents the true neutralisation point. (In case of weaker polybasic acids which yield different results with different indicators one can merely say that the acid behaves as monobasic towards one indicator, dibasic towards another, and so on.) It is evident that one molecular weight of an acid which is n basic should require n molecular proportions of sodium hydroxide to neutralise it. Thus, if W grams of the acid require, for neutralisation, W_1 grams of sodium hydroxide,

$$W : W_1 = M : 40 \times n,$$

where M is the molecular weight of the acid and n is its basicity.

(C) On adding molecular quantities of sodium or potassium hydroxide to one molecular weight of an acid in dilute aqueous solution, there will be a definite quantity of heat liberated which in many cases will be independent, or nearly so, of dilution. In the case of a strong monobasic acid the quantity of heat so liberated will be a maximum, a further quantity of alkali producing no particular increase in the heat evolution. In case of a dibasic acid, a second molecular proportion of the alkali will produce a further, considerable, heat evolution, and so on. If

therefore the molecular weight of the acid is known, one may at once gain information as to its basicity by observing the thermal effects produced on adding successive molecular proportions of the alkali. In the cases of a few dibasic acids the amount of heat liberated on adding two molecular proportions of alkali is almost exactly double of that obtained on adding one molecular proportion (e.g. H_2PtCl_6 and H_2SiF_6). In others, the heat evolved on adding one molecular proportion of the alkali is either greater than half the quantity evolved on adding two molecular proportions (e.g. H_2SO_3, H_2SeO_3, H_2CO_3, $H_2B_2O_4$) or is less (e.g. H_2SO_4, H_2SeO_4, $H_2C_2O_4$, $H_2C_4H_4O_6$).

If the molecular formula of the acid is not known we cannot of course directly determine the basicity of this method; we can however state the basicity *per* formula-weight. Thus if we were ignorant of the molecular weight of monochloracetic acid, this thermal method would at any rate shew us that, if the acid is regarded as $C_2H_3ClO_2$, it is monobasic, if $C_4H_6Cl_2O_4$, it is dibasic, and so on.

Thomsen obtained a large number of interesting results by the application of this method and, although some of his conclusions have to be modified in order that the phenomena may be interpreted in accordance with the ionic dissociation hypothesis, the main facts established are of very considerable importance. A few examples may be mentioned here in illustration of the application of his method.

Hydrosulphuric acid was always stated to be a dibasic acid on the evidence that a large number of metallic sulphides can be isolated as solids in which the whole of the hydrogen of the acid has been replaced by metal. But when one gram molecular weight of hydrosulphuric acid is mixed with one gram molecular weight of sodium hydroxide in dilute aqueous solution, the quantity of heat evolved (7738 gram calories) is practically identical with that evolved when the same quantity of the acid is mixed with twice this proportion of sodium hydroxide; i.e. two molecules of the alkali give rise to no more heat than one molecule. Hence the acid is, under these conditions, to be regarded as monobasic. It is true that compounds such as Na_2S can be isolated as solids,

but thermal measurements indicate that these undergo partial hydrolysis when dissolved; thus $Na_2S + H.OH = Na.SH + NaOH$.

Orthophosphoric acid gave the following results:

$$H_3PO_4.Aq,\ NaOH.Aq = 14800,$$
$$H_3PO_4.Aq,\ 2NaOH.Aq = 27100,$$
$$H_3PO_4.Aq,\ 3NaOH.Aq = 34000,$$
$$H_3PO_4.Aq,\ 6NaOH.Aq = 35300.$$

On the assumption then that hydrogen is replaced by sodium, these results appear to indicate that, as regards the first and second molecule of sodium hydroxide added, orthophosphoric acid behaves as a well-marked dibasic acid under the given conditions. The comparatively small quantity of heat due to the addition of the third molecule of alkali, and the fact that the quantity is somewhat increased by a still further proportion of it, might be interpreted to mean that after two atoms of hydrogen have been replaced by metal, the acidic function of the third atom is considerably weakened and its behaviour is then analogous to that of other weak acids, i.e. its 'salt' undergoes partial hydrolysis and this is to some extent retrograded by increasing the active mass of the alkali. [The interpretation in terms of the ionic hypothesis will be referred to below.]

Arsenic acid behaves in a manner which is quite analogous.

Examined in a similar way, phosphorous acid behaves as a dibasic acid and hypophosphorous acid, monobasic. Arsenious acid cannot be obtained, but addition of sodium hydroxide to arsenious oxide in solution shews, that for each atom of arsenic the resulting acid is monobasic.

The application of this thermal method to a study of the basicity of periodic acid led to interesting results. The acid had previously been regarded as monobasic, its formula being represented as HIO_4, or the crystallised acid as $HIO_4.2H_2O$. It appeared strange, however, that, although the salt KIO_4 results from the action of chlorine on potassium iodate in presence of potassium hydroxide, a similar treatment of sodium iodate gives rise to the salt $Na_2H_3IO_6$. The latter was, consequently, sometimes looked upon as a basic salt, i.e. as $NaIO_4.NaOH.H_2O$.

Thomsen, however, obtained the following thermal values on the addition of potassium hydroxide to crystallised periodic acid:

$$H_5IO_6 . Aq, \quad KOH . Aq = 5150,$$
$$H_5IO_6 . Aq, \quad 2KOH . Aq = 26590,$$
$$H_5IO_6 . Aq, \quad 3KOH . Aq = 29740.$$

Since the average heat evolution on neutralising many acids is of the order of 13000 or 14000 heat units *per* atom of hydrogen replaced, these results were considered to shew that two-fifths of the hydrogen in H_5IO_6 is normally replaceable by metals, and to indicate this the formula was written as $H_2(H_3IO_6)$. But since the molecular weight of the acid is unknown, the facts mentioned are equally consistent with any multiple of this formula; the acid might for example be tetrabasic, $H_4(H_6I_2O_{12})$. The latter formula indeed appeared probable, as a minimum, in consequence of the isolation of such salts as $Ag_4I_2O_9$. In order to account for the very different quantities of heat evolved by the addition of the first and second molecules of potassium hydroxide, it was suggested that the acid salt $KH(H_3IO_6)$ is unstable, losing water and becoming the 'anhydro-salt' KIO_4, and that the deficiency is due to the heat used up in the dissociation. On adding the second molecule of alkali the normal salt is formed and the water again appropriated.

$$H_2(H_3IO_6) + KOH = KH(H_3IO_6) + H_2O,$$
$$KH(H_3IO_6) = KIO_4 + 2H_2O,$$

and
$$KIO_4 + KOH + H_2O = K_2(H_3IO_6).$$

The different results obtained in preparing the potassium and sodium periodates are then, probably, simply due to the comparatively sparing solubilities of the 'anhydro' potassium salt and the normal sodium salt respectively.

(D) The equivalent conductivity of the solution of a sodium salt of an acid increases as the dilution becomes greater (**63**). Ostwald established the approximate empirical rule that for the sodium salt of a monobasic acid, the difference between the equivalent conductivity at dilutions of one equivalent in 32 litres and one equivalent in 1024 litres, is about 10 units; for the sodium salt of a dibasic and, the difference is about 20 units, for the sodium salt

of a tribasic acid it is about 30 units and so on. Generally, if Δ is the difference between the equivalent conductivities at the dilutions mentioned, the basicity of the acid $=\frac{\Delta}{10}$. The results were confirmed as far as pentabasic acids. Thus, for the salts of pyridine mono-, di-, tri-, tetra- and penta-carboxylic acids, he obtained respectively, as the difference between the equivalent conductivities at the dilutions mentioned, the numbers 10·4, 19·8, 31·0, 40·4 and 50·1.

The application of this method has already given many results of interest. Thus, Kremann and Decolle [*Monatsh.* 1907 (28) 917] find that the value of Δ for sodium fluoride is 20·8. This result lends support to the view that hydrofluoric acid should be regarded as a dibasic acid. [A similar conclusion has often been drawn from other properties of the acid, such as the formation of the comparatively stable salt KHF_2 and the complexity of the molecule in the gaseous state at low temperatures (compare page 91). The latter arguments might, however, be extended to acetic acid.]

Persulphuric acid was at one time regarded as a monobasic acid HSO_4 and determinations of the basicity by the method now described appeared to support this formula. But it was subsequently shewn by Bredig [*Zeit. Physikal. Chem.* 1893 (12) 230] that the results had been calculated from earlier experiments into which an error had been introduced. His own determinations shewed clearly that the acid is dibasic having the formula $H_2S_2O_8$. A similar conclusion had been arrived at by Löwenherz, whose cryoscopic and conductivity determinations with potassium persulphate indicated the dissociation into three ions rather than two. Bredig found also that potassium permanganate and potassium perchlorate give a corresponding value for Δ, and he concludes therefore that potassium permanganate is the salt of a monobasic acid, i.e. its formula is $KMnO_4$ (see page 36). Whetham [*Phil. Trans.* 1900 (194) 357], arrives at a similar conclusion.

(E) Information with regard to the basicity of an acid may sometimes be gained by observations of the lowering of freezing point, rise of boiling point, etc., of the aqueous solution. The acidic hydrogen is *ex hypothesi* ionisable and consequently, if we know the molecular weight of the acid and can determine the number of ions into which the acid, or its normal salt, dissociates, we can find

the basicity. In the case of acids themselves, however, it must be remembered that complete ionisation of a polybasic acid may only occur at extreme dilution, and under such circumstances the methods referred to are not sufficiently exact.

(F) Experience indicates that only polybasic acids are capable of dissociating into their anhydrides and water by the action of heat alone. In the case of monobasic acids it is necessary to make use of a dehydrating agent (e.g. the preparation of nitric anhydride from nitric acid) or to proceed in some more indirect way (e.g. the preparation of acetic anhydride from acetic acid). Hyponitrous and hypochlorous acids were at one time regarded as exceptions to this statement, but the first named was afterwards shewn to be dibasic and the formation of hypochlorous anhydride from its acid has never been demonstrated.

This generalisation has been employed as an argument for doubling the molecular formula of iodic acid, since this acid readily yields its anhydride when heated to 170° Some support is given to this view by the isolation of acid salts, such as KHI_2O_6, although salts corresponding to a still more complex formula have been obtained. Groschuff [*Zeit. Anorg. Chem.* 1905 (47) 331] finds by cryoscopic determinations, that the apparent molecular weight, in aqueous solution, varies very considerably with the concentration. In a 1 per cent. solution the acid appears to exist principally as the ions of the simple form, HIO_3, whereas in concentrated solutions there is evidence that more complex molecules are present.

Practical Work.

1. Determination of the basicity of acids.

(*a*) The given acids are treated in the manner described above (A), page 244, in order to ascertain the number of different salts, of a univalent metal, which they are capable of yielding.

(*b*) Solutions of different acids are given for determination of the basicities of the acids by the method of titration (B), page 245. The concentration of the solution and the molecular weight of the acid is, in each case, stated.

2. General methods of preparation of acids.

Students who are not already familiar with the work, take this opportunity of making experiments illustrating some of the most typical methods of obtaining acids from the usual sources.

(*a*) *From elements.* The preparation of iodic acid from iodine by oxidation with nitric acid.

(*b*) *From anhydrides.* The action is investigated of water on phosphoric pentoxide and on acetic anhydride.

(*c*) *From salts.* An aqueous solution of orthophosphoric acid is prepared from common sodium phosphate ($Na_2HPO_4.12H_2O$) by precipitation with lead acetate, decomposition of the precipitate, after thorough washing, with hydrogen sulphide, filtering off lead sulphide and boiling off excess of the reagent.

A solution of chloric acid is prepared from barium chlorate by decomposition with dilute sulphuric acid. A weighed quantity of the salt is dissolved in water and the calculated quantity of standard acid is added. Or, the result may be attained in a qualitative way if the solutions are carefully adjusted. In this case it is best to add a very slight excess of the acid and then remove this excess by cautious addition of baryta-water; any slight excess of the latter may afterwards be got rid of by careful treatment with carbon dioxide.

Various other problems of a similar character may be set, the success of the operations being tested by the purity of the specimens obtained and, in some cases, by the yield.

CHAPTER XVIII.

ACIDS (*continued*).

77. 'Strength' of Acids.

It is a matter of common observation that different acids, when taken in equivalent quantities and under similar conditions may vary very considerably in the extent to which they exhibit the properties which have been described above as 'acidic.' A variety of different terms have been employed to express this relative property, the commonest being *affinity*, *activity*, *avidity*, and '*strength*.'

The term 'affinity,' although still much used in this connection, is open to objection because of the loose way in which it has generally been applied. (See page 167.) 'Activity' may perhaps lead to misconception, since the word is frequently used in a sense other than the restricted one now under consideration. Thus, it is often said in reference to the action of acids on metals, that nitric acid is more 'active' than hydrochloric acid; yet in respect of the general property in question, the two are equal. The term 'avidity' was employed by Thomsen to mean 'greediness for base' and it is perhaps best to reserve the expression for reference to this particular property. 'Strength' is of course liable to be confused with 'concentration'; in volumetric analysis, for example, these two terms are often regarded as synonymous. But if we employ 'concentration' strictly in the sense of 'mass per unit volume' (i.e. grams per c.c., grams per litre, moles per litre, etc., as occasion requires), there will be no harm in making use of the word 'strength' to denote the 'acidic' property now under discussion. A large number of different methods have been used

in comparing the 'strengths' of acids and a brief account may be given here of some of those which are best known and of most general application.

(*a*) The idea of comparing the relative strengths of two acids by ascertaining whether one can 'turn the other out' from its combination with a base, is perhaps the oldest of all. In a qualitative way, this was for a long time regarded as a satisfactory and sufficient test, no attention being paid to the conditions under which the process of 'turning out' was effected. Thus sulphuric acid was regarded as the strongest of all acids, since salts of all other acids could be converted into sulphates by suitable treatment with sulphuric acid. Nitric acid was, for the same reason, said to be stronger than silicic acid; but since potassium nitrate when heated to redness with sand yields potassium silicate, it was supposed that, at the high temperature employed, the order was reversed, silicic acid being the stronger. The investigators of those days appear to have entirely lost sight of the fact that, in order to make a fair comparison, it is necessary to retain all the reacting substances in the same sphere. It is an obviously unfair competition, for example, if we distil potassium nitrate with sulphuric acid, since the nitric acid, owing to its greater volatility, is continually removed from the field of action.

Another point of importance which was entirely overlooked is that the changes are limited and reversible and that, in order to carry out a satisfactory test, one must proceed in a quantitative way, estimating not merely the possibility of replacing one acid by the other, but also the extent to which the replacement is accomplished under the equitable conditions above indicated.

(*b*) These necessary conditions will be fulfilled if we allow one equivalent weight of each acid to react with one equivalent weight of a base in dilute aqueous solution, all the reacting substances being soluble and, when equilibrium is established, determine the proportion of base which is appropriated by each acid. Evidently, in order to make this determination we must employ some method which causes no disturbance in the equilibrium; isolation of the resulting salts by crystallisation, or estimation of the remaining free acids by titration, etc., would obviously be useless. Thomsen first succeeded in accomplishing a successful solution of this

problem by making use of the fact that the heats of neutralisation of many acids are different and that this difference may be sufficiently great to afford a practical indication of the ratio in which the base is divided between the acids. Thus, let Q be the thermal value observed when the two acids HA_1 and HA_2 simultaneously react, in equivalent quantities, with one equivalent of the base MOH; let the heat of neutralisation of HA_1 with this base be h_1 and that of HA_2, with the same base, be h_2. Then if x equivalents of the base are appropriated by the acid HA_1, $1-x$ equivalents will be taken by the acid HA_2, so that

$$Q = xh_1 + (1-x)h_2 \text{ or } x = \frac{Q-h_2}{h_1-h_2}.$$

A far more convenient method of proceeding, however, is to act with one acid on the salt of the other acid, the substances being taken in equivalent quantity. Evidently the final distribution will then be the same as in the experiment last mentioned. Thus, using the same symbols as before, if we allow one equivalent weight of the acid HA_1 to react with one equivalent weight of the salt MA_2, and x is again the proportion of base finally appropriated by HA_1, the thermal effect observed, Q, will be the algebraical sum of the positive quantity xh_1 and the negative quantity xh_2. A simple way of regarding the matter is to imagine that the acid HA_2 is partly 'un-neutralised' and the acid HA_1 partly neutralised. If the process were completed, we should obtain the thermal value h_1-h_2; but since only the portion x (equivalents) of MA_2 is un-neutralised, the thermal result is $x(h_1-h_2)$. Hence

$$x = \frac{Q}{h_1-h_2}.$$

In order, therefore, to find x, the amount that is of the base which is appropriated by the acid HA_1, we must know the *difference* between the heats of neutralisation of the two acids with the given base. It is not necessary, however, to know the actual values h_1 and h_2, and it is, in certain cases, more convenient to obtain this difference by an indirect method. This may be done by taking the difference between the thermal values of the reaction of each acid with the salt of the other acid. Thus, the final distribution of the base will be the same whether we start with the two free acids and the base, in equivalent quantities, or if we allow either HA_1 to react with MA_2 or HA_2 to react with MA_1. Hence the

thermal value of the change HA_1, MOH, HA_2 will be equal to that of the total change (HA_1, MOH)+(MA_1, HA_2), and again, that of the total change (HA_2, MOH)+(MA_2, HA_1). By subtraction, therefore, we obtain

$$(MA_1, HA_2) - (MA_2, HA_1) = (HA_2, MOH) - (HA_1, MOH).$$

Instead of employing the thermal method as a measure of the changes in question we may make use of the fact that the neutralisation of an acid by a base is attended with alteration of *volume*. Ostwald, in 1878, made a large number of determinations of the ratio of distribution of bases between acids in this way, and he shewed that the method has certain advantages in that the changes of volume are more easily determined, and shew greater differences for different acids, than the corresponding thermal changes. The method of calculating the results is entirely similar. Other physical properties, such as the refraction equivalent, may be utilised for the same purpose.

The ratio of the quantities of base appropriated by each acid, under the conditions of the experiments above referred to, was called by Thomsen the ratio of the *avidities* of the acids. Thus, if the salt of the first acid is acted upon by an equivalent quantity of the second acid and it is found that x equivalents of the base are appropriated by the second acid, the ratio of the avidities will be $\frac{1-x}{x}$. Regarding the matter in light of the law of mass action we have, in the change

$$MA_1 + HA_2 \rightleftarrows MA_2 + HA_1$$

when equilibrium is attained, $(1-x)$ equivalents of MA_1 and $(1-x)$ equivalents of HA_2, since they react in equivalent quantity, and x equivalents each of MA_2 and HA_1. Consequently, $k(1-x)^2 = k'x^2$ or $\frac{k'}{k} = \frac{(1-x)^2}{x^2}$. It follows therefore that the ratio of the velocity constants $\frac{k'}{k}$ is equal to the square of the ratio of the avidities, in the sense above defined.

In order to assign a definite numerical value to each acid, representing its avidity, Thomsen took the avidity of hydrochloric acid as unity; in this case, experiment gives for sulphuric acid the

avidity 0·49. That is to say, if one equivalent of a base, such as sodium hydroxide, is competed for by one equivalent, each, of hydrochloric and sulphuric acids, the base will be distributed between the two acids in the ratio of 1 : 0·49. Hydrochloric acid is therefore, in this sense, about twice as 'strong' as sulphuric acid, since it appropriates about $\frac{2}{3}$ of the base. [The announcement of this result was most unfavourably received by many chemists of the time, since they had, from the faulty considerations referred to in (*a*), conceived the fixed idea that sulphuric acid was the strongest of all acids. It had also been assumed that the stronger the acid, the greater must be its heat of neutralisation. This idea was finally disposed of by Thomsen's results since hydrofluoric acid is one of the weakest acids but has the highest heat of neutralisation.]

Nitric acid was found to be as strong as hydrochloric acid; its avidity therefore = 1. The numbers obtained for some other common acids were as follows: Hydrobromic 0·89, Hydriodic 0·70, Trichloracetic 0·36, Oxalic 0·24, Monochloracetic 0·09, Hydrofluoric 0·05, Acetic 0·03, Boric 0·01, Silicic 0, Hydrocyanic 0.

Ostwald, by his volume method, obtained much the same order, but the values in certain cases were notably different. Thus he found for trichloracetic, monochloracetic and acetic acids the number 0·80, 0·070 and 0·012 respectively.

From these numbers we can calculate at once the ratio in which a base will divide itself between any two acids under the conditions laid down. Thus, if we act upon one equivalent of sodium monochloracetate with one equivalent of trichloracetic acid, we shall have, using Ostwald's numbers, $\frac{1-x}{x} = \frac{0{\cdot}07}{0{\cdot}80}$, whence $x = 0{\cdot}92$. That is to say, the trichloracetic acid will appropriate 92 per cent. of the base. Ostwald shewed conclusively that the relative avidity of an acid is independent of the nature of the base.

(*c*) Instead of investigating the division of a base between two acids in a homogeneous medium we may cause an acid to act upon excess of an 'insoluble' salt and estimate the amount of free acid which is liberated from this salt by the action, assuming of course that the first acid forms a soluble salt with the given base. Thus Ostwald allowed various acids to act upon excess of calcium oxalate, or zinc sulphide, and estimated the liberated oxalic acid by

titration with potassium permanganate, or the liberated hydrogen sulphide by means of iodine.

In these experiments it is shewn that the stronger the acid is, the more oxalic acid, or hydrogen sulphide, does it replace and the order obtained, under similar conditions, is the same as that arrived at by the methods previously described. But the important observation was here made that, whereas the stronger acids gave practically the same result at different dilutions, the values for the weaker acids increase considerably with dilution, the increase being more marked the weaker the acid is.

From the results of this method we can calculate the relative values of the ratio $\frac{k}{k'}$ for different acids, at a specified dilution, in a manner analogous to that given above. Thus, taking one equivalent of the first acid, we find, when equilibrium is attained, that x equivalents of oxalic acid are liberated from the calcium oxalate. The active mass of the solid calcium oxalate being constant ($=c$) we shall have the relation

$$k(1-x)c = k'x^2.$$

In making a similar experiment with the second acid, we find that $\mathbf{x}$ equivalents of oxalic acid are liberated, and consequently

$$\mathbf{k}(1-\mathbf{x})c = \mathbf{k}'\mathbf{x}^2.$$

Hence
$$\frac{k}{k'} = \frac{x^2}{c(1-x)} \quad \text{and} \quad \frac{\mathbf{k}}{\mathbf{k}'} = \frac{\mathbf{x}^2}{c(1-\mathbf{x})},$$

so that
$$\sqrt{\frac{k}{k'}} : \sqrt{\frac{\mathbf{k}}{\mathbf{k}'}} = \frac{x}{\sqrt{1-x}} : \frac{\mathbf{x}}{\sqrt{1-\mathbf{x}}}.$$

This method of comparing the strengths of acids has an advantage over the methods previously described in that the value of x can be directly determined by chemical analysis.

(*d*) The hydrolytic decomposition of salts by water has long been recognised as affording, in certain cases, a means of comparing the strengths of acids. Thus, Berthelot in 1875 [*Comptes Rendus* (81) 844], reasoning from his thermochemical results, came to the conclusion that weak acids are those whose salts are decomposed by water, the degree of decomposition progressively increasing as the dilution increases and diminishing if excess of either acid or base is added. An acid was therefore weaker the more its salt, with a given base, was hydrolysed and it was proposed to estimate the extent of this hydrolysis by ascertaining the extent to which the

heat of neutralisation was diminished by dilution. At the present time, this hydrolytic method is still employed to a considerable extent, but its application is practically limited to the very weak acids and the degree of hydrolysis is estimated by more refined and reliable means. (See page 290.)

(*e*) A large number of methods for comparing the 'strengths of acids depend on the measurement of reaction velocity in chemical changes which are known to be accelerated by acids. The acid in these cases appears, as a rule, to act catalytically and the rate of change is often proportional, or nearly so, to the concentration of a given acid. If different acids are compared under similar conditions the rate is generally proportional to the 'strength' of the acids and the 'order of merit' drawn up in this way usually coincides remarkably well with that deduced from the methods previously described. Regarding the matter again from the point of view of mass action, one may consider that in the experiments so far described, the ratio of the velocity coefficients, k and k', is arrived at by the statical or equilibrium method, whereas, in the processes now under consideration the velocities are directly compared, i.e. we employ the so-called kinetic method. It is evident that the latter method cannot be employed in the ordinary process of neutralisation of acids and bases, since the rate of change is far too rapid. But we may make use of a variety of other reactions, which are suitable for investigation by the time method, if we assume that the accelerative action of the acid in these cases is due, as in the neutralisation of bases, to the 'acidic' function of the acid.

Some of the best known of these 'velocity methods' are the following:

Inversion of cane sugar. The character of this change has already been referred to (see page 134). In the application of the reaction to the comparison of the 'strengths' of acids, a solution of cane sugar (20 per cent.) is mixed with an appropriate quantity of the acid to be measured [e.g. equal volumes of the sugar solution and a normal solution of the acid], the mixture is introduced into the polarimeter tube, kept at a constant temperature, say 25°, and the angle of rotation is measured at stated time intervals. The process is allowed to continue until the inversion is complete and

the difference between the initial and final readings is then proportional to the total quantity of sugar inverted. If a_0 is the initial reading, a_n the reading at the time t_n and a_∞ the final reading when the inversion is complete, the velocity constant k, for a reaction of the first order, will be

$$k = \frac{1}{t_n} \log_e \frac{a_0 - a_\infty}{a_n - a_\infty}$$

Making similar experiments with a series of different acids, the order of the velocity constants obtained will be a measure of catalytic influence of the acids in accelerating the inversion process.

Hydrolysis of methyl acetate. The change

$$CH_3COOCH_3 + HOH = CH_3COOH + CH_3OH,$$

like that of the inversion of cane sugar, is very greatly accelerated by the addition of acids and the acceleration is found to be proportional to the 'strength' of the acid, when other things are equal. The progress of the change can be very easily followed by direct titration and the reaction is a remarkably sensitive one, the influence of a very minute proportion of 'acidity' (i.e. in terms of ionisation, a very minute concentration of hydrogen ions) being distinctly perceptible. For these reasons the change in question is very extensively used for the object under discussion and it may be well here to describe, in some detail, the method of working.

Steamed flasks are employed and the solutions are kept at some constant temperature as in the saponification experiment described on page 142. The various acids to be examined are made up to a concentration of $\frac{N}{2}$. A convenient volume, say 50 c.c., of each acid is introduced into a separate flask and the flasks are kept in the thermostat for about 10 minutes at say 25°, being held in position by means of leaden weights, suitably fitted, or by other device. Each flask should be closed by a paraffined cork to prevent any loss by vaporisation. A measured volume of methyl acetate (say 2·5 c.c.) is now added to each flask, and the mixtures are thoroughly shaken; a measured quantity, say 5 c.c., of the mixture is then immediately withdrawn, run into pure

(CO_2-free) water (about 50 c.c.) and titrated with standard barium hydroxide, all the usual precautions being taken to prevent access of carbon dioxide. At definite time intervals, further equal portions of the mixture are withdrawn, run into water and titrated in the same way. The times may be taken at the moment when the solution is run into the water; the intervals should be at first, say, 15 minutes and may be increased as the reaction proceeds.

We thus obtain a series of readings C_0, C_1, C_2, C_3..., representing the quantities of barium hydroxide used in the titrations, corresponding to the time intervals t_0, t_1, t_2, t_3.... After several such observations have been recorded, the mixture remaining in the flask is allowed to stand at the constant temperature for at least 24 hours (48 hours is preferable) and a final titration is then made in the same way as before.

If C_0 is the initial titration, C_n the titration after the time-interval t_n and C_∞ is the final titration, it is evident that the initial concentration of the methyl acetate is proportional to $(C_\infty - C_0)$ and the concentration after the time t_n is proportional to $(C_\infty - C_n)$. Therefore, since the reaction is of the first order (see page 135), we shall have

$$k = \frac{1}{t_n} \log_e \frac{C_\infty - C_0}{C_\infty - C_n}.$$

[It is not necessary to reckon from the initial reading; one may start for example from C_1 after the interval t_1.]

Hydrolytic decomposition of amides. Water tends to decompose amides in the sense $R.CONH_2 + HOH = R.COOH + NH_3$; but here again the change is in most cases entirely inappreciable owing, presumably, to the low reaction velocity. A small quantity of either acid or alkali, however, at once makes the change apparent.

[The changes which occur under these circumstances cannot, however, be regarded as catalytic; when an acid HX is added we have $R.CONH_2 + HOH + HX = R.COOH + NH_4X$, or if a base, MOH, is present, $R.CONH_2 + MOH = R.COOM + NH_3$.]

Ostwald compared the influence of various acids as regards their capability of accelerating this change and the results gave an order agreeing, on the whole, well with that obtained by other methods, but the process is somewhat complicated by secondary

reactions. He employed acetamide for these experiments and estimated the progress of the change by measuring the nitrogen evolved when the mixture was treated with sodium hypobromite; this reagent liberates the nitrogen from ammonia, but not from acetamide.

Decomposition of diazo-compounds. The typical action of water upon diazonium salts results in the replacement of the N_2X group by OH, with evolution of free nitrogen. Thus, in the case of benzene diazonium chloride, we have

$$C_6H_5N_2.Cl + HOH = C_6H_5OH + HCl + N_2.$$

A somewhat similar change occurs when water reacts with diazo-ethylacetate, thus:—

$$CHN_2.COOEt + HOH = CH_2OH.COOEt + N_2.$$

These changes take place with extreme slowness, at low temperatures, but are greatly accelerated by the presence of acids, the accelerative influence being dependent on the concentration of the acid, or, if different acids are compared under similar conditions, on the 'strengths' of the acids.

The reactions are readily followed by estimating the volumes of nitrogen evolved and the velocity-constants can in this way be determined for the various acids. The changes are so sensitive to acids that they are sometimes recommended as delicate qualitative tests for the presence of hydrogen ions. [Compare, for example, Fraenkel, *Zeit. Physikal. Chem.* 1907 (60) 202.]

Experiment shews that the *electric conductivities* of aqueous solutions of acids are closely connected with their 'strengths' as determined by the various methods described, the equivalent conductivities being roughly proportional to the 'acidic' function. Arrhenius first shewed in a quantitative manner the connection between the chemical activity of electrolytes and their conductivities and Ostwald afterwards clearly demonstrated the remarkably close proportionality between the conductivities of acids and their behaviour as catalysts in accelerating various reactions.

78. Ionic interpretations. In terms of the hypothesis of electrolytic dissociation, the acidic properties are, as previously

stated, due to the hydrogen ions which the acid yields on ionisation. In all the previously described methods of comparing the 'strengths' of acids it is therefore assumed that the measurements must be interpreted as being dependent upon the relative values of the dissociation constants of the acids, i.e. on their relative degree of ionisation under the conditions of dilution, etc., which obtained in the experiments. In the cases of the inversion of cane sugar, or catalysis of methyl acetate, it is not easy to understand why hydrogen ions should produce the effects in question and there are some considerable difficulties in accepting this simple interpretation (compare page 178). As regards the hydrolytic action of water on salts, the ionic explanation is far more complete and satisfactory. The degree to which the salts of different acids, with the same strong base, are hydrolysed in solution depends, according to this hypothesis, not on the circumstance that the stronger acid forms a more stable salt—one, that is, which can better resist the decomposing action of water—but on the relative degrees of ionisation of the acids at the dilution employed. (See page 292.)

The method of comparing the 'avidities' of two acids by allowing them to compete for an insufficient amount of base can be interpreted in a quantitative manner according to the hypothesis of ionisation, but the general problem becomes a complicated one, since we have to consider the equilibrium between each acid and its ions, each salt and its ions, and the influence of the common ions in affecting the degrees of ionisation. When a dilute solution of a strong acid is added to the salt of another equally strong acid, the system consists mainly of the constituent ions, these being in equilibrium with very small proportions of the non-ionised molecules and consequently there will be practically little change in the equilibrium on mixing. But if a strong acid is added to the salt of a weak acid, the hydrogen ions of the strong acid unite with the anions of the weak acid until the solution becomes isohydric with respect to the two acids. The result of the mixing has been therefore, that a notable proportion of the weak acid has been formed at the expense of the salt and the strong acid. In Thomsen's experiment then we are comparing, not the striving of the two acids to appropriate the base, but rather the different

extents to which the two acids tend to become ionised at the dilution employed, the metal playing a comparatively unimportant part. If the experiment is made by adding an insufficient amount of base to the two acids, in dilute aqueous solution, each acid will be 'concerned with' the base in the sense that the hydrogen ions of the acids tends to combine with the hydroxyl ions of the base. The anions of the acids will also tend to combine with the metal of the base to form salts, but since these are usually highly ionised, this latter effect is comparatively insignificant.

If it be assumed that the law of mass action is obeyed, it can be shewn that the ratio of distribution of a base between two weak acids is equal to the ratio of square roots of the dissociation constants of the acids. In order to illustrate the usual method of proof the following simplified example is generally given.

Suppose that two weak monobasic acids compete for a monacid base in dilute aqueous solution. Let the three substances be taken in equal molecular proportions, i.e. one gram molecule of each, and let the volume of the mixture be V. When equilibrium is attained we shall have present in the solution the two salts MA_1 and MA_2, which are largely ionised, and the remaining portions of the two acids HA_1 and HA_2. These acids being weak, were only slightly ionised to start with, and after equilibrium has been reached they will be still less so, since each is in presence of its own salt; the concentration of hydrogen ions in the resulting solution will therefore be extremely small.

Let $(1-x)$ and x be the quantities (measured in gram equivalents, or in moles) of the base which are 'concerned with' the two acids HA_1 and HA_2 respectively, and c be the small quantity of hydrogen ions present. The 'unused' portions of the two acids will then be x and $(1-x)$ respectively. Further, let it be assumed that the salts MA_1 and MA_2 are ionised to the same degree $=a$ (since this is generally found to be the case with salts of this type). Then the total quantity of the salt MA_1 will be $(1-x)$, and of this a portion $a(1-x)$ will exist in the ionised condition; similarly, the ionised portion of MA_2 will be ax.

In addition to the non-ionised portions of the two salts, the solution will therefore contain the quantities x of the acid HA_1, $(1-x)$ of the acid HA_2 (both practically non-ionised), $a(1-x)$ of the anion A_1, ax of the anion A_2 and c of hydrogen ions.

As regards the equilibrium between each acid and its ions we shall have, respectively,

$$K_1 x = \frac{a(1-x)c}{V} \quad \text{and} \quad K_2(1-x) = \frac{axc}{V},$$

when K_1 and K_2 are the dissociation constants of HA_1 and HA_2 respectively. Dividing one by the other, we obtain

$$\frac{K_1}{K_2} = \frac{(1-x)^2}{x^2}.$$

If m_1 and m_2 represent the degrees of ionisation of the two acids themselves, respectively, when they are dissolved separately at this same dilution V, the dissociation constants are

$$K_1 = \frac{{m_1}^2}{(1-m_1)\,V} \quad \text{and} \quad K_2 = \frac{{m_2}^2}{(1-m_2)\,V}.$$

But since the acids are very weak, we may regard the quantities $(1-m_1)$ and $(1-m_2)$ as practically equal to unity, so that

$$\frac{1-x}{x} = \frac{m_1}{m_2},$$

i.e. the ratio of 'distribution' is equal to the ratio of the degrees of ionisation of the two acids when they are dissolved separately at the dilution employed in the experiment.

As regards electric conductivity, it might not at first sight be apparent why there should be such a close parallelism between the acidic properties of a solution and its equivalent conductivity, since the current is conveyed by both the anion and kation. From the relation $\lambda_v = m\,(U+V)$, it might appear conceivable that a weaker acid could conduct better than a stronger one if it happened that the mobility of its anion were greater than that of the other acid, i.e. that the smaller value of m might be more than compensated by the greater value of U. But experiment shews that this never happens to be the case. The mobility of the hydrogen ion is always very much greater than that of the anion, being about five times as great as the most mobile anion yet investigated and it happens, therefore, that the equivalent conductivity is roughly proportional to the concentration of the hydrogen ions.

If we wish to compare numerically the 'strengths' of various acids taken at the same equivalent concentration, we have to determine, in terms of this hypothesis, the relative concentration of hydrogen ions in the various solutions. Assuming that the acids behave as binary electrolytes, the concentration of hydrogen ions which they produce are simply proportional to the degrees of ionisation of the various acids at the dilutions specified. The degrees of ionisation may be determined, as previously stated, by osmotic effects, such as freezing point depression, etc.; in the case of weak acids, however, the conductivity method is by far the most accurate and convenient.

In the methods so far considered the object has been to make a comparison of the strengths of different acids under

similar conditions of dilution. If the equivalent concentrations are not the same, such comparisons would, in themselves, be meaningless, at any rate from a quantitative point of view. But if it can be shewn that the 'acidic' properties vary with dilution according to some definite law, it becomes possible to compare the strengths although the determinations are made at unequal concentrations. With weak acids, this happens to be the case; the degree of ionisation—and consequently the concentration of hydrogen ions and the acidic properties—varies in a regular manner with dilution. In such cases, it is found, as previously stated, that, in dilute solutions, the law of mass action can be applied to the process of ionisation as to other processes of chemical change and, knowing the degree of ionisation at one state of dilution, we can therefore calculate its value at another. More than this, the law enables us to express the 'strength' of any acid, of the class mentioned, at a given temperature, by a single numerical constant. The expression of this relationship in the simple form already referred to (see page 211) is known as Ostwald's dilution law and the constant k is termed the 'dissociation constant' of the acid.

The practical determination of the dissociation constant by the conductivity method will be dealt with in a future section.

In addition to the well-known methods of comparing or measuring the 'strengths' of acids which have been considered in the foregoing sections, a brief reference may be made to the use of colour indicators for this purpose. Salm, for example [*Zeit. Electrochem.* 1906 (12) 99], shews that the concentration of hydrogen ions in a solution may be determined by comparing the colour given by a suitable indicator with that given by a standard solution of some acid in which the value has been determined by the conductivity method. Litmus, methyl-orange, p nitrophenol, alizarin, etc., were used as indicators. The latter indicator, for example, is said to change from yellow to orange at a concentration of hydrogen ions between 1×10^{-5} normal and 1×10^{-6} normal, from orange to red between 1×10^{-7} and 1×10^{-10} and from red to violet between 1×10^{-13} and 1×10^{-14} normal. Similar experiments were made by Eijdman [*Rec. Trav. Chim.* 1906 (25) 83], Kastle [*Am. Chem. Jour.* 1905 (33) 106] and, more recently, by Veley [*Trans. Chem. Soc.* 1907, 153 etc.].

In conclusion mention may be made of a method of comparing the 'strengths' of acids by a process which has the advantage of extreme simplicity of working although it involves the use of a somewhat expensive reagent [Fenton and Jones, *Trans. Chem. Soc.* 1901, 91]. Experiment shews that the hydrazone of oxalacetic acid when heated in aqueous solution readily loses carbon dioxide, becoming converted into the hydrazone of pyruvic acid

$$\begin{array}{lcl} CH_2.COOH & & CH_3 \\ \dot{C}:N_2HPh & = & \dot{C}:N_2HPh + CO_2 \\ \dot{C}OOH & & \dot{C}OOH \end{array}$$

whereas, in presence of a sufficient concentration of hydrogen ions no carbon dioxide is evolved, but instead a molecule of water splits off with formation of pyrazolone carboxylic acid

$$\begin{array}{lcl} CH_2.COOH & & CH_2.CO \\ \dot{C}:N_2HPh & = & \dot{C}:N.\dot{N}Ph + H_2O \\ \dot{C}OOH & & \dot{C}OOH \end{array}$$

With an insufficient concentration of hydrogen ions, both changes take place side by side, the proportion of the pyrazolone carboxylic acid to pyruvic acid hydrazone increasing as the hydrogen ion concentration becomes greater. Consequently, if we compare the effects of various different acids at the same equivalent concentration, the amounts of carbon dioxide finally evolved will give an approximate, inverse, measure of the relative strengths of the acids.

The connexion between chemical constitution and 'strength' in acids will be referred to in a future section.

Practical Work.

A, *B* and *C* are $\frac{1}{2}$ normal solutions of three different acids. Their 'strengths' are compared by the method of hydrolysis of methyl acetate described on page 259. It is convenient to conduct all the operations simultaneously and students are therefore recommended to work together in groups, each taking charge of one series of observations.

CHAPTER XIX.

SALTS.

79. THE word salt appears to have been used in the first instance to mean the solid residue obtained by evaporation of sea water; the name was afterwards employed for various soluble solids which were supposed to have a resemblance to sea salt. On the dualistic conception of salts, already referred to on page 237, a distincton had eventually to be made between salts formed by union of the oxide of a metal with the oxide of a non-metal and substances like common salt. Berzelius used the names amphi-salt and haloid-salt for the two classes respectively; in both classes the proximate constituents were considered to be a positive and a negative part.

According to more recent views, a salt is commonly defined as a compound formed from an acid by replacement of its 'acidic' hydrogen, whole or part, by a metal or electro-positive radicle. [In these terms therefore the definition of an acid must precede that of a salt.] It is the custom now to make the further restriction that a salt must be capable of behaving as an electrolyte in aqueous solution or, in some cases, in the fused state. The alkyl derivatives of acids, such as ethyl acetate or ethyl chloride, are consequently excluded. Accordingly, all salts are electrolytes; the converse proposition that 'all electrolytes are salts' (Hittorf) has often been insisted upon, acids being salts of hydrogen and bases, being regarded as salts of the acid H.OH. Since 'metal' and 'non-metal,' 'electro-positive' and 'electro-negative,' are to a large extent relative terms, it is evident that there must often be a difficulty in drawing a sharp line in classifying substances as salts or 'not salts.' Compounds which are largely decomposed or hydrolysed by water are often excluded; thus the chlorides of phosphorus are, for this reason, not regarded as salts. Yet if we

compare the action of water on the chlorides of phosphorus, arsenic, antimony and bismuth, it is evident that the difference is one of degree; it appears therefore somewhat arbitrary to include, as salts, the chlorides of the two latter and to exclude those of the former. Urea hydrochloride is usually classed as a salt; yet it undergoes hydrolysis to the extent of about 90 per cent. in a decinormal solution (at 25°).

Similarly, it is often said that the 'binacetates' and 'quadroxalates' (**74**) are not 'true' salts since they are at once decomposed by water.

80. Classification.

It may perhaps be of interest to refer briefly to each of the classes into which salts are commonly divided, in order to draw attention to certain points of detail.

Normal salts are those in which all the 'replaceable' or 'acidic' hydrogen of the acid has been replaced by the metal or electropositive radicle. [The term 'neutral' salt was formerly used to mean the same thing but it is obviously incorrect, only the normal salts of the strongest acids and bases being neutral in the stricter sense. Even potassium sulphate is not correctly a neutral salt. See page 287.]

It is evident that difficulties may arise in the application of this definition to certain particular cases owing to the want of precision in the general use of the term 'basicity.' Which, for example, is the normal sulphide of potassium or the normal orthophosphate of sodium? (See page 246.)

Acid Salts are those, derived from polybasic acids, in which only part of the 'acidic' hydrogen has been replaced; they still therefore retain acidic properties. It does not of course follow that this acidic character can be demonstrated by all indicators. Thus towards litmus, sodium bicarbonate—an acid salt—is powerfully alkaline. Upon the older dualistic view, acid salts were regarded as compounds of a base with more than one 'equivalent' of an 'acid.' Thus acid sodium sulphate was represented as $NaO.HO.2SO_3$, i.e., in modern symbols, $Na_2O.H_2O.2SO_3$; acid sodium carbonate would be $Na_2O.H_2O.2CO_2$ and so on. Hence the names 'bisulphate' and 'bicarbonate.'

Much discussion arose at one time in connection with certain compounds whose composition is that of an acid salt *minus* water. Thus potassium bichromate was generally looked upon as $2KHCrO_4 - H_2O$ and borax as $Na_2H_2B_4O_8 - H_2O$; the term *anhydro*-salt was generally used for such compounds and they were considered to be salts derived from the same parent acid as the normal salts K_2CrO_4 and $NaBO_2$. It is usual now, however, to look upon these compounds as salts of entirely different acids, potassium bichromate being derived from 'bichromic acid' $H_2Cr_2O_7$ and borax from pyroboric acid $H_2B_4O_7$. (See page 235.)

Acid salts of dibasic acids when dissolved in water appear to ionise in the first instance as binary compounds, e.g.

$$MHX \rightleftarrows \dot{M} + HX';$$

at greater dilution the anion HX′ may undergo further dissociation into $\dot{H} + X''$; the extent to which the latter change proceeds depends not only on the dilution but also on the strength of the acid. This property is made use of in the preparation of certain products of higher oxidation than the original acids, e.g. persulphates and perborates.

Basic salts may be looked upon in two or three different ways. According to the older view, a basic salt is a 'molecular' compound of a normal salt with a base. Thus basic bismuth chloride might be looked upon as the normal salt $BiCl_3$ united with the base Bi_2O_3; basic cupric sulphates as $CuSO_4 . CuO$ [or $CuSO_4 . Cu(OH)_2$] $CuSO_4 . 2CuO$ [or $CuSO_4 . 2Cu(OH)_2$] and so on. One alternative view, which now appears to find most favour, is to regard a basic salt as a normal salt in which part of the negative radicle, or group, has been replaced by oxygen or hydroxyl; basic bismuth chloride is then BiOCl, and basic cupric sulphates

$Cu_2O(SO_4)_2$ [or $Cu(OH)SO_4$] and $Cu_3O_2(SO_4)$ [or $Cu_3(OH)_4SO_4$] etc.

This may be stated in another way by considering that basic salts are compounds derived from metallic polyhydroxides by replacement of part of the hydroxyl by acidic groups, or else, are salts of basic groups such as (BiO), (Cu_2O), etc.

The molecular weights of such compounds are of course unknown and there is perhaps little to choose between the alternative views. The older method of representation certainly

appears to have the advantage of simplicity in those cases where a whole series of basic salts is known. Thus there are said to be thirteen oxychlorides of mercury $x\mathrm{HgCl_2}.y\mathrm{HgO}$.

Basic salts may be formed either by directly acting upon a normal salt with a base (e.g. by boiling a solution of cupric sulphate with cupric hydroxide), by addition of a limited quantity of a base to a normal salt (e.g. by adding sodium hydroxide to cupric sulphate in about the ratio $\mathrm{CuSO_4}:\mathrm{NaOH}$ and boiling), or by partial hydrolysis of a normal salt (e.g. by adding water to bismuth chloride).

81. *Double salts.* It often happens that two single salts may combine together in some simple molecular ratio to give a compound which, in the solid state, has properties—such as solubility, crystalline form, density, colour—which are distinct from those of the constituent single salts. In dilute aqueous solution, however, a difference of properties no longer exists. The conversion of two single salts into a double salt is a reversible process and in each case there is a definite transition temperature on one side of which the double salt, and on the other the mixture of the two single salts, is the stable system.

This transformation is usually attended, on the whole, with either dehydration or hydration, i.e. the number of molecules of water of crystallisation in the double salt is usually either less or greater than the sum of the numbers contained in the two single salts. Entirely distinct from these true double salts are the isomorphous mixtures of salts, i.e. solid solutions or 'mixed crystals' of two isomorphous salts. In these the molecular ratio of the two may be continuously varied and the properties, which vary continuously with the composition are, additively, those of the constituents. Experience shews that salts which form these mixed crystals never form double salts and, conversely, those which form double salts never give mixed crystals.

Double salts may be derived from (*a*) two different metals and one acid [e.g. the alums $\mathrm{M'M'''(SO_4)_2}.12\mathrm{H_2O}$ and the vitriols $\mathrm{M'M''(SO_4)_2}.6\mathrm{H_2O}$], (*b*) two different acids and one metal [e.g. $\mathrm{Hg(NO_3)_2}.2\mathrm{HgS}$, $\mathrm{PbCl_2}.3\mathrm{PbS}$ and $\mathrm{PbI_2}.2\mathrm{PbCl_2}$], (*c*) two different metals and two different acids [e.g. $\mathrm{MgSO_4}.\mathrm{KCl}.3\mathrm{H_2O}$].

The first type (*a*) is by far the most common. The specific properties of a double salt, as distinct from those of the two single salts, are sometimes very striking; thus green $CuCl_2.2H_2O$ with colourless LiCl gives a red double salt $CuCl_2.LiCl.2H_2O$, and green cupric acetate with colourless calcium acetate gives the dark blue double salt $CaCu(CH_3CO_2)_4.8H_2O$.

A dilute aqueous solution of a double salt shews all the properties of the constituent ions and is therefore identical with a mixture of dilute solutions of the two single salts. In concentrated solutions, however, there is evidence that a double salt may to some extent exist as such. Thus it is possible under certain conditions, to be mentioned below, for a double salt to be in equilibrium at different temperatures with its saturated solution, i.e. it may have a definite solubility curve—a property which is generally considered to depend upon the equilibrium between a solid with molecules of its own kind in solution. Freezing point and conductivity determinations also shew a considerable difference, in strong solutions, from the results calculated for the sum of the depressions, or conductivities, which would be produced by the two single salts. The possibility has of course to be considered that the double salt may behave in the first instance as a complex single salt; e.g. potassium alum may ionise in the first instance as $\dot{K} + [Al(SO_4)_2]'$. [See, for example, Jones and Caldwell, *Amer. Chem. Jour.* 1901 (25) 349.]

The reversible transformation of a double salt into two other salts may be easily demonstrated in the case of di-potassium cupric chloride $2KCl.CuCl_2.2H_2O$ which, when heated to 92°, breaks up into $CuCl_2.KCl$ and KCl and water, partial liquefaction taking place. The original double salt is blue, whereas after decomposition it is fairly easy to distinguish the brown needles of potassium cupric chloride and the white cubes of potassium chloride. In this case the di-potassium double salt is the stable form *below* the transition temperature and the same is true of some others, such as cupric calcium acetate (75°) and Rochelle salt,

$$KNaC_4H_4O_6.4H_2O\,(55°).$$

But in many cases the double salt is the stable form *above* the transition point, e.g. carnallite $MgCl_2.KCl.6H_2O$ (−21°), and

astracanite $MgSO_4.Na_2SO_4.4H_2O$ (22°). The thermal change accompanying the transition may be either positive or negative and the effect observed is largely due to hydration or dehydration, i.e. the thermal effects due to other circumstances of the change are comparatively insignificant. It is consequently possible in most cases to predict the sign of the thermal change from the chemical equation. Thus when carnallite is formed from $MgCl_2.12H_2O$ and KCl there is, on the whole, a splitting off of $6H_2O$, and when Rochelle salt is formed from sodium tartrate ($2H_2O$) and potassium tartrate ($\frac{1}{2}H_2O$) there is, taking one formula weight of each of the single salts, a combination with $5\frac{1}{2}H_2O$. We shall expect, therefore, that heat will be absorbed in the first case and evolved in the second case. Applying now the principle of le Chatelier (page 159) one can foretell with tolerable certainty the direction of the change as the transition temperature is passed. Since a rise of temperature favours an endothermic change—and conversely—carnallite should be formed and Rochelle salt should be decomposed, with rising temperature. In the case of ordinary alum, the formation of $2[KAl(SO_4)_2.12H_2O]$ from K_2SO_4 and $Al_2(SO_4)_3.18H_2O$ is attended with a combination of $6H_2O$, so that the double salt is stable below the transition point.

The condition of double salts when completely dissolved in water has already been briefly referred to. The case becomes more complicated, however, if we have to consider the behaviour of a solid double salt in contact with a limited quantity of water. It is possible for the solid double salt and the two solid single salts to exist together, in stable equilibrium, with the saturated solution produced and the vapour; but this is possible only at one particular temperature, i.e. the transition point. If the temperature is raised or lowered one or more of the solids will disappear. If it should happen that the two single salts have the same solubility in the solution, it is possible for the double salt to dissolve 'unchanged'; i.e. on raising or lowering the temperature, in the direction in which the double salt is the stable form, the double salt will have a definite solubility at a given temperature, the solid double salt remaining undecomposed. In this case it is possible therefore to have the solid double salt alone in equilibrium with its saturated solution near the transition point.

In most cases, however, the two single salts have different solubilities and the saturated solution formed, when the double salt is treated with a little water, at about the transition point, will contain the two single salts in a ratio different from that in which they exist in the double salt. The solid remaining will therefore be a mixture of the double salt with the less soluble single salt; when this happens, it is usually said that the double salt is 'decomposed by water.' When carnallite, for example, is treated with a little water at ordinary temperature, some of the solid dissolves and a mixture of potassium chloride and unaltered carnallite remains. On cooling the mixture the solution in contact with these two solids is found to have a definite composition at a given temperature, and at no temperature can we have solid carnallite alone in equilibrium with the saturated solution. If the mixture is cooled below $-21°$ the solid carnallite will all disappear and, if the quantity of water is not too large, we should then have solid potassium chloride and magnesium chloride, $MgCl_2.12H_2O$, together in equilibrium with the saturated solution and vapour. At $-21°$, carnallite, potassium chloride, magnesium chloride ($12H_2O$), the saturated solution and aqueous vapour can all exist together in equilibrium. The behaviour of astracanite is very similar; $Na_2SO_4.10H_2O$ is less soluble than $MgSO_4.7H_2O$ and the former separates as a solid when the double salt is treated with a little water just above the transition point. The saturated solution so obtained contains therefore more magnesium sulphate than sodium sulphate. But the solubilities of the salts vary not only with the temperature but also with the composition of the solution, i.e. the presence of one salt in solution influences the solubility of the other. As the temperature rises, the solution in contact with astracanite and sodium sulphate alters in composition, becoming relatively richer in sodium sulphate, and at 25° the molecular ratio of the two is the same; i.e. the solution now contains the two salts in the same proportion as that existing in the double salt. At, and above, this temperature solid astracanite can 'dissolve unchanged'; that is to say, we can have equilibrium between solid astracanite alone and its saturated solution at different temperatures, the composition of the solution being the same as that of the double salt and the concentration being constant for a given temperature.

There is an interval then between 22° and 25° during which astracanite, although on the stable side of the transition point, cannot exist in stable equilibrium with the saturated solution unless one of the solid single salts (the less soluble) is also present. This interval of temperature is called the transition interval. It is limited, on the one hand, by the transition point and, on the other, by the temperature at which the solution in equilibrium with the two solids (double salt and less soluble single salt) contains the two single salts in the same proportion as that existing in the double salt. In other words, it is the interval between the temperature at which the double salt begins to be formed from the two single salts and the temperature at which it ceases to be 'decomposed' by water. The greater the difference in the solubility between the two single salts, the wider, as a rule, is the transition interval and, in some cases, the upper limit (or lower limit in case the double salt is the stable form below the transition point) can never be attained. This happens in the double salts $2KCl.CuCl_2 2H_2O$, $PbI_2.KI.H_2O$, carnallite and some others, none of which can dissolve 'unchanged' at any temperature—at any rate under ordinary pressures.

The behaviour of double salts in contact with their aqueous solutions can be most clearly expressed in terms of the phase rule and the subject will be referred to again in that connection. (See Chapter XXIII.)

The student is recommended to read the article on 'Double salts' by Miss Freund in *Science Progress*, 1907 (5) 135. Also E. F. Armstrong, *B. A. Report*, 1901, 262.

82. *'Complex' single salts* have already been referred to (see page 230) It may be advisable, however, to add a few supplementary remarks here in dealing with the classification of salts. There are numerous instances of compounds which can be formulated as double salts and can sometimes be produced, like these, by mere admixture of solutions of two single salts, but which exhibit certain specific properties entirely distinct from those of double salts. In salts of this class it is found that, even in dilute aqueous solution, the characteristic reactions of some of the ions of the single salts disappear, either entirely or to a considerable extent. In addition to this, the aqueous solutions are found to have new or specific properties which are not possessed by the

solutions of the original salts separately. Thus by mixing together solutions of ferrous sulphate and excess of potassium cyanide a salt, *potassium ferrocyanide*, can be obtained in the crystalline condition which, when dissolved in water, fails to give the reactions either of iron or of a cyanide; on the other hand it has remarkable specific properties (prussian blue reaction, etc.). From its mode of formation and empirical composition it might well be regarded as a double salt, $Fe(CN)_2.4KCN$, but the properties mentioned would thus be entirely inexplicable. The solution does, however, give the ionic reactions of potassium; it is assumed therefore that the iron and cyanogen groups together form a complex anion and that the compound is the potassium salt of a complex acid. *Potassium chromi-oxalate* $K_3[Cr(C_2O_4)_3]$ (prepared by digesting chromium hydroxide with acid potassium oxalate, or by reducing potassium bichromate with oxalic acid) was at one time regarded as a double salt $Cr_2(C_2O_4)_3.3K_2(C_2O_4)$. In a solution of this salt the ionic reactions of chromium, and of oxalates, are practically absent since no precipitate is obtained either with alkalis or with calcium chloride (the latter does, however, shew a very slight indication after a time). *Potassium platini-chloride*, $K_2(PtCl_6)$, formerly regarded as $PtCl_4.2KCl$, is completely precipitated by two molecular proportions of silver nitrate, whereas if it were a double salt, as formerly supposed, it should require six molecules. The precipitate, however, is not silver chloride at all but silver platini-chloride; moreover, it has been proved that on electrolysis the platinum moves with the chlorine to the anode.

Potassium ferri-oxalate is analogous to potassium chromi-oxalate, but in this case the reaction with calcium chloride is well marked although, on electrolysis, it has been proved that the iron appears at the anode. The solid salt is bright green—entirely different therefore from all ferric salts. In this instance, then, it appears that the aqueous solution does behave to a limited extent as would the double salt $Fe_2(C_2O_4)_3.3K_2(C_2O_4)$, but that it also has distinct specific properties.

It is evident that a hard and fast line cannot always be drawn between the two classes and that usually the change, simple double salt $\rightleftarrows$ complex single salt, is reversible, the extent of the change depending on the nature of the substances and on the

concentration, temperature, etc. Thus in a solution of potassium ferri-oxalate we have the equilibrium

$$Fe_2(C_2O_4)_3 . 3K_2(C_2O_4) \rightleftarrows 2K_3[Fe(C_2O_4)_3].$$

Some other well-known examples of complex single salts are the following. $K[Ag(CN)_2]$ formed by dissolving silver cyanide in a solution of potassium cyanide. This gives no indications of silver ions (e.g. with sodium chloride). On electrolysis the silver goes, with the CN groups, to the anode; this circumstance is supposed to explain the difference between the character of the metallic silver deposited in electro-plating, where this salt is employed, and that obtained by electrolysis of ordinary silver salts. It is possible that in the former case the metal results as a secondary product, i.e. from the action of the potassium, produced at the kathode, on the surrounding solution, whereas in the latter case the silver is the primary product at the kathode. $K[Ni(CN)_4]$ is obtained when nickel cyanide is dissolved in potassium cyanide; the formation of the complex ion is here indicated by the solution having a yellow colour, instead of the green colour characteristic of $\ddot{N}i$ ions. It exhibits the ionic reactions of nickel only to a limited extent; thus it gives no precipitate of nickel hydroxide with alkalis, but does so with mercuric oxide or oxycyanide. $K_3[Co(CN)_6]$ in solution shews none of the characteristic reactions of cobalt or of cyanides; hence its formation is taken advantage of in the separation of nickel and cobalt, since the nickel compound produced under like circumstances can, as above indicated, give ionic reactions of nickel with certain reagents.

83. The state of salts in solution.

In studying the condition of a single salt in aqueous solution, several important phenomena have to be taken into consideration, such as ionisation, hydration, hydrolysis, the formation of complex ions and so on. The problem becomes of course more complicated when two different salts are present and we have then, in addition to the above phenomena, to enquire whether mutual interaction occurs and to consider the possibility of the formation of double salts or of complex single salts, the interchange of radicles and the mutual influence of the ions on the degrees of ionisation of the salts. All of these problems are included in speaking generally

of the 'state of salts in solution'; the expression has, however, often been used exclusively in reference to the interchange of radicles when solutions of two different salts are mixed together. This latter problem has for a long time engaged the attention of chemists; if we mix, for example, solutions of the salts AB and CD in aqueous solution, what happens? Before the advent of the hypothesis of ionisation, the three possibilities which presented themselves were (*a*) complete interchange, so that the resulting solution would contain only AD and CB, (*b*) partial interchange, the solution then containing all four salts, and (*c*) no change. Obviously the problem could not be efficiently investigated by attempting to isolate any of the salts, since equilibrium would be disturbed by their removal; many ingenious attempts were therefore made to throw light upon the question by indirect methods.

Gladstone's experiments on the interaction of ferric salts and thiocyanates were amongst the first which appeared to give a quantitative proof that interchange had taken place and that this interchange was partial (see p. 156). The fact that a green solution is obtained when cupric sulphate is treated with hydrochloric acid was considered to prove that some interchange had occurred since hydrated cupric chloride was known as a green salt and cupric sulphate as a blue one. When borax is titrated with sulphuric acid, using litmus as indicator, the wine-red colour characteristic of the weak boric acid appears at once and this eventually gives place to the bright red colour produced by strong acids. It was stated that this change of colour coincides with the addition of the exact equivalent of sulphuric acid necessary to combine with the soda, and hence it was concluded that entire interchange had taken place. Berthelot attempted to investigate the problem by thermal methods. Thus if we find independently the heats of formation of AB, CD, AD and CB in aqueous solution to be h_1, h_2, h_3 and h_4, respectively, we should, on mixing AB with CD, expect to obtain the thermal change represented by $(h_3 + h_4) - (h_1 + h_2)$ if complete interchange took place, or a corresponding fraction of this value if the interchange is partial. In this way he endeavoured to shew, for example, that complete interchange is effected when zinc nitrate is mixed with sodium acetate—'the strongest acid going to the strongest base.'

Hess, however, previously shewed that dilute aqueous solutions of neutral salts when mixed give, generally, no appreciable thermal effect (Law of 'Thermoneutrality'). This is of course easily intelligible in terms of the hypothesis of ionisation; the salts both being nearly completely ionised before and after mixing. It is sometimes the custom now to dismiss the consideration of this problem in these terms and to say that no further explanation is needed, i.e. that 'no acid is united with any base.' But this applies of course only to extremely dilute solutions; as regards stronger solutions the problem still remains. Theoretically, if we know the dissociation constants of the two salts, and the concentrations, we can calculate the distribution of the non-ionised parts and the ions of each salt; unfortunately, however, it is just in the cases under consideration—strong solutions of metallic salts—that the law of mass action does not hold.

The problem of the reciprocal action of salts assumes a different aspect if we consider a system in which the solid salts are in equilibrium with their saturated solution. Here the actual solid salts can be separated and identified, the distribution of metals and acid radicles in the solution is then no longer a matter of concern. In the study of these 'reciprocal salt pairs' when one speaks of one pair being stable at a given temperature, etc., reference is made to the solid salts only; the distribution of the constituents in the solution being disregarded. In the case of two salts AB and CD which are capable of mutual interaction, there is, in general, a definite transition temperature at which the four solid salts AB, CD, AD and CB can co-exist in equilibrium with the saturated solution and aqueous vapour. One of the pairs (say AB and CD) is the stable system below this temperature and the other pair (say AD and CB) above it. But just above or below this transition temperature it is not possible to obtain equilibrium between one salt pair, saturated solution and vapour. In order to obtain a saturated solution which has a definite concentration at a given temperature, one of the other salts must be present also. Thus if AB and CD are kept in contact with a limited quantity of water at a temperature just below transition point, a certain amount of double decomposition will take place and either AD or CB will separate in the solid

state. There is a certain interval of temperature, above or below the transition point in which, for equilibrium, it is necessary to have three solid salts present. Beyond this interval, however, equilibrium can be established when only two solid salts are present, i.e. *AB* and *CD* or *AD* and *CB*, as the case may be, can give rise to a saturated solution having a definite concentration for a given temperature. This transition point and transition interval are quite analogous to those considered in the case of double salts, but at the transition point we have, in the present case, four different solids instead of three, and during the transition interval three different solids instead of two.

Practical Work.

1. Exercises are given in the general methods of preparing metallic salts; for example, by action of acids on hydroxides, oxides or carbonates and by double decomposition of salts. Students must make it their object to obtain pure specimens well crystallised (when possible) and in good yield.

2. A general investigation is made on the behaviour of the commoner metals towards hydrochloric, sulphuric, nitric, and acetic acids and 'aqua regia.' The effects of dilution and of temperature are carefully studied, the character of the resulting salt is identified (whether -ous or -ic) if necessary, and the nature of the gaseous products is examined.

3. The usual method of classification of salts is illustrated by the preparation of specimens of (for example) (*a*) normal potassium oxalate, (*b*) acid potassium oxalate, (*c*) bismuth oxychloride and basic cupric sulphates, (*d*) alums and 'vitriols,' (*e*) potassium ferrocyanide.

4. Various transformations of salts are practised. For example, the preparation of zinc acetate from zinc sulphate, cuprous chloride from cupric sulphate, chromic chloride (in solution) from potassium bichromate, and so on.

CHAPTER XX.

BASES.

84. HAVING defined the terms 'acid' and 'salt,' a base is generally said to be a compound which, when acted upon by an acid, yields a salt *plus* water. This definition will, however, include both oxides and hydroxides of metals, and it is often now the custom to consider that a true base must contain hydroxyl, just as an acid must contain hydrogen; in this sense the basic oxides are regarded as 'anhydrides' of the true bases. It must be noticed also that the definition suggested is not applicable to ammonia, aniline, pyridine, etc., although these substances are often called bases; these, by action of acids, yield salts but not water also. Hence their 'basic' behaviour is usually explained by assuming their combination with water to form ammonium hydroxide, 'anilonium' hydroxide, and so on.

By *basic character* is generally understood 'ant-acid' character, a base having the property of annulling or 'neutralising' the properties described above as 'acidic.' The term *alkaline* is often used in the same sense, although this word is sometimes restricted to the property of producing certain colour changes in indicators.

The expression 'acidity of a base' is used in the same way as 'basicity of an acid'; it might shortly be defined as the number of molecules of a monobasic acid with which one molecule of the base is capable of reacting. This number is generally determined by the 'isolation of salt' method which was previously described, and the results so obtained are consequently, to the same extent, indefinite. To ascertain the number as regards the reaction of a base in solution, one may of course proceed by thermal determinations in a manner quite analogous to that employed in finding the basicity of an acid.

There are numerous reasons for considering that bases are hydroxy-compounds, but they are mostly indirect. For example: it is found in the case of most organic oxygen-containing acids that the typical action of phosphorus halides is to introduce one atom of halogen in place of one atom of oxygen and one atom of hydrogen. This replacement of O and H by X, may often be effected, in one molecular weight of the acid, as many times as the acid is basic, e.g. with phosphorus pentachloride, acetic acid yields CH_3COCl and succinic acid yields $C_2H_4(COCl)_2$. It is natural therefore to conclude that the 'basic' hydrogen atoms of the acids are intimately associated with oxygen. Alcohols behave in a similar way, O and H, collectively, being replaced by halogen. Alcohols can also react with acids, under appropriate conditions, to give esters, and the number of different esters which an alcohol can yield with a monobasic acid coincides with the number of times that the phosphorus halide can replace an oxygen and a hydrogen atom by a halogen atom. Hence both alcohols and the oxygen-containing acids are represented as containing the OH group. But the formation of esters from alcohols is in many respects quite analogous to the formation of salts from bases. [It was at one time the custom, in fact, to call esters 'etherial salts,' but they are now differentiated from salts owing to their non-electrolytic character.] Hence both alcohols and inorganic bases are represented as $R^n(OH)_n$ where n is the 'hydricity' of the alcohol on the 'acidity' of the base. It must be remembered, however, that the evidence for the presence of the hydroxyl group in bases is often far less conclusive than in the case of alcohols. In the action of hydrochloric acid on, say, slaked lime, there is little to choose between the two equations

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$

and

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

For convenience in classification and for systematic representation of the reactions, there is a considerable advantage in writing the formulæ of hydrated metallic oxides as hydroxides, but it must not be supposed that such formulæ are firmly established by experiment.

[Attention may here be drawn to the fact that, until quite recently, many chemists employed the term 'hydrate' in an

ambiguous way; $Ca(OH)_2$, for example, was called calcium hydrate, and yet $CuSO_4 . 5H_2O$ was called a hydrate of cupric sulphate. The word meant then either 'compound of hydroxyl' or 'compound of water.' The calcium compound mentioned may of course be regarded as $CaO . H_2O$, but then it is a hydrate of *calcium oxide*, not of *calcium*.]

A 'normal' hydroxide of a metal is regarded as one in which all the available valencies of the metal are combined with hydroxyl, i.e. $M^n(OH)_n$. If, on the other hand, we regarded the substances as compounds of the oxides with water, the general formula will be $M^{2n}O_n . nH_2O$; that is there will be as many molecules of combined water as there are atoms of oxygen in the formula employed for the oxide. [It must be observed that it is only in comparatively few cases that these 'normal' hydroxides are actually obtained when the metallic hydroxides are prepared by precipitation, etc.; the proportion of water being, usually, more or less variable, i.e. their composition is $(M^{2n}O_n)_x (H_2O)_y$.]

[Oxides of the type $\left(M^nO_{\frac{n}{2}}\right)_x$ are classified as basic oxides. Observe that the valency n of the metal is that deduced from the composition of the salts which are produced in the change, oxide + acid = corresponding salt + water *only*.]

Compounds of this 'normal' type derived from non-metals are usually called ortho-acids, e.g. orthosilicic acid $= Si(OH)_4$ or $SiO_2 . 2H_2O$, orthoboric acid $= B(OH)_3$ or $B_2O_3 . 3H_2O$. [Unfortunately, however, this terminology is not always strictly adhered to; orthophosphoric acid for instance should be $P(OH)_5$ instead of $PO(OH)_3$.] A similar definition may be applied to various organic acids if the restriction is made that the typical nucleus of the acid must be preserved, e.g. orthoformic acid $= HC(OH)_3$ and orthoacetic acid $= CH_3 . C(OH)_3$.

85. 'Strength of bases.'

The remarks previously made with regard to the question of 'strength' in acids, apply, to a large extent, also to bases. (*a*) One may, for example, compare the strengths of two bases by allowing them to compete, in equivalent quantity, for a limited amount of an acid. Berthelot made measurements

of this kind by the thermal method; he shewed, for example, that in the competition for an acid between equivalent weights of soda and ammonia, the former base appropriates practically the whole of the acid; also that ammonia and methylamine divide the acid between them in almost equal proportions [*C. R.* 1880 (91) 139]. (*b*) Various 'velocity' methods may be employed, more particularly those in which the rate of saponification of esters is measured. (*c*) The order of the electric conductivity of solutions of bases also gives a rough measure of their relative strengths. (*d*) In the case of weak bases, the degree of hydrolysis of the salt of the base with a strong acid will also afford a measure of the strength of the base (see page 293). (*e*) Various colorimetric methods of comparing the strengths of bases have been employed in a manner analogous to that referred to under Acids (page 265). Menschutkin, for example, in 1883 attempted to compare the strengths of bases, such as potash, aniline and triethylamine, by the effects produced when alcohol is added to their aqueous solutions in presence of phenolphthalein as indicator. Veley has recently [*Trans. Chem. Soc.* 1908, 411 and 1909, 1] succeeded in comparing the strengths of several weak bases by colorimetric observations, using methyl orange as indicator.

Ionic interpretations. A base, in terms of the theory of electrolytic dissociation, is a substance which can yield hydroxyl ions when dissolved in water and the strength of a base is measured by the concentration of these ions at a given dilution. If therefore we can ascertain the degree of ionisation m of the base at a given dilution V, we can express the strength numerically as the dissociation constant of the base, i.e. for a monacid base, $\frac{m^2}{(1-m)V} = K$. The degree of ionisation can be obtained, as in the case of acids, by osmotic methods, or better, by the conductivity. There is of course the same difficulty with regard to strong bases as with strong acids in that the dilution law is not obeyed.

The order of the electric conductivities of bases is less approximately proportional to their degrees of ionisation than is the case with regard to acids, since, although the mobility of the hydroxyl ion is relatively large in comparison with the positive

ions, or kations, the difference is less marked than that between the mobility of the hydrogen ion and the anions. This will be apparent from the following list of the relative mobilities of some of the commoner ions at 18°, as determined by Kohlrausch:

H 318, OH 174, Br 67·6, I 66·4, Cl 65·4, (NO_3) 61·7, K 64·7, (NH_4) 64·4, Ag 54, Na 43·5, ½ Ba 57·3, ½ Sr 54, ½ Ca 53.

The fact that esters, such as methyl or ethyl acetate, are the more rapidly saponified the stronger the base employed, is explained by regarding hydroxyl as the active agent; the essential change, for example, in the saponification of ethyl acetate would be regarded as

$$EtA + OH' = EtOH + A'.$$

This hypothesis is to some extent supported by the observation that with the strongest bases the rate of saponification of the ester is nearly independent of the nature of the kation. Determinations of the relative strengths of bases by this method were first made by Warder in 1881, and afterwards, in a more reliable way, by Ostwald. In solutions containing one equivalent weight in 40 litres, at 25°, Ostwald obtained the following relative numbers for the velocity constants:

LiOH 165, NaOH 162, KOH 161, TlOH 148, NEt_4.OH 131, NEt_3 22, NEt_2H 26, $NEtH_2$ 19, $NMeH_2$ 19, NMe_3 7·3.

The substituted ammonias are therefore all stronger than ammonia itself, but the influence of the number of similar replacing groups is not always quite regular. The remarkable difference between the fully substituted ammonium hydroxide and the amines, or ammonia, is probably connected with the circumstance that the incompletely substituted ammonium hydroxides are able to dissociate into free amine and water. Thus the weakness of ammonia in solution, as a base, is due to the small concentration of hydroxyl ions present; this, however, may depend not only on the small value of the dissociation constant of NH_4OH but also on the readiness with which NH_4OH dissociates into NH_3 and H_2O.

[In determining the relative strengths by this method it is found that complications may arise in the case of ammonia and

amines, owing to an influence exerted on the rate of change by the ammonium salt, or amine salt, produced and the numbers are therefore calculated for the initial change.]

Bredig shewed, by the conductivity method, that the compounds PMe_4OH, $AsMe_4OH$ and $SbMe_4OH$ are strong bases, their strength being of about the same order as that of NEt_4OH or NMe_4OH. These compounds may be regarded as derivatives of PH_3, AsH_3 and SbH_3 (or rather of the hydroxides PH_4OH, AsH_4OH and SbH_4OH which are presumed to be formed when they act as bases). Here again therefore the effect of the replacement has been to convert extremely weak bases into strong ones.

Practical Work.

1. A study is made of the usual methods for preparing metallic hydroxides. Quicklime is first 'slaked' with water and the resulting calcium hydroxide is made into 'milk of lime' by rubbing it with a sufficient quantity of water. A solution of sodium (or potassium) carbonate (about 1 in 12) is then heated to boiling in an iron vessel and the calcium hydroxide is gradually added in small portions at a time, until a portion of the clear liquid (after settling of the solid) gives no effervescence when treated with an acid.

Note that the change is a 'reversible' one, and the conditions have therefore to be carefully observed. A slight excess of calcium hydroxide may be added, for although this compound is appreciably soluble in pure water, its solubility is greatly diminished by the large concentration of OH'. (Compare page 218.)

2. The solution of sodium (or potassium) hydroxide obtained in this way, is now used for the preparation of various other metallic hydroxides, which are sparingly soluble in water, by precipitation from their salts.

3. A comparison is made in the behaviour of solutions of ammonia and of sodium (or potassium) hydroxide upon various metallic salts. [For example, upon solutions of

$$FeCl_3,\ MgSO_4,\ CuSO_4,\ NiSO_4,\ CoCl_2,\ CaCl_2,\ \text{etc.}]$$

The reagents are added gradually until in excess; the results are carefully noted and the theoretical explanations studied.

4. Experiments are made with the given oxides with a view of ascertaining in each case whether, according to its general behaviour, the oxide should be more appropriately classified as basic oxide, peroxide, acidic oxide or a compound of two of these classes.

CHAPTER XXI.

NEUTRALISATION AND HYDROLYSIS

86. Neutralisation.

The term 'neutral' has been generally used, in connection with solutions of salts, etc., in somewhat vague fashion to mean neither 'acidic' or 'alkaline'; the test for this condition, however, has depended almost entirely upon the behaviour towards indicators so that the same substance might be acidic, neutral or alkaline, according to the indicator employed. The hypothesis of ionisation enables us to give a more precise meaning to the term; since 'acidity' is due to hydrogen ions and 'alkalinity to hydroxyl ions it follows that 'neutrality' will be attained when the concentration of these two ions is equal (or where both ions are absent). The neutralisation of an acid by a base consists, in terms of this theory, in the combination of hydrogen ions of the acid with hydroxyl ions of the base to form water; if therefore the acid (HX), the base (MOH) and the resulting salt (MX) are all completely ionised, under the conditions employed in the experiment, the process of neutralisation would be simply represented as

$$\dot{H} + X' + \dot{M} + OH' = \dot{M} + X' + HOH, \text{ i.e. as } \dot{H} + OH' = HOH.$$

These conditions practically exist when the strongest acids react with the strongest bases in dilute aqueous solution. If the acid or base, or both, are not completely ionised to start with, i.e. if they are only moderately strong, the change will consist not exclusively in the combination of $\dot{H}'$ with OH since further ionisation must occur before the process is practically completed. In the case of very weak acids and bases the process is incomplete, i.e. a portion of the weak acid or base, or both, remains un-ionised.

The heats of neutralisation of the strongest acids with the strongest bases are found to be practically the same—about 13700 gram calories for one gram equivalent, each, of acid and base. Hence the heat evolved in these cases is assumed to be that due to the combination of $\dot{H}$ with OH'. Any deviation from this constant heat of neutralisation is, in the case of moderately strong acids and bases, attributed mainly to the thermal change attending the completion of the ionisation. Thus, if a moderately strong acid is neutralised by one of the strongest bases and the heat of neutralisation is found to be Q calories, it is assumed that $(13700 - Q)$ represents the thermal change attending the ionisation of that portion of the acid which was originally un-ionised. The heats of neutralisation of some of the commoner acids by sodium hydroxide are as follows:

HCl 13700, HNO_3 13700, HI 13700, HBr 13800, $HClO_3$ 13800, $CH_3.COOH$ 13400, $\frac{1}{2}H_2SO_4$ 15700, HPO_3 14300, $H(PH_2O_2)$ 15100, HF 16300.

It will be observed that the deviation from the 'constant' 13700 is sometimes positive and sometimes negative. This circumstance was, at one time, regarded as affording a powerful argument against the ionic explanation of neutralisation, since it was tacitly assumed that ionisation must be an endothermic process, i e. that heat must be absorbed when a compound dissociates into its ions. If this were the case the heat of neutralisation should never be greater than 13700 and the deficiency from 13700 should be greater the weaker the acid. But Arrhenius was able to shew, as has previously been stated, that the heat of ionisation may be either positive or negative; in the majority of cases the process of ionisation is an exothermic one. The heat of ionisation of hydrofluoric acid, for example, calculated from the rate of change of dissociation constant (measured by conductivity) with temperature, by means of van 't Hoff's formula, was found to be +3200; this number subtracted from the heat of neutralisation as determined by Thomsen, gives a number not far from the common constant. All acids therefore which have a greater heat of neutralisation than 13700 must ionise with evolution of heat. (Compare page 213.)

In pure water we have an ideal example of a neutral liquid; yet it can be shewn in various ways that both hydrogen ions and hydroxyl ions are present, of course in equivalent amounts. Water is therefore both an acid and a base. The concentration of hydrogen and hydroxyl, although exceedingly minute, has been measured in various ways, and the results of the determinations shew a remarkably close agreement. Kohlrausch shewed that the conductivity of distilled water becomes less and less the more carefully it is purified, but a limit is eventually reached; the purest water obtainable therefore has a measurable conductivity. The same author and Heydweiler found for the purest water the specific conductivity $0{\cdot}043 \times 10^{-6}$ at 18°. [From determinations of the influence of temperature on the conductivity they calculated that for absolutely pure water the value would be $0{\cdot}0386 \times 10^{-6}$ at 18°.] From this number, if we know the mobilities of hydrogen and hydroxyl, we can calculate the degree of dissociation of water.

Another method depends on the determination of the rate of hydrolysis of methyl acetate in pure water. As this change proceeds, the concentration of hydrogen ions increases and that of the hydroxyl ions diminishes; but experiment shews that the change is accelerated much more by hydroxyl than by hydrogen, the influence of the former being about 1400 times as great as that of the latter. Hence the reaction velocity will reach a minimum when the concentration of the $\dot{H}$ is 1400 times as large as that of the OH'. By determining this minimum velocity and the amount of free acid present, Wijs calculated the degree of dissociation of pure water [*Zeit. Phys. Kal. Chem.* 1893 (12) 167]. Other methods depend on the determination of the degree of hydrolysis of salts and on the measurement of the electromotive force of an acid-alkali cell.

From Kohlrausch's numbers the concentration of the hydrogen ions, and of the hydroxyl ions, in pure water is, in gram-ions per litre, $0{\cdot}8 \times 10^{-7}$ at 18° and $1{\cdot}09 \times 10^{-7}$ at 26°. Pure water then, is about a ten-millionth normal solution of hydrogen ions and the same of hydroxyl ions. From the law of mass action we have $\dot{H} \times OH' = K H_2O$, the symbols being used here to denote the respective concentrations, and K being the dissociation constant of water. Since, however, the concentration of the non-ionised

water is enormous in comparison with that of the ions, its active mass may be taken as constant; the product of the concentrations of H and OH is therefore constant and is usually called the dissociation constant of water ($= K_w$).

If we know the value of K_w at different temperatures we can calculate the heat of ionisation by means of van 't Hoff's formula $\frac{d.\log K}{dT} = -\frac{Q}{RT^2}$, and the results so obtained agree well with the value found from the heats of neutralisation of the strongest acids and bases. [As a matter of fact the converse process was first made use of, i.e. Kohlrausch and Heydweiller calculated the change of K_w with temperature by making use of the neutralisation constant, $Q = 13700$.]

87 Hydrolysis.

All chemical changes in which water takes an essential part as indicated by the chemical equation, other than by direct addition (hydration), are generally referred to as 'hydrolytic' actions. For example, the action of water on cane-sugar to produce dextrose and laevulose, on starch to produce various dextrins and maltose, on nitriles or on amides to produce ammonium salts of corresponding acids, on esters to produce alcohols and acids, on halogen derivatives to produce hydroxy-compounds, or on salts to produce acids and bases—all of these changes are spoken of as 'hydrolytic.' The term is also used for the decomposition of various complex naturally occurring substances, such as proteins, glucosides, etc., when they are acted upon by acids, or by enzymes, in presence of water.

We shall confine ourselves, mainly, in the present instance to a brief consideration of the hydrolytic action of water upon salts—a change referred to as salt-hydrolysis or simply, as hydrolysis ('hydrolytic dissociation' is sometimes used but is evidently open to objections).

The action of the strongest acids upon strongest bases takes place in aqueous solution 'completely' in the sense that, if exactly equivalent quantities are taken, our methods of qualitative and quantitative analysis are unable to detect any trace of acid or base

remaining. If either the acid or the base, or both, are weak, it is easy to shew that the change is incomplete and reversible or,

$$\text{acid} + \text{base} \rightleftarrows \text{salt} + \text{water}.$$

Until a comparatively recent date the only conclusive methods of practically demonstrating the reverse change, the hydrolysis of salts, were those which depended upon the removal of one of the products from the sphere of action. The hydrolysis of bismuth chloride, for example, can be shewn by isolation of the precipitated oxychloride; that of ferric chloride can be demonstrated by dialysis of its aqueous solution, hydrochloric acid diffusing through the membrane and colloidal ferric hydroxide eventually remaining behind. The hydrolysis of many ammonium salts and of sodium phenoxide may be shewn by mere distillation with water, the ammonia or phenol respectively, being identified in the distillate. The hydrolysis of borates is indicated by the fact that in very dilute solution borax will precipitate silver oxide instead of borate, from a solution of silver nitrate; that of potassium cyanide can be detected by the odour of hydrocyanic acid obtained on heating its aqueous solution. Such experiments, however, shew nothing with regard to the extent to which the change would occur in a homogeneous system; equilibrium might have been attained when a millionth part of the salt was hydrolysed and the equilibrium would then be shifted by the removal of one of the products, further hydrolysis thereby resulting.

An interesting experiment is described by Emich [*Ber.* 1907, 1482] by which the hydrolytic decomposition of sodium chloride may be demonstrated. A small quantity of sodium chloride is introduced into a platinum crucible heated to bright redness and a drop or two of water is then added so that the water assumes the spheroidal state. After about half a minute the drop of water remaining is quickly transferred to a vessel containing a very weak blue litmus solution; the residue remaining in the crucible is dissolved in water and tested with dilute red litmus. The result shews that the first mentioned aqueous solution is acid and the residue alkaline.

When, however, it is desired to shew the existence of hydrolysis in aqueous solution and to measure its extent, methods must be

employed which cause no disturbance of the equilibrium. The want of neutrality in a solution of a normal salt is generally regarded as a qualitative proof that hydrolysis has occurred; it is possible, however, in certain cases for a salt to undergo hydrolysis and yet for the solution to remain neutral. The quantitative methods of ascertaining the extent or degree of hydrolysis will be referred to below.

Ionic explanation.

The decomposition of a salt by water into free acid and free base may be looked upon as an example of the division of a base between two acids, one of which is water. There is nothing new in this conception of the process; Thomsen, for example, explained in this way the fact that the heat of neutralisation of very weak acids, like silicic acid, diminishes as the proportion of water is greater. Water, he regarded as a monobasic acid H.OH analogous to hydrosulphuric acid H.SH and when sodium silicate was dissolved in water, the silicic acid and the water competed for the base. In the case of stronger acids the 'avidity' of the acid H.OH was immeasurably small in proportion, so that the effect of this competition was unrecognisable, whereas the avidities of silicic acid and water were somewhat of the same order.

In terms of the ionisation hypothesis the general idea is the same but the 'division of a base between two acids' is regarded quite in a different way, as was indicated above (see page 262). If we consider the case of the salt of a very weak monobasic acid HX with a strong monacid base MOH, the change which takes place on hydrolysis is then to be regarded as depending upon the total result of the various equilibria represented by

$$(1)\ \mathrm{HOH} \rightleftarrows \dot{\mathrm{H}} + \mathrm{OH}', \qquad (2)\ \mathrm{MOH} \rightleftarrows \dot{\mathrm{M}} + \mathrm{OH}',$$

$$(3)\ \mathrm{HX} \rightleftarrows \dot{\mathrm{H}} + \mathrm{X}' \quad \text{and} \quad (4)\ \mathrm{MX} \rightleftarrows \dot{\mathrm{M}} + \mathrm{X}'.$$

The salt MX and the strong base MOH are both largely ionised at moderate dilution and the hydrolysis will consequently be mainly conditioned by the active masses and dissociation constants concerned in the changes $\mathrm{HOH} \rightleftarrows \dot{\mathrm{H}} + \mathrm{OH}'$ and $\mathrm{HX} \rightleftarrows \dot{\mathrm{H}} + \mathrm{X}'$. The concentrations of $\dot{\mathrm{H}}$ and OH' in water are of course extremely small, whereas that of X' is considerable; hence if the dissociation

constant of HX is small, the $\dot{H}$ ions from the water will rapidly be used up in formation of slightly ionised HX, further ionisation of HOH resulting. The principal change taking place may therefore be approximately represented as

$$\dot{M} + X' + H{\cdot}OH \rightleftarrows \dot{M} + HX + OH'.$$

The result is therefore that in the solution obtained there is a considerable concentration of OH′ in excess of $\dot{H}$, i.e. the solution becomes alkaline.

Conversely, if we start with the salt MX of a strong acid HX and a weak base MOH we shall have, to a large extent,

$$\dot{M} + X' + H{\cdot}OH \rightleftarrows M{\cdot}OH + X' + \dot{H},$$

so that the resulting solution will be acid

In regarding the matter from a quantitative standpoint it is of course necessary to take into consideration the influence of all the reacting substances upon the final equilibrium. A simple approximate calculation may be made, however, if we assume that the salt MX and the strong base (or the strong acid as the case may be) are practically completely ionised. Thus, taking the salt MX of a strong base and very weak acid, let one molecule of the salt be dissolved in water and let V be the volume of the solution, K_a the dissociation constant of the acid and x the degree of hydrolysis of the salt when equilibrium is established. Since the acid is very weak (and since moreover its degree of ionisation is further reduced by the presence of a considerable concentration of X′ ions) we may regard it as being practically non-ionised. The active mass therefore of the free acid may be taken as $\frac{x}{V}$. The part of the salt which remains un-hydrolysed is, according to our assumption, practically completely ionised; hence the active mass of the X′ ions is $\frac{1-x}{V}$.

The active mass of the OH′ ions may be taken to be the same as that of the free acid, $= \frac{x}{V}$, since the acid and base are produced in equivalent quantity and the base is, by assumption, completely ionised. In order to find the concentration of the $\dot{H}$ ions we make use of the relation $\dot{H} \times OH' = K_w$ (see page 290). The active mass of the H ions will therefore be $\frac{K_w}{OH'}$, i.e. in our present example, $\frac{K_w V}{x}$.

We shall have therefore the active masses

$$\dot{H} = \frac{K_w V}{x}, \quad OH' = \frac{x}{V}, \quad HX = \frac{x}{V} \text{ and } X' = \frac{1-x}{V}.$$

As regards the equilibrium $HX \rightleftarrows \dot{H} + X'$, there will be the relation

$$\frac{x}{V} K_a = \frac{K_w V}{x} \cdot \frac{1-x}{V} \quad \text{or} \quad \frac{K_w}{K_a} = \frac{x^2}{(1-x)V} \tag{1}.$$

From this calculation it is evident that the degree of hydrolysis of the salt of a weak acid and strong base will depend on the relative values of the dissociation constants of the acid and of water; the smaller the dissociation constant of the acid the greater the hydrolysis. The formula also shews that if the degree of hydrolysis is small, i.e. if $(1-x)$ does not differ much from unity, the degree of hydrolysis will vary nearly as the square root of the dilution. This last result follows of course, just as well if we regard the process in the old way as consisting in the decomposition of the salt by water into acid and base (see page 152).

If both the acid and the base, from which the salt is derived, are weak the salt will be hydrolysed to a greater extent than in the cases previously mentioned. If we take the simplest example where both acid and base are so weak that we may regard them as practically non-ionised in the solution obtained, and if as before we regard the non-hydrolysed part of the salt as completely ionised, we shall have, practically,

$$\dot{M} + X' + H \cdot OH \rightleftarrows M \cdot OH + HX.$$

Taking as before one molecule of the salt MX, the concentrations, when equilibrium is established, will be

$$\frac{1-x}{V} \text{ of } \dot{M}, \quad \frac{1-x}{V} \text{ of } X', \quad \frac{x}{V} \text{ of HX and } \frac{x}{V} \text{ of MOH}.$$

Therefore as regards the equilibrium between the base and its ions,

$$\frac{x}{V} \cdot K_b = \frac{1-x}{V} \cdot OH'$$

when K_b is the dissociation constant of the base and the symbol OH' represents the concentration of the hydroxyl ions.

Similarly for the acid we shall have

$$\frac{x}{V} \cdot K_a = \frac{1-x}{V} \cdot \dot{H}.$$

Multiplying the first by the second,

$$K_b \cdot K_a = \frac{1-x}{x} \cdot \frac{1-x}{x} \cdot OH' \cdot \dot{H} = \frac{(1-x)^2}{x^2} \cdot K_w \tag{2}.$$

Observe that in this case V cancels out; i.e. the degree of hydrolysis is independent of the dilution.

We may express these relations in terms of acid, base and salt as follows: Let A, B and S represent the concentrations of the free acid, free base, and un-hydrolysed salt respectively, when equilibrium is established. Then for the hydrolysis of the salt of a weak acid and strong base, or of a weak base and strong acid, $\frac{A \times B}{S}$ is constant. But when both acid and base are very weak

$\frac{A \times B}{S^2}$ is constant, since the concentrations of M and of X in the formula (2) are practically the same as that of the un-hydrolysed part of the salt.

88. Determination of the degree of hydrolysis.

Any method which serves to estimate the concentration of free acid, or free base in the solution, without disturbance of the equilibrium, will give a direct measure of the degree of hydrolysis. Titration with alkali or acid is of course out of the question, but it is possible in some cases to obtain, approximately at any rate, quantitative results by observation of the depth or tint in the colour produced by certain indicators (see page 265). In the case of the salt of a weak base and strong acid one may employ the various velocity methods for determination of the concentration of hydrogen ions, such as the inversion of cane sugar or catalysis of methyl acetate. [See Walker and Wood, *Trans. Chem. Soc.* 1903, 484.] For salts of weak acids and strong bases, the hydrolysis of esters is suitable since as previously stated this change is particularly sensitive to hydroxyl ions.

If we know the dissociation constant of water and of the weak acid or base, we may calculate the degree of hydrolysis of its salt (with a strong base or acid respectively) by means of the formula given above. [See for example Walker, *Trans. Chem. Soc.* 1900, 5 and *Zeit. Physikal. Chem.* 1900 (32) 137.]

Another method is based on the measurement of the equivalent conductivities of the salt at dilutions of 32 litres and 1024 litres (see page 248). In the case of the sodium salt of a weak monobasic acid, for example, if hydrolysis occurs, Δ will exceed 10 units, the increased conductivity at the greater dilution (in excess of the normal increase) being attributed to the liberation of free base.

It may happen that either the acid or the base produced on hydrolysis may be soluble in some solvent, such as benzene, which is only partially miscible with water. If then we have previously determined the partition coefficient of this acid, or base, between benzene and water (see page 318) the degree of hydrolysis of the salt may be determined by shaking up its aqueous solution with benzene and ascertaining the concentration of the acid, or base, in the resulting benzene solution. [See Farmer, *Trans. Chem. Soc.* 1901, 863.]

89. Psuedo acids and psuedo bases.

A considerable number of compounds are now known which are themselves non-electrolytes and neutral and in which hydrogen cannot be directly replaced by metals, but which are capable of undergoing tautomeric change by which they become acids. Examples are found in the nitroparaffins, nitrophenols, nitrolic acids, oximino-ketones, quinone-oximes, etc. Thus nitromethane $CH_3.NO_2$ is a normal nitro-compound which has no acid reaction, very slight electric conductivity and gives no colour with ferric chloride. In contact with baryta water, in equivalent quantity, at 0°, the conductivity of the solution gradually falls, shewing that the strong base is slowly neutralised. Alcoholic sodium hydroxide yields the salt of the composition CH_2NaNO_2 and this gives a red colour with ferric chloride. Again, when the barium salt is gradually titrated with hydrochloric acid, using methyl-orange as indicator, the pink colour of the indicator is shewn on each addition of the acid but it disappears again and only becomes permanent when the acid has been added in equivalent quantity; the resulting solution now gives no colour with ferric chloride shewing that the original form of the substance has been reproduced. There seems to be little doubt that these results are due to the reversible change of $CH_3.NO_2$ into $CH_2:N\begin{matrix}O\\ \diagdown OH\end{matrix}$, the latter having acidic properties. In this acid, and in nearly all other cases, only one of the forms can actually be isolated but Hantzsch and Schultze have succeeded in obtaining two forms of phenyl-nitro-methane. One of these is a crystalline substance which behaves as an electrolyte and is a strong acid; in contact with acids it changes into an oily isomer which is neutral and non-electrolytic. Slow neutralisation may be observed when this oily substance is brought into contact with alkalis, since it then passes gradually into the acidic form, i.e. $C_6H_5CH_2.NO_2$ becomes $C_6H_5CH:N\begin{matrix}O\\ \diagdown OH\end{matrix}$.

Substances which behave in the manner here indicated are called by Hantzsch pseudo acids. They are characterised not only by the phenomenon of slow neutralisation but in many other

ways, amongst which the following may be referred to. [See Hantzsch, *Ber.* 1899, 575; 1902, 210, etc.]

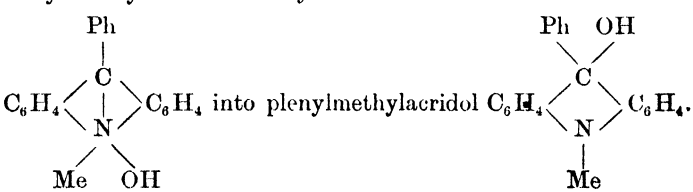
(*a*) The original non-electrolytic compound may be colourless and the salts of the acidic form coloured; this happens for instance, in the case of violuric acid $CO\langle^{NH—CO}_{NH—CO}\rangle C=N.OH$ which in the free state is colourless but forms salts which are red, blue, etc. Phenolphthalein appears to be another example (see page 305).

(*b*) The original neutral substance does not form a compound with ammonia in a non-ionising solvent but does so in presence of water, etc.

(*c*) If the neutral, or feebly acid, original compound gives salts which are neutral or feebly basic, i.e. which are not hydrolysed or scarcely hydrolysed, the compound is a pseudo acid. [Compare, however, Kauffman, *Zeit. Physikal. Chem.* 1904 (47) 618.]

(*d*) Pseudo acids have an abnormally large positive temperature coefficient of conductivity and (*e*) do not combine directly with water or alcohol but may yet indirectly yield stable hydrates or alcoholates.

Pseudo bases are compounds which have not themselves basic properties but which by action of acids undergo tautomeric change, becoming strong electrolytes of the ammonium hydroxide type. Alkalis effect the reverse change, the hydroxyl group which in the strong basic form was attached to nitrogen, now becomes attached to carbon. An example given by Hantzsch is the slow transformation of phenylmethylacridinium hydroxide



90. Amphoteric electrolytes. A considerable number of compounds are known which can behave as acids towards bases and as bases towards acids. Amongst inorganic compounds we have familiar examples in the hydroxides of zinc, aluminium, chromium, lead, etc. According to the ionisation hypothesis these substances must be capable of yielding both hydrogen ions and hydroxyl ions.

Zinc hydroxide, for example, appears to ionise as $(ZnO_2)'' + 2\dot{H}$ and also as $\ddot{Z}n + 2OH'$, aluminium hydroxide as $(AlO_2)' + \dot{H}$ (perhaps also as $(AlO_3)''' + 3\dot{H}$, etc.) and as $\ddot{A}l + 3OH'$; lead hydroxide appears to give $(PbO_2)'' + 2\dot{H}$, $(PbO.OH)' + \dot{H}$, $\ddot{P}b + 2OH'$ and $(PbOH)^{\cdot} + OH'$. In alkaline solution therefore, the metal forms part of a complex anion whereas, in acid solution, it behaves as a kation or it may form part of a complex kation.

Particularly interesting and important examples of amphoteric electrolytes are furnished by the simple amino-acids, such as glycine, leucine, asparagine, etc.; and many of the proteins also exhibit this character. The acidic character of amino-acids is evident from the fact that they form salts with bases and that they undergo esterification with alcohols; the basic character is seen in their capability of forming well marked salts with acids. Thus glycine not only yields metallic salts but also the ester, hydrochloride, and ester-hydrochloride

$$NH_2.CH_2COOEt, \qquad HCl.NH_2CH_2COOH$$

and

$$HCl.NH_2.CH_2COOEt.$$

In aqueous solution, glycine must therefore, presumably, yield both hydrogen ions and hydroxyl ions, and if we regard the nitrogen bases in solution as hydroxy-compounds (see page 281) the non-ionised molecule of glycine in solution must be

$$OH.NH_3.CH_2COOH.$$

Since this ionises as an acid and also as a base, we shall have

$$OH.NH_3CH_2COOH \rightleftarrows (OH.NH_3CH_2COO)' + \dot{H}$$

and also

$$OH.NH_3CH_2COOH \rightleftarrows (NH_3CH_2COOH)^{\cdot} + OH'.$$

In addition, the amphoteric electrolyte will 'neutralise itself,' the acidic part reacting with the basic part to form a salt. There is the possibility that two molecules of the electrolyte may interact in this way or that the salt formation may occur in a single molecule; in the latter case we should obtain the 'internal salt,'

$$\begin{array}{l} CH_2 - NH_3 \\ | \quad\quad | \\ CO - O \end{array}$$

[This 'self-neutralisation' of an amphoteric compound may be supposed also to occur in the case of the inorganic substances

referred to above; thus when aluminium chloride reacts with sodium aluminate in aqueous solution, the aluminium hydroxide which is precipitated is derived from both compounds and may be regarded as aluminium aluminate $Al(AlO_3)$.]

Generally, then, if an amino-acid is dissolved in water we shall have present the non-ionised acid H.R.OH, the 'internal salt' and the ions H, OH', (ROH)' and (HR)'. The simple dilution law of Ostwald is not obeyed in these cases but it has been shewn by Walker [*Proc. Roy. Soc.* 1904 (73) 155 and (74) 271] that it is possible to express the concentration of the various ions present in terms of the concentration of the non-ionised substance, the dissociation constants of the substance as an acid and as a base, respectively, and the dissociation constant of water.

A compound which has considerable interest in this connection is cacodylic acid $(CH_3)_2 As\begin{matrix}=O\\ \diagdown OH\end{matrix}$ which from its general behaviour one would naturally classify as an amphoteric electrolyte. It has well marked acidic properties as shewn by the isolation of its metallic salts and by the fact that it can be sharply titrated with caustic alkalis, using phenolphthalein as indicator; it does not, however, form salts with ammonia. On the other hand, it combines directly with acids forming, for example, a hydrochloride, nitrate and hydrofluoride; the presence of hydroxyl ions in its aqueous solution is indicated by its accelerating influence on the bi-rotation of dextrose. [Compare Zawidzki, *Ber.* 1903, 3325.] It will be noticed that the formula given only contains one atom of hydrogen and its amphoteric character cannot therefore be represented, as in the amino-acids, on the type H.R.OH. According to Hantzsch [*Ber.* 1904, 1076], however, the compounds formed with acids are not derived from cacodylic acid itself but from its hydrate, e.g. the hydrochloride is not

$$(CH_3)_2AsOCl,$$

as it should be if cacodylic acid acts as a base, but

$$(CH_3)_2As(OH)_2Cl.$$

He considers therefore that the substance is not really an amphoteric electrolyte, but that in aqueous solution there is equilibrium

between cacodylic acid, which behaves as an acid and its hydrate, which acts as a base.

91. Indicators.

The methods of demonstrating the presence of free acid or free base in aqueous solutions, have already been referred to in the foregoing chapters. We shall consider here the application of some of these methods for practical purposes, such as for the indication of the point of neutrality in qualitative and quantitative analysis. For such purposes, use is made, almost exclusively, of certain organic substances which undergo a marked change of colour when their acid solutions are made alkaline or their alkaline solutions are made acid. There are, it is true, a few acid-alkali indicators which depend on the reactions of inorganic compounds, e.g. the liberation of iodine from a mixture of an iodide and iodate, or the change of chromate to bichromate, by action of acids. Measurements of the electric conductivity may also be employed with the same object, as was first suggested by Kohlrausch. Thus Küster has shewn that on titrating a dilute solution of hydrochloric acid with caustic soda, the conductivity diminishes at first owing to the replacement of the rapidly moving hydrogen ions by the more slowly moving sodium ions (see page 284); after the neutral point is passed, however, the conductivity again increases owing to the presence of the hydroxyl ions as well as to the increase in the sodium ions. The 'end point' in the titration is therefore that where the conductivity is at a minimum.

It must not be supposed that the 'end-point' observed in acid-alkali titration, when a colour indicator is used, necessarily corresponds with 'neutrality' in the strict sense of the term. Thus at 24° the concentration of hydrogen ions × the concentration of hydroxyl ions = 10^{-14} gram ions per litre; in a neutral solution the concentration of each is therefore 10^{-7}. But the concentration of hydrogen ions at which methyl orange changes colour lies between 10^{-4} and 10^{-5}; and in the case of litmus it is about 10^{-6}. In order to define the condition of acidity, alkalinity or neutrality in a solution, Salm proposes to refer always to the concentration of hydrogen ions. From conductivity and colorimetric

measurements, it appears that the minimum concentration of hydrogen ions is contained in a solution of 6·7 normal caustic potash and the maximum concentration, in 5·8 normal nitric acid. [*Zeit. Electrochem.* 1904 (10) 113.]

Before proceeding to discuss the theory of the behaviour of colour indicators, it may perhaps be advisable to draw attention to the nature and composition of a few of the organic compounds which are commonly employed for this purpose.

Most of these are definite chemical compounds of known constitution whilst others are more or less indefinite mixtures which contain some colour-giving constituent.

Red cabbage, which is probably one of the oldest known indicators, is used as a tincture, which has a violet colour; it turns red with acids and green with alkalis and is fairly sensitive. The composition of the colouring matter is not exactly known.

Litmus dissolves in water giving a blue solution, in alcohol it is purplish blue. The principal colouring matter contained in its solution is a substance called 'azolitmin' which has the composition $C_7H_7NO_4$. Its varying colour changes with strong and weak acids and with alkalis are of course already known.

Phenolphthalein is a white crystalline substance, nearly insoluble in water but soluble in dilute alcohol. It is particularly well suited for the titration of the weakest acids with strong bases but is practically useless for weak bases such as ammonia. Ammonium salts interfere with its delicacy as an indicator. The constitution of phenolphthalein will be referred to below. The pink colour produced by alkalis is destroyed by excess of alkali and is also discharged by alcohol.

Methyl orange. The sodium or ammonium salts of *p*-dimethyl-aminoazobenzene *p*-sulphonic acid,

$$(CH_3)_2N.C_6H_4.N:N.C_6H_4.SO_3H,$$

are sold under various names and include methyl orange, helianthine, Tropæolin D, Poirrier's orange III, mandarin orange, etc. These salts dissolve easily in hot water and very slightly in alcohol. This indicator is practically unaffected by weak acids.

Congo-red is the sodium salt of tetrazodiphenyl-naphthionic acid $(C_6H_4)_2(N_2)_2(C_{10}H_5)_2(NH_2SO_3H)_2$. It is a reddish brown

substance, easily soluble in water and in alcohol which gives a blue colour with strong acids and red with alkalis; it may be used for estimating strong mineral acids in presence of organic acids, since the latter generally do not affect it. Aluminium sulphate may, it is said, be titrated as free sulphuric acid, using this indicator.

Lacmoid is a substance prepared by heating resorcinol with sodium nitrite. Its composition is stated to be $C_{12}H_9NO_4$ but its constitution is not known. This reagent is sometimes called 'Weselsky's indicator'; it is a brown or violet powder easily soluble in alcohol, sparingly soluble in water. In neutral or alkaline solution it is blue, or blue-violet; acids change it to red. Its character much resembles that of litmus but is, in certain cases, perhaps more delicate.

Para-rosolic acid, also known as 'aurin' or corallin. The commercial product is a mixture of several substances. The pure compound is a triphenylmethane derivative $(OH.C_6H_4)_2C:C_6H_4:O$ (see page 305). It is insoluble in water but soluble in alcohol. Alkalis turn it rose-red and acids change the colour to yellow. The presence of ammonium salts interferes with the delicacy of this indicator.

Turmeric contains a colouring matter known as curcumin $C_{14}H_{14}O_4$ which is coloured reddish brown by alkalis and yellow by acids. It is now more used as a reagent for the detection of boric acid than as an acid-alkali indicator, although it may have some advantages for the latter purpose.

p-Nitrobenzeneazo-a-naphthol sulphonic acid is recommended by Hewitt as a delicate acid indicator, alkalis changing the yellow colour to purple. It has advantages over phenolphthalein in that excess of alkali does not destroy the colour and that alcohol does not affect it.

92. Theory of indicators. All the organic substances which are employed for this purpose are to be regarded either as weak acids or weak bases, and the colour changes observed are usually understood to depend on the fact that the free acid or free base has a different colour from that of its salts. In terms of the ionisation hypothesis this is expressed by saying that if the indicator is an acid, the colour of the non-ionised compound is different from that

of its anion, if it is a base the non-ionised molecule has a colour different from that of its kation. This exceedingly simple and popular explanation, due to Ostwald, may be stated in the following way.

Suppose the indicator to be an acid HX; this when dissolved will undergo ionisation $HX \rightleftarrows \dot{H} + X'$ and the equilibrium will be regulated by the law of mass action, that is, $Kc = ab$. In the case of phenolphthalein, HX is colourless whilst X′ is pink; but since the acid is such a weak one, the very slight amount of ionisation which occurs when the compound is dissolved does not yield a sufficient concentration of X′ to produce a visible effect. If, however, a strong base is added, the OH′ ions combine with the $\dot{H}$ ions of the phenolphthalein, thus destroying the equilibrium between the latter and its ions; the concentration a is diminished and the concentration b must therefore increase and c diminish, i.e. further ionisation takes place. The final result then, is practically represented as

$$HX + \dot{M} + OH' = \dot{M} + X' + HOH,$$

so that the colour of X′ becomes apparent.

Since phenolphthalein is such a weak acid an extremely small concentration of free hydrogen ions will be sufficient to reverse this effect. The reason why phenolphthalein is not applicable to the titration of weak bases is explained by the hydrolysis of the resulting salt. Thus, if ammonia solution is run into an acid, using phenolphthalein as indicator, a considerable concentration of ammonium ions will be formed in solution; after the quantity of ammonia added is exactly equivalent to the acid originally present, the next drop of ammonia will yield scarcely any free hydroxyl ions since the degree of ionisation of NH_4OH will be 'suppressed' by the (NH_4) already present. Hence considerably more than the equivalent quantity of ammonia will be necessary before the pink colour is apparent. For the same reason the presence of ammonium salts is to be avoided even when strong bases are titrated by means of this indicator.

The undissociated molecule of methyl orange is pink and its anion is yellow*; as an acid it is considerably stronger than phenolphthalein and, in its aqueous solution, the concentration

* Compare, however, Küster, *Zeit. Anorg. Chem.* 1897 (13) 136.

of the anions is sufficient to affect the colour, hence the solution is orange. A notable concentration of hydrogen ions is necessary to 'suppress' the anions practically completely, in this case; so that in titrating weak acids which give only few hydrogen ions, this necessary concentration is never reached and the complete pink colour is not obtained. On the other hand, a very minute concentration of OH' in excess of the calculated quantity necessary to neutralise the acid which is being estimated, will suppress the hydrogen ions of the methyl orange sufficiently to cause an appreciable increase of ionisation of the indicator, so that a sharp colour change is obtained when titrating weak bases.

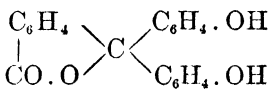
In titrating orthophosphoric acid, the concentration of H' which results from the change $H_3PO_4 = \dot{H} + (H_2PO_4)'$ is sufficiently great to suppress the ionisation of methyl orange to a point where the pink colour is apparent; in the second stage, however, $(H_2PO_4)' = \dot{H} + (HPO_4)''$ the $\dot{H}$ concentration is not sufficient for methyl orange but is sufficient for phenolphthalein. It is stated that even the concentration of $\dot{H}$ in the third stage $(HPO_4)'' = \dot{H} + (PO_4)'''$ is sufficiently great to suppress the ionisation of trinitrobenzene so that with this indicator orthophosphoric acid may be titrated as a tribasic acid (Salm).

The colour changes of other indicators are explained in a similar way: thus the colour of non-ionised molecule of congo-red is blue and the anion is red, in litmus the anion is blue and the non-ionised part red.

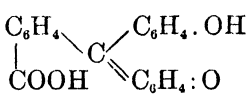
This simple interpretation of the colour changes in indicators has been subjected to severe criticism; it is contended on the one hand that it gives an insufficient explanation of all the facts and further, that the phenomena can all be explained equally well by reference to tautomeric changes in constitution which, in compounds of this class, are known to be brought about by acids and alkalis. With regard to the behaviour of phenolphthalein for instance the objections are raised (*a*) that the colourless solution of the indicator itself should become coloured on large dilution, and (*b*) that a solution of it made just perceptibly pink by a trace of alkali should become colourless when evaporated to dryness, since the first operation would increase ionisation and the second operation would suppress it. Neither of these effects, however, can

be observed. The solid silver salt of phenolphthalein is coloured and in this, ionisation appears to be excluded. The fact that excess of alkali lessens or destroys the pink colour of alkaline phenolphthalein has been got over by assuming that the pink compound is itself an acid and that a colourless salt is formed when sufficient excess of base is present (McCoy) but Green shews that the colour is not restored when the cold mixture is neutralised with acetic acid and again rendered alkaline [*Trans. Chem. Soc.* 1904, 398]. The last named author also shews [*Ber.* 1907, 3724] that quinolphthalein, which is analogous, yields a coloured methyl ester, which is of course non-ionised.

The alternative so-called chemical explanation refers the changes of colour only to the tautomeric change from the colourless 'lactoid' form of the substance to a coloured quinonoid form. Thus the usual constitutional formula for phenolphthalein (dihydroxyphthalophenone) is

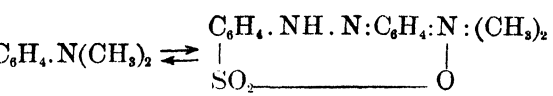


and this, according to Ostwald's explanation, behaves, at first at any rate, as a monobasic acid, the hydrogen atom of one of the OH groups becoming ionic and the remainder constituting the coloured anion. The alternative explanation is that this lactoid form is colourless and that under the influence of alkalis it undergoes a change of constitution, being converted into the quinonoid modification



acids effecting the converse change.

In the case of methyl orange, the change might be represented as being due to the formation of an internal salt, which is pink, thus,



[See Hewitt, *The Analyst*, March, 1908.]

Although opinions still differ and difficulties have yet to be explained, it is now being generally recognised that the two views are not necessarily antagonistic and that these tautomeric changes, which are admitted, do not in any way preclude ionisation. According to Hantzsch these indicator substances are to be regarded as pseudo acids or pseudo bases, the original compound therefore having a different constitution to that of the salts which it produces under the influence of alkalis. Phenolphthalein on this view is not itself an acid; it is a colourless compound which can be readily transformed by alkalis into an isomer which has acid properties and whose anion is coloured.

Practical Work.

1. Standard solutions are given of the following acids: boric, orthophosphoric, sulphurous, hydrosulphuric, acetic. Titrations, with standard caustic soda, are made with each acid using, in each case, various indicators. The results obtained are tabulated and compared. In the case of boric acid the influence of glycerol is also studied.

2. Aqueous solutions of various normal salts are examined by indicators with the object of ascertaining the occurrence of hydrolysis. The following salts may be taken as examples:

KCN, CH_3COONa, Na_2HPO_4, NaH_2PO_4, $Na_2B_4O_7$, $Al_2(SO_4)_3$, $CuSO_4$, $FeCl_3$, $Hg(NO_3)_2$, NH_4Cl.

3. Approximate experiments are made with the object of ascertaining the dilutions at which different acids yield the same colour tint, under similar conditions, with methyl orange.

Compare, for example, hydrochloric acid with oxalic and acetic acids.

4. The different sensitiveness of various indicators may also be illustrated by the experiment suggested by Nernst. A very dilute solution of barium hydroxide is mixed with methyl formate $\left[50\text{ c.c. of }\frac{N}{1000}\ Ba(OH)_2 \text{ to } 0{\cdot}5\text{ c.c., or } 1\text{ c.c., of the ester}\right]$; a few drops of the indicator are added and the time noted at which the colour change occurs. Compare, in this way, litmus, phenolphthalein, cyanine, *p*-nitrophenol and methyl orange.

CHAPTER XXII.

SOLUTION.

93. It was at one time the custom to employ the word solution only in reference to homogeneous mixtures obtained by dissolving solids, liquids or gases in liquids: the resulting mixture being also liquid. The term is now employed in a wider sense and includes all homogeneous mixtures, of two or more substances, the composition of which is continuously variable within certain limits. We can have therefore solutions of gases in solids or solids in solids as well as solutions of solids, liquids or gases in liquids.

In such a homogeneous mixture or solution, consisting, for example, of two substances, one of the components is usually spoken of as the solvent and the other as the solute. Such a distinction although convenient in particular cases is quite arbitrary and, when the proportions of the two are not very different, is unnecessary and out of place. In the case of a salt dissolving in water one might to some extent regard the resulting mixture either as a solution of salt in water or of water in salt. If the salt is more soluble as the temperature rises, cooling the strong solution will cause the separation of solid salt leaving a stronger 'solution of water' behind, just as cooling the weak solution causes ice to separate, leaving a stronger solution of salt.

Solutions of solids in liquids.

If excess of a crystalline solid is finely powdered and added to a limited quantity of water, the salt will continue to dissolve, and its concentration in solution continue to increase, until, if the temperature is kept constant and excess of salt is still present, a maximum concentration will be arrived at and the process of dissolution will cease.

[If to each solid we ascribe a definite 'solution pressure' at a given temperature the solution will become saturated when this

maximum solution pressure is equal to the osmotic pressure of the substance in solution.]

This maximum concentration is called the solubility of the solid in the given solvent at the temperature in question.

The solubility may be expressed in different ways. It is usual to define it as the weight of the solute which, in the saturated solution, is dissolved by 100 parts by weight of the *solvent*. For certain purposes, however, it may be convenient to express the value as the weight of solute in a given volume of the solvent or as the weight of solute in a specified weight or volume of the *solution*.

It is particularly to be noticed that the solubility refers to the concentration which is reached when the solution is in contact with the particular solid in question. If that solid is absent the expression is meaningless.

For every temperature therefore in which the solid is in equilibrium with its saturated solution there will be a definite concentration of solution. There will also be a definite vapour pressure. That is, if the temperature is altered both the solubility and vapour pressure will alter, but for any given temperature there is a corresponding solubility or concentration and a corresponding vapour pressure. [Two components in three phases.]

If, however, the vapour is absent, that is if the solid and solution only are in contact (e.g. in a closed vessel) it will be found that the solubility at a given temperature is not dependent on the temperature only since it varies also with the pressure. The effect of pressure is comparatively very slight; for example, an increase of 160 atmospheres in pressure makes a difference of about 1 per cent. in the solubility of ammonium chloride. As solubilities are usually determined in open vessels, the influence pressure is in most cases neglected, since the pressure can be regarded as constant—i.e. one atmosphere.

Practically then, the solubility of a solid is constant at a given temperature and is independent of the amount of solid present. It can be shewn, however, theoretically and demonstrated practically that there is a limit to the truth of this statement, since the solubility depends also upon the state of division of the solid. Thus extremely fine powders may be more soluble than large crystals. [Compare Hulett, *Zeit. Physikal. Chem.* 1901 (37) 385.]

The solubility of most solids increases with rise of temperature but the rate of increase is very different for different substances. Potassium chloride is about twice as soluble at 100° as it is at 0°, the increase of solubility being proportional to the temperature increase; potassium chlorate is about 14 times more soluble at 100° than at 0° and here the solubility increases more rapidly than the rise in temperature. The solubility of sodium chloride increases only very slightly between 0° and 100°. In some cases the solubility becomes less as the temperature increases, at any rate between certain intervals. Well-known examples of this behaviour are found in calcium citrate, isobutyrate and sulphate, anhydrous sodium sulphate and thorium sulphate tetrahydrate. Sometimes a minimum solubility is reached at a certain temperature (e.g. sodium sulphate at 120° and calcium sulphate at about 240°) beyond which the salt again becomes more soluble with rise of temperature.

The solubility of crystallised sodium sulphate $Na_2SO_4.10H_2O$ increases rapidly with rising temperature up to 32·5° being at this temperature nearly 10 times as soluble as it is at 0°. The solubility curve cannot be followed beyond this point since the solid salt at this temperature loses its water of crystallisation. The curve at higher temperatures refers therefore to the solubility of the anhydrous salt Na_2SO_4. Formerly it was supposed that the solution changed its character at this temperature, i.e. contained the hydrate only below 32·5° and the anhydrous salt only above this temperature; no such change is indicated, however, by any of the properties of the solution; these properties change quite continuously and shew no break at the temperature mentioned. Since the solubility refers only to one particular kind of solid it is evident that we are dealing with two entirely distinct solubility curves, that of the solid hydrate and of the solid anhydrous salt. It is, in fact, possible to shew the continuation of the curve of solubility of the anhydrous compound below the transition point since the solid does not immediately become re-hydrated as the temperature falls. The solution below 32·5° will always contain more salt than a saturated solution of the hydrate, i.e. it is supersaturated with respect to the latter. Only at the transition point can the two solids, hydrate and anhydrous salt, exist in

equilibrium with the saturated solution and vapour. [Two components and four phases.]

94. Supersaturated solutions. If no solid is present there is of course no longer any question of a definite solubility. By saturating a solution at a given temperature and then carefully cooling (or heating) to a temperature at which the given solid is less soluble, it is easy to obtain supersaturated solutions. These are comparatively stable, but on addition of a mere trace of the solid, the excess of solid separates out and a normally saturated solution remains, i.e. equilibrium is established between the solid and solution.

The quantity of solid which is able to bring about the crystallisation of a supersaturated solution is extremely minute, i.e. of the order of a millionth of a milligram. It must be identical or isomorphous with the substance which crystallises out.

When a supersaturated solution of sodium sulphate is cooled to about 5° another hydrate, $Na_2SO_4 . 7H_2O$, separates out. This salt is at all temperatures more soluble than the salt $Na_2SO_4 . 10H_2O$; i.e. its saturated solution is always supersaturated with respect to the latter salt. If then to the solid heptahydrate in contact with its saturated solution a small quantity of the decahydrate be added, solid decahydrate will continue to separate out until the solution is normally saturated with respect to that salt. The solution will therefore become unsaturated with respect to the heptahydrate; this therefore dissolves and the solution is again supersaturated as regards the decahydrate. This continues until the solid heptahydrate has all dissolved, decahydrate taking its place.

If the concentration of a supersaturated solution, at a given temperature, is greatly in excess of that of a normally saturated solution at that temperature, crystallisation may often be induced, even without the addition of a 'nucleus,' by mechanical disturbance, e.g. by friction. Such solutions are said to be in the 'unstable' condition, that of the ordinary supersaturated solution being described as 'metastable.' The latter are only unstable under the one condition, namely, that the particular kind of solid is present.

In the case of sodium sulphate decahydrate it is not possible to say where is the line of demarcation between the metastable and unstable condition. For the heptahydrate however and for the anhydrous salt there appears to be a definite supersolubility curve, i.e. a curve representing the temperature at which solutions of different concentrations will crystallise when cooled with constant shaking or friction. A similar 'metastable limit' has been shewn in many other cases. [Compare Miers and Isaacs, *Trans. Chem. Soc.*, 1906, 413. Hartley and others, *ibid.* 1906, 1028; 1908.]

95. The thermal change which takes place when a solid is dissolved in a liquid may be either positive or negative. A very considerable evolution of heat results, for example, when caustic potash is dissolved in water; whereas the dissolution of ammonium nitrate or ammonium sulphocyanate is attended with so great an absorption of heat that water may easily be frozen by this means. [This may be easily shewn by dissolving the solid in a small quantity of water contained in a thin glass dish, the under surface of which is in contact with a drop or two of water.]

By the heat of solution of a solid in a liquid, say water, is meant the quantity of heat absorbed or evolved when one formula weight of the solid is dissolved. But this will have different values according to whether the solid is dissolved in a large excess of water or is just dissolved to saturation. It will be different again if the solid is dissolved in its (nearly) saturated solution. The latter value is equal to the heat of precipitation but of opposite sign and can in this way be determined.

It can be shewn by thermodynamic reasoning that if the heat of solution *in the latter sense* is positive, the substance will, at constant pressure, be less soluble as the temperature rises (e.g. Na_2SO_4) and conversely those substances whose heat of solution is negative will become more soluble with rising temperature (e.g. $Na_2SO_4 . 10H_2O$). [Compare pages 159 and 162.] If the substance dissolves without thermal change then, at constant pressure, the solubility will not change with temperature. Cupric chloride at first appeared to afford an exception to this rule since its solubility increases with increasing temperature and

yet its heat of solution appeared to be positive. The latter value had been determined, however, by dissolving the salt in much water; it was afterwards shewn that heat of solution becomes less as the quantity of water used is smaller and, in the nearly saturated solution, the heat of solution is negative.

The influence of pressure on solubility can be predicted in a similar way. When, at constant temperature, the substance dissolves with contraction in volume (e.g. $CuSO_4.5H_2O$, NaCl or K_2SO_4) the solubility is increased by increasing pressure. Conversely the solubility of a substance which dissolves with expansion in volume (e.g. NH_4Cl) is diminished by increased pressure. The influence of pressure is, as previously stated, extremely slight.

The solubility of a given solid in a given liquid depends therefore upon the temperature and to some extent on the pressure. No satisfactory general statement can be made with regard to the dependence of solubility on the chemical nature of the solid and of the solvent. It may be noticed in passing, however, that an element which is sparingly soluble in many solvents will often dissolve easily in certain liquid compounds into whose composition the given element enters [e.g. sulphur in carbon disulphide or in chloride of sulphur, phosphorus in phosphorus trichloride]. Most hydroxy-compounds dissolve in water and are sometimes more soluble the greater the proportion of hydroxyl. [e.g. Benzene is nearly insoluble in water; phenol, very slightly soluble; hydroquinone more soluble, and pyrogallol extremely soluble.] The aliphatic acids and alcohols also become less soluble as the series is ascended. Most alcohols dissolve in ordinary ethyl alcohol and nearly all hydrocarbons dissolve in benzene.

Certain general relationships are sometimes noticed between the solubilities of salts of a series of metals and the atomic weights of the metals, but the order may also depend on the acid radicle. e.g. The sulphates and chlorides of Mg, Ca, Sr, Ba are less soluble with increasing atomic weight but the solubility of their hydroxides is in the reverse order.

In many cases there is a connection between solubility and fusibility; in certain groups of isomeric acids, for example, the solubility is in the same order as the fusibility and the same is true of their salts. [Carnelly and Thomson, *J. Chem. Soc.*, 1888, 782.]

PRACTICAL WORK.

Determination of the solubility of solids.

In order to prepare a saturated solution it is necessary that every effort should be made to facilitate the equilibrium between solid and solution, and for this object the most important conditions are, 1st, a fine state of division of the solid, and 2nd, the continued agitation of the mixture. For the latter purpose mechanical stirrers should be employed. Two methods have been employed in order to arrive at the required result. One consists in keeping the solid in contact with the solvent at the required temperature until saturation is reached; the other method is to nearly saturate the solution at a higher, or lower, temperature at which the solid is more soluble and then bring the mixture, still containing excess of solid, to the required temperature. The second method is more rapid but is less reliable and the results are usually too high. The first method, which is now generally adopted, will give results which are too low unless sufficient time is allowed; in some cases it may be weeks or even months before real saturation is attained. The only way in which the final state can be ascertained is to make repeated determinations of the concentration until constancy is obtained.

Since the smaller particles of the solid are the first to dissolve, it is advisable after the process of saturation has gone on for some time, to add fresh portions of the finely powdered substance. The concentration of the saturated solution is ascertained by withdrawing a portion of the clear solution and estimating the contents by any suitable method. e.g. (1) By evaporation to dryness and weighing the residue. This method can only be employed if the solution leaves a residue of definite and known composition on evaporation. (2) By chemical analysis, volumetric or otherwise. In this case it is necessary to remember that the saturated solution is, as a rule, much too strong for direct titration, etc., and must first be diluted to a known volume; an aliquot part of the diluted solution is then taken for analysis. (3) By specific gravity determination. Here it is of course necessary to be supplied with tables giving the concentrations corresponding to the specific gravities.

If the solubility is to be determined at about the ordinary temperature the liquid may be withdrawn from the saturation vessel by means of an ordinary pipette or tube. [If filtration is necessary the first few drops of the filtrate must be neglected since a certain amount of the solute is retained by the paper and the solution which first passes through is less concentrated.] When the solubility is determined at a temperature at which the substance is more soluble than it is at the ordinary temperature, the solid may separate out during the transference; in this case it is best to employ Landolt's pipette. (Fig. 20.) In many cases, however, it will be sufficient to warm the ordinary pipette which is used for transference to the weighing bottle.



Fig. 20.

EXP. 1. *Determine the solubility of crystallised oxalic acid at the temperature of the given thermostat.*

In order to save time the mixture of salt and water has been kept in agitation in the bath for some hours before the demonstration. More finely powdered solid is to be added and the agitation continued, before the determination is made.

About 2 or 3 c.c. of the saturated solution is withdrawn and transferred to a weighed stoppered bottle. After cooling (if necessary) the bottle and saturated solution are weighed. Weight of saturated solution taken $= W_1$. The contents are then transferred to a measuring flask and made up to the given volume (say 500 c.c.) with distilled water. 10 c.c. of this diluted solution is then titrated with standard potassium permanganate, in presence of excess of dilute sulphuric acid, in the usual way. [Or it may be titrated with standard sodium hydroxide if preferred.] From the result the total quantity of oxalic acid ($C_2H_4O_2.2H_2O$) is calculated $= W_2$.

The solubility expressed in grams of oxalic acid per 100 grams of solvent, is then

$$\frac{W_2 \times 100}{W_1 - W_2}.$$

A similar determination is afterwards made at some other temperature.

EXP. 2. *Determine the solubility of ammonium chloride at the given temperature.*

Proceed as in the last experiment. Dilute the weighed quantity of saturated solution to 500 c.c. and titrate 5 c.c. or 10 c.c. of the diluted solution with $\frac{N}{10}$ $AgNO_3$ using potassium chromate as indicator.

EXP. 3. Prepare supersaturated solutions of sodium sulphate and of sodium thiosulphate and observe the results of adding traces of various salts to the solutions obtained.

EXP. 4. Observe the temperature changes which result when the following solids are mixed with small quantities of water. Caustic potash, potassium nitrate, ammonium sulphocyanate, anhydrous sodium sulphate, hydrated sodium sulphate

$$(Na_2SO_4 10H_2O).$$

An instructive experiment may be made, in a rough quantitative manner, by observing the thermal changes which take place when the salts Na_2HPO_4, $Na_2HPO_4 . 7H_2O$ and $Na_2HPO_4 . 12H_2O$ are dissolved, under approximately identical conditions, in the proportion of their formula-weights.

96. Solutions of liquids in liquids. Mixtures of liquids may be divided with regard to their mutual solubility into three classes: namely those which are (1) non-miscible, (2) partially miscible, and (3) miscible in all proportions.

Probably there is no perfect example of a mixture of the first class; even mercury and water may perhaps dissolve one another to a minute, but so far inappreciable, extent. Benzene and water, or carbon disulphide and water, afford further instances; they are not absolutely immiscible but for practical purposes may be considered as mixtures belonging to the first type. When distilled, such mixtures will yield distillates containing the two constituents in a constant proportion for any given temperature. The vapour pressure of the mixture at a given temperature will be practically equal to the sum of the vapour pressures of the constituents separately and the mixture will therefore boil at a lower tempera-

ture than either constituent, since the atmospheric pressure is supported by both constituent vapours. The quantities which distil over will be proportional to the partial pressures multiplied, by the vapour densities or $\frac{W_1}{W_2} = \frac{P_1 d_1}{P_2 d_2}$. Consequently, if we know, from previous observation, the vapour pressure of one constituent (say water) at the temperature in question and also its vapour density, we can determine the vapour density of the other constituent. This principle has been suggested by Wanklyn, Naumann and others as a method of determining molecular weights, but it has not found much application.

Mixtures of the second type, are those which dissolve one another to a limited extent and separate into two phases; when equilibrium is established, one of these phases is a saturated solution of *a* in *b* and the other, of *b* in *a*. At a given temperature therefore there will be a constant ratio between the concentrations in the two phases which will be quite independent of the total quantity of each constituent which is present. The vapour pressure of such a mixture at a given temperature will be constant and will be less than the sum of the partial pressures, since the vapour pressure of each pure liquid is lowered by the presence of the other in solution. It can be shewn, theoretically and practically [Konowaloff, *Wied. Ann.* 1881 (14) 219], that the vapour pressure, and the ratio of the components in the vapour, of each liquid phase is the same. On distilling a mixture of this type, at a given temperature, a liquid of constant composition will pass over as long as two liquid phases are present.

In some cases the solubility of *a* in *b* and of *b* in *a* both increase as the temperature rises and it may happen that the composition of each layer will in this way become more and more alike until at a given temperature they become identical and complete miscibility results. The temperature at which this happens is called the critical solution temperature. In other cases both solubilities may decrease as the temperature increases. In this case a 'lower critical solution temperature' is possible. Or one may increase and the other diminish; the solubility of ether in water, for example, diminishes and that of water in ether increases, as the temperature rises.

In terms of the phase rule we have, in this type of mixture, two components in three phases. The system is therefore univariant and for a given temperature both the vapour pressure and the concentrations must have fixed values. These values are quite independent of the proportions in which the two components are present so long as the two liquid phases continue to exist.

In liquid mixtures of the third type, those which are miscible in all proportions, we shall have two components existing in only two phases. The system is then bivariant and both the composition and vapour pressure may be altered at a given temperature. If at a given temperature the composition of the liquid remains unaltered the vapour pressure will have a fixed value, but if the composition alters the vapour pressure will alter correspondingly.

The vapour pressure of a mixture of this type is never equal to the sum of the vapour pressures of the two constituents. It may (*a*) lie between the two for all concentrations; a mixture of methyl alcohol and water is of this kind. It may be (*b*) greater than that of either constituent or (*c*) less. In (*a*) a nearly complete separation by fractional distillation is possible. In (*b*) a maximum vapour pressure is reached at a certain concentration and on repeated fractional distillation the first portion of the distillate will have this concentration, i.e. the minimum boiling point mixture first distils over unchanged. In (*c*) the composition alters on distillation until a mixture having the minimum vapour pressure, or highest boiling point, remains; on further distillation this mixture distils over unchanged in composition.

A mixture of propyl alcohol and water is an example of (*b*); in this case the mixture containing about 75 per cent. of the alcohol has the lowest boiling point or highest vapour pressure. If a solution stronger or weaker than this is distilled, the 75 per cent. mixture tends to come over first, leaving a residue stronger or weaker, respectively, in the alcohol.

Examples of (*c*) are found in mixtures of formic, nitric, hydrofluoric, hydrochloric, hydrobromic or hydriodic acids with water. Any mixture of formic acid and water has a higher boiling point, or lower vapour pressure, than either constituent alone. On distillation of the mixture either water or formic acid will first come over until the residue contains about 70 per cent. of the acid.

This mixture has the highest boiling point and on further distillation it comes over unchanged in composition.

These constant boiling mixtures of apparently constant composition were at one time regarded as chemical compounds. Roscoe however in 1860 [*Liebigs Annalen* (116) 203] shewed that the composition is only constant if the external pressure is constant. Thus, in the case of nitric acid the maximum boiling point mixture contained 66·7 per cent. of acid if boiled under a pressure of 75 mm., 68 per cent. under 760 mm. and 68·6 per cent. under 1200 mm.

Increase of pressure gives a mixture of greater concentration in the cases of nitric and hydrofluoric acids, but of less concentration in the cases of hydrochloric, hydrobromic and hydriodic acids. If a mixture could be realised in which the concentration of the constant boiling product was unaffected by pressure it would be difficult to distinguish it from a true chemical compound. It might also by chance happen that such a mixture would have its constituents present in some simple ratio of their formula weights and if so the distinction from a compound would be practically impossible. [In this connection read Ostwald's Faraday Lecture, *Trans. Chem. Soc.* 1904, 506.]

97. Distribution or Partition Law. When a solute is shaken up with two non-miscible, or partially miscible, solvents it will distribute itself between the two. A familiar illustration of this statement is afforded by the usual process of extracting aqueous solutions (e.g. of certain organic substances) with ether; the process, it will be remembered, has to be repeated many times, shewing that the ether does not remove the whole of the solute even though it is very soluble in ether and only slightly soluble in water.

The laws which regulate this phenomenon were investigated by Berthelot and Jungfleisch in 1872 [*Ann. Phys. Chim.* (4) 26, 396].

It is found, when equilibrium is attained, that if the solute retains the same molecular state in both solvents, the ratio of the concentrations (e.g. moles per litre) in the two solvents is constant for a given temperature and independent of the total quantities. This ratio is called the partition coefficient or ratio of distribution.

If c_1 and c_2 represent the concentrations in the two solvents respectively, then $\frac{c_1}{c_2} = K$.

If several different solutes are present each will distribute itself in a constant ratio as though the others were absent. Or, again, if the solute undergoes dissociation, each of the dissociation-products will distribute itself in the above manner.

When the solvents are non-miscible, the ratio of the solubilities of the solute in the pure solvents separately is the same as the distribution ratio. With ether and water this is not the case since the two solvents concerned in the experiment are a saturated solution of ether in water and of water in ether.

When the solute undergoes polymerisation or association in one of the solvents, i.e. when its molecular state is different in the two solvents—the above ratio is no longer constant. Phenol, for example, undergoes association in benzene solution but not in water and the ratio of the concentrations in these two solvents is found to alter as the actual concentrations alter.

Suppose that in the process of polymerisation or association n single molecules unite to form one complex molecule, the process being limited and reversible, and suppose further that in the experiment under consideration the degree of association is large —that is, most of the molecules exist in this associated condition. Let the concentration of the solute in the first solvent, in which all the molecules are single, be c_1 and that in the second solvent, where association occurs, be c_2. There will now be single molecules in both solvents and these will distribute themselves according to the above law; their concentration in the first solvent is c_1. In order to find their concentration in the second solvent one may apply the law of mass action; in the reversible process of association above mentioned if a and b are the concentrations of the single and the associated molecules respectively, $a^n = Kb$ or $\frac{a}{\sqrt[n]{b}}$ is constant. The concentration of the single molecules in the second solvent is therefore proportional to the nth root of the concentration of the complex molecules (which is practically the total concentration) in this solvent and consequently,

$$\frac{c_1}{\sqrt[n]{c_2}} = K.$$

In this way then one may find the degree of complexity of the associated molecules with respect to the simple molecules. A series of determinations are made of the values of c_1' and c_2 using different quantities of the solvents or solute and the value of n is taken which gives the nearest approach to constancy in the above ratio.

Practical Work.

Determination of partition coefficients. (1) e.g. Of succinic acid between ether and water, (2) of iodine between benzene and water, and (3) of benzoic acid between benzene and water, at the temperature of the given bath.

A series of observations is made in each case, taking different total concentrations. The concentrations are determined after equilibrium is established, by separating the two solutions, withdrawing a given volume of each and titrating in the usual manner.

Standard barium hydroxide and sodium thiosulphate are given.

98. Solutions of solids in solids. If we define a solution as a homogeneous mixture of two or more substances the concentration of which may be continuously varied within certain limits (with a corresponding continuous change in certain properties of the mixture) it is evident that we have numerous examples of solid solutions. For example, many alloys, the hard steels (martensite), glasses and mixtures of crystals of isomorphous substances such as alums, vitriols, etc.

[If, however, true solids are regarded as being essentially crystalline, glasses are in reality supercooled liquids.]

The term solid solution was first given by van 't Hoff to the intimate and apparently homogeneous mixtures of solvent and solute which separate in certain cases from liquid solutions on freezing. The normal lowering of the freezing point occurs when pure solvent separates on freezing; if, however, solute and solvent together separate in the solid state, the remaining solution will not be so concentrated as in the previous case. If the solid mixture separating contains more of the solute than the remaining liquid, the solution will be diluted instead of being strengthened by freezing, and the freezing curve will therefore rise with

increasing concentration. When the solid mixture which separates is poorer in solute than the remaining liquid the freezing point will fall with increasing concentration, but the depression will be less than the normal.

A distinction is sometimes made between these dilute solid solutions and isomorphous mixtures since it is considered that, in the latter case, diffusion of the solute in the solvent is not possible, since it is held in position as part of the crystal. The term 'mixed crystal' is often used to indicate either class but is sometimes found confusing since it might suggest two phases instead of one.

That diffusion can take place in solids is seen in the passage of hydrogen through palladium, of carbon (or carbon monoxide) through hot iron, and in Roberts-Austen's well-known experiment of the diffusion of lead in gold [*Proc. Roy. Soc.* 1900 (67) 101].

In dilute solid solutions it would appear probable that the laws of solution and of osmotic pressure may be applied in the same manner as in liquid solutions. And in this way one may gain information as to the molecular weights of substances in solid solution. The solid which freezes out from a solution of thiophene in benzene is an isomorphous mixture whose concentration always bears a constant ratio to that of the liquid solution, i.e. it obeys the simple partition law and consequently the molecular weight of the thiophene is the same in the solid and liquid solutions.

Küster* attempted to determine the molecular weight of β naphthol in solid naphthalene by this method. These two substances form a continuous series of isomorphous mixtures with one another; β naphthol is soluble in water but naphthalene is not. On shaking up the isomorphous mixture, of known composition, with water, the β naphthol will divide itself between the liquid and solid solvent and the ratio of the concentrations c_1 and c_2 can be determined experimentally.

The value found for $\frac{c_2}{c_1}$ was not constant but altered with the concentration of the solid mixture taken. Numbers not far from constant, however, were obtained for the ratio $\frac{\sqrt{c_2}}{c_1}$ and the author

* Küster, *Zeit. Physikal. Chem.* 1895 (17) 357.

concludes that the molecular weight of β naphthol in the solid solution is double of that in the aqueous solution. In the latter it has the single formula, so that the molecular weight in its solid solution corresponds to $(C_{10}H_7.OH)_2$. Since it appears probable that substances in isomorphous mixture have the same degree of molecular complexity, it may further be concluded that the molecules of the solid naphthalene are also double, i.e. $(C_{10}H_8)_2$.

In solids as in liquids we may have degrees of miscibility. Some solids, such as the alums or vitriols, may mix homogeneously in any proportion. In some cases there may be limited miscibility, the two substances crystallising, when apart, in different forms but crystallising together in a single form, within certain limits of relative concentration. Beryllium sulphate, for example (tetragonal), can crystallise with Beryllium selenate (rhombic) in the tetragonal form until the proportions are 7·33 to 1. Further addition of the selenate gives rise to a heterogeneous mixture until the proportion rises to 4 of the sulphate to 1 of the selenate; beyond this proportion miscibility again results, the crystals now being of the rhombic form. Probably, as in the case of partially miscible liquids, these solids may become completely miscible at some definite temperature, i.e. the 'isodimorphism' may change to isomorphism.

Cases are known (e.g. with calcite and magnesite) in which a double salt may be formed at a certain relative concentration which crystallises differently from either of the single salts and is not miscible with them. [See van 't Hoff's Lectures, vol. I. 55.]

99. Solutions of gases in liquids. When an excess of a gas is shaken up with a limited quantity of a liquid, the quantity of gas which will dissolve depends upon the temperature, the pressure of the gas in question, and the nature of the gas and of the liquid.

The solubility of a gas in a liquid is in all * cases smaller as the temperature is higher; this is to be expected since all gases appear to dissolve with evolution of heat. (Compare le Chatelier's

* Bunsen stated that in the cases of hydrogen dissolving in water and oxygen or carbon monoxide dissolving in alcohol, the solubility is independent of the temperature between 0° and 25°. These results have been contradicted by Timofejeff [*Zeit. Physikal. Chem.* 1890, 141]. The inert gases show a minimum solubility at certain temperatures.

principle.) The rate of change of solubility with temperature does not follow any general law.

The solubility may vary enormously according to the nature of the gas and liquid. Thus, at 0° one volume of water will dissolve about 0·02 volumes of nitrogen, 0·04 of oxygen, 1·8 of carbon dioxide, 80 of sulphur dioxide, and 1149 of ammonia. In alcohol the solubilities are in many cases much larger, but the numbers are not proportional. Gases which are the more easily liquefied are, in general, the more soluble.

In the cases of those gases whose solubility is small, which do not chemically react with the solvent, and which do not undergo association or dissociation when dissolved, the mass of gas which can be dissolved by a given quantity of a solvent is directly proportional to the pressure, at a given temperature. (Henry's Law.) In the case of mixed gases each dissolves in proportion to its partial pressure. (Dalton's Law.) Gases which are very soluble at the temperature in question do not follow this law; sulphur dioxide, for example, only begins to obey the law above 40° and ammonia above 100°. Deviations also occur at high pressures. The law appears therefore to hold only for dilute solutions. [Compare the laws of osmotic pressure.]

It was formerly supposed that deviation from Henry's law necessarily indicated the chemical combination of the gas and solvent. Carbon dioxide, for example, dissolves in water at ordinary temperatures and pressures in accordance with the law; but at high pressures and low temperatures considerable deviations occur. At one time it was considered a sufficient explanation to say that these deviations were due to the formation of a chemical compound, such as carbonic acid H_2CO_3. A similar explanation was given in the case of oxygen dissolving in the blood. It was supposed that these cases were analogous to the dissociation of, say, calcium carbonate where the pressure of the gas is a function of the temperature only and independent of the masses. The phenomena are, however, of a different type; in the system lime chalk and carbon dioxide three phases are present, whereas the solution of carbon dioxide in equilibrium with the gas consists of only two phases, and the system, since there are two components, is bivariant.

Deviations from the law may be due to chemical changes; but it does not follow that the formation of a chemical compound is necessarily excluded if the gas dissolves in accordance with Henry's law. The relation between the gas pressure and the concentration, when a chemical compound is formed in solution, is of a complicated character*. It will depend on (*a*) the number of molecules of solute which combine with the solvent to give a single molecule of the compound, e.g.

$$nX + y\mathrm{H_2O} \rightleftarrows X_n(\mathrm{H_2O})_y,$$

(*b*) the degree of dissociation of this compound in the liquid and if volatile, in the vapour also. The reduction of the effective mass of the solvent has also to be considered (see page 359) especially if y is large. For special cases the concentration might be proportional to the pressure. In many cases, however, the deviations from Henry's law can be simply explained, without making use of hypotheses as to the formation of compounds, if it be assumed that the molecular state of the solute is different in the gas and solution. In the case of carbon dioxide, for example, it is probable that the compressed gas is in an associated condition such as C_2O_4. [Compare partition law, page 318.]

The solubility of gases is usually expressed numerically in terms of the *volumes* of gas and solvent; in the case of the very soluble gases, however, it is generally more convenient to define it in terms of the masses as was done in expressing the solubilities of solids. Bunsen's 'coefficient of absorption' represented the volume of the gas corrected to 0° and 760 mm. which is dissolved by unit volume of the solvent at the pressure of 760 mm. If, for example, v c.c. of gas at $t°$ and P mm. are dissolved by V volume of solvent the corrected volume of the gas will be

$$v \times \frac{273}{273+t} \times \frac{P}{760}.$$

But by Henry's law the amount dissolved at a pressure of 760 mm. will be $\frac{760}{P}$ times this quantity or $v \times \frac{273}{273+t}$. [That is, the *volume* dissolved is independent of the pressure.] The coefficient of absorption is therefore $\frac{v}{V}\frac{273}{273+t}$.

* In reference to this question see Richardson, *Phil. Mag.* 1904 (7) 266.

Ostwald proposes a much simpler coefficient, namely $\frac{v}{V}$ which is called the 'solubility' of the gas. It represents the volume of the gas which is dissolved by unit volume of the solvent at a specified temperature. In other words it denotes the ratio of the concentrations in the liquid and in the gas itself at the given temperature. This ratio is evidently independent of the pressure and of the absolute volumes of gas or liquid and depends only on their nature and on the temperature.

The fact that the ratio of the concentrations is constant at a given temperature at once reminds us of the partition law as regards the distribution of a solute between two solvents; in fact Henry's law may be regarded as an example of the partition law, where one of the phases is gaseous.

Gases are as a rule less soluble in salt solutions than in pure water but there are exceptions. The solubility of carbon dioxide in a solution of sodium phosphate was said by Pagenstecher, in 1840, to be greater than in pure water and Setschenoff states that the solubility of carbon dioxide in a 0·6 per cent. solution of common salt ('physiological salt solution') at 15° is greater than in pure water. The last-named author considers that salts in their influence on the solubility of carbon dioxide may be divided into two classes. In one class, e.g. phosphate or borate, a part of the gas is absorbed not in accordance with Henry's law and this part is greater as the concentration of the salt increases. In the other class (e.g. chlorides, sulphates, nitrates) the gas dissolves in accordance with Henry's law and the absorption diminishes as the concentration of the salt increases.

The solubilities of indifferent gases such as oxygen, hydrogen and nitrous oxide are always lower in salt solutions than in pure water and the extent to which the solubility of these gases is diminished by various salts appears to be the same for each gas. It has been suggested that the cause of the diminished solubility may be the hydration of the salt, i.e. that the salt appropriates some of the water and that this combined water has no longer power to dissolve the gas. Attempts have been made in this way to throw light upon the yet obscure question as to the existence of hydrates in aqueous solution. (See page 360.)

100. Solutions of gases in solids.

A gas may be 'taken up' by a solid in various ways; it may, for example,

(A) dissolve in the solid to form a homogeneous solid solution with it; (B) form two or more solid solutions which are only partially miscible; (C) form a chemical compound with the solid, or (D) it may become condensed on the surface of the solid, or 'adsorbed.'

If the gas and solid are placed in contact in a closed vessel and the apparatus is so arranged that the pressure of the gas may be varied, it is possible in many cases to distinguish between the various phenomena referred to, by observation of the relation between the gaseous pressure and the quantity of gas taken up by the solid.

(A) If the gas forms a single homogeneous solid solution with the solid, the concentration of the gaseous constituent in this solid solution will, at a given temperature, vary with the pressure of the gas above it, the concentration becoming greater as the pressure is greater. If we draw a pressure-concentration diagram, taking the pressures as ordinates, this relation will be indicated by a curve or line slanting upwards in some such form as that represented by *oa* in the following figure.

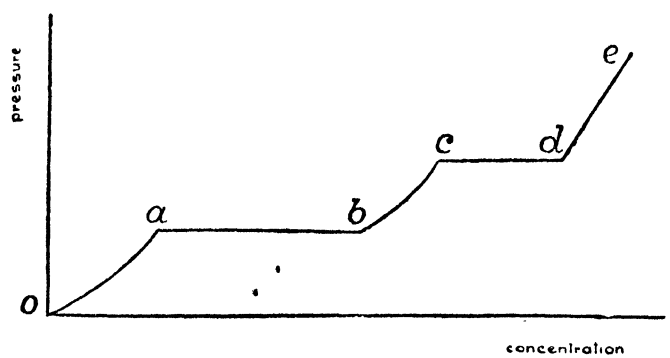


Fig. 21.

When the gas dissolves in this way, and has the same molecular state in both phases, Henry's law will be obeyed and the concentration in the solid will be directly proportional to the

concentration in the gas, i.e. to the pressure of the gas. We shall have therefore $\frac{P}{C} = K$.

If, however, the gas changes its molecular state in dissolving the relation will be less simple. Thus if its molecular formula in the gaseous state is A and in the solid solution A_n, the relation will be $\frac{P}{\sqrt[n]{C}} = K$. Or, if the molecular state in the solid is A and that in the gas A_n the relation will be $\frac{C}{\sqrt[n]{P}} = K$. (See page 319.)

(B) There is the possibility, theoretically at any rate, that the gas may first dissolve, forming a solid solution, and that, on increasing the concentration, a point may be reached at which a second solid solution is formed which is only partially miscible with the first; the case would then be analogous to that of, say, phenol and water or ether and water (page 316). For a constant temperature then the pressure would remain constant although the concentration continued to increase (line *ab* in the above diagram). The effect of increasing the concentration would be to alter the relative amounts of the two solutions, i.e. with increasing concentration the relative amount of the second solid solution would increase; but the gaseous pressure, and the relative concentrations in the two solid solutions, would remain constant for a given temperature. Beyond a certain concentration, however, the first solid solution would entirely disappear, being converted into the second, and, when this is the case, the pressure would again increase as the concentration became greater (curve *bc*). The concentrations at which the discontinuities, represented at *a* and *b*, would occur will of course be constant for a given temperature but will be different for different temperatures; at a certain temperature the two solutions would become completely miscible and the pressure would then rise with the concentration as before.

(C) The gas may first dissolve, forming a solid solution as in (A). If the solid can form a solid chemical compound with the gas, the formation of this compound will begin when, at a given temperature $t°$, the pressure P of the gas reaches, or exceeds, the pressure of dissociation of the compound at $t°$. If the chemical compound is non-miscible with the rest of the solid present, the

pressure will now remain constant although the concentration of the gas in the solid increases (line *ab*). When, however, the whole of the solid is converted into the chemical compound the pressure will again rise as the concentration is increased (see page 118). Possibly the gas might then dissolve in this compound to form another solid solution, the pressure rising with concentration (curve *bc*) and eventually another compound might be formed (line *cd*) and so on. Probably, however, the more common case is that represented in the following figure

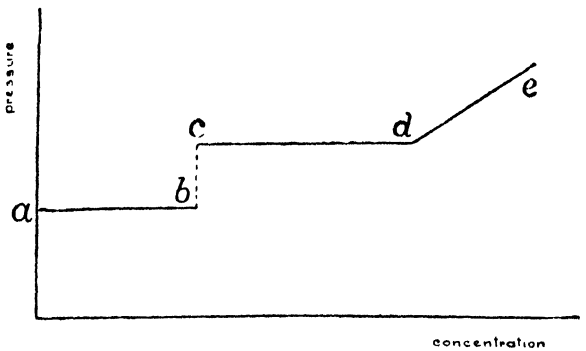


Fig. 22.

in which the gas is not dissolved as such to form a solid solution, but when the pressure reaches the necessary value P, at $t°$, forms a chemical compound. The pressure then remains constant, at $t°$, until sufficient gas has been introduced to convert all the solid into the chemical compound (point *b*). Further addition of the gas will then increase the pressure without altering the concentration in the solid (line *bc*). If now a second chemical compound can be formed containing a greater proportion of the gaseous constituent (and whose dissociation pressure at $t°$ is therefore greater than that of the first compound), the addition of more of the gas will only cause the pressure to rise until its value reaches that of the dissociation pressure of this second compound (point *c*); after this, the pressure will again remain constant with increasing concentration. When the whole of the solid is converted into the second compound (point *d*) the pressure will again rise. If a third compound can be formed the same thing may be repeated, the line becoming vertical and again horizontal as before. (Compare

page 119.) Or possibly the gas might again dissolve as a solid solution (line *de*).

These relationships become much more easily intelligible when they are interpreted in terms of the phase rule, and examples illustrating some of the cases above referred to will be discussed, in that connection, in the next chapter.

(D) The fact that gases condense, in some way on the surface of solid substances is of course well known and may be illustrated by the familiar experiment of immersing a clean glass rod in hot water and observing the formation of gas bubbles on the surface. That this condensation is confined to the surface only appears probable from the fact that the amount of gas which can be so condensed is proportional to the amount of surface. [The gas appears to be 'held' in this way with remarkable tenacity; it is stated that in order to entirely remove the gas from a glass surface it must be heated in a vacuum almost to redness.] It is to be expected therefore that fine powders and porous solids will take up far greater quantities of gas than compact solids; platinum-black, charcoal and spongy platinum are generally mentioned in illustration of this. The more easily liquifiable gases are the more readily absorbed by such substances and for this reason charcoal is largely employed in separating gaseous mixtures. Ammonia, hydrogen chloride, hydrogen sulphide, etc., are most readily absorbed, hydrogen, nitrogen, argon, etc., comparatively slightly and helium least of all.

It is usual to regard this condensation as taking place only at the bounding surface between the solid and the gas and to explain it as a surface tension effect. The same interpretation is frequently put upon the analogous property of solids to take up substances from solutions. The name 'adsorption' is given to all such phenomena to distinguish them from those referred to above under A, B and C, in which the gas, etc., enters the mass of the solid itself, and to which the general term 'absorption' or sometimes 'occlusion' is applied. Unfortunately, however, there is considerable difficulty in attempting to make a distinction of this kind and there exists, at the present time, much difference of opinion with regard to the matter. Until recently, there have been comparatively few experimental data to go upon in attacking

this problem; even now the available data are principally concerned with the adsorption of substances from solutions and various interpretations are put upon the results. The only cases in which exhaustive experiments have been made on the absorption of gases by solids are those of (1) charcoal and carbon dioxide, oxygen, etc., (2) palladium and hydrogen, and (3) the undoubtedly chemical examples such as the absorption of carbon dioxide by lime, oxygen by barium oxide, water vapour by anhydrous salts and ammonia by calcium chloride or silver chloride.

It may be of interest here to give a brief outline of these experiments (1) and (2), and in addition to say something about the adsorption from solutions. The chemical examples referred to in (3) have already been mentioned in previous Chapters and will be again considered in connection with the phase rule.

101. Examples.

Gases in charcoal. The earliest quantitative experiments on the absorption of gases by charcoal appear to have been made by de Saussure in 1814. He observed that Henry's law is not obeyed in these cases and it is now shewn by Travers [*Proc. Roy. Soc.* 1906 (78) 9] that his numbers for oxygen nearly correspond to the relation $\frac{\sqrt[4]{P}}{C} = K$. This author has made measurements of the absorption of carbon dioxide and of hydrogen by charcoal between the temperatures 100° and − 190°. Tabulating his results in terms of the formula $\frac{\sqrt[n]{P}}{C} = K$, he finds in the case of carbon dioxide that n is almost exactly 3 at 0° and 2 at 100°. Probably at higher temperatures $n=1$; if so, carbon dioxide will then dissolve in charcoal in accordance with the simple distribution law. Hydrogen at − 190° was found to behave similarly to carbon dioxide at 0°, i.e. constancy is obtained for the relation $\frac{\sqrt[3]{P}}{C}$. It is evident that if we attempt to interpret these results by supposing that the gas has a different molecular complexity in the solid and gaseous phases, as above suggested, we should have to assume that hydrogen, which is present in the gaseous phase as H_2, must be dissociated into

fractions of an atom in the solid charcoal. [Compare the case of palladium-hydrogen mentioned below.] Travers is inclined to the opinion that when the gas is brought into contact with the solid, the gas diffuses slowly into the solid and that equilibrium is determined by the formation of a 'diffusion column,' the concentration of the gas in the solid decreasing as the distance from the surface increases. The alternative view is that the gas does not actually enter into the mass of the charcoal and that the phenomenon is one merely of surface adsorption*. The well-known property of charcoal in removing colouring matters, etc., from solutions appears to be analogous to its property of 'taking up' gases in the manner here mentioned and elucidation of the general question is being now sought principally in the study of the behaviour of various solids towards aqueous solutions.

Palladium and hydrogen. The fact that large quantities of hydrogen may be taken up by metallic palladium was first observed by Graham in 1866. He found that palladium foil which had previously been heated in a vacuum 'occluded' 376 times its volume of hydrogen at the ordinary temperature, 643 times its volume at 90—97° and 526 times its volume at 245°. The quantities occluded depend, however, on the physical condition of the metal, and on the pressure, as will be indicated below. Graham considered that the hydrogen became condensed to a kind of metal, which he called 'hydrogenium,' and that this formed an alloy with the palladium.

The influence of pressure upon the 'occlusion' was not studied by Graham; but investigations in this direction were made by Troost and Hautefeuille in 1874. It was found by these authors that at a given temperature, e.g. 100°, the pressure at first increased as the concentration of the hydrogen in the palladium became greater, but beyond a certain point, the pressure remained nearly constant or rose only slowly, with increasing concentration, throughout a certain range, after which it again began to rise more rapidly. Similar results were obtained at other temperatures. They concluded from these results that hydrogen first dissolves physically in the metal and, when a certain pressure is reached, combines with the metal to form a chemical compound, which compound can itself dissolve hydrogen physically. The maximum concentra-

* Compare McBain, *Phil. Mag.* 1909 (18) 916.

tion obtained, before the pressure began to rise more rapidly, corresponded roughly to about 600 volumes of hydrogen in one volume of palladium; taking the atomic weight of palladium as about 105 and its specific gravity as about 12, this would represent a ratio of about two atoms of palladium to one of hydrogen. They assumed therefore that the compound had the formula Pd_2H. Ramsay, Mond and Shields [*Proc. Roy. Soc.* 1897 (62) 290] found that after strong ignition the metal could take up as much as 852 volumes of hydrogen, the ratio then corresponding more nearly to the formula Pd_3H_2. Palladium-black, they found, could absorb over 1000 volumes. Graham had shewn that when palladium foil is used as a kathode in the electrolysis of dilute sulphuric acid, it can take up 935 volumes of hydrogen. The quantity absorbed by colloidal palladium is even greater [Paal and Amberger, *Ber.* 1905 (38) 1394].

So far, it will be noticed that, apart from the relative composition of the 'alloy,' the only evidence in favour of the formation of a chemical compound was based upon the observation that, for a given temperature, the pressure remained nearly constant, i.e. nearly independent of the concentration of the hydrogen contained in the solid. Until a comparatively recent date, in fact, behaviour of this kind was regarded as definite proof of a chemical combination between gas and solid. A chemical compound dissociating into a solid and a gas must obey Devilles' law of dissociation (page 117)—that the dissociation pressure is a function of the temperature and independent of the quantities present—and conversely, it was supposed that if the pressure remained constant for different concentrations, a chemical compound must be present. It will be seen, however, that the latter conclusion does not necessarily follow.

Hoitsema was the first to point out that the property mentioned is also capable of another explanation, namely that two non-miscible solid solutions may be formed (see above). In the present case therefore the hydrogen may at first dissolve forming a single homogeneous solid solution, and, on further addition of hydrogen, two solid solutions may be formed, one of which is richer in hydrogen than the other. At a given temperature further addition of hydrogen will then only alter the relative amounts of the two solid solutions, the amount of the richer solution

growing at the expense of the poorer solution; the pressure of the gaseous hydrogen, and the relative composition of the two solutions, will remain constant. These relations will be easily understood by application of the phase rule (following Chapter).

It may be asked then, is there no way of distinguishing the two systems, namely (1) solid solvent, chemical compound and gas; and (2) two solid solutions and gas? By reference to the diagram on page 334 it will be seen that information with regard to this point may usually be obtained by a study of the pressure-concentration curves at different temperatures. For, if a chemical compound is present, the pressure remains constant with increasing concentration in the solid, until the whole of the solid is converted into the compound, after which it again rises. The concentration at which this takes place should be the same at all temperatures. If, however, we are dealing with a system of the second kind, the point at which this rise commences—i.e. the point at which the two solid solutions become completely miscible—will be different at different temperatures.

Further investigations of the relation between pressure and concentration in the system palladium-hydrogen at different temperatures were made by Roozeboom in 1890 and, more particularly, by Hoitsema in 1895 [*Zeit. Physikal. Chem.* (17) 1]. The last named author gives an elaborate summary of all the results and shews that they afford very strong, if not absolutely conclusive, evidence against the hypothesis that a chemical compound is formed. The following diagram will give an idea of the general type of the pressure-concentration curves obtained.

With regard to the first portions of the curve, i.e. when the concentration is small, it is shewn that between 100° and 150°, the relation between pressure and concentration is expressed approximately by the relation $\frac{\sqrt{P}}{C} = K$. From this it is concluded that under these conditions hydrogen dissolves in palladium as single atoms. As the concentration increases the results approximate more nearly to $\frac{P}{C} = K$ and it is supposed that the gas then begins to dissolve as H_2. Travers, however, (*loc. cit.*) draws attention to the objection referred to above, that if this mode of

reasoning is adopted, hydrogen would appear to dissolve in charcoal in fractions of atoms.

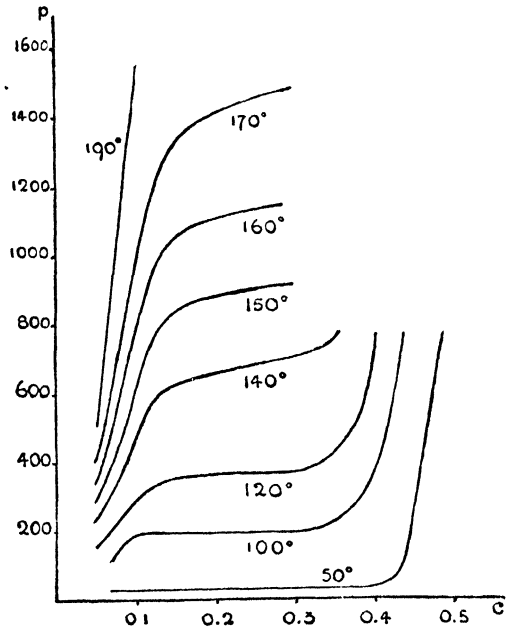


Fig. 23.

In conclusion, it may be mentioned that Shields [*Proc. Roy. Soc. Edin.* 1898, 169] shewed that the electromotive force of the combination, palladium containing little hydrogen—dilute sulphuric acid—palladium containing much hydrogen, was zero. The arrangement does not therefore behave like a true concentration cell, as it might be expected to do if the hydrogen were merely dissolved. He considers that the result is more in accordance with the view that a chemical compound is formed, in which case the E.M.F. would be independent of the quantity of the compound.

102. Adsorption from solutions.

The well-known property which charcoal possesses of removing colouring matters from solutions is generally considered to be entirely analogous to its power of absorbing gases, and, in this case also, considerable difference of opinion exists as to the nature of

the phenomenon. If an aqueous solution of some solute, such as iodine, picric acid, organic dye-stuff, etc., be shaken up with charcoal the concentration of the solute in the solution is, as a rule, diminished; other solids, such as silk, cotton, clay and most other substances, of a colloidal character, behave similarly. In such cases 'positive adsorption' is said to occur. Instances are known, however, in which 'negative adsorption' occurs, i.e. the concentration is increased; this happens, for example, when a solution of sodium chloride is shaken with charcoal.

The amount of solute taken up by the solid is not found to be directly proportional to the concentration of the solution, but follows some more complicated law; generally the amount taken up is relatively greater as the concentration is less. Thus when ferric hydroxide is shaken up with a solution of arsenious oxide, a certain quantity of the latter will be removed from the solution, and equilibrium will be established between the arsenious oxide adsorbed in the ferric hydroxide and that in solution. Calling the concentration in the ferric hydroxide C_1 and that in solution C_2 experiment shewed that, for different initial concentrations, $\frac{C_1^5}{C_2} = 0{\cdot}631$, shewing that relatively more will be adsorbed as the solution is weaker. In many other cases expressions of a similar kind have been found to hold; thus in the adsorption of picric acid by silk, Walker and Appleyard [*Trans. Chem. Soc.* 1896, 1334] found constancy for the relation $\frac{S}{\sqrt[2.7]{W}}$ in which S is the concentration of the acid in the silk and W is that in the water.

It would appear that in a large number of typical instances the relation may be expressed by the general formula

$$\frac{x}{a} = KC^m,$$

where x is the mass adsorbed, a is the adsorbing surface (usually estimated from the weight of adsorbing material) and C is the concentration of the solute; K and m are constants depending on the temperature and the nature of the solute*.

These phenomena have been explained in various ways. There is, for example, the solid solution theory which supposes that the

* The exponent m is generally, but not invariably, less than unity; its value often falls between 0·5 and 0·8.

substance is dissolved in the solid. Witt, for instance, regards a dyed fibre as a solid solution of the dye and shews that, in many cases where a certain dye has a different colour in the solid state and in solution, the colour of the dyed fabric is that which it has in solution and not that which it has as a solid. Certain dyes exhibit fluorescence when dissolved but not when solid, and, in these cases, it is found that materials dyed with these substances may shew marked fluorescence.

If the process of adsorption consists in the formation of solid solutions the constancy of such expressions as $\frac{S}{\sqrt[n]{W}}$ could sometimes be explained by supposing that the dissolved substance has a different molecular state in the two solvents. In other cases, however, such an explanation appears to be inadmissible; thus in the example mentioned of picric acid and silk, the molecular weight of picric acid should be about three times as great in water as in silk, whereas cryoscopic, etc., measurements indicate the simplest formula for picric acid in aqueous solution.

Secondly, there is the view that adsorption is due to chemical combination between the solid and solute. In this case it might be expected that the concentration of the solution should, when equilibrium is established, remain constant within certain limits, at a given temperature, although further quantities of the solute are added, just as the pressure of carbon dioxide remains constant in its equilibrium with lime and chalk. It does not follow, however, that this evidence is conclusive. [Compare p. 327, also Robertson, *Zeit. Chem. Ind. Kolloide*, 1908 (3) 49.]

The third view, which now appears to be the most popular, is that adsorption is a surface-tension phenomenon, being dependent upon a change in surface-tension between solid and liquid.

The treatment of the subject, from this point of view, on the theoretical side is not simple. From thermodynamical considerations Gibbs deduced an equation connecting concentration surface-tension and quantity adsorbed which, in a somewhat modified form, may be stated as

$$\Gamma = -\frac{c}{RT}\frac{ds}{dc}.$$

Here c is the concentration of the solute in the bulk of the solution, s is the surface-tension at the interface and Γ, the 'adsorption coefficient,' i.e. the mass

of solute per square centimetre of dividing surface in excess of what would have been there had no adsorption occurred. [See Lewis, *Phil. Mag.* 1908 (15) 499.]

According to this theory, it can be shewn that if the presence of the solute diminishes the surface energy of the film, at the surface of contact, the solute will tend to accumulate in this film, and conversely; the theory accounting in this way for positive and negative adsorption respectively.

A considerable number of experiments have recently been made by various authors with a view of testing these different theories. Freundlich [*Zeit. Physikal. Chem.* 1906 (57) 385], for instance, has studied the adsorption of many organic and inorganic compounds by charcoal, and he considers that the results are capable of being explained in terms of Gibbs' theory. Lewis, on the other hand, (*loc. cit.*) has investigated the matter by studying the condensation of certain dyes or salts on the surface of drops of a liquid hydrocarbon, and he finds that there is considerable discrepancy between the observed and calculated results. Bayliss [*Biochem. Journ.* 1906 (1) 175] has studied the adsorption of various electrolytes by protein substances, and although his results are mainly interpreted in terms of Gibbs' theory he considers that, in certain cases, the formation of solid solutions and of compounds may play an important part. Freundlich's results appeared to shew that the amount of the adsorption is independent of the nature of the adsorbing substance although it depends on the solute and solvent, but Davis [*Trans. Chem. Soc.* 1907, 1666] finds that even the same substance in different conditions may have different adsorbing power; thus, as regards the adsorption of iodine by carbon, different results are obtained with different varieties of charcoal. He considers that the process consists of a surface condensation, which is instantaneous, and a diffusion into the interior, with formation of solid solution, which may proceed for weeks or months.

PRACTICAL WORK.

(1) *Determination of the solubilities of certain gases.* The apparatus by which the solubilities of the less soluble gases have been determined are described in the lecture. In place of the original apparatus of Bunsen (absorptiometer) the simpler apparatus of Heidenhain and Meyer, as modified by Ostwald, which is shewn in the following figure, is now generally employed.

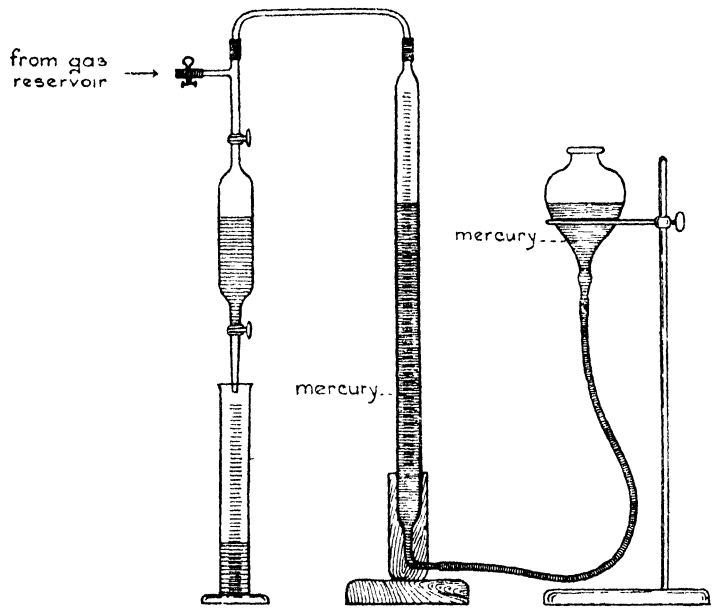


Fig. 24.

Neither of these forms of apparatus would be applicable for the determination of the solubilities of the very soluble gases, such as ammonia or hydrogen chloride. In these cases the method of Roscoe and Bunsen is employed. The thin glass vessel, bent in the following form (fig. 25), has a capacity of about 50 c.c. The vessel, clean and dry, is first weighed and a convenient quantity of the solvent, say about 30—40 c.c., is then introduced. The gas, dried if necessary, is then passed into the solvent, the vessel being immersed in a bath at the required temperature, until saturated. The ends *a* and *b* are then sealed (or drawn off and sealed, the parts of course being retained) and the whole is

weighed. The vessel containing now a known weight of the saturated solution is broken under a sufficient excess of a suitable solution and the quantity ascertained by titration. In the case of ammonia it is broken under an excess of standard acid (say 100 c.c. N H_2SO_4 conveniently diluted) and the residual acid determined by back titration with soda, using methyl orange or

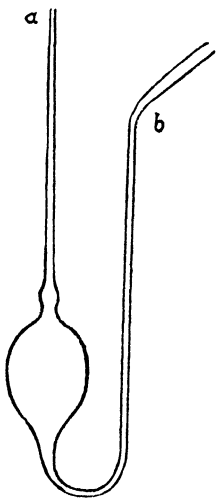


Fig. 25.

litmus as indicator. In determining the solubility of hydrogen chloride the vessel may be broken under water and the acid directly titrated. [If great accuracy is required corrections must be applied for the weight of air displaced and the weight of moist vapour filling the spaces.]

(2) Qualitative experiments are made on the adsorption by charcoal of gases and of colouring matters from solutions.

The adsorption of iodine by charcoal may be studied quantitatively as follows. Into several stoppered bottles, introduce equal weights (say, 2 grams) of animal charcoal (washed, dried and ignited) and 50 c.c. of alcohol. Now add measured volumes (say 40 c.c., 25 c.c., 10 c.c....) of a normal alcoholic solution of iodine diluted with alcohol so that the total volume of liquid in each bottle is 100 c.c. Allow to stand for 24 hours, with frequent shaking, and titrate 10 c.c. of each clear solution with $\frac{N}{10}$ thiosulphate. From the results calculate, in each case, the total weights of iodine adsorbed and left in solution.

CHAPTER XXIII.

THE PHASE RULE.

103. NUMEROUS instances have been mentioned in the foregoing chapters of chemical and physical equilibrium in systems which are heterogeneous, i.e. in which there is a surface of separation between certain parts of the system, and the parts separated are physically or chemically different. As examples, one may refer to the equilibrium between calcium carbonate and its products of dissociation; steam, hydrogen, iron and oxide of iron; a soluble solid, its aqueous solution and aqueous vapour; double salt, two single salts, solution and vapour, and so on.

The conditions of equilibrium in such systems have been briefly dealt with in terms of the general laws, so far considered, which are applicable to both homogeneous and heterogeneous systems; such as the law of mass action and the principle of le Chatelier. In the case of heterogeneous systems, however, it becomes possible also to regard the conditions of equilibrium, from another point of view, in terms of the Phase rule of Gibbs.

It would of course be entirely out of place here to attempt to present anything like a complete account of this important law. It is expected that the serious student will be proceeding with his studies of the well-known standard works on the subject, such as those of Findlay or Bancroft. In the present instance we must content ourselves with the statement and explanation of a few provisional definitions and the discussion of some applications of the phase rule to well-known chemical problems.

The terms employed in stating the phase rule in its usual form, *phase, constituent, component,* and *degree of freedom,* require careful consideration. There is little difficulty in understanding

the meaning attached in this connection to the word *phase*. The phases are 'the homogeneous parts of the heterogeneous system or 'the mechanically separable parts which are themselves homogeneous.' Ice, liquid water and water vapour are three phases which may under certain conditions co-exist in equilibrium with one another. Iron, oxide of iron and the gaseous mixture of steam and hydrogen constitute three phases in the equilibrium referred to previously. A gaseous mixture is always to be regarded as a single phase since each portion of it is physically and chemically identical with any other part. A similar remark applies to an isomorphous mixture in the solid state and to a mixture of completely miscible liquids. [Discrete particles of the same substances, e.g. coarse lumps or powders, are of course to be regarded as a single phase for the same reason, although they may, in one sense, be said to be 'mechanically separable.']

The term *constituent* may be used in reference to the phase rule to denote the primary substances out of which the system under consideration is composed. It is a matter of indifference whether we regard our system as being constituted from the primary atoms, groups or molecules; the rule is, in fact, independent of atomic or molecular hypotheses. In the equilibrium between sodium sulphate and water, for example, we might regard the constituents as being the substances denoted by the symbols

Na, S, O and H; Na, (SO_4) and H_2O;
Na_2O, SO_3 and H_2O, or Na_2SO_4 and H_2O.

The *number of components* may provisionally be defined as the least number of the constituents out of which all the phases of the system can be constituted. It must particularly be noticed that, for the purpose of defining the system in terms of the phase rule, the choice of constituents, as regards their nature, is immaterial so long as this least *number* can be correctly stated. Thus in the system sodium sulphate—water, we may have as possible phases, the anhydrous salt, decahydrate, heptahydrate, solution, aqueous vapour and solid ice, and all of these can be obtained from sodium sulphate and water, either singly or collectively. Similarly they are all obtainable from Na_2O, SO_3 and H_2O or Na, SO_4 and H_2O, but here we should evidently select an unnecessarily large number

of constituents since two only are sufficient. Observe that each of the constituents which is chosen as a component according to this definition, must be capable either by itself or in combination, or homogeneous mixture, with other components, of constituting one or more phases of the system; that is to say, it must not dissociate into two or more non-miscible parts having a different composition It may, however, dissociate, reversibly, in a single phase and yet be regarded as a component; thus, in the system last referred to, water would still be regarded as a component even if it could be partially dissociated in the vapour state under the conditions considered. Again, the ionisation of the sodium sulphate in solution would in no way interfere with its title as a component; the reason for this will be apparent from what follows.

Another way of defining the term is to say that the components are those constituents which have an independently variable concentration. Such a definition certainly has the advantage of brevity but, in the present writer's experience, it is very liable to be misunderstood. An illustration may perhaps serve to make the meaning clear. If we take weighed quantities of sodium sulphate and water in a closed vessel, in such proportion that excess of solid is present, and subject the system to variations of temperature and pressure, we know in all cases what are the total amounts of the two substances contained in the vessel, although they may partly be in a state of combination with one another. We may now add further weighed quantities of one or the other substance and we shall still know the total concentrations under varying conditions. Under suitable conditions, hydrate of sodium sulphate will be formed as a solid phase but the quantity of this will depend on the temperature and pressure; i.e. its 'concentration' is not independently variable and it cannot therefore be regarded as a component. None of the constituents Na, H, O, S, SO_3, SO_4, or Na_2O are independently variable since if the concentration of any one of them is varied, that of one or more of the others must also vary with it in some fixed proportion.

The case may be stated more generally in the following form*. It is evident that if we represent the constituents of

* See Trevor, *J. Physical Chem.* 1896 (1) 22; Bancroft, *The Phase Rule*, page 226.

our system as the elementary substances which are present, there will, in general, be certain necessary relationships between the weights of some of them. Thus, in the system referred to above, whatever the conditions may be under which we study the system, there must always be, in the phases in which these constituents occur, 46 parts of sodium to 96 parts of (SO_4) and again, there must always be 2 parts of hydrogen to every 16 parts of oxygen, other than that contained in the SO_4 group. We have therefore two *limitations* and four *constituents*. If, on the other hand, we regard the constituents as Na_2O, SO_3 and H_2O, there is the necessary limitation that for every 62 parts of Na_2O there must always be present 80 parts of SO_3. Hence we have three constituents and one limitation. Substituting copper sulphate for sodium sulphate, the same remarks would apply provided we start with copper sulphate and water and consider only the equilibrium between these two substances. If, however, we take varying quantities of sulphuric acid and copper oxide, the limitation referred to does not obtain; there will then be three constituents, if we consider them as CuO, H_2O and SO_3, and no necessary limitation.

The rule for finding the number of components ($= C$) is therefore to state the number of constituents ($= m$) and, from the known chemical relationships, find the number of limitations ($= n$). We shall then have $C = m - n$. As further examples, consider the following cases. If we study the equilibrium in the system—potassium chloride, magnesium chloride—and regard the elements as constituents, there is evidently one necessary limitation, namely, that the quantity of chlorine present must always be chemically equivalent to the potassium and magnesium jointly. If, on the other hand, we consider the constituents to be the two salts, there is no necessary limitation. On either view therefore the number of components is two

Consider now the system—potassium chloride, sodium bromide. Here there is evidently one limitation, namely, that the quantity of (potassium + sodium) must be chemically equivalent, collectively, to the (chlorine + bromine) collectively. Hence there are four constituents and one necessary limitation, so that the number of components is *three*. It is unnecessary to decide *which* are the components; the number is all that is required.

Degrees of freedom or 'Variance' of the System. In a one component system, three phases can co-exist in stable equilibrium only at one particular temperature and pressure—e.g. ice, water and aqueous vapour, only at 0·0076° and 4·6 mm.; whereas two phases may co-exist at various temperatures provided that the pressures are suitably adjusted; for each temperature, that is, there must be a corresponding pressure. If, however, we dissolve a substance, such as common salt, in the water the equilibrium of the system, now a two-component one, will depend not only on the temperature and pressure but also on the concentration of the dissolved substance; it is now possible to have various pressures at the same temperature provided that the concentration is suitably adjusted. In order that the system may be perfectly 'defined' it is necessary arbitrarily to fix either temperature and pressure, temperature and concentration, or pressure and concentration; the third factor will then adjust itself to a definite value.

The capability of the various phases of a system to exist together in stable equilibrium depends then upon certain variable factors such as the temperature, pressure and, when the phases have a variable composition, the 'concentration' or composition of these phases. A system in which the phases present can only co-exist in stable equilibrium when each of these factors has a particular value, is said to have no *degree of freedom*, or to be *non-variant.*

In a *univariant* system any one of these variable factors can be arbitrarily fixed; the other factors will adjust themselves to corresponding fixed values and the system will then be perfectly defined. If we choose to fix the temperature, for example, at a certain value, the equilibrium between the existing phases can only be maintained if the pressure and concentration adjust themselves to certain definite values. In a *bivariant* system, two of the factors must be arbitrarily fixed before the system is defined—and so on.

104. Having briefly considered the meanings of these three terms—the number of components (C), the number of phases (P) and the degrees of freedom (F)—we may state the phase rule in the usual way, namely

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

It is questionable whether anything would be gained by attempting to give here a simple explanation of the way in which this 'rule' is deduced from thermodynamic considerations. We shall, for the present, take the rule for granted, since we are now concerned only with its applications to certain chemical and physical problems. In the following illustrations, the examples are selected principally from instances of heterogeneous equilibrium which are of special interest from the chemist's point of view, most of which have been referred to in previous chapters.

1. *Common salt and water.* The possible phases are, in this case, solid salt*, ice, aqueous solution of the salt and aqueous vapour. The system is clearly a two-component one and it follows that these four phases can only co-exist at one particular temperature, pressure of the vapour and concentration of the solution.

If we cool down a solution of common salt, either salt or ice will begin to separate at a certain temperature, the solution therefore becoming weaker or stronger respectively. Eventually the solution remaining will have a concentration of about 36 grams of salt in 100 grams of water, when, on further cooling, both ice and salt will separate. The temperature will then be about $-21°$ and the vapour pressure 0·73 mm. The system is now non-variant and, if any one of the three conditions is altered, the equilibrium between the four phases can no longer exist. If we continue to remove heat from the system, ice and salt continue to separate in the proportion in which they existed in the saturated solution and, as long as the four phases are present, the temperature remains constant. The solid mixture of ice and salt obtained in this way was regarded by Guthrie as a chemical compound, since the solution appeared to have a definite freezing point and the composition of the solid appeared to be absolutely constant. If, however, the vapour phase is removed and the remaining 'condensed system' is subjected to varying pressures, it can be shewn that the composition of the solid and the freezing point of the solution are not really constant, i.e. they vary somewhat with the pressure. Here, in fact, we have two components in three phases, so that the system is now univariant; we may therefore alter

* The hydrate $NaCl.2H_2O$ is said to separate from the saturated solution at about $-10°$.

one of the conditions provided the other two suitably adjust themselves.

Further proof that these so-called 'cryohydrates' are not chemical compounds is afforded by the fact that they are not really homogeneous; in the case of coloured salts, the crystals of salt and ice can be distinguished when the mixture is examined under the microscope.

If, starting from the 'cryohydric point,' we add heat to the system, one of the solid phases will first disappear; ice, if the solid salt is present in excess, or salt, if the ice is in excess. The system will then be univariant. If, for example, the ice first disappears, we shall have left solid salt, saturated solution and vapour; this system can now remain in equilibrium throughout a certain range of temperature, but for each temperature there must be a definite vapour pressure and a definite concentration of the solution. If the quantity of solid salt is not too large and if the solubility rises with increasing temperature, the solid will all disappear, when a certain temperature is reached, and we shall then have present only two phases, i.e. unsaturated solution and vapour. The system has now two degrees of freedom; we may, for example, alter both the temperature and the concentration at will, within certain limits so that we can have varying concentrations at the same temperature or the same concentration at varying temperatures; but the third condition, the vapour pressure, must in each case adjust itself correspondingly.

If we consider the case of two metals which, in the liquid state, are miscible but which form no compounds with one another and which are non-miscible in the solid state, e.g. zinc and cadmium, we may follow the conditions of equilibrium in a manner quite analogous to that used in the foregoing example. Thus, at a certain temperature (270°), the four phases, solid zinc, solid cadmium, liquid alloy and vapour, may co-exist in equilibrium, the composition of the alloy and the vapour pressure having their definite values. The temperature at which this non-variant system exists is, in this case, called the 'eutectic point' and the mixture of the composition which then exists is called an eutectic alloy. In the case of metals which in all proportions form solid solutions, or mixed crystals (see page 320), it is evident that the

solid which separates on cooling will constitute only a single phase, so that there can be no eutectic point, i.e. the system is never non-variant. This subject will be further considered in a future section.

Lime, chalk and carbon dioxide. From the rules mentioned above, it is evident that this is a two-component system, whether we choose to regard it as made up of lime and carbon dioxide or of the elements carbon, calcium and oxygen with one necessary limitation—namely that the oxygen present must always be chemically equivalent to the calcium and carbon collectively. The possible phases (if we exclude the reputed compounds $2CaO.CO_2$ and $4CaO.3CO_2$, see page 118) are the two solids, lime and chalk, and carbon dioxide gas. When all of these are present the system will be univariant and for each temperature there will be a fixed pressure of the gas. There is no relative concentration to consider here since each phase has an invariable composition. If the pressure of carbon dioxide is reduced continuously, at a suitable given temperature, e.g. by pumping away the gas, the whole of the chalk will eventually be decomposed and only two phases will remain; under these conditions, then, lime could exist together with carbon dioxide at a given (sufficiently high) temperature under different pressures of the gas. A similar remark applies to the case when sufficient carbon dioxide is pumped into the apparatus to convert all the lime into chalk. The example previously mentioned of barium oxide, barium dioxide and oxygen, may be dealt with in similar terms.

Sodium bicarbonate. If pure sodium bicarbonate is heated in a closed vessel, it will be found that the gaseous mixture of carbon dioxide and water vapour has a definite, constant pressure for a given temperature. The system therefore behaves as if it were univariant. If, however, we add an excess of one of the gaseous constituents, for example, if we introduce more carbon dioxide, the pressure at a given temperature is no longer constant, but will depend on how much extra carbon dioxide is added. There are different ways of looking at these facts in terms of the phase rule. We may, for instance, regard the constituents as Na_2CO_3 and H_2CO_3, since all the phases can be constituted from these; there is no necessary limitation between the ratio of these, and the behaviour as a univariant system will not be altered if we

introduce an excess of sodium normal carbonate. Or, we may consider the constituents to be Na_2O, CO_2 and H_2O, with the limitation that the two latter are present in a necessary chemical ratio. On either view the system will be a two-component one, with three phases. If, however, excess of carbon dioxide is added, the necessary limitation referred to no longer exists and the system is a three-component one and, with the three phases, will be bivariant.

Ammonium chloride, etc. It has previously been mentioned that when solid ammonium chloride is heated in a closed vessel to a suitably high temperature, so that the substance is partially vaporised, there is a constant vapour pressure for a given temperature which is independent of the quantity of solid remaining and of the quantity of vapour. The system is to be regarded as having one component, since every part of the system has the same composition; the fact that the vapour consists mainly of the products of dissociation, does not affect the case at all. We may therefore either regard the system as constituted from NH_4Cl, or from NH_3 and HCl with the necessary limitation that the two latter must be present in the ratio of 17 to 36·5 parts by weight. We have therefore one component in two phases and the system is univariant.

Quite similar remarks apply to *phosphorus pentachloride* or *chloral hydrate.*

If in any of these cases excess of one or other product of dissociation is added, the pressure is no longer a function of the temperature only; the system is now bivariant since the number of components has been increased to two, owing to the removal of the restriction that the dissociation products must be present in equivalent quantity. Similar considerations apply to the dissociation of *mercuric oxide.* If this substance is heated in a closed vessel to such a temperature that it partly decomposes into mercury and oxygen, that the mercury is entirely vaporised and that some solid mercuric oxide remains, there will be two phases, the solid undecomposed oxide and the gaseous mixture of oxygen and mercury. Experiment shews that here again, under these conditions, there is a fixed vapour pressure for a given temperature. The system has one component for reasons analogous to those given in the previous cases; either HgO, or Hg and O with one

necessary limitation. Addition of excess of oxygen, or excess of mercury vapour, will cause the system to become a bivariant one and the vapour pressure will no longer be dependent on the temperature alone. If, however, at a suitable temperature, sufficient excess of mercury is added, so that some of it remains in the liquid state, there will be three phases present and the system becomes again univariant.

In all the cases last mentioned there is, it is true, another way of looking at the matter. Thus, it has been objected that there is no real difference between the system formed by heating ammonium chloride and that obtained by mixing together hydrochloric acid and ammonia, except that in the first case one is tied down to a certain fixed proportion between the constituents. The system, it is suggested, is really a *two*-component one in both cases, but in the former an arbitrary limitation has been introduced, so removing one of the degrees of freedom. The question then turns upon the opinion whether the introduction of this restriction is, or is not, arbitrary. (Compare page 318.)

Double salts. The complex character of the various states of equilibrium which may exist when a double salt is brought into contact with a limited quantity of water, has already been referred to on page 270. With the assistance of the phase rule, such equilibria become much more easily intelligible, particularly when illustrated by means of diagrams and models. (These are shewn in the lecture and will be found in the text books above mentioned.) We must, in the present instance, confine ourselves to only a few remarks of a preliminary character. Consider the case of a double salt of the commoner type, one, that is, which is derived from two different metals and one acid. In the systems produced by treating this salt with a small quantity of water, there may arise various phases, according to the conditions which obtain. We may have as solid phases, the double salt itself, the two single salts and ice; these salts may be anhydrous, or may give rise to one or more solid hydrates. Thus, for example, in the case of carnallite, the solid phases may be, the double salt, potassium chloride (anhydrous), magnesium chloride with 12, 8, 6, 4 and 2 molecules of water of crystallisation, respectively, and ice. In addition, there may be the saturated aqueous solution and aqueous vapour. The system

is a three-component one for the reasons above mentioned (i.e. water, KCl and $MgCl_2$; or water, K, Mg and Cl with the one necessary limitation that the potassium and magnesium are together equivalent to the chlorine).

For a non-variant system, five phases must therefore be assembled; this can occur for instance at $-34{\cdot}3°$ (cryohydric point) when ice, KCl, $MgCl_2.12H_2O$, aqueous solution and vapour can co-exist in equilibrium. The aqueous solution then has a definite concentration and the vapour pressure a fixed value. Or again, at $-21°$, the transition point, the five phases, carnallite, KCl, $MgCl_2.12H_2O$, aqueous solution and vapour can co-exist. The aqueous solution will have a fixed composition

$$(H_2O : MgCl_2 : KCl = 1 : 0{\cdot}066 : 0{\cdot}005)$$

and the vapour pressure will again have a definite value.

It is usual, however, to consider such cases as 'condensed systems' (i.e. those in which the vapour phase is absent, or is not concerned), since the solubility determinations are made in open vessels under atmospheric pressure. Since the influence of pressure is very slight, the atmospheric pressure may be regarded as constant. Under these circumstances we exclude one of the degrees of freedom and one of the phases, so that the relationship, in terms of the phase rule, remains unchanged.

[Note that the *transition point* refers to that temperature, in a *condensed system*, at which a new phase makes its appearance and can co-exist in equilibrium with the phases which were already present.]

To obtain a univariant system, we must assemble four phases (or three if we are considering the condensed system at constant pressure). Hence in order that the concentration of the solution in contact with the solid may have a constant value at a given temperature, as the temperature is varied, two solid phases must be present. This is illustrated in the case of carnallite by the fact that, in order to have the solid double salt in equilibrium with the saturated solution, it is necessary to have one of the solid single salts also present. [It is true that in certain cases (i.e. when the two single salts are equally soluble or when the temperature is beyond the transition interval) it is possible to obtain a pure

saturated solution of the double salt, one, that is, when the solid has the same composition as the salt in solution. But we may then regard the system as a two-component one, since the two constituents, water and the double salt, are sufficient to constitute all the phases.] Other univariant systems may also exist; thus we may have equilibrium at different temperatures, within certain limits, between the two solid single salts, solution and vapour, or between either single salt, ice, solution and vapour.

The case of *reciprocal salt pairs* may be considered in a similar way. If we have the two salts AB and CD in contact with water and the salts are capable of double decomposition, the system is a four-component one, since the four salts AB, CD, AD and CB are to be regarded as a system of three components. For a non-variant system, we must therefore assemble six phases and for a univariant system, five phases. At the transition point the four solid salts, solution and vapour can co-exist in equilibrium. On either side of this point, one or other pair is the stable one, but in order that these two solid salts may be in equilibrium with the solution at different temperatures, one of the other solid salts must be also present, i.e. a fifth phase is necessary. Beyond the transition interval, however, equilibrium can exist between the two salts, solution and vapour; here the system becomes a three-component one, since the two salts no longer interact appreciably, and four phases constitute a univariant system.

Steam and iron. The equilibrium system containing iron, oxide of iron, water vapour and hydrogen, referred to on pages 116 and 154, must be regarded as a three-component one; the constituents are iron, oxygen and hydrogen and between these there is no necessary limitation. If we assemble the three phases, iron, oxide of iron and the gaseous mixture of hydrogen and water vapour, the system must be bivariant. We have then to account for the much-quoted results obtained by Deville, and later by Pruener and others, which shewed that the ratio of the partial pressures of hydrogen and steam at a given temperature was constant. The variable factors of the system may be regarded as the temperature, concentration of the gaseous mixture and total pressure (temperature, ratio of the two partial pressures and the sum of the partial pressures), or as the temperature, and the two partial pressures. We should expect therefore that any two of

these three variables might have arbitrary values assigned to them, when the third variable would then assume a corresponding value. In the experiments referred to we find a particular case, for one of the partial pressures, that of the water-vapour, was kept constant; consequently, when the temperature was also fixed, the third variable, the pressure of the hydrogen, adjusted itself correspondingly.

Palladium and hydrogen. When a gas is brought into contact with a liquid or solid and some of the gas dissolves forming a homogeneous liquid solution or solid solution, there are two components in two phases and the system is bivariant. At a given temperature, therefore, both the pressure of the gas and concentration of the solution can be varied; for a given pressure and a given temperature there must be a fixed concentration, but if the temperature is fixed and the pressure is altered, the concentration will alter correspondingly. The concentration may vary directly as the pressure (Henry's law) or otherwise (see page 326). If, however, the circumstances are such that a third phase separates, the system becomes univariant. Thus, if hydrogen dissolves in palladium to form a single homogeneous solution, the system is bivariant; whereas if a chemical compound is found, which is non-miscible, or only partly miscible, with the rest of the palladium, the system is univariant and, for a given temperature, the pressure will be constant; the only result of attempting to increase the pressure will be the formation of more of the compound. When, however, all the palladium is converted into the chemical compound, there will again be only two phases, and the system again becomes bivariant; at a given temperature then, the pressure will increase as the concentration becomes greater. If therefore experiment shews that the pressure is a function of the temperature and is independent, within certain limits, of the concentration, the inference is that three phases are present. It does not follow, however, that the two solid phases are of necessity the chemical compound and the unaltered palladium, since two non-miscible solid solutions of hydrogen in palladium would equally well account, so far, for the facts (see page 327).

Until a comparatively recent date it was always supposed that obedience to the 'law of dissociation' gave conclusive proof of chemical combination between gas and solvent; conversely, obedience to Henry's law was regarded as evidence that no chemical compound was formed. We have already seen that in

neither case is the evidence certain; there is the possibility of accounting for two solid phases independently of chemical combination in the first case and, in the second, the formation of a chemical compound is not inconsistent with the obedience to Henry's law (see page 324).

105. Hydrates.

The hydrate of a substance (R) is generally understood to be a chemical compound of the substance with water ($m\mathrm{R}.n\mathrm{H_2O}$) which can be formed reversibly from these constituents, i.e.

$$m\mathrm{R} + n\mathrm{H_2O} \rightleftarrows m\mathrm{R}.n\mathrm{H_2O}.$$

[Thus $\mathrm{CuSO_4}.5\mathrm{H_2O}$ is a hydrate of copper sulphate and $\mathrm{Cl_2}.9\mathrm{H_2O}$ is a hydrate of chlorine*. 'Carbohydrates,' however, are not now regarded as hydrates of carbon; $\mathrm{NH_4NO_2}$ is not considered to be a hydrate of nitrogen, nor is KOH usually regarded as a hydrate of potassium oxide, since the changes $\mathrm{NH_4NO_2} = 2\mathrm{H_2O} + \mathrm{N_2}$ and $\mathrm{K_2O} + \mathrm{H_2O} = 2\mathrm{KOH}$ can be effected only in one direction.]

In most cases the ratio of m to n is a simple one, but this is by no means necessary. The term 'complexity of a hydrate' is used somewhat ambiguously in this connection; a complex hydrate might be understood to be one in which n is large relatively to m, or m relatively to n; or again one in which both m and n are large. In the most usual cases, one molecule of R is found to combine with 1, 2, 3... molecules of water; in other cases, however, we find formulae with $\frac{1}{2}\mathrm{H_2O}$, i.e. two molecules of R to one of water, and so on.

Recognition of hydrates. If by the action of a substance (R) on water a product is obtained which, on heating, again gives (R) and water, it does not of course follow from this alone that it is a true hydrate. If, however, this product is homogeneous and has a definite crystalline form, solubility, colour, melting point, etc., a constant composition and contains the two constituents, R and $\mathrm{H_2O}$, in some fairly simple ratio of their formula-weights, the evidence that it is a hydrate is usually considered to be sufficient.

* The number of molecules of water in this compound has been variously stated as 8, 9 or 10.

But since the mistake was made in regarding 'cryohydrates' as chemical compounds, chemists have been somewhat nervous of relying only upon evidence of this kind. It must be remembered, however, that in the so-called cryohydrates, these conditions were not really fulfilled; the composition, for example, of the solid cryohydrate is not really constant, since it can be to some extent altered by pressure. Similar remarks apply to the constant boiling point mixtures referred to on page 317.

Application of the phase rule affords evidence of a more conclusive nature in the cases where it happens that a hydrate forms a distinct phase, but not otherwise. To illustrate this application, one may refer to the example usually given of the hydrates of copper sulphate.

According to evidence of the kind mentioned above (e.g. isolation of a substance of constant composition in which the formula-weight ratio is a simple one), the existence of the following hydrates of copper sulphate has been assumed.

(1) The monohydrate; obtained by heating the pentahydrate to 100—105°.

(2) The dihydrate; said to be obtained by keeping the pentahydrate in a vacuum at 20° for some days (Thorpe and Watts).

(3) The trihydrate; prepared by pouring a cold concentrated solution of copper sulphate into sulphuric acid of sp. gr. 1·7 (Thorpe and Watts) or by keeping the pentahydrate in dry air at 25—30° (Magnier de la Source).

(4) The pentahydrate prepared in the usual way by crystallising the aqueous solution.

(5) The hexahydrate; obtained by Lecoq de Boisbaudran by 'sowing' a super-saturated solution of the pentahydrate with a crystal of $NiSO_4.6H_2O$.

(6) The heptahydrate; obtained from the mother liquor in the preparation of the hexahydrate, by addition of a crystal of $FeSO_4.7H_2O$.

If, however, we study the equilibrium between copper sulphate and water vapour, by subjecting the anhydrous salt to the action of gradually increasing quantities of the vapour, or by gradually removing water vapour from the fully hydrated compound, the problem can be dealt with in a manner analogous to that indicated

in the previous sections. Thus if each hydrate forms a distinct phase (i.e. is non-miscible with the other hydrates, or the anhydrous salt), the system will become univariant when two different hydrates, or one hydrate and the anhydrous salt, are present together with the vapour. When this is the case, the pressure of the vapour should be constant for a given temperature as long as the three phases are present. If therefore we start with the highest obtainable hydrate and, at a constant temperature, gradually remove water vapour, allowing the system to come to equilibrium after each withdrawal, the pressure should remain constant as soon as the first portion of the hydrate has begun to dissociate since the three phases, higher hydrate, next lower hydrate and vapour, are present. The pressure should then remain constant until the whole of the higher hydrate has been dissociated; at this point the system will become bivariant, since only two phases are present, but further withdrawal of water vapour will cause dissociation of this lower hydrate and the system will again become univariant. The pressure now attains a new value and again remains constant as long as any of this second hydrate remains. The pressure-concentration curve will therefore be of the type indicated in the first portion of that in figure 22, page 328, the breaks occurring at the composition of the respective hydrates. The system will become univariant also if sufficient water is present to dissolve a portion of the solid hydrate, i.e. if the solid is in equilibrium with its saturated solution and the vapour. In this case the presence of new hydrates may often be indicated by breaks of continuity in the temperature-concentration curve (solubility curve). A study of the pressure-concentration curves of copper sulphate when the hydrated salt is gradually dehydrated at a given temperature, reveals the existence of only *three* hydrates $CuSO_4 . 5H_2O$, $CuSO_4 . 3H_2O$ and $CuSO_4 . H_2O$. Thus at 50° the 'tension of dissociation' of the pentahydrate (i.e. the vapour pressure in the system pentahydrate, trihydrate, vapour) is 47 mm.; that of the trihydrate (trihydrate, monohydrate, vapour) is 30 mm. and of the monohydrate (monohydrate, anhydrous salt, vapour) 4·7 mm. It does not follow, however, that this evidence alone necessarily excludes the possibility of the existence of other hydrates. It is quite possible that a lower hydrate might, at

a certain temperature, have a greater dissociation pressure than a higher hydrate and in this case it would, at that temperature, decompose, giving rise to the higher hydrate (plus another hydrate or anhydrous salt). Thus if at 50° the tetrahydrate should happen to have a greater vapour pressure than the pentahydrate, it would be unstable and would decompose into the pentahydrate and trihydrate.

Chlorine hydrate is obtained in crystals when chlorine gas is passed into water at 0°. Much discussion has taken place as to its nature; from its crystalline character, apparently constant composition and apparently definite ratio of the formula weights, it has been regarded as a true hydrate of chlorine. [Bromine forms a similar compound and sulphur is said to form a hydrate $S_8 . H_2O$; with these exceptions no hydrate of an elementary substance has been obtained.] Others have regarded this substance as a compound (or mixture?) of hydrochloric acid, hypochlorous acid and water, on the assumption that the action of chlorine on water is analogous to that of its action on a cold solution of caustic alkali; when the temperature rises these two acids react giving chlorine and water.

This solid crystalline substance can exist up to 9·6° when the chlorine pressure is 760 mm.; if the temperature is raised it decomposes into chlorine and water. But under lower pressures the temperature of complete decomposition is lower, and conversely. The 'hydrate' then, has a definite dissociation pressure for a given temperature. Under a chlorine pressure of 244 mm. at −0·24°, the hydrate can exist in equilibrium with solid ice, saturated solution and the gaseous phase, moist chlorine. If, however, the temperature or the pressure is altered, one of the phases disappears. These facts clearly indicate that the solid 'hydrate' behaves as a distinct homogeneous substance, since the two components, chlorine and water, yield a system which is univariant when the 'hydrate,' saturated solution and gas, are present and a non-variant system when ice is also present. The results, however, do not definitely prove that the solid is a hydrate of chlorine, i.e. they are not inconsistent with the hypothesis that the solid is a chemical compound of hypochlorous acid, hydrochloric acid and water which can reversibly dissociate into chlorine and water.

106. Hydrates in aqueous solution. From what has been said above, it is evident that there is no particular difficulty in recognising a solid hydrate; the specific properties, fixed composition, simple molecular ratio, definite tension of dissociation (in presence of lower hydrate or anhydrous substances), definite solubility and so on, usually give sufficiently conclusive evidence. Even if the solid hydrate cannot be actually isolated, its formation can often be detected by methods such as those indicated above (e.g. by breaks in the pressure-concentration curve or in the solubility curve).

The problem becomes much more difficult, however, when we wish to ascertain whether a hydrate exists in a homogeneous solution. It is evident that the phase rule can give us no information here, since the solution will behave as a single phase whether a hydrate is formed or not. Thus when carbon dioxide dissolves in water we shall obtain a bivariant system whether it dissolves as CO_2, C_2O_4 or H_2CO_3, etc.

The fact that a given substance forms a solid hydrate when acted upon by water does not necessarily prove that this hydrate still exists when the substance is completely dissolved in water. We cannot say, off-hand and without further evidence, that an aqueous solution of chloral, for example, contains chloral hydrate. If some of the solid hydrate is also present, in equilibrium with the saturated solution, there is indeed every probability that *some*, at any rate, of the hydrate exists in the solution; but this may be only a small fraction of the whole. [Compare, for example, the vaporisation of ammonium salts; page 154.]

The methods by which this problem has been attacked are all more or less indirect and, although on the whole there appears to be a balance of evidence in favour of the existence of hydrates in aqueous solution, it cannot be said that we are approaching a final settlement of the question.

It will only be possible here to indicate, in a brief manner, a few of the experiments which have been made in this direction; the hydration of ions has already been briefly referred to (page 216). The idea that solution consists in a kind of loose chemical combination between solvent and solute, is a very old one, but no attempts to test the idea in a definite and quantitative manner appears to have been made until 1887. Mendelejeff then published his well-known experiments on the relationships between

concentration (c) and specific gravity (s) in certain aqueous solutions, in which he shewed that abrupt discontinuities or actual breaks occur at certain points. His method was to plot the differential coefficients $\frac{ds}{dc}$ against the percentage composition and the diagram so obtained was found to consist of five straight lines shewing breaks at concentrations represented by

$H_2SO_4 . H_2O$, $H_2SO_4 2H_2O$, $H_2SO_4 6H_2O$ and $H_2SO_4 . 150H_2O$.

Pickering, later, made an extensive series of observations in this direction and his results when tabulated according to Mendelejeff's method failed to shew any breaks, the curve so obtained being continuous, although irregular. The effect of a second differentiation was then examined and discontinuities or breaks were found at eleven points. Some of the hydrates supposed to be indicated by these breaks were extremely complex; thus while excluding Mendelejeff's

$H_2SO_4 . 6H_2O$ and $H_2SO_4 . 150H_2O$,

they seem to shew the existence of

$H_2SO_4 . 1600H_2O$ and $H_2SO_4 . 5182H_2O$.

The conclusions arrived at in this way have been the subject of much adverse criticism, some attributing the supposed discontinuities to experimental error and others, whilst admitting the discontinuities, considered that they could be interpreted in other ways*. The examination of the relation between concentration and various other physical properties (viscosity, thermal effect on mixing, electric conductivity, etc.) has also given indications of breaks of continuity. Kohlrausch, for example, studied the change of electric conductivity with concentration in solutions of sulphuric anhydride in water and shewed that two minima occurred at the concentrations corresponding to

$SO_3 . H_2O$ and $SO_3 . 2H_2O$.

Since pure substances have a lower conductivity than mixtures, this result is taken as a proof of the existence of these two hydrates in solution.

So far all the experimenters seemed to regard hydrate formation as a completed change; the sulphuric acid, for example, was

* Compare Lowry on the 'Hydrate theory of' Solutions.' *Science Progress*, 1908, 145.

considered to combine with all the water present, up to a certain limit, and little attention seems to have been paid to the possibility that the change might be of a limited and reversible character.

If the solvent combines reversibly with the solute forming a homogeneous solution, there is no reason to expect any abrupt change of continuity any more than one would look for discontinuities in the combination, say, of phosphorus trichloride and chlorine. The case is of course entirely different where a new phase makes its appearance or disappearance, as in the solubility curves obtained when the actual solids are present.

The deviations from the normal freezing point depressions, or boiling point elevations, in strong aqueous solution, have been extensively studied by H. C. Jones and his colleagues with the object of throwing light upon the question of hydrate formation. They consider not only that their results afford evidence for the existence of hydrates in solution but also that the method can, when aided by conductivity measurements, give an approximate indication of the composition of the hydrates formed. In the earlier part of the work, Jones and Chambers, for example [*Am. Chem. Journ.* 1890 (22) 5], from observations on the freezing points and conductivities of solutions of metallic chlorides and bromides, came to the conclusion that these substances take up part of the water, forming complex compounds with it, and thus remove it from the field of action, as far as freezing point lowering is concerned. The complex so formed, which is probably very unstable, then acts as one molecule in lowering the freezing point of the remaining water*. The theory of hydrates in aqueous solution here suggested is essentially different from that of Mendelejeff. The latter supposed that definite chemical compounds having definite composition were formed when the necessary proportion of water was present and that intermediate compounds did not exist; whereas Jones considers that a compound, such as calcium chloride, can form all the possible hydrates from one or two, up to at least 30 molecules of water, the composition being determined, at a constant temperature, by the concentration of the solution.

Another method by which the problem has been attacked,

* A full account of these, and of more recent investigations, will be found in H. C. Jones' *Hydrates in Aqueous Solution* (Washington), 1907.

depends upon the observation that the solubility of gases, liquids or solids in water, may be diminished by the addition of certain foreign substances and that this diminution often appears to be the greater when the foreign substance is one which, from other considerations, is regarded as being more capable of hydration. Thus Smirnoff [*Zeit. Physikal Chem.* 1907 (58) 667] determined the quantities of various salts required to cause the separation of butyric acid from a strong aqueous solution; he assumed that owing to the combination of the salt with part of the water, the effective proportion of water is lowered so that, when sufficient salt is added, the butyric acid solution may become saturated. Similar experiments were made by Rothmund [*loc. cit.* 1900 (83) 401] on the diminution of solubility of phenylthiocarbamide. Sulphates and carbonates were found to have the greatest effect and nitrates the least. The order of the depressions so obtained is the same as that produced by the same salts on the solubilities of certain other solutes such as ethyl acetate, carbon dioxide, etc. The lowering of the solubility of gases, such as hydrogen, nitrous oxide, nitrogen, etc., by the addition of electrolytes and non-electrolytes has been examined by Steiner, Knopp, Hüfner, Philip, Caldwell and others. Knopp, for example, studied the lowering of the solubility of hydrogen, in water, which was produced by the addition of chloral hydrate. He found that the absorption co-efficient falls regularly as the concentration of chloral hydrate increases. Philip shews, however, [*Trans. Chem. Soc.* 1907, 713] that if the results are calculated for the number of grams of water actually present instead of the volume of the solution, the solubility of the hydrogen appears to be almost the same as in pure water. The chloral hydrate therefore has not decreased the effective water to any extent. But if similar experiments are made with cane sugar, the decrease of effective water is very noticeable, the numbers indicating that one molecule of cane sugar 'puts out of action' about 6·7 molecules of water when the concentration is 16·67 per cent. and 5·4 molecules when the concentration is 47·6 per cent.; the degree of hydration of the sugar appears therefore to be less in the stronger solution. It must be remembered, however, that the results are capable of other interpretations.

Marie and Marquis [*C. R.* 1903 (136) 684] determined the solubility of sodium chloride in sodium sulphate solutions be-

tween 14·8° and 34·28°, and obtained a perfectly continuous curve shewing no break or change of direction at 32·38°, which is the transition point for the system $Na_2SO_4 . 10H_2O$ and the anhydrous salt. They conclude therefore that the hydrate does not exist in solution. Perman [*Trans. Chem. Soc.* 1902 (81) 489] finds that anhydrous sodium sulphate and anhydrous potassium sulphate have, approximately, an equal effect in raising the vapour pressure of ammonia from aqueous solutions, a result which appears to indicate that if the potassium salt is not hydrated, as generally supposed, neither is the sodium salt.

Compare also Holmes and Sageman, *loc. cit.* 1909 (95) 1919.

For a discussion of the general question, see *Trans. Faraday Soc.* 1907 (3) Part 2. Also, Washburn, *Res. Lab. Phys. Chem. Mass. Inst. Tech. Quart.* Dec. 1908.

Practical Work.

In connection with this lecture students sometimes make determinations of the transition points of such systems as

$$Na_2SO_4 . 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$$

and $$K_2Mg(SO_4)_2 . 6H_2O + H_2O \rightleftarrows K_2SO_4 + MgSO_4 . 7H_2O$$

by the dilatometric and thermometric methods. For the sake of economy in time and apparatus, the experiments are arranged and set up by the demonstrator, the students making the necessary sets of observations. [For details see van 't Hoff's *Lectures*, Part I. pp. 25 and 82 or Findlay's *Practical Physical Chemistry*, p. 269.]

CHAPTER XXIV.

DIFFUSION.

107. Diffusion of Gases. The interdiffusion of two gases has been illustrated in the lecture by means of the well known experiments (e.g. placing a jar of air over bromine vapour, etc.). If we allow free communication between two gases, A and B, placed for example in a tall cylindrical vessel, one over the other, at the same temperature and pressure, we shall have two streams of gas flowing past one another, each gas tending to equalise its partial pressure in all parts of the vessel. The rate at which each gas moves across an area of the cylinder will depend on the rate of decrease of its partial pressure, i.e. of its density, in the direction of its flow; also, on the temperature and on the nature of the gas.

If we imagine the gas so arranged that, at the commencement of the operation, A is above B, that the layers in horizontal planes have equal density, and that the density of A at a distance x above a horizontal plane is c, then the mass (Q) of A which passes in unit time downwards through unit area of a horizontal plane at the height x, is proportional to the gradient of c, or

$$Q = K\frac{dc}{dx},$$

K is here called the 'interdiffusity' of the gases A and B.

If we pass a gas, or mixture of gases, through a solid plate which is perforated by small holes, the solid itself being impervious to the gas, the result obtained will depend on the size of the holes and the thickness of the solid.

(a) If the plate is extremely thin and the holes are not too small, the gas, or gas mixture, will pass through as a whole; the process is then called *effusion*.

It can be shewn theoretically that the rate of effusion of a gas into a vacuum is proportional to $\sqrt{\frac{P}{D}}$, where D is the density of the gas and P is the pressure; consequently for different gases under the same pressure, the rates of effusion are inversely as the square roots of the densities—(i.e. the times taken for equal volumes to pass through the hole, under the same conditions, are directly as the square roots of the densities). This principle was applied by Bunsen for the determination of the densities of gases, the rate of effusion of the gas whose density is required being compared with that of a gas whose density is known.

(*b*) If a gas, or gas mixture, is forced through a thick plate which is pierced with holes which are not too small, but which are small in comparison with the thickness of the plate, the results are of a more complicated character and are analogous to those which Graham obtained when the gases are forced through capillary tubes; the process in this case is called *transpiration.* Graham forced the gases through capillary tubes of various dimensions into the receiver of an air pump and observed the times required to reach a definite pressure. He found that similar results could be obtained with a tube of any diameter if a certain length were given to it. The relative time of transpiration increases with rise of temperature, but appeared to be independent of the pressure and of the material of the tube. If a mixture of gases is subjected to transpiration the mixture, as in the case of effusion, passes as a whole; there is no separation of the constituents. He concluded from these results that the tube becomes lined with a film of the gas and that the laws regulating the phenomenon depend on the viscosity of the gas. In some cases, gases of equal density have equal transpiration rates; thus the rates for carbon dioxide and nitrous oxide are about equal and again, for nitrogen and carbon monoxide. But nitric oxide appears to have the same rate as nitrogen and that of hydrogen is little more than twice that of nitrogen. Some of Graham's results, representing the volumes transpired in equal times, are as follows:

O_2,	air,	N_2,	NO,	CO,	N_2O,
1·00,	1·107,	1·141,	1·141,	1·145,	1·33,

HCl,	CO_2,	Cl_2,	SO_2,	H_2.
1·35,	1·37,	1·50,	1·53,	2·28.

(*c*) When gases pass through plates of compressed graphite, unglazed earthenware, or certain other porous solids, the effects are in certain respects different from those mentioned in the previous cases. Here the holes or pores are extremely fine and the gaseous molecules find their way through independently of one another; in mixtures of gases therefore, a partial separation can be effected if the densities are different. The rates of diffusion (i.e. the volumes which pass through in a given time, measured at a standard pressure) of different gases, under these circumstances, were found by Graham to be directly proportional to the difference of pressure on the two sides of the plate and inversely as the square roots of the densities of the gases.

Thus if we take two different gases A and B at the same temperature and pressure and compare their rates of diffusion R_1 and R_2 when they are allowed to pass through a porous diaphragm, of the kind mentioned above, using the same apparatus in each case, we shall find that

$$R_1 : R_2 = \sqrt{d_2} : \sqrt{d_1}.$$

This relation is easily accounted for in terms of the kinetic theory of gases, since the rate at which the gases pass through the minute pores of the diaphragm will be proportional to the average velocities, v_1 and v_2, of their molecules. Since the two gases are at the same temperature, $M_1v_1^2 = M_2v_2^2$, where M_1 and M_2 are the molecular weights respectively of A and B (see page 8), and since densities are proportional to the molecular weights,

$$d_1R_1^2 = d_2R_2^2.$$

Graham established this law experimentally by allowing the different gases, at some standard pressure, to pass into a vacuum through a plate of unglazed earthenware or compressed graphite; plaster of Paris does not answer so well, probably because the results are complicated by transpiration. Different forms of apparatus were used for this purpose, one of which is indicated in figure 26.

Applications. The process of diffusion has been largely employed by chemists as a means of effecting a partial separation of gases of different densities; it may be used, for example, for the purpose of distinguishing methane from a mixture of equal

volumes of ethane and hydrogen; these having the same percentage composition and the same density, might easily be mistaken for one another. Experiments have already been referred to in which the process of diffusion has been made use of for the purpose of investigating the nature of mixed gases or vapours; e.g. ammonium chloride (page 20), calomel (page 23) and water (page 122). Ramsay and Rayleigh employed diffusion as one of the methods of

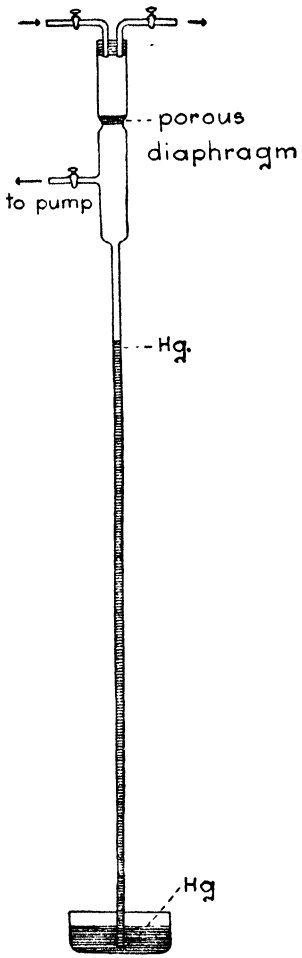


Fig. 26.

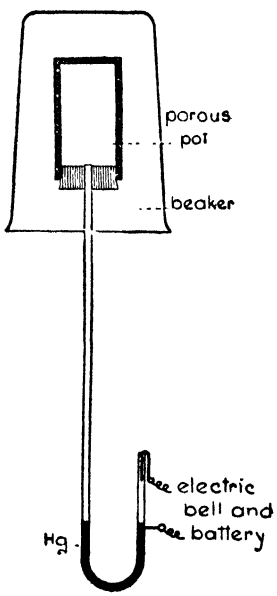


Fig. 27.

shewing that so-called atmospheric nitrogen is a physical mixture. Helium also, was separated from the gases of clèveite by this means and shewn to be homogeneous by the fact that further diffusion did not alter its density [Ramsay and Travers, *Proc. Roy. Soc.* 1898 (52) 316].

Ansell's method of indicating the presence of marsh gas in coal mines has been illustrated in the lecture by means of the apparatus shewn in figure 27.

In addition to these and numerous other qualitative applications, the process of diffusion has been employed for the determination of the densities of gases; diffusion through porous diaphragms does not appear to be suitable however [see Travers, *Study of Gases*, page 289] but free diffusion or, as above stated, effusion through a small hole in a thin plate may be applied for the purpose. Soret's well known method of proving the molecular formula for ozone is based on this principle, *Ann. Chim. Phys.* 1868 (13) 257.

He first attempted to carry out the experiments in porous vessels, but it was at once evident that the mere passage of the gas through the porous material had the effect of destroying a considerable proportion of the ozone. The method eventually adopted may be described briefly and superficially as follows:

Two glass cylinders of equal capacity are taken; and the mouth, or open end, of each is fitted with a glass plate through which a hole is drilled; the cylinders are then superposed, mouth to mouth, and, by suitably rotating the glass plates, communication between the contents of the two jars can be established or shut off at will. Suppose that the upper cylinder contains pure oxygen and the lower cylinder a mixture of oxygen with some more dense gas A. When communication is established, the gas A will begin to diffuse into the upper cylinder; at the end of a definite (short) time interval, let the quantity so diffused be v. It may be assumed (and this assumption appears to be confirmed by experiment) that, if V is the quantity of the gas A which was originally present in the lower cylinder, the ratio $\frac{v}{V}$ will be independent of the value of V, provided the time interval is always the same and the same apparatus is used. An exactly similar experiment is now made with the same quantity V of a second gas B, in place of A, and the quantity of it which is found in the upper cylinder, after the same time interval as before, is v_1. The ratio $\frac{v_1}{V}$ will also be constant and independent of the value of V. If now the time interval is very short, the ratio of these two values,

$\frac{v}{V} : \frac{v_1}{V}$, will be inversely as the square roots of the densities of the two gases *A* and *B*.

In the experiments made by Soret, the mean value of the ratio $\frac{v}{V}$ for ozone, prepared electrolytically, was 0·2708 and that for chlorine 0·2270. Hence if x is the density of ozone,

$$\sqrt{x} : \sqrt{35{\cdot}5} = 2270 : 2708,$$

whence x=about 24.

Attempts have been made in recent years to apply the diffusion method to the determination of the molecular weight of the radium and thorium emanations. Thus Makower [*Phil. Mag.* 1905 (vi) (9) 56] compared the rates of diffusion of these emanations with the rates of diffusion of oxygen, carbon dioxide and sulphur dioxide and obtained numbers indicating a molecular weight of about 99 for radium emanation. Perkins [*Amer. Journ. Science,* 1908 (iv) (25) 461] compared the rates of diffusion of mercury vapour and the radium emanation and found for the latter a molecular weight of about 235.

Mention must also be made of the passage of gases through certain solids which are not porous in the sense employed in the previous section. The passage of hydrogen through palladium has already been referred to on pages 30 and 331. Hydrogen readily passes through red hot platinum, iron or nickel and oxygen through red hot silver. It does not appear certain whether gases other than hydrogen can pass through platinum; it has been stated that sulphur compounds contained in a coal gas flame may find their way through the walls of a platinum crucible. Carbon monoxide readily diffuses through hot iron and the poisonous gas may in this way pass through the walls of an iron stove and so contaminate the atmosphere. This property of carbon monoxide probably plays an important part in the manufacture of steel by the cementation process.

Gases all appear to pass through india-rubber to some extent, but the property differs very considerably for different gases and bears no relation to the densities of the gases. Thus Graham found that the volumes of nitrogen, air, oxygen, hydrogen and carbon dioxide which pass through india-rubber, in the same time, are as 1 : 1·149 : 2·556 : 5·5 : 13·58.

The passage of gases through non-porous substances, of the kinds here referred to, is often attributed to the formation of chemical compounds which are of a 'loose' or easily dissociable character, formation taking place where the pressure of the gas is greater and dissociation where the pressure is less. Compare page 31.

108. Diffusion of liquids. If pure water is carefully introduced on to the surface of a strong aqueous solution of some salt, or other solute, contained in a tall cylinder and the mixture is kept at rest, there will be a gradual passage of the solute into the water; this process will continue, the concentration of the weaker solution increasing and that of the stronger solution diminishing, until the whole mixture has a uniform composition. [The existence of this movement in liquids appears to have been first clearly recognised by Parrot in 1815.] By using coloured solutes, such as potassium bichromate or copper sulphate, the progress of the change can be easily observed. Compared to the interdiffusion of gases, this is of course an extremely slow process; if the cylinder above referred to were a metre long, the attainment of complete mixture might be a matter of several years, if all external forces were excluded. In order to study the phenomena of diffusion in liquids in a quantitative manner, a variety of different methods have been employed. Graham (1851) was the first to attempt accurate measurements in this direction. A wide-mouthed jar, of about 200 c.c. capacity, was nearly filled with the salt solution to be examined; it was then carefully filled to the top with water, placed in a larger vessel and surrounded by water (about 1 litre) until the level of the water was about 3 cm. above the mouth of the jar. The whole arrangement was then left at rest for a considerable time, after which the jar was closed with a glass plate and removed; the quantity of the salt contained in the water of the outer vessel was then determined.

Various methods were afterwards devised by which the concentration of the solution at different parts of the diffusing system could be estimated without disturbance or removal of any of its parts. Thus Hoppe-Seyler, and also Voigt, allowed a sugar solution

to diffuse into water contained in a rectangular vessel and determined the concentration of the layers at certain points by means of a saccharimeter. Lord Kelvin made approximate measurements of a similar kind by estimating the densities of the solutions at various points; he did this by introducing a number of glass beads, containing air, of different mean specific gravities and observing the position of the stratum in which each bead floated. A much more accurate method was employed by Weber, which depends upon the principle that when two plates of the same metal are placed in a salt solution of different concentrations, an electromotive force is produced which is proportional to the difference of concentrations, provided this difference is small. Long compared the diffusion of various salts by passing a stream of pure water through a U tube which was immersed below the surface of the salt solution, communication with the solution being established by means of an orifice at the bottom of the U tube. The quantities of the salt carried away by the constant stream of water in a given time were then estimated. [For a more recent method, see Clack, *Phil. Mag.* 1908 (16) 863.]

As a result of the above mentioned experiments, and many others, several important generalisations were formulated. Thus Graham observed (*a*) that the quantities of a salt which diffused in a given time from solutions of different initial concentrations were, approximately, directly proportional to these concentrations, (*b*) that the rate of diffusion was greater at a higher temperature, (*c*) that each salt appeared to have its own specific rate of diffusion and (*d*) that when two different salts were allowed to diffuse simultaneously in the same solution, each appeared to diffuse independently of the other; if the rates of diffusion of two salts were sufficiently different therefore, it appeared that a partial separation could in this way be effected.

The most important generalisation however, from a quantitative point of view, was that put forward by Fick in 1855. The evidently close resemblance between diffusion and conduction of heat appears to have been noticed by Berthollet in 1803 but Fick, guided by Fourier's theory of heat conduction, was the first to state the laws of diffusion clearly in a mathematical

form. A complete theoretical treatment of the subject is by no means simple and cannot of course be attempted here. One may give an idea of the general character of the laws of diffusion in an approximate way, as follows.

Suppose that the solution is contained in a cylindrical vessel, the concentration of the solute diminishing gradually from bottom to top, and horizontal layers having uniform concentration.

Then the small quantity Q of the solute which diffuses in the small time interval across a very thin stratum (thickness c) of the liquid depends directly on the difference in concentration of the solute on the two sides of the stratum, the time (t), the area (a) of the cross section and a constant K, and inversely on the thickness of the stratum. The constant K depends on the nature of the solute and solvent; also on the temperature and, to some extent, on the concentration of the solution.

More exactly, if s is the concentration at a point x and $s + ds$ that at the point $x + dx$

$$\delta Q = - Ka \frac{ds}{dx} \delta t,$$

K is here called the diffusion coefficient; it may be defined simply as the quantity of solute which diffuses through a stratum of unit area and unit thickness in unit time, when unit difference of concentration is maintained between the two sides of the stratum. *Fick's law* is similarly expressed by saying that the quantity of solute which diffuses through a given area is directly proportional to the difference of its concentration in two areas infinitely near to one another.

According to the theory first put forward by Nernst in 1888, the driving force upon which the phenomenon of diffusion depends is the osmotic pressure of the solute; the rate of diffusion is then proportional to the difference between the osmotic pressures of the solutions of unequal concentration, as indicated by Fick's law. The extreme slowness of diffusion in liquids as compared to gaseous diffusion is explained by the enormous frictional resistance offered by the liquid. Since the driving force can be calculated from the laws of osmotic pressure and the rate of diffusion can be experimentally measured, it is possible to calculate the frictional

resistance. In this way it has been estimated that the force required to drive one gram molecular weight of urea through water with a velocity of a centimetre per second, at 7·5°, is equal to the weight of about 2500 million kilograms; in the case of cane sugar at 18° the force required would be equal to about 4 million tons.

CHAPTER XXV.

THE COLLOIDAL STATE.

109. THE systematic study of the colloidal state of matter began with the researches of Graham on liquid diffusion [*Annalen*, 1851 (77) 56. *Phil. Trans.* 1861 (151) 183]. It may be mentioned however that many substances which are now classified as colloids had been recognised and studied in much earlier times. Thus colloidal gold in the form of 'Purple of Cassius' was known in 1685; extensive investigations of colloidal gold were made by Richter in 1802 and by Faraday in 1857.

From the results of his experiments on the rates of diffusion of a large number of acids, salts, bases and organic substances, Graham was led to compare the property of liquid diffusion with that of volatility; thus he says: "the range in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapour tensions." Potassium sulphate, caustic potash, sugar, alcohol, magnesium sulphate, etc. vary considerably in their diffusion rates but they all belong to the 'volatile' class as regards diffusion. The comparatively 'fixed' class is represented by a different order of chemical substances marked out by the absence of power to crystallise and their extremely slow diffusion. As examples of the latter class he mentions silicic acid, aluminium hydroxide, starch, dextrin, gums, caramel, tannin, albumen and gelatine. The last named substance, which appeared to be a typical example of the class, suggested the name 'colloid' (*κόλλα*, glue). Graham fully recognised that the distinction between this class of substances and 'crystalloids' was not sharply defined, but the very great differences in properties

between the extreme members appeared to offer an obvious justification for making the classification. An idea is given of the greatly differing diffusion rates by the following list, the numbers given indicating the relative times required for the diffusion of equal quantities:

Hydrochloric acid 1; common salt 2·33; cane sugar 7; albumen 49; caramel 98. From Graham's results Stephan calculates the following numbers for the diffusion coefficient taking a day as the unit of time:

Hydrochloric acid 1·74 (at 5°); common salt 0·76 (at 5°); cane sugar 0·31 (at 9°); albumen 0·06 (at 13°); caramel 0·05 (at 10°).

[e.g. in a solution of cane sugar where the concentration at each horizontal layer differs from that one centimetre above it by 1 gram per c.c., the sugar diffuses upwards at the rate of 0·31 grams through each square centimetre per day, at 9°.]

General Character of Colloids.

It has been shewn from the investigations of Graham with gelatine and of Voigtländer with agar-agar, that crystalloids can diffuse through jellies or membranes of these colloidal substances with a velocity closely approaching that at which they diffuse through pure water, whereas colloids themselves appear to be nearly or entirely unable to pass. This circumstance was regarded by Graham as an important distinction between the two classes; thus he says, "of all the properties of liquid colloids, their slow diffusion in water and their arrest by colloidal septa are the most serviceable in distinguishing them from crystalloids." Amongst other properties Graham refers to the following:

They are often largely soluble in water, yet they are held in solution by a most feeble force. Fluid colloids always appear to have a 'pectous' modification (πηκτός, curdled) into which they often pass under the slightest influences. Colloids appear to be singularly inert in their capacity as acids and bases and, indeed, in all chemical reactions. Their 'equivalents' (i.e. reacting weights) are always high although the ratio of the elements may be simple; as an illustration, 'gummic acid' is mentioned, whose simplest formula appeared to be $C_{12}H_{22}O_{11}$ but whose reacting weight must be very much greater, as indicated by the small

amount of alkali necessary to neutralise it [see page 4]. Referring to the general inability of colloids to assume the crystalline form, it is stated that "an extreme departure from the normal condition appears to be presented by a colloid holding such a high place in its class as albumen. In the so-called blood crystals of Funke, a soft gelatinous albuminoid body is seen to assume a crystalline contour. Can any facts more strikingly illustrate the maxim that in nature there are no abrupt transitions and that distinctions of class are never absolute."

"Another and eminently characteristic quality of colloids is their mutability"; they may be compared to super-cooled liquids or to super-saturated solutions.

The foregoing extracts and quotations from Graham's papers are given here in order to shew that, notwithstanding the enormous amount of attention which has since been given to the subject of colloidal chemistry, especially within the last 15 years, our conception of the general properties of colloids has undergone little change.

Whilst clearly recognising the absence of any abrupt line of demarcation between crystalloids and colloids, Graham regarded the latter as a distinct class of *substances*; thus he says, "the colloidal character is more than a modification of the physical condition of the solids"; nevertheless he refers to the transition from colloidal to crystalline state. It is quite evident in view of more recent investigations that we have no right to regard one individual as a colloid and another as a crystalloid. A large number of substances which are typically crystalloid, in Graham's sense, have recently been obtained in the colloidal condition. Thus Weimarn [*Zeit. Chem. Ind. Kolloide*, 1908 (3) 89 and 282] shews that gelatinous precipitates are often obtained when a substance separates rapidly from a solution in which it is very sparingly soluble; the character of the precipitate will in fact depend on various factors, such as rate of formation, solubility of the solid phase, viscosity of the medium, etc. This author considers that the amorphous condition has no real existence, the so-called amorphous substances being sponge-like aggregates of minute crystals. He shews that by adding a solution of the thiocyanate of an alkali or alkaline earth metal, in a mixture of amyl alcohol

and ether, to an acid, dissolved in the same solvent, the gelatinous modifications of sodium, potassium, calcium, barium, and strontium chlorides, nitrates or sulphates may be obtained. Neuberg obtained colloidal barium sulphate and carbonate by the interaction of barium hydroxide in methyl alcoholic solution with sulphuric acid and carbon dioxide respectively, *Biochem. Zeit.* 1906 (1) 166, and the present writer shewed that sodium dihydroxytartrate can be obtained in the gelatinous, water-soluble, form by action of sodium ethylate on the free acid in alcoholic solution. [*Proc. Camb. Phil. Soc.* 1905, XIII. 73.]

The existence of a substance in the gelatinous condition is clearly no indication that a high molecular weight should be assigned to the substance as an individual, as was at one time supposed. In addition to the examples above quoted, it may be mentioned that Fischer shewed [*Ber.* 1907 (40) 3715] that glycyl-valine anhydride has a great tendency to separate from its solutions in a gelatinous form; yet its molecular weight is found, by the cryoscopic method, to have about the value 156 as indicated by the simplest formula. On the other hand we have further evidence of the existence of undoubtedly colloidal substances in the crystalline state in crystalline egg albumen and serum albumen etc. [see for example, Hofmeister, *Zeit. Physiol. Chem.* 1891 (14) 165], and it would appear that the colloidal and crystalline states may perhaps be possible for all matter.

Other characteristic properties of the colloidal condition will be referred to in the following sections.

110. Nature of colloidal solutions.

Graham regarded the distinction between crystalloids and colloids as being dependent on 'intimate molecular constitution,' suggesting that the colloid molecule may be constituted by the grouping together of a number of smaller crystalloid molecules. He considered a colloidal solution to be *homogeneous* and states that the phenomena of the solution of a crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. This view was held by many of the subsequent observers; Schulze for example regarded the colloidal solutions of arsenic sulphide as true solutions and explained the difference between these forms

and insoluble arsenic sulphide by supposing that they were allotropic modifications.

Barus and Schneider in 1891 made a series of experiments on colloidal silver, with reference especially to its optical behaviour, electric conductivity and the conditions of its 'sedimentation'; from their results they concluded that the so-called solution consists of extremely fine particles of normal silver which were able to remain suspended owing to the tenacity of the medium. A similar view as regards colloidal gold had been put forward by Richter in 1802. These opinions were strongly opposed at the time and a lively discussion took place between the supporters of the 'solution' theory and the 'suspension' theory of colloids, the question turning largely upon the homogeneity of the solutions, i.e. whether they were to be regarded as one-phase or two-phase systems. It must be observed however that it is extremely difficult to draw a sharp line between homogeneity and heterogeneity; a solution may for example appear to be chemically and (in all other respects) physically identical in every part and yet may be optically heterogeneous.

Results of considerable importance in this direction were obtained by Picton and Linder in their studies of the modes of preparation and the properties of colloidal solutions of various metallic sulphides [*Trans. Chem. Soc.* 1892, 114, 137, 148 and 1895, 63]. By allowing a solution of arsenious oxide to flow into a saturated solution of hydrogen sulphide, they obtained a colloidal solution of arsenious sulphide which contained as much as 11 or 12 grams As_2S_3 per litre. This solution could be kept for months without precipitation, was capable of diffusion and could be filtered through a porous pot; when microscopically examined it appeared perfectly homogeneous. A colloidal solution of antimony sulphide prepared in a similar way from tartar-emetic was incapable of diffusion or filtration through a porous vessel. The latter solution when examined under a powerful microscope did not at first reveal the existence of any particles, but did so after standing for some days.

But both of these solutions when examined by the 'Tyndall' method gave indications of the existence of particles; when a beam of lime light was passed through the solutions the track of

the beam was marked by a soft yellow or red glow, the light of which, when examined by a Nicol's prism, was found to be completely polarised. The presence of particles was indicated in a similar way in colloidal solutions of mercuric sulphide and ferric hydroxide, but not in silicic acid or molybdic acid. 'Congo red' (whose molecular weight is about 700), cellulose dissolved in Schweitzer's solution, and starch, all gave well marked polarised beams.

In addition to the modification of arsenious sulphide mentioned above, they obtained other grades, the differences in properties depending evidently on the size of the particles. Thus they divide the modifications obtained into four classes; (α) has aggregates visible under the microscope, (β) invisible but not diffusible, (γ) diffusible but not filterable and (δ) diffusible and filterable but scattering and polarising a beam of light.

Siedentopf and Zsigmondy in 1893 devised the arrangement known as the ultramicroscope*, by means of which particles much too small to be perceptible under the most powerful microscope, used in the ordinary way, can be rendered visible as points of light. They were able also to make an approximate estimate of the size of the particles whose existence was thus revealed.

[A particle whose dimensions are below the limit of microscopic visibility (or rather, resolvability) is described as '*ultramicroscopic*.' This in practice corresponds to a diameter of about $\frac{1}{4000}$ mm. $= \frac{1}{4}$ of a micron. (A micron is $\frac{1}{1000}$ mm. and is denoted by μ.) An ultramicroscopic particle which can be revealed by the ultramicroscope is said to be *submicroscopic*; otherwise it is *amicroscopic*. Zsigmondy also refers to the particles themselves as 'ultramicrons,' 'submicrons' and 'amicrons.' The limit, under the most favourable conditions, for the submicron, is about 5×10^{-7} cm. $= 5$ millionths of a millimetre $= 5\mu\mu$.]

Colloidal solutions, when examined in this way, nearly all shew the presence of submicroscopic particles and all the experiments go to prove that between true solutions, colloidal solutions and suspensions, there is no sharp line to be drawn. Zsigmondy proved, in fact, that colloidal solutions of gold can be obtained, the

* For details, see Zsigmondy's *Colloids and the Ultramicroscope*. Translated by J. Alexander.

dimensions of whose particles may vary continuously within very wide limits, the end members on one side forming microscopically visible suspensions and, on the other side, subdivisions which are amicroscopic and behave as true solutions; Linder and Picton's solutions of arsenious sulphide appear to be similarly constituted. It is true that in certain typically colloidal solutions, no ultramicroscopic particles can be observed; this however does not prove the absence of particles of such dimensions, since the method of observation depends on the existence of a sufficient difference in the refraction and dispersion coefficients of the particles and the medium; the more nearly these properties approach in the two phases, the larger must the particles be in order that they can be ultramicroscopically distinguishable.

Lobry de Bruyn in 1900 [*Rec. Trav. Chim.* (19) 251] emphasised the view that there is no real distinction between true solutions and colloidal solutions and that there is no true criterion of homogeneity or heterogeneity in a liquid. The same author and Wolff [*loc. cit.* 1904 (23) 155] shewed in fact that there is some evidence of optical heterogeneity in solutions of cane sugar and raffinose when they are examined by means of a powerful cone of light. Further, it has been demonstrated by de Bruyn and Calcar (*loc. cit.* 218) that solutions of sodium sulphate when subjected to centrifugalisation become more concentrated at the peripheral end of the tube and may even be caused, in part, to crystallise out. This experiment recalls at once the well known phenomenon of the separation of colloids from these solutions by centrifugalisation.

On the whole then it would appear that the long continued discussion as to whether colloidal solutions are, or are not, homogeneous is of little avail unless the term homogeneity is strictly defined.

The prevailing opinion at the present time is that colloidal solutions are to be regarded as heterogeneous two-phase systems and that the peculiar properties of colloids are principally due to their very great specific surface—i.e. the quotient of surface by volume.

These peculiar properties are connected, to a large extent, with phenomena which occur at the surface (e.g. surface tension, electric charge and adsorption) and it is therefore to be expected that

'colloidality' will become more pronounced as the subdivision of the particles is increased. As an illustration of the rapid increase of surface with continued subdivision, the following example may be considered.

A cube the length of whose side is L has a total surface $6L^2$ and a volume L^3; the specific surface is therefore $\frac{6}{L}$. If therefore one cubic centimetre of a solid is symmetrically subdivided into 1000 cubes the length of side of each cube will be 1 mm., the total surface 60 square centimetres and the specific surface 60. If this subdivision were continued until the side of each cube had a length μ, the total surface would be 60,000 square centimetres and the specific surface 60,000—and so on.

To give an idea of the magnitude of the specific surface of a typically colloidal substance, it may be mentioned that Lobry de Bruyn, from the investigations referred to above, estimated the diameter of the starch molecule as about 5 $\mu\mu$. If then one cubic centimetre of dry starch were subdivided in solution until its particles had molecular dimensions, the total surface would amount to some hundreds of square metres.

111. Classification of colloids.

The terminology proposed by Wolfgang Ostwald [*Chem. Centr.* 1907 II. 120] is extremely convenient when referring to the systems with which we are here concerned. If, in a two-phase system, one of the phases is continuous and coherent while the second phase is distributed throughout the first in the form of fine subdivisions or particles, the first phase is called the *dispersion medium* and the second the *disperse phase*. When the dispersion medium is a *liquid* and the disperse phase a solid, the system is called a *suspension*; if the disperse phase is liquid, the system is an *emulsion* or 'milk,' and if the disperse phase is gaseous the system is called a *foam*. If the dispersing medium is a *gas* and the disperse phase a liquid the system is a *mist*, whilst if the disperse phase is solid the result is called a *dust*. Similarly we may have gases, liquids or solids dispersed in *solids* and so on.

The various systems referred to are called 'dispersoids.' The dispersoids which we are now considering may be broadly classed

in the following three groups according to their 'degree of dispersity.'

(*a*) True, or coarse, suspensions and emulsions; size of particles greater than 0·1 μ; specific surface less than 5×10^4.

(*b*) Colloidal solutions; size of particles between 0·1 μ and 1 $\mu\mu$; specific surface between 5×10^4 and 5×10^6.

(*c*) Molecular dispersoids (and ion dispersoids); size of particles 1 $\mu\mu$ or less; specific surface greater than 5×10^6.

It must of course be remembered that a classification of this kind is only arbitrary; the degree of dispersity is, in the same system, a changing quantity and in some cases—for example in the colloidal solutions of gold and of arsenious sulphide above mentioned—there may be present, in the same solution, particles of the disperse phase whose size varies continuously from that of coarse suspensions to the dimensions here classed as molecular.

Amongst other methods of classification which have been suggested, brief reference may be made to the following:

Noyes distinguishes between 'colloidal solutions' and 'colloidal suspensions'; the former are viscous, gelatinising colloid systems which are not easily coagulated by salts, whilst the latter are not viscous, not gelatinising and are easily coagulable. The classification includes most organic colloids in the first class and the colloidal metals, sulphides and many hydroxides in the second. These classes are in fact often referred to as 'organic colloids' and 'inorganic colloids.' Perrin considers that the distinction between these classes is dependent upon the relationship, or attraction, between disperse phase and dispersing medium and proposes to call the first class 'hydrophile' colloids and the second 'hydrophobe' colloids. Since, however, the dispersing medium need not necessarily be water, the names are altered to *lyophile* and *lyophobe*.

The lyophobe colloids are evidently nearly allied to the coarser suspension in their sensitiveness to coagulation by electrolytes, lesser viscosity, easily observed Brownian movements etc. and the fact that the precipitates obtained on coagulation are solids. Bearing in mind also that the subdivisions of gold and of arsenious sulphide can be obtained in all grades of dispersity—from that of coarse suspensions to that of 'submicrons' and apparently even

'true' solutions—there appears to be every reason to regard the lyophobe colloids as being solid-liquid systems, i.e. a solid disperse phase in a liquid dispersing medium. (Although no sharp line can be drawn between these lyophobe colloids and true suspensions, the latter are broadly distinguished by the far greater readiness with which they undergo spontaneous sedimentation.) On the other hand there is a considerable amount of evidence in favour of the view that the lyophile colloids such as albumen, gelatine etc. are liquid-liquid systems; their properties may to a large extent be explained in fact by regarding them as mixtures of two partially miscible liquids in the neighbourhood of the critical solution temperature (see page 316)*. Upon this view, solutions of lyophobe colloids stand in the same relation to 'true' (coarse) suspensions as those of lyophile colloids stand to true emulsions. Accordingly many authors now refer to the two classes of colloidal solutions as *suspensoids* and *emulsoids*.

Although the disperse phase in emulsoid solutions is probably liquid, it does not follow that on coagulation it will necessarily appear in the liquid state; whether it appears as a liquid or solid will depend on various conditions; thus certain emulsoids appear as solid powders when their solutions are precipitated by excess of alcohol, but as jellies, oils, etc. when slowly coagulated.

Friedländer shewed that, from the same three components, one may obtain either an emulsion or suspension according to the method of treatment. Thus if a little water is added to an alcoholic tincture of colophony, an opalescent colloidal-like solution

* The similarity between solutions of emulsoids and mixtures of liquids near the critical solution temperature is exhibited in various ways. Thus, opalescence, which is often a characteristic property of lyophile colloids, has been observed in certain liquid mixtures at the critical temperature, and some degrees above it, and appears to be due to the presence of minute drops [Rothmund, *Zeit. Physikal. Chem.* 1908 (63) 54]; this effect is diminished or increased by the addition of foreign substances and changes of temperature. The temperature-coefficient of the viscosity of liquid mixtures in this region of the critical point is much greater than beyond it and this coincides with the fact that the influence of temperature on the viscosity in emulsoids, and in true emulsions, is very great in comparison with other liquids. Further, it has been shewn that in certain lyophile colloidal solutions, the submicroscopic particles become less evident at greater dilution; on the above view, this fact can be accounted for by supposing that the two liquid phases become more alike in composition and refractive power as the dilution increases. Compare pages 316 and 378.

is obtained and a similar solution results when the tincture is dropped into a large bulk of water. But further addition of water in the first case yields an emulsion whilst, in the second case, the addition of a larger proportion of the tincture gives rise to the separation of the solid resin.

It may be mentioned here that the particles recognisable in dispersoids, if not too large, are always found to be in rapid movement. Such movements were first observed by R. Brown in 1827 and they appear to be common to all small solid or liquid particles suspended in liquid or gaseous media provided the size of the particles is not greater than about 0·01 mm. At one time it was supposed that these motions were due to inequalities of temperature or to the action of light, but this appears to have been disproved. The movements are spontaneous and continuous; their velocity increases with the temperature and with decrease of the size of the particles; it also depends upon the nature of the medium in which the particles are suspended, being largely influenced by its viscosity.

Picton noticed these movements in the microscopically visible particles contained in his colloidal metallic sulphide solutions and Zsigmondy has more recently extended the observations to the submicrons in colloidal gold etc. In the latter case the appearance of the movement is said to be of a somewhat different character; the ordinary Brownian movements, i.e. those of the larger particles, or microns, are described as being of a trembling or vibratory kind whereas that of the ultramicrons is translatory in a zig-zag fashion and is of a 'jumping, dancing and dashing' nature. The results of this and the more recent work of Einstein, Smoluchowski, Svedberg, Perrin and others, have lent considerable support to the view that the phenomena are due to the movements of the molecules of the fluid medium, the general character of the movement being that which the kinetic theory ascribes to molecules. Perrin [*Ann. Chim. Phys.* 1909 (18) 5] prepared suspensions of gamboge in water which consisted of particles nearly of the same size. By allowing the particles to settle under the influence of gravity, determining the distribution of the particles in layers at different heights, and estimating the weight and diameter of each particle, he found that the law of distribution with height indicated that each particle had the same average kinetic energy of movement as the molecules of the liquid in which it was suspended.

112. Coagulation.

Colloidal solutions must all be considered as unstable (or metastable) systems in that they tend in course of time to gelatinise, solidify or precipitate etc. These changes can usually be brought about more or less instantaneously by various influences, depending on the nature of the case; amongst these may be mentioned (*a*) change of concentration of the solution, (*b*) mechanical agitation, centrifugalisation etc., (*c*) temperature change,

(*d*) addition of electrolytes, (*e*) addition of non-electrolytes. Graham in fact compared colloid solutions to supercooled liquids or supersaturated solutions and regarded the effect of addition of a foreign substance as the acceleration of a change already in progress. The deposition of solid or liquid particles from undoubted suspensions (such as clay in water) resembles in many respects the separation of colloids from their solutions and may often be brought about by similar influences.

Under the influence of the various causes mentioned, a colloid may separate from its solution as a powder or as a gelatinous or flocculent precipitate, or the whole solution may set to a firm jelly. The phenomena have been called by various names, such as coagulation, flocculation, precipitation, gelatinisation, setting etc. and although attempts are being made to restrict each of these terms to particular or special cases, it is not yet possible to define the terms accurately, since they are still very frequently used in a loose general way. It happens that in many cases the precipitated or coagulated substance can again be brought into solution if the circumstances of its precipitation are reversed. Thus a solution of gelatine or agar-agar may be solidified by cooling and redissolved again on warming, and certain emulsoids etc. which have been precipitated by salts can be again brought into solution if the salt is carefully removed by dialysis. But in another, larger, class it is found that the process is irreversible and the separated substance can only be again brought into solution by going through the complicated process by which it was originally obtained. (Gelatinised silicic acid, for example, might have to be dried, fused with alkali and the resulting silicate decomposed, under proper conditions, with acids.) See however page 402.

Hardy therefore proposes to classify colloids as *reversible* and *irreversible* in the above sense; the term 'coagulation' is, according to this mode of classification, restricted to the separation of an irreversible colloid and the solidification of gelatine etc. is termed 'setting.' A difficulty may arise here owing to the fact that unless the particular influence is stated, a given colloid may, in certain cases, be reversible or irreversible according to the nature of the influence, e.g. according to the nature of the electrolyte employed to precipitate it. It may happen, again, that

moderate cooling may lead to the solidification in a reversible way, but extreme cooling may cause a change in the nature of the colloid, so that it then becomes irreversible; this is said to be the case with gelatine.

For this reason, Zsigmondy proposes to refer the capability of reversion only to *one* influence—namely, desiccation at the ordinary temperature. According to this, dextrin, gum arabic, most albumens and molybdic acid are reversible, whilst most inorganic colloidal sulphides and hydroxides, and colloidal metals, are irreversible.

It would be preferable, probably, to use the words reversible and irreversible to signify that the *change of state* in a colloidal system can or cannot be restored by bringing it back to the original conditions, rather than to speak of the particular *substances* as reversible or irreversible. The question of time has also to be considered; the reversion may be a very slow process and by selecting some arbitrary time limit, say days or weeks, the capability of reversion might be overlooked. On the other hand it is considered by some that all colloids are irreversible in the sense that the colloidal state is an unstable one and that, given time enough, they would all assume the crystalline condition. Graham appears to have regarded the matter in this light when he states that "the mineral forms of silicic acid deposited from water, such as flint, are often found to have passed during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition. The colloidal is, in fact, a dynamical state of matter; the crystalloid being the statical condition."

The phenomena of coagulation or flocculation in dispersoids (using this term in the sense above indicated) by means of electrolytes may conveniently be divided into two classes, as follows:

I. It is found that solutions of many organic colloids, notably those of the 'lyophile' or emulsoid type (albumens, globulins, etc.) are, when in the pure state, not sensitive to the addition of small traces of metallic salts, whilst they may be precipitated with more or less completeness by concentrated solutions of appropriate neutral salts when these are added in sufficient excess. The precipitation in this case will depend, as regards rate and completeness, on the nature of the emulsoid and of the salt and also

on the concentration of the salt; precipitation may begin at a certain salt-concentration but may require a much higher concentration for its completion. Thus Kauder states that the precipitation of globulins by ammonium sulphate begins at a salt-concentration of 24 per cent. but requires a concentration of 36 per cent. to complete it. In a mixture of emulsoids of this kind, the concentration necessary for complete precipitation may vary very greatly for the different constituents and in such cases the process of fractional 'salting out' can be used to separate them. Thus the addition of a 35 per cent. solution of ammonium sulphate to blood serum separates the globulins and on increasing the concentration of the salt to 70—80 per cent., the albumens are precipitated.

It was generally considered that the concentrations of a salt required for complete precipitation were in the inverse order of the molecular weights of the proteins precipitated; thus peptones, which owing to their diffusibility are considered to have a relatively low molecular weight, are not precipitated by ammonium sulphate. Fischer and his colleagues, however, have shewn that some polypeptides of comparatively simple composition can be precipitated by ammonium sulphate.

The quantity of salt required for complete precipitation of a substance, of the kind mentioned, appears to be dependent, in an additive way, on the nature of the ions of the salt. Thus for the complete precipitation of pure albumen, the precipitation-capability of the anions mentioned increases in the order (CNS), I, Br, (NO_3), Cl, (CH_3CO_2), SO_4 and the kations in the order NH_4, K, Na, Li. The precipitation of albumens etc. in the manner here described is a 'reversible' process: if the salt is removed by dialysis, or if the solution is sufficiently diluted, the precipitated substance becomes again soluble.

II. The behaviour of most inorganic colloids, such as the colloidal metals, colloidal sulphides and many colloidal hydroxides, towards the addition of electrolytes, is of a different character. Here comparatively minute quantities of the electrolyte can effect the precipitation or coagulation, the process being, in most cases, irreversible. Even coarse suspensions, such as clay or mastic

in water, behave very similarly. The concentration of an electrolyte which is necessary to produce this effect, although very small in comparison with that required in the salting out method, must, in this case also, reach a certain minimum value, which may vary very considerably with the nature of the electrolyte and of the colloid, or suspension, used.

H. Schulze in 1882 studied the behaviour of various metallic salts towards colloidal solutions of arsenious sulphide. He shewed that for each salt there is a dilution beyond which it ceases to cause precipitation and further, that the precipitating powers of the various salts examined depended chiefly on the nature of the metal and only slightly on the acid radicle. He found also that the precipitating power increased in a remarkable manner with the *valency* of the metal, being least for salts of the alkali metals and greatest for aluminium, chromic and ferric salts (Schulze's rule). Linder and Picton greatly extended these observations (*loc. cit.* 1895, 64), using for the purpose the γ modification of arsenious sulphide.

The following values were obtained for the relative number of molecules of various sulphates required to produce coagulation, the numbers being referred to aluminium chloride as unity.

Al	Fe‴	Cr‴	Ca	Zn	Ni	Fe″	Mg	H
0·6	1·5	1·25	26·0	27·3	26·8	32·7	34·1	750

NH_4	K	Li	Na
778	1000	1020	1110

Thus 0·6 molecule of aluminium sulphate possesses the same coagulative power as 750 molecules of sulphuric acid or as 1000 molecules of potassium sulphate. The molecular coagulative powers are inversely proportional to the number of molecules required to produce coagulation. The average values calculated from Schulze's experiments, of the coagulative powers for univalent, divalent and trivalent metallic kations, appears to be about 1:30:1650, and from some of Picton and Linder's results, 1:35:1023. The actual values however differ with the degrees of ionisation of the salts etc. and no extreme accuracy can be expected owing to the nature of the method of observation. Whetham points out [*Phil. Mag.* 1899 (48) 474] that if we make certain assumptions as to

the nature of the coagulative process, the theoretical values for the relative coagulative powers should be in the ratio $1 : n : n^2$, a result which agrees remarkably well with the average experimental numbers, which are approximately 1 : 32 : 1024. [Linder and Picton found that quadrivalent ions are abnormal in this respect [*loc. cit.* 1905 (87) 1906]. For a suggested explanation, see Burton, *Phil. Mag.* 1906 (12) 472.]

The results so far mentioned indicate, as Schulze observed, that the coagulative power of a salt depends chiefly on the nature of the metal. It must be noticed however that results which point to this conclusion have all been made with colloidal solutions of metallic sulphides, colloidal metals, etc. Hardy afterwards [*Proc. Roy. Soc.* 1899 (66) 110 and *Zeit. Physikal. Chem.* 1901 (33) 385] shewed that with certain other colloids the coagulative powers of salts depend principally on the nature of the *anion* and he formulated an important generalisation which connected these phenomena with the sign of the electric charge of the colloid.

Before stating the nature of these results, it will be necessary to refer briefly to the behaviour of colloidal solutions in an electric field. It was observed by Reuss in 1809 that if a sufficiently strong current is passed through water, or a very dilute aqueous solution of an electrolyte, in which the electrodes are separated by a porous diaphragm, such as an unglazed earthenware pot, the liquid will pass through the diaphragm towards the kathode until a certain equilibrium pressure is reached. This phenomenon, which is known as electric endosmose, is exhibited also by various other liquids. Wiedemann afterwards shewed that this pressure, when equilibrium is attained, is proportional to the difference of potential on the two sides of the porous diaphragm and is greater the higher is the specific resistance of the liquid. The pressure and the direction of flow are however dependent on the nature of the liquid and the solid; thus in a glass capillary tube, oil of turpentine moves towards the anode, but if the tube is lined with sulphur, it flows in the opposite direction. If the solid is free to move as well as the liquid, the two will wander in opposite directions; this behaviour has been observed in the case of solid particles suspended in a liquid, the direction depending on the nature of the solid and liquid.

This phenomenon, now generally spoken of as 'kataphoresis*,' has some resemblance to ordinary electrolysis in its general character and it can best be understood if we suppose that the liquid and the particles of the solid have opposite electric charges. [There is no definite evidence to shew whether the particles are actually discharged at the electrode; in certain cases it has been found that the particles are repelled from both electrodes and collect in the middle of the liquid. Compare, for example, Lehmann, *Zeit. Physikal. Chem.* 1894 (14) 301.] In order to account for the existence of these electric charges, it has been suggested that they are due to the ions of water (see page 289); thus in the case where the solid wanders to the anode, it may be supposed that OH ions attach themselves in some way to the solid particles, so that the process of kataphoresis would consist in the transfer of H ions to the kathode and of the particles with the associated hydroxyl to the anode. In the opposite case hydrogen ions attach themselves to the particles, thereby giving them a positive charge, and hydroxyl ions wander in the other direction. An alternative is to regard both electric endosmose and kataphoresis as electrocapillary phenomena. [See, for example, Lamb, *B. A. Report*, 1887, 495.]

Not only coarse mechanical suspensions but nearly all colloidal solutions exhibit this kataphoretic behaviour. As regards aqueous suspensions or solutions, it is found that quartz, mastic, sulphur, selenium, and the colloidal forms of metals and metallic sulphides, all wander to the anode; whilst most metallic hydroxides wander to the kathode. Silicic acid in alkaline solution goes to the anode and in acid solution to the kathode; certain substances in suitable mixtures of alcohol and water are electrically indifferent. Pure albumen in water is also indifferent; but Hardy shews that by addition of traces of alkali or acid it will move to the anode or kathode respectively. Colloidal substances and suspensions are referred to as 'electropositive' or 'electronegative' according as they wander to the kathode or anode.

Hardy shewed [*Proc. Roy. Soc.* 1900 (66) 110 and *Zeit. Physikal. Chem.* 1900 (33) 385] that dialysed silicic acid, mastic, or proteid treated with alkali, wander to the anode and that, with these, the precipitating powers of various metallic salts depend,

* Sometimes, as kataphoresis or anaphoresis according to direction.

as in the examples quoted above, on the valency of the metal. But if the proteid is treated with acid, so as to render it 'electro-positive,' the powers of salts to coagulate it are found to depend, not on the metal, but upon the valency of the acid radicle; sulphates, for example, have a greater precipitating power than chlorides. Results of a similar kind were obtained with colloidal ferric hydroxide. It appears therefore that only those ions are active in bringing about the coagulative process whose electric charge is of opposite sign to that of the colloid. (Hardy's rule.) The influence of electrolytes on the difference of potential between colloid particles and dispersion medium has been accounted for in different ways. One view is that the colloid particles adsorb a larger proportion of the most rapidly moving ions and so assume the charge of these; thus in presence of acid, the colloid will take up a larger proportion of hydrogen ions, thus assuming a positive charge, and in presence of bases it will take up hydroxyl ions and become negative, see page 284.

This explanation is supported to some extent by Freundlich's observation that in many cases the faster moving ions are more effective in coagulation; thus acids are more effective than their salts (of univalent metals). Also, the same author shews that there is often a direct parallelism between the precipitating powers of ions and their capability of being adsorbed by charcoal; in these cases therefore, the faster moving ions are more adsorbed and have greater precipitating power, but there appear to be many exceptions to this generalisation. It would appear difficult to account, in terms of this explanation, for the fact, above mentioned, that most solids when suspended in water, move to the anode, since the faster moving hydrogen ions should be most adsorbed. In order to get over this difficulty, some have suggested that perhaps the water employed in the experiments always contained traces of alkali (e.g. from the glass vessels), but even admitting this, the behaviour of ferric hydroxide, etc., suspended in, presumably, similar water, would have to be explained.

Billitzer [*Zeit. Physikal. Chem.* 1903 (45) 307; 1905 (51) 129] accounts for the phenomena in a different way. Reference is made to the fact that many typical colloids are amphoteric in

character (see page 297) and this property is probably shared to some extent even by silicic acid, ferric hydroxide, etc. This addition of an acid to a substance of this class would give a salt which ionises into a positively charged colloidal complex and the acid anion; a base on the other hand would yield a salt capable of ionising into a negatively charged complex anion and the metal. Since a very small proportion of acid or base is sufficient to produce the effects mentioned, these two results might be indicated as

$$R_nHX \rightleftarrows R_nH + X' \text{ and } R_nOHM \rightleftarrows R_nOH + \dot{M}.$$

When an instabilising electrolyte is added, it is supposed that these complex ions are attracted by the negative or positive ions, respectively, of the electrolyte, which they tend to adsorb on their surfaces. The instabilising ions of the electrolyte thus act as condensation nuclei and, when the mass of the resulting aggregate reaches a certain limiting magnitude, precipitation occurs. [See also Hardy, *Proc. Roy. Soc.* 1907 (79) 413 and 1909 (81) 38.]

The process of coagulation of a colloid appears to take place in two stages; in the first place the smaller particles collect themselves together into larger aggregates and the latter then settle under the action of gravity. At the surface of separation of disperse phase and dispersion medium surface tension comes into play, and if other disturbing forces are absent, the tendency will be for the surface to become smaller; the lesser particles will therefore tend to aggregate together into larger ones, as in the formation of rain drops. If however the particles are electrically charged, the available electric energy will be greater as the surface is smaller so that, for this reason, the tendency will be for the surface to become larger, thus reducing or counteracting the influence of surface tension and so retarding coagulation. It might be expected therefore that removal or neutralisation of the electric charge would 'set free' the influence of surface tension and so favour coagulation. As mentioned above, the addition of alkali or acid to certain colloids will change the direction of movement of the colloid in an electric field; thus in a colloidal system in which the particles are charged electronegatively, the gradual addition of an acid will decrease their 'negativity' and eventually will make

them electropositive; there exists therefore some point at which the particles and the fluid in which they are immersed are *isoelectric*. Hardy shews that as this isoelectric point is approached, the particles are seen to grow in size and the stability of the colloidal system diminishes; at the isoelectric point the system appears to be least stable and coagulation or precipitation occurs.

Notwithstanding the importance of this observation, it must be observed that there appear to be notable exceptions to the rule namely, that the minimum stability coincides with the point at which the difference of potential between disperse phase and dispersion medium is zero. Thus Billitzer finds that colloidal platinum, which moves towards the anode, can be made to travel in the opposite direction by the addition of alcohol, whilst potassium chloride does not alter the difference of potential; yet coagulation is brought about rapidly by the addition of potassium chloride and only very slowly by alcohol. Dialysed, neutral albumen again, which shews no kataphoretic behaviour, is nevertheless stable. The stability of a colloidal solution depends, in fact, upon many other factors, the influence of which may be more pronounced than that due to the potential difference above mentioned. (See below.)

113. Gels and Sols. The term *gel* is generally used in reference to the precipitated or coagulated colloid, whether it happens to be 'jelly-like' or not; even the solid which is separated from a coarse suspension is spoken of as a gel. The term may include substances therefore which are jellies, powders, amorphous precipitates, slimes, etc.

The use of the term *gelatinisation* however is now generally restricted to the phenomenon of 'setting to a jelly' which is observed in many colloidal solutions of the emulsoid class, and some authors still further limit the term to the cases in which this process is of a reversible nature. In most cases gelatinisation is brought about by lowering the temperature and the resulting jelly again dissolves when the temperature is raised; this is the case, for example, with gelatine or agar-agar. But the opposite effect has been observed with casein; when small quantities of calcium salts are added to a slightly alkaline solution of casein, the mixture gelatinises on warming and redissolves on cooling

(Ringer). There appears to be, in many respects, a clear analogy between the gelatinisation of an emulsoid and the 'unmixing'—or separation into two phases—of mixed liquids in the region of the critical solution temperature; in both cases, for instance, it has been shewn microscopically that the initial process consists in the separation of minute liquid droplets which then gradually increase in size. The fact that gelatinisation may be brought about by lowering or raising the temperature, according to the nature of the substance, at once recalls the behaviour of mixed liquids referred to on page 316.

The structure of jellies has been investigated microscopically by Hardy and by Bütschli and from their results it is evident that jellies are to be regarded as two-phase heterogeneous systems. The configuration of the jelly and the parts played by the original disperse phase and dispersion medium will depend however, in a remarkable way, on the concentration. Hardy shewed that when a dilute aqueous alcoholic solution of gelatine is cooled below 20°, the drops which separate are relatively rich in gelatine; these appear to solidify and begin to adhere to one another, eventually building up an open network structure, in the interstices of which the liquid dispersion medium is contained. But with a concentrated solution of gelatine the result is of a different character; here the liquid phase which separates is less viscous and poorer in gelatine and the dispersion medium becomes a solid (or semi-solid) continuous framework containing hollow spherical spaces which are filled with the liquid. These two types of jelly are often referred to as having the 'net' structure and 'honeycomb' structure, respectively.

The minute structure of those gels which are obtained in the form of amorphous opaque precipitates is of course unknown; these products shew however certain points of resemblance with jellies, especially as regards the obstinacy with which they retain the dispersion medium and the enormous shrinkage in volume which they experience when dried.

Graham regarded gels as chemical compounds; the hydrogel of silicic acid for example was looked upon as a hydrate. By action of alcohol, the water could be replaced and an 'alcogel' formed; sulphuric acid similarly replaced the water yielding a 'sulphagel.'

This question has been investigated by van Bemmelin [*Zeit. Anorg. Chem.* 1896 (13) 233, 1898 (18) 14, 1899 (20) 85] who made a series of observations on the relations between vapour pressure and concentration in a large number of colloidal precipitates and jellies. In the case of silicic acid he found that when the transparent gel is slowly dehydrated at 15°, the vapour pressure falls quite continuously and the substance remains transparent. Since there is no constant vapour pressure for a given temperature, the two-component system is bivariant and only two phases appear to be present. The gel behaves therefore as a solid solution and not as a hydrate (unless the improbable assumption is made that the hydrate and dehydrated substance are completely miscible). When however the dehydration is relatively rapid and the vapour pressure has fallen to 5 mm. the remaining gel becomes opaque and the vapour pressure then varies only very slightly during further dehydration up to a certain point; beyond this, the gel again becomes transparent. The composition of the gel when the vapour pressure is 5 mm. is approximately $SiO_2.2H_2O$ and the result might appear to indicate the existence of a hydrate of this composition. It is very questionable however whether the phase rule can be strictly applied to such cases since the condition of a colloidal phase is not completely defined in terms of temperature, pressure and concentration of the components. More probably the change in direction of the curve and in the appearance of the gel is due to structural changes of the kind referred to above. With the gelatinous or precipitated forms of various other substances such as ferric, aluminium and cupric hydroxides, which were often regarded as true hydrates, the same author has usually obtained continuous dehydration curves at a given temperature. (See page 326.)

The re-absorption of water by the dried gels varies in character for different colloids. Gelatine for example at 25—30° absorbs water forming a colloidal solution, but at lower temperatures it swells up to a jelly. Cellulose swells but does not dissolve. [This swelling of cellulose may produce enormous pressures, as seen in the use of wedges of dry wood, which, when moistened, may overcome pressures of hundreds of tons.] In the case of silicic acid, van Bemmelin found that the dehydration was irreversible, in the

sense that the dried product (up to 5 mm.) when placed in saturated water vapour, never became hydrated to the same extent as before; below 5 mm. however the process appeared to be reversible. With ferric hydroxide, the dehydration is throughout irreversible.

It was mentioned above, that the researches of Graham, Voigtländer and others, lead to the conclusion that the rate of diffusion of crystalloids in gelatinised colloids is almost the same as in pure water. Reformatzki further shewed that the rate of hydrolysis of methyl acetate is, within one per cent., the same in gelatinised agar-agar as in water. Later observers however have found that these general statements require modification in that the rate of diffusion, or of reaction, depends to a considerable extent on the concentration of the jelly (also upon its age etc.). This difference in property is no doubt closely connected with the structure of the jelly, which, as above mentioned, depends upon the concentration; it is to be expected that diffusion would be more free in the liquid phase and that the open network offers less obstruction than the closed honeycomb structure.

Further, it should be mentioned that the diffusion of one colloid in another is by no means impossible, as is sometimes supposed; thus Henri and Gompel shew that colloidal silver can pass through certain emulsoid membranes [*C. R. Soc. Biol.* 1906 (61) 362] and it is well known that many enzymes, which are of a colloidal character, can readily diffuse in jellies.

The fact that diffusion, and many chemical changes, can take place readily in a colloidal medium, even when the latter is in the solid condition, is of considerable importance in the technical application of colloids. The changes taking place during the developing and fixing of a photographic plate may be cited as an example; also the use of gelatinised solutions of soluble gun cotton, alone or with nitroglycerine, as explosives and of solutions of electrolytes in gelatine for 'dry' galvanic cells.

The term *sol* was originally used by Graham for colloidal solutions in general; since however these may be formed in solvents of various kinds, a distinction was afterwards made between hydrosols, alcosols, etc. Schneider in 1892 proposed the name *organosol* for the solution of a colloid in an organic solvent; for these solutions, he used such symbols as Ag (ethyl alcohol), Au_2S

(ethyl alcohol), the name of the dispersion medium being written in brackets after the chemical symbol of the disperse phase. Solutions of this kind may sometimes be obtained by replacing one solvent by another; thus the organosol Ag (ethyl alcohol) was prepared by coagulating Carey Lea's silver hydrosol (see page 402) with alcohol, thoroughly draining the precipitate in a Pasteur's tube and dissolving the product in alcohol. Many organosols can be obtained by interaction of salts, etc., in organic solvents; e.g. HgS (ethyl alcohol) is prepared by acting upon mercuric cyanide with hydrogen sulphide in alcohol and Cu_2S (benzene) by interaction of hydrogen sulphide and the copper derivative of acetoacetic ester in benzene; they may also be obtained by methods analogous to Bredig's preparation of platinum hydrosol (page 187).

114. Adsorption compounds.

The gel which is precipitated from a colloidal solution by the addition of an electrolyte is always found to contain a small quantity of one of the ions of the electrolyte; experiments made with 'negative' and 'positive' colloids indicate that the ion thus carried down is always of opposite sign to that of the colloid. Thus Linder and Picton shewed that when colloidal arsenious sulphide (negative) is coagulated by means of barium chloride or calcium chloride, a portion of the metal is carried down with the precipitate whilst the total quantity of chlorine present in the solution remains constant. From their results, they concluded that the quantities of various metals thus carried down, under similar conditions, by a given colloid, stand to one another in chemically equivalent ratio. The metallic constituent carried down with the precipitate could not be removed by washing with water; by digestion however with a solution of another metallic salt, a complete exchange could be effected, the replacement taking place in chemically equivalent proportions. These replacements appeared to be conditioned by mass action, for if calcium chloride is used as coagulator, the calcium contained in the resulting precipitate can be replaced by cobalt, whilst if a cobalt salt is employed, the cobalt in the precipitate can be replaced by calcium. The authors regarded the precipitates thus obtained as chemical compounds; it must be remembered however that a similar co-precipitation, of one of

the ions of the coagulator, occurs even in the case of coarse suspensions, such as that of clay in water.

Analogous co-precipitation can take place of one colloid with another; this may occur even with electrically neutral colloids but it appears to be much more marked if the two colloids have electric charges of opposite sign. Thus if colloidal solutions of arsenious sulphide (negative) and ferric hydroxide (positive) are mixed together, the gel produced will contain both constituents; their proportion in the gel will depend on their relative concentrations in the original mixture and it is thus possible to prepare a series of these 'colloidal complexes' of continuously varying composition. Complete precipitation is said to take place when the total negative charge of the one constituent neutralises the total positive charge of the other.

The nature of these 'adsorption compounds' has already been referred to in Chapter XXII; although the generally prevailing view is that they are surface-condensation products, it must be remembered that, in many cases, the possibility of the formation of chemical compounds or of solid solutions is not excluded.

Many substances which at one time were regarded as true chemical compounds have recently come to be looked upon as adsorption products. Thus, 'Purple of Cassius' (which at one time was considered to be aurous stannous stannate) is, according to Zsigmondy, an adsorption compound of colloidal gold and colloidal stannic acid. The darkened products obtained in photographic silver printing are perhaps of the same nature and the so-called sub-chlorides of potassium and sodium (which result for example by the action of kathode rays on the ordinary chlorides or by action of the metal on the fused chlorides) appear to be solutions of the colloidal metals. The precipitate obtained on mixing solutions of arsenious acid and ferric acetate was regarded by Bunsen as a basic ferric arsenite $4Fe_2O_3.As_2O_3.5H_2O$, but according to Biltz, it is an adsorption compound of continuously variable composition [*Ber.* 1904, 3138]. (See page 335.) Many precipitated metallic hydroxides are considered by van Bemmelin to be adsorption compounds of the oxides with water and not true hydrates of the oxides since, as previously mentioned, they give a continuous dehydration curve at a given temperature. (Foote

[*J. Amer. Chem. Soc.* 1908 (30) 1388] proposes to regard precipitated ferric or aluminium hydroxides as solutions of liquid water in the oxides, i.e. as solutions of liquid in solid.) Much discussion has taken place from time to time with regard to the nature of the blue substance formed by starch and iodine, opinions being divided as to whether it is a chemical compound, solid solution or surface-adsorption compound. The latter view appears to be supported by the fact that the amount of iodine taken up from a solution by starch varies with the concentration in a manner which is typical of adsorption phenomena (page 335) and also that a product, which is apparently similar, is obtained by the action of iodine on colloidal lanthanum acetate.

The formation of adsorption compounds plays an important part in many technical processes. As examples may be mentioned the fixation of colouring matters, either with or without mordants, the clarification of syrups by charcoal, sewage precipitation, tanning, etc. In enzyme-action, there appears to be conclusive evidence that combination of some kind takes place between the enzyme and the 'substrate' (i.e. the substance upon which the enzyme exerts its activity) and the undoubtedly colloidal character of enzymes lends strong support to the view that this combination is of the adsorption kind. Many instances occur in ordinary analytical work in which the formation of adsorption compounds may influence the result; familiar examples are the 'carrying down' of zinc or manganese in the third group, and the difficulty found in many cases of washing a precipitate completely free from traces of a constituent of the precipitant.

115. Stability of colloids.

In addition to the influences of temperature and concentration, the stability of a colloidal system depends, as above indicated, on various conditions (sometimes called 'stabilising' factors) amongst which the following may be briefly noticed:

(*a*) The apparent coincidence between the minimum stability and the isoelectric point has already been referred to.

(*b*) The *degree of dispersity* of the dispersed phase has evidently a prominent influence in determining the stability of such systems; this is at once apparent if one compares the varying

degrees of stability of the different modifications of colloidal gold or of arsenious sulphide. Broadly speaking, it would appear that the greater the degree of dispersity, and consequently, the greater the specific surface, the greater is the stability.

(*c*) The *viscosity of the medium* has also an important influence; by increasing this the stability becomes greater. The addition of a viscous substance, such as glycerine, to an aqueous solution of a colloid will often increase its stability; also, insoluble substances such as silver chloride or chromate may be obtained in colloidal form by dissolving them in strong solution of cane sugar (Lobry de Bruyn).

(*d*) The stability of a colloidal system is also connected, according to Perrin [*C. R.* 1903 (137) 564], with the *dielectric constant* of the medium and possibly therefore with its ionising power [see page 215]. According to this view it is only the strongly ionising media which yield stable 'sols.' There appear however to be many exceptions.

(*e*) According to Burton [*Phil. Mag.* 1906 (11) 425], the stability of certain metal 'sols' is conditioned by the relation between the electrochemical character of the disperse phase and the chemical composition of the dispersion medium. Thus, the more electronegative metals, platinum, gold and silver, could be obtained as 'sols' by Bredig's method (page 187) in water or in ethyl malonate (the particles being then negatively charged) but not in alcohol; whereas lead, tin and zinc gave sols in alcohol (the particles then being positively charged) but not in ethyl malonate. It is suggested that for the formation of such sols of the more negative metals, the dispersion medium must contain an ionisable hydrogen atom and for the more positive metals, ionisable hydroxyl must be present.

(*f*) *'Stabilising' ions.* It was mentioned above that the addition of electrolytes may bring about the coagulation or precipitation of colloidal solutions, the suspensoids and true suspensions being extremely sensitive in this respect. Consequently it is to be expected that when a colloidal solution is prepared by means of some chemical interaction, one should, if stability is desired, take every care to remove the last traces of electrolytic reaction products—e.g. by dialysis. Although this

appears to be true in many cases there are some notable exceptions and more recently some authors have even been led to the conclusion that traces of electrolytes are essential to the stability. [See Duclaux, *J. Chim. Phys.* 1907 (5) 29 and 1909 (7) 405. Jordis, *Monat. Sci.* 1904 (18) 797.]

Graham found that colloidal silicic acid "is more durable the longer it has been dialysed" and the same appears to be true of neutral albumen. On the other hand, it has been shewn that Bredig's platinum hydrosol is rendered more stable by the presence of a small amount of alkali and even coarse suspensions of clay or charcoal are said to be similarly affected. It is stated also that the hydrosol of ferric hydroxide, prepared by hydrolysis of basic ferric chloride, becomes less stable if every trace of hydrochloric acid is dialysed away. According to Freundlich, Bechhold and others, negative colloids or suspensions (e.g. arsenious sulphide or clay) are coagulated by hydrogen ions but are either unaffected, or are rendered more stable, by hydroxyl ions; positive colloids, on the other hand, such as ferric hydroxide, are coagulated by hydroxyl and 'stabilised' by hydrogen ions. Lottermoser has also shewn [*Chem. Centr.* 1906, ii. 1597] that colloidal solutions of silver halides may be obtained by interaction of silver nitrate with the respective salts, or free acids, provided one of the ions of the required sol is kept in suitable excess.

The remarkable fact therefore appears to be clearly established that the presence of electrolytes may have either a stabilising or an instabilising influence according to the nature of the case. The result is conditioned, no doubt, by the nature and proportion of the electrolyte and colloid and depends, probably, on changes of potential difference between disperse phase and dispersion medium which may be brought about by the electrolyte in the manner previously indicated; a complete explanation however, applicable to all observed cases, is yet wanting.

(*g*) *Protective colloids.* It frequently happens that the stability of a given, slightly stable, colloidal solution may be enormously increased by the presence of another colloid. Most, if not all, of the instances in which this phenomenon has been observed, are those in which a *suspensoid*, which otherwise is easily coagulated by electrolytes, temperature change, increase

of concentration, etc., becomes largely indifferent to these coagulative agencies if a colloid of the *emulsoid* type is present. The stability of the system so produced may become, in fact, as great as that of the emulsoid itself. This phenomenon is evidently quite of a different type to the mere stabilising by increase of viscosity of the dispersing medium (*c*), since the protective effect may often be brought about by the presence of minute proportions of the emulsoid, whereas comparatively large proportions of the viscous material are required in the latter case. As examples of this protective action it may be mentioned that most of the metal hydrosols can only exist in a relatively stable condition when very dilute; on attempting to concentrate the solution by evaporation beyond a certain point, coagulation occurs; in the presence of albumen, starch, dextrin, etc. however, very concentrated solutions may be obtained. The coagulation of hydrosols of metallic oxides and sulphides, and even of some coarse suspensions, by electrolytes, may be prevented in a similar way; one milligram of gelatine is said to be sufficient to prevent the precipitation of a litre of colloidal gold by sodium chloride.

The protective powers differ however considerably for various colloids.

Zsigmondy has made comparisons of this property in the following way. It is found that a colloidal gold solution prepared in a special way is comparatively stable and may be heated to 100° without change; it is of a bright red colour, but the addition of electrolytes changes its colour to blue, after which it quickly deposits metallic gold. This change can be prevented by the addition of a suitable quantity of a protective colloid and in making the comparisons, the quantity of the latter which is just insufficient to prevent the change was determined. The term 'gold figure' is used to mean the weight of protective colloid which is just insufficient to prevent the colour-change, from red to violet, of 10 c.c. of the bright red gold solution by the addition of 1 c.c. of a 10 per cent. solution of sodium chloride.

The following are some of the gold figures obtained:

gelatine ·005—0·01, egg albumen 0·1—0·25, gum arabic 0·1—4, starch 4—25 (according to quality), dextrin 6—20, urea ∞, sugar ∞.

It appears that the determination of these gold figures may serve the purpose of characterising various proteins, such as albumens, globulins, albumoses, etc., and of detecting in them the presence of impurities. Thus crystallised albumen gave the numbers 2—8 whilst amorphous albumen gave 0·03—0·06.

Little is known with regard to the nature of this protective action; it is evidently not due to change in viscosity, for the reason above mentioned, neither can it be explained by an alteration of sign or quantity in the electric charge, since the same colloid may sometimes 'protect' either a positive or negative colloid.

The 'umhüllungstheorie,' of Quincke and Bechhold, accounts for the phenomenon by supposing that the particles of the less stable colloid become coated with a thin layer of the protective colloid and that the attraction of these particles for one another, and consequently their tendency to aggregate, becomes thereby lessened. Since the protective colloid is usually, or perhaps invariably, an emulsoid (i.e. one in whose solution the disperse phase is liquid) we may regard the whole system as consisting of particles of the less stable colloid (usually a suspensoid) in contact with two non-miscible liquids. From the principle that the available surface energy tends to a minimum, it follows that if the surface tension at the surface of separation of suspensoid particle and dispersion medium exceeds the sum of the tensions at the surfaces of separation, suspensoid-emulsoid and emulsoid-dispersion medium, the emulsoid will spread itself out between the suspensoid particles and the medium, thus forming an intermediate layer.

[Thus, designating the three phases, suspensoid, dispersion medium and emulsoid by 1, 2 and 3 and the tensions at the surfaces, in the order mentioned, as a_{12}, a_{13} and a_{23} respectively, the condition that 3 spreads itself between 1 and 2 is that $a_{12} > a_{13} + a_{23}$.]

Quincke shewed that this relation does actually exist in the case of mastic, gelatine and water, a system in which the protective action of gelatine can be easily demonstrated. In further support of this theory, Michaelis and Pinoussohn (1906) state that on bringing together suspensions and certain colouring matters which act protectively, they have observed a diminution in the number of the ultramicroscopic particles of the protective colloid. Bayliss has observed similar phenomena in the case of congo-red. Although the protective colloids which have been principally studied are organic substances, there are many instances in which inorganic colloids may behave in a similar way. Silicic acid and

zirconium hydroxide, for example, are found to exert a protective action on colloidal gold and the supporters of the theory above indicated consider this fact as evidence in favour of regarding these substances as colloids of the emulsoid class.

The protective property of colloids, and of electrolytes, has many important practical applications. The so-called 'emulsion' used for coating photographic plates, prepared by interaction of ammonium bromide and silver nitrate in gelatine solution, may be looked upon as a colloidal suspension of silver bromide which is 'protected' by a colloid. In Carey Lea's colloidal silver, obtained by reducing silver salts with various agents, such as tartrates, ferrous salts, dextrin, tannin, etc., under appropriate conditions, the colloidal solution is protected either by electrolytes or colloids, according to the mode of formation. It is possible in this way to obtain a colloidal product, soluble in water, containing 95 per cent. of silver. The so-called 'collargol,' used in medicine, appears to be a similar product; it contains about 87 per cent. of silver, together with protein substances, etc.

Paal obtains concentrated and relatively stable colloidal solutions of silver, platinum gold, etc. by reducing their salts in presence of 'protalbinates' and 'lysalbinates' (products prepared by the action of alkalis on egg albumen). The palladium hydrosol so obtained can take up much larger quantities of hydrogen than the compact metal or even palladium-black.

Peptisation. Many of the factors enumerated in the foregoing section may be effective, not only in giving increased stability to a colloidal solution which has already been prepared or which is in the act of formation, but also, in many cases, may be able to bring a substance which is otherwise insoluble, or nearly so, into the state of a colloidal solution. A remarkable instance of this property was first pointed out by Graham who shewed that gelatinised silicic acid can again be brought into the condition of a colloidal solution by the influence of a minute proportion of caustic soda; thus 1 part NaOH in 10,000 parts of water, at 100°, brought into solution 200 parts of silicic acid (estimated dry). This process was compared by Graham to the digestion of albumen —the "liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid"—and hence the use of the term *peptisation.*

Similar effects may be produced in a large number of cases, not only by the influence of electrolytes, but also by colloids themselves; it is now usual therefore to speak of 'peptisation by ions' and 'peptisation by colloids.'

As examples, the following may be referred to. By hydrolysis of stannic chloride, and dialysis, a hydrogel of stannic acid is obtained which is practically insoluble, but can be brought into colloidal solution by the addition of a minute quantity of ammonia. Colloidal ferric hydroxide precipitates a solution of albumen or of colloidal arsenious sulphide; the precipitates produced however dissolve again if an excess of the ferric hydroxide is added. Many hydroxides which are otherwise insoluble may be brought into the state of colloidal solution by treatment with salts containing a common ion; thus a solution of colloidal thorium hydroxide can be obtained by treating the precipitated hydroxide with thorium nitrate (Müller). It is shewn however by Szilard, that similar results may sometimes be arrived at by use of salts which contain no ion in common; he, somewhat inappropriately, calls such products 'heterogeneous colloids.' The last named author finds that coagulated albumen dissolves on heating with thorium nitrate solution; the product gives neither the reactions of thorium or albumen and it is suggested that the process is a kind of inorganic 'digestion' of the albumen and that the latter is converted into albumose or perhaps into peptone. [*Journ. Chim. Phys.* 1907 (5) 495.]

The peptisation by means of small quantities of salts or alkalis has been utilised in preparing colloidal solutions of various highly infusible oxides for the purpose of constructing filaments for electric lamps (Kužel).

116. Molecular weight of substances in the colloidal state.

Having regard to the slowness of diffusion and the generally inert character of typically colloidal substances and to the fact that the reacting-weights of many of them (e.g. gummic acid) must be represented by a multiple of the simplest formula weights, Graham was led to conclude that complexity of the molecule was essential to the colloidal condition. He says, for example, "The

enquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules and whether the basis of colloidality may not really be this composite character of the molecule." It is to be noticed that he refers to the molecular state of a substance when in the colloidal condition. The expression 'molecular weight of a colloid,' although frequently met with, is apt to be misleading; as mentioned above, various substances, to which we usually assign the simplest molecular formulæ, may be obtained in the colloidal state.

Further it must be evident that, even granting the applicability of the methods used, any single value assigned to the molecular weight of a particular colloid can, in most cases, be of little importance, since "the small parts which move about as a whole" in a colloidal solution, may have very different and varying magnitudes.

A large number of determinations have, nevertheless, been made, from time to time, with the object of calculating the molecular weights of colloids by the application of the usual methods. Cryoscopic, or vapour pressure, determinations are extremely unsatisfactory for this purpose, since the very small depressions observed might well be ascribed to the, highly probable, presence of electrolytic impurities. Direct measurements of osmotic pressure, using a membrane of parchment-paper, are more reliable since these impurities are, in this case, able to dialyse away and do not affect the measurement, i.e. the membrane is permeable to electrolytes but not to colloids.

In all these attempts, however, a further difficulty arises in that the proportionality between osmotic effect and concentration, upon which the calculation of the molecular weight depends, does not hold in colloidal solutions. The osmotic pressure for example does rise with increasing concentration, but not proportionally; and as regards lowering of the vapour pressure, the effect of change of concentration sometimes leads to altogether abnormal results. Thus the sodium salts of the higher fatty acids, which behave as colloids, give, in dilute solution, a lowering of the vapour pressure which becomes *smaller* as the concentration increases and eventually may become zero. [Smits, *Zeit. Physikal. Chem.* 1903 (45) 608.]

It may be of some interest to mention here a few of the results which have been obtained by various authors who have worked in this direction.

Picton and Linder found that the colloidal forms of various metallic sulphides gave no depression of the freezing point of water; a measurable osmotic pressure was observed in the case of colloidal arsenious sulphide, a semi-permeable diaphragm of copper ferrocyanide being employed. With various emulsoids the results are much more marked. Thus Pfeffer found for gum arabic the osmotic pressures 69, 259, 700 and 1190 millimetres, corresponding to the percentage concentrations of 1, 6, 14 and 18. Calculating the molecular weight by comparison with cane sugar under like conditions these numbers give values of about 2570, 4110, 3540 and 2680 respectively.

Weymouth Reid [*Journ. Physiol.* 1905 (33) 13] measured the osmotic pressure of purified hæmoglobin, using a gelatine diaphragm, and obtained a mean value of 3·86 mm. at 15° for a one per cent. solution; this gives a molecular weight of about 45,000. [In the solution employed, no ultramicroscopic particles could be detected and the author considers therefore that it should be regarded as a true solution.] Other observers using a similar method obtained much lower values for the molecular weight.

Bayliss [*Proc. Roy. Soc.* 1909 (81) 269], using a diaphragm of parchment, obtained osmotic pressures for Congo-red which agree with the value calculated on the assumption that it exists in true solution in the state of single molecules. The solutions are not resolvable by the ultramicroscope, although the substance is generally regarded as colloidal in that, for example, it does not pass through parchment.

Moore and Roaf [*Biochem. Journ.* 1906 (2) 34] shewed that the osmotic pressure of a 10 per cent. gelatine solution was 70 mm. at 30°, it is greater at higher temperatures, but the increase is larger than that required by theory. Further, they found that if the solution has previously been heated to 70°—80°, the osmotic pressure at 30° is considerably higher than before.

The influence of electrolytes on the osmotic pressures of colloidal solutions has been studied by Lillie [*Am. Journ. Physiol.* 1907 (20) 127] who employed solutions of albumen and gelatine

for the purpose. He shewed that salts often depress the osmotic pressure to an extent depending on the nature of the anion and of the kation, the depression being usually greater for polyvalent ions in both cases. In some instances the osmotic pressure is raised instead of lowered. The presence of non-electrolytes has little if any effect. Bayliss also found that the addition of electrolytes caused a marked depression of the osmotic pressure of Congo-red; he suggests that this effect is due to the aggregation of the molecules to particles and consequent diminution of the effective concentration.

Attempts to determine the molecular weights of colloidal substances by the cryoscopic method were first made by Brown and Morris in 1888. These authors drew attention to the difficulties which arise owing to the very small depressions which are obtained, but they concluded, nevertheless, that the molecular complexity of these compounds is very great indeed. For the lowest, dextrin, they obtained a molecular weight of about 6480 and, from the proportions of dextrin and maltose resulting from the hydrolytic decomposition of starch, they estimated the molecular weight of starch to be five times this number, i.e. 32,400, or 200 times the simplest empirical formula weight. Sabanéeff obtained the values 800 for tungstic acid, 1100 for tannin, 14,000 for egg albumen and 45,000 for silicic acid; whilst Gladstone and Hibbert found 1700 for caramel, 1800 for gum arabic and 6000 for ferric hydroxide. In all these cases it is evident that a very considerable concentration is required in order to yield a marked depression; thus in the case of albumen 44·5 grams in 100 grams of water only gave a depression of 0·06°. As an indication of the variable results obtained by different observers it may be mentioned that for glycogen the values 1625, 10,000 and 140,000 were found by Sabanéeff, Jackson, and Gatin-Gružewska, respectively.

Sabanéeff in 1891 proposed to classify colloids according to their molecular weights and he relied for this purpose principally on the values obtained by the cryoscopic method. Colloids whose molecular weights exceed 30,000 were called by him 'higher' or 'typical' colloids; these, it was said, become coagulated when their aqueous solutions are frozen. Included in this class were silicic acid, starch, ferric hydroxide and (probably) colloidal metallic sulphides.

The 'lower' colloids, with molecular weights less than 30,000, were unchanged by freezing; to this class were assigned tungstic acid, tannin, glycogen, inulin, etc.

117. Preparation of colloidal solutions.

If we adopt the system of classification of dispersoids suggested on page 380 it is evident that the general methods of obtaining substances in the state of colloidal solution may be divided into two groups. Thus, if we start with true solutions and, by some reaction, produce the required colloidal solution, the operation is accompanied by a *diminution* in the degree of dispersity, since a part of the system is brought down from the region of molecular (or ion) dispersoid to that within the limits arbitrarily assigned to colloids ($0{\cdot}1\mu$ to $1\mu\mu$). If on the other hand the substance is, to start with, a compact solid or coarse powder, the degree of dispersity has to be *increased* in order to bring it to the colloidal state. These two processes are usually referred to as *condensation* and *dispersion* methods respectively.

The condensation method is of course by far the most usual and numerous examples have already been mentioned of colloidal solutions obtained in this way. Generally, the required substance is produced from a solution of one of its crystalloid compounds by means of such chemical changes as reduction, hydrolysis or double decomposition. The necessary conditions for obtaining, and maintaining, the substance in the sol condition depend, as above indicated, on various factors, such as temperature, concentration, insolubility of the required substance in the dispersion medium employed, rate of formation, absence of instabilising electrolytes and, in certain cases, on the presence of protective colloids, stabilising ions, viscous substances, etc. It generally, but not invariably, happens that when the chemical change employed gives rise, in addition to the colloidal substance, to an electrolyte, the latter exerts an instabilising influence. Thus, where arsenious sulphide* results from the change $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$, in aqueous solution, a sol is at once obtained; whereas if aluminium hydroxide is produced by the interaction of an aluminium salt and ammonium hydroxide, the resulting ammonium salt acts as an

* O_2, according to Linder and Picton, a hydrosulphide such as $8As_2S_3 . H_2S$.

instabilising factor and the aluminium hydroxide is obtained in the form of a gelatinous precipitate. If however this precipitate is washed quite free from the ammonium salt, the precipitate partially redissolves as a sol. Similar phenomena occur in the case of many other precipitations in which electrolytes are produced, or are originally added, and the partial redissolving of the washed precipitate may lead to errors in analytical work, if due precautions are neglected.

As examples of dispersion methods of obtaining colloidal solutions, reference may first be made to the so-called 'mechanical dispersion'; thus certain colouring matters such as indigo and ultramarine, which are first obtained as coarse powders, may, by continued grinding, become capable of giving suspensions which are so fine that they no longer undergo spontaneous sedimentation. Cellulose fibres also may, by 'grinding to death' (*totmahlen*) become so finely divided that the moist material is converted, on drying, into a horny substance. Bredig's method of obtaining colloidal metals (page 187) is often regarded as a direct dispersion process, i.e. as a 'tearing to pieces' of the solid metal. Some consider however that the metal is actually vaporised and that in the rapid cooling of the vapour, the less stable or colloidal form first appears (compare the preparation of phosphorus, mercuric iodide, etc.) and, electrolytes being absent, this form persists. It has been shewn by Svedberg [*Ber.* 1909, 4375] that certain metals can be brought into the state of colloidal solution, in which submicroscopic particles can be detected, by exposing a clean surface of the metal, covered with the dispersion medium, to the action of ultra-violet light. Silver, copper, tin and lead readily yield sols in this way, but with platinum, aluminium and cadmium, little or no effect was obtained. The 'peptisation' phenomenon referred to on page 402 must also be included as a dispersion process and the same may be said of the redissolving of the well washed precipitates mentioned above. Finally, mention should be made of the fact that in addition to methods depending upon condensation or dispersion, it is possible in some cases to prepare one sol from another by chemical interaction. Thus for example by the action of hydrogen sulphide, the hydrosol of stannic acid can be converted into the hydrosol of stannic sulphide.

For further information the student should consult Wolfgang Ostwald's *Grundriss der Kolloidchemie* (1909), or Müller's *Allgemeine Chemie der Kolloide* (1907).

A useful summary on Colloid Chemistry by H. R. Procter will be found in the *Report of the British Association*, 1908, page 201.

Practical Work.

1. Qualitative experiments are made, using the ordinary forms of apparatus, on the unequal rates of diffusion of various gases (e.g. air and hydrogen, air and carbon dioxide), the gases being allowed to diffuse into one another through a porous closed vessel fitted with a manometer.

Approximate quantitative determinations are also made of the relative rates of diffusion of two gases—say oxygen and hydrogen—using the apparatus indicated on page 365, fig. 26.

2. Some applications of dialysis for chemical purposes are illustrated by:

(*a*) The preparation of a solution of silicic acid.

A solution of sodium silicate is poured into a considerable excess of dilute hydrochloric acid and the mixture is subjected to dialysis. The process is allowed to continue for some days with frequent renewal of the outside water, and the diffusate is tested, from time to time, with silver nitrate.

(*b*) As an illustration of the application of dialysis in analytical work, a solution is given to be tested for arsenic, strychnine, etc., which is made by mixing a small quantity of one of these 'poisons' with a large excess of some colloidal matter, such as boiled starch. The mixture is dialysed and tests made with the diffusate.

3. Colloidal solutions of certain metallic sulphides are prepared according to the method of Picton and Linder.

(*a*) Arsenious oxide is dissolved in hot water or in a solution of potassium hydrogen tartrate (about 2 grams As_2O_3 to 500 c.c. of solution) and the cold solution is allowed to run into an excess of saturated solution of hydrogen sulphide.

(*b*) A moderately dilute solution of tartar-emetic is employed in the same way.

The solutions obtained are freed from excess of hydrogen sulphide by means of a current of hydrogen and, if necessary, dialysed to remove salts.

4. A colloidal solution of gold is prepared according to Zsigmondy's receipt; 120 c.c. of the purest distilled water are boiled in a Jena glass vessel; 2·5 c.c. of a 0·6 per cent. solution of $HAuCl_4.3H_2O$ and 3·5 c.c. of 0·18 normal K_2CO_3 are then added and 3 to 5 c.c. of commercial formalin (diluted considerably with water) is slowly introduced.

The result should be a bright red solution which is permanent. The preparation however requires extreme care and seldom succeeds unless the instructions are strictly followed. A red solution may also be obtained by using, in place of formalin, a few drops of a solution of phosphorus in ether (prepared by diluting a saturated solution to 5 times its volume). The phosphorus solution is added to the cold mixture and this is then heated to boiling until the odour of ether has disappeared. Good results are obtained if a few drops of the red solution prepared in this way are used to 'inoculate' the solution prepared by Zsigmondy's process, the addition being made before the formaldehyde is introduced.

5. With the colloidal solutions obtained in 3 and 4 approximately quantitative experiments are made on the precipitating powers of various metallic salts (e.g. NaCl, $BaCl_2$, $MgSO_4$ and $FeCl_3$), standard solutions of these being given.

The influence of protective colloids may be illustrated by comparing the coagulating power of an electrolyte with and without the previous addition of a minute quantity of dilute agar-agar solution.

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		O=16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	75·0
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·09
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·1
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	81·8
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	7·00
Lutecium	Lu	174
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·0

		O=16.
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20
Nickel	Ni	58·68
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·0
Platinum	Pt	195·0
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·62
Sulphur	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·42
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	128
Ytterbium (Neoytterbium)	Yb	172
Yttrium	Y	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

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